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TREATISE ON

GENERAL AND INDUSTRIAL

INORGANIC CHEMISTRY

ALSO BY DR. MOLINARI

TREATISE ON

GENERAL AND INDUSTRIAL

ORGANIC CHEMISTRY

TRANSLATED BY

T. H. POPE, B.Sc., A.C.G.I., F.I.C.

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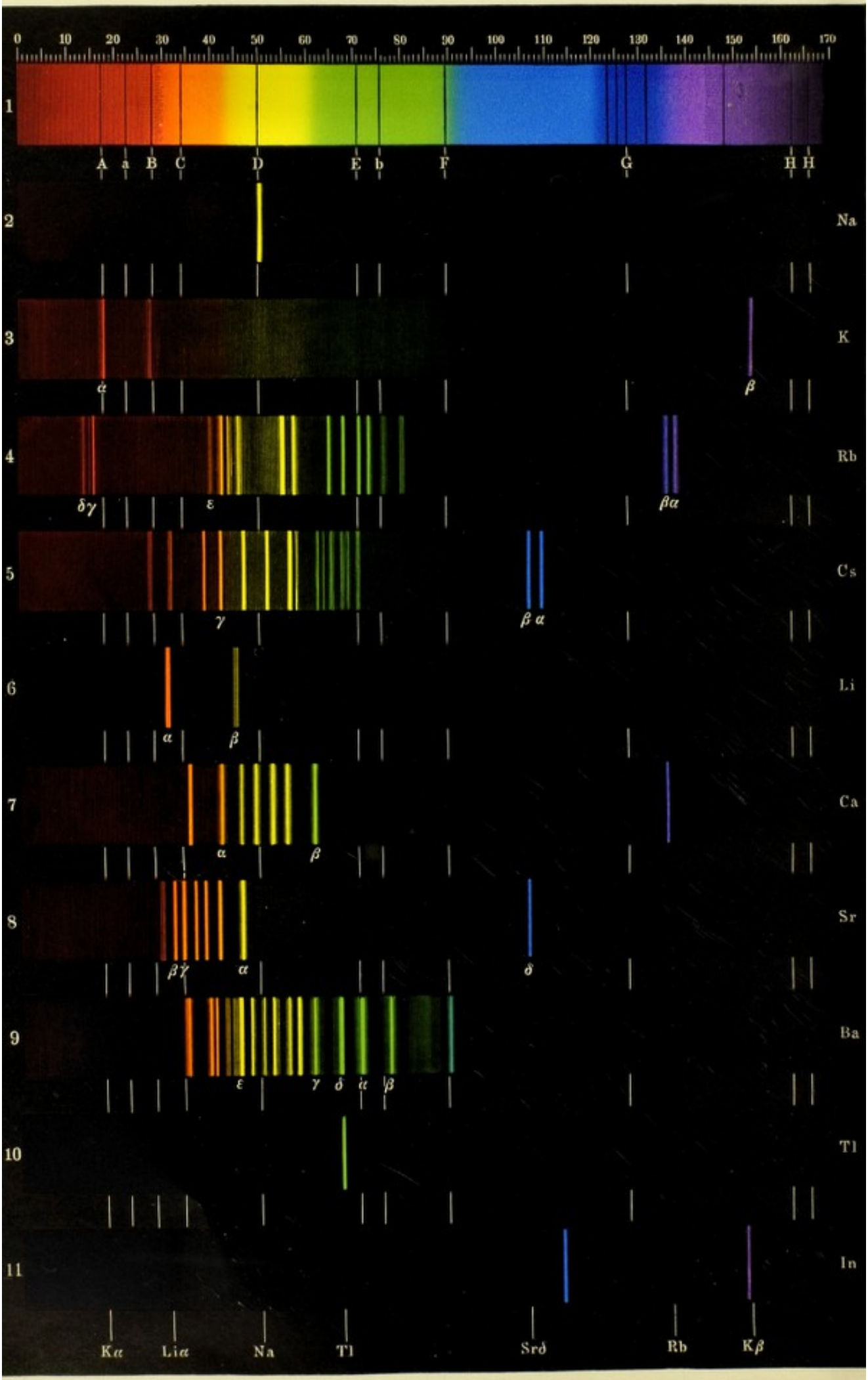
506 Illustrations

Spectroscopic Plate.



TREATISE ON
GENERAL AND INDUSTRIAL
INORGANIC CHEMISTRY

BY

DR. ETTORE MOLINARI

Professor of Industrial Chemistry to the Society for the Encouragement of Arts and Manufactures and of Merceology at the Commercial University Luigi Bocconi at Milan

THIRD REVISED AND AMPLIFIED ITALIAN EDITION

TRANSLATED BY

DR. ERNEST FEILMANN

B.Sc., Ph.D., F.I.C.

WITH 280 ILLUSTRATIONS IN THE TEXT
ONE CHROMOLITHOGRAPHIC PLATE
AND TWO PHOTOTYPE PLATES

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TRANSLATOR'S PREFACE

In this translation the original text has been adhered to as faithfully as possible, even where the views or explanations of the author are not such as would meet with unqualified acceptance by all chemists. Where it seemed especially desirable a *Translator's Note* has been interpolated as such.

Prices have generally been given in English currency per ton, where the substance in question is sold in large quantities, and in English currency per kilogramme in the case of fine chemicals ; the pound sterling has been taken as equal to twenty-five lire.

Temperatures are always given in Centigrade degrees, and it has not been considered necessary to add the abbreviation "C." In the case of other abbreviations for units of volume, mass, &c., the abbreviations in the Chemical Society's and Society of Chemical Industry's recognised Journals have usually been followed.

The decimal system of weights and measures has been retained throughout, the decimal and English tons being practically identical for the purposes for which they are used in this work.

ERNEST FEILMANN

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PREFACE TO THE THIRD EDITION

In this new edition almost all the more important chapters of the book have been revised. Thus certain sections, such as those on cement, superphosphates, the utilisation of atmospheric nitrogen, white lead, steel, and water (including appendix at the end of the volume) have been considerably amplified on account of the practical and theoretical importance of these subjects, which increases daily. The chapter on cement, for example, may be useful in giving some idea of the various chemical, mechanical, and economic problems which are to-day involved in chemical industry on a large scale.

The statistics have been brought up to date so that they may offer to the reader a summary, which is sometimes very suggestive, of the progress and circumstances of the principal chemical industries of Italy and other countries.

In this third edition, apart from the inclusion of various analytical methods of testing the more important chemical products, numerous patents have been cited, because, apart from the new processes or new practical successes which are often embodied in them, they always contain a new idea which tends to advance the progress of chemistry in its practical applications. In these references we have cited the German patents by preference because, as is well known, these are controlled by a special technical commission, which, with rare exceptions, ensures that they are to be taken seriously, an assurance which is often wanting in the patents granted by other countries without any such guarantee.

The book thus amplified will perhaps be better capable of enabling the young chemist to prepare himself for practical activity, and may stimulate those engaged industrially, who are somewhat slower in accepting the results of chemical progress, to advance with a more eager stride.

THE AUTHOR

PREFACE TO THE FIRST EDITION

During the last century chemistry has been one of the most powerful factors of progress, civilisation, and improvement in all countries, some of which have derived from its study their most important sources of wealth and activity. Germany is still benefiting from the beneficent impulse given by Liebig to chemical studies, and it was in Germany that the scientists of other countries studied their science in that school of chemistry to which Liebig, Hofmann, and Kekulé gave a scientific and entirely theoretical impulse.

To-day, however, this mode of study does not correspond to modern requirements, because industrial problems have become specialised and intensified to such an extent, under the impulse of constant progress from day to day and the pressure of strenuous international competition, that pure theory encounters grave difficulties in finding a path through the complex and multiform organism of modern chemical industry. It is therefore necessary to-day to recognise, in general treatises at least, the more salient, marvellous, and brilliant methods which permit one to pass rapidly from the more abstract theoretical conceptions to the more important practical applications.

The young chemist should be initiated with much care into those exercises which link theory and practice together.

This necessity has led chemical teaching in a new direction.

General and inorganic chemistry should no longer be a simple and arid exposition of fundamental laws and of the properties of innumerable known substances, but should possess a soul which brings it into contact with the vital activities around which it clings. In a course of general inorganic chemistry all the applications which have been made of the fundamental laws and of the properties of substances should be studied. The chemical text-books which have been used until now do not correspond sufficiently to these requirements, and it is only since a couple of years that attempts have been made to reform this state of affairs and to carry into practice the improvements which have been urgently demanded from several quarters.

In 1903 already the University of Berlin prescribed an examination in applied chemistry even for the students of pure chemistry, and in Italy, Gabba at the Chemical Society of Milan, Cannizaro at the Chemical Congress at Turin in 1902, and Ciamician in his inaugural discourse to the students at the University of Bologna in 1903, have amplified the urgent necessity of modifying the character of university chemical studies by special consideration of practical applications.

The author came to the same conclusions two years ago, when he was charged with the arrangement of a general course of inorganic chemistry at the Milan Polytechnic, as he had taken special notice, during several years of industrial activity, of the almost general lack of success of our young chemists when faced with practical applications of chemistry, an insuccess which explains the slow progress and sometimes even the ruin of many Italian chemical industries. Our young chemists themselves cannot be blamed for this lack of success. which is due to the erroneous direction of their training.

And if anything is to be attempted in Italy it should not be an imitation of that which has been done in other countries in the past, but should start

at the point at which other countries have arrived in order to proceed otherwise and profit by the experience of others.

The present treatise took its rise from these considerations, and has no other pretensions than to be an attempt to initiate a work of reform in the teaching of chemistry in the hope that others may follow and carry out its objects better.

The first sections of the work are devoted to a short historical sketch of the progress of chemistry, which may perhaps be of interest to students because this branch of chemistry is ordinarily very incompletely or even incorrectly treated in other text-books.

I have prefaced the special and systematic portion by a theoretical portion, which explains the principal fundamental laws. This portion is not especially suited for the instruction of those completely ignorant of chemistry, but appears to me, on the other hand, to offer advantages to those students of secondary institutions who have already an elementary knowledge of chemistry gained during their previous studies in high schools and technical institutes.

In the development of the descriptive portion, I have often turned back to the more important fundamental laws and completed their elucidation as well as possible. Thus the exposition of the phase rule is illustrated and completed in the chapter on sulphur, and the laws of mass action are illustrated in the section on the manufacture of catalytic sulphuric acid, and are again referred to at various other points.

The third portion, which deals with the metals, is preceded by a section on the fundamental laws of electro-chemistry and by an amplification of the electrolytic theory of solutions.

The book closes with a short summary of the periodic system of the elements.

In the special portion I have always endeavoured to emphasise very briefly those industrial processes which deal with the preparation of the more common compounds. In the case of some of those which take part in large scale industrial operations, I have treated them rather more extensively in order to impart an idea of the character which the more important applications of chemistry assume in practice. I have done this in the case of hydrogen, which is destined to have an important industrial future, in the case of water in its very varied uses, of sulphuric acid, soda, chemical fertilisers, &c.

By means of the ordinary text-books it is difficult for the student to form a conception of the greater or lesser importance of any one compound compared with others. Many, for example, do not know whether arsenious anhydride has other applications than that of destroying rats or that other more tragic one which solves many intricate human problems; whether phosphorus has other uses than for the heads of matches, or whether hydrogen serves other purposes than the inflating of balloons. I have endeavoured to indicate as completely as possible the varied applications of each substance, and have summarised their present and past importance by means of statistics. In the case of each substance I have indicated its commercial price without any desire to offer a commercial price-list of chemical products, but merely for the sake of orientation, as quite often it is not known whether a cubic metre of oxygen costs 2*d*. or 4*s*., whether ammonia costs more or less than nitric acid, copper more or less than aluminium or nickel, &c. In general nothing is available with regard to the prices of chemical products than the fantastic price-lists of the pharmacists.

I have purposely omitted the description of ordinary laboratory apparatus, because this is only of subsidiary importance for the young student, as an

aid to the professor in imparting knowledge, and may be found in special works. I have substituted for this cumbersome material simple and illuminating sketches of industrial apparatus and processes which I have collected from the best works on chemical technology (Muspratt, Dammer, Bertsch, Lunge, &c.) from patents or directly from practice in works which have been visited by me in Italy and other countries.

Thus the student will become accustomed to comprehend those means by which processes pass from the experiments of the school and from more abstract scientific considerations to the more important industrial applications. Practical disappointment and disastrous failure, due to too dogmatic and simple conceptions acquired during the teaching of the schools, will be spared to many in the future. They will learn how one passes from the retort and the beaker to the more wonderful devices of modern technology, and how in the course of chemical processes in practice one must not only take the main reactions which are ordinarily found in the books into account, but also the secondary reactions, special conditions of temperature, pressure and time, and the proportions of the reacting substances. These are all conditions which may decide the success or failure of an entire industry.

I am far from believing that this book may be considered as a treatise on chemical technology, but it is my conviction that industrial chemistry must start from the foundations of general chemical culture embodied in this treatise, in order to enter into all the technical and economic conditions of manufacture of the more important compounds and in order to place the young chemist in a position to assume the direction of and collaboration in our chemical industry with more success and utility.

THE AUTHOR

MILAN

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PART I. GENERAL

EVERYTHING which exists, everything which directly or indirectly influences our senses, constitutes Nature or the universe, of which we ourselves form part.

It is now admitted that the one fundamental essential constituting Nature is none other than Energy, which, in various qualities and in its many transformations and combinations, also changes into that well-defined form which constitutes the innumerable substances of the universe.

39 Bodies formed of one or more substances influence one another reciprocally in various ways, and the perception of their forms and their properties is all relative to the nature of the organism which is influenced by them. Thus the forms and qualities which we perceive in the bodies around us are relative to our sensitive faculties or to the special constitution of our organism, but there is nothing to prove that these bodies have, in any absolute sense, the forms and properties which we attribute to them.

If we consider abstractly imaginary organisms quite different from ourselves or from members of the animal kingdom to which we belong, then the nuclei of energy which constitute bodies as we know them will manifest themselves to these hypothetical organisms in quite a different shape and manner.

These abstract considerations do not, however, modify the methods of perception of nature by the human organism, so that all the researches and all the deductions and victories of the natural sciences retain a general and positive value for mankind.

The distinction which was once made between matter and energy is not rigorous and has been generally abandoned in favour of the more general conception of energy as the sole real entity.[1]

A *body* is a part of space in which there are indissolubly united certain quantities of energy of distance (*weight*), energy of motion (*mass*), and energy of volume (*volume*).

Bodies are formed of various *substances*, which are in their turn manifestations of chemical energy, variously grouped in different compounds and distinct from other forms of energy by which, however, they are usually accompanied (thermal, electric, mechanical, and radiant energy, &c.); the magnitude of this chemical energy is measured by the product of two inseparable factors, the factor of capacity (*mass*)[2] and the factor of intensity (*chemical affinity* or *chemical potential*, which is the cause of all chemical reactions).

The specific properties of substances are represented by the quotient of two factors, intensity and capacity.

[1] In fact, if we analyse the inner nature of matter we must at once admit that we perceive the objects of the exterior world (and we may add that we acquire consciousness of our own existence) solely in virtue of the influence exercised by these objects on our senses. Now the causes of our perceptions are the qualities and properties (due to various forms and differences of energy) which we consider to be inherent to matter (light, the various colours and physical state are all forms of energy); but if we for a moment imagine matter divested of all these properties in order to see what remains, we find that there is nothing perceptible, that is to say, we cannot then demonstrate the existence of matter. That energy alone should exist, without matter, would appear to be a contradiction of the law of gravitation, to which matter itself is said to be subjected; but gravitation is only a form of energy, which can only manifest itself by contrast with other forms of energy. In fact gravitation is, more exactly stated, energy of distance.

In ordinary language the use of the word matter is so well established that it is impossible to always avoid its use, without, however, invalidating what we have said above.

[2] Whilst all the masses concerned in the various forms of mechanical energy are equivalent and homogeneous, in chemical energy the masses are of varying nature and characterise the various simple substances (elements).

I

Bodies are distinguished from one another by variable properties only (form, magnitude, &c.) ; thus, for example, a cube of sugar is a body, because it has an inherent, well-determined form, that of the cube, which constitutes a variable property, because the cube may be more or less large. The component—sugar—on the other hand, is a substance with well-defined and invariable specific properties. In fact, on breaking up the cube, the sweet taste characteristic of sugar still remains, and this property does not disappear even when the sugar is dissolved in water.

Thus, again, a beaker, mirror, bottle, &c., are all bodies, very distinct from one another in form and size, but all constituted of the same material, glass, with invariable specific properties.

The descriptive natural sciences, botany, anatomy, zoology, crystallography, &c., study more especially the internal and external forms of bodies, whilst the speculative natural sciences, physics and chemistry, mainly study substances and their specific properties, their transformations and combinations.

More exactly, physics is the study of all the modifications which the properties of substances can undergo without durably losing any of their specific properties, that is to say, without being transformed into other substances.

Chemistry, on the other hand, studies the stable modifications of the properties of substances when these lose any of their specific properties and acquire others, that is, when they are transformed into other substances.

On heating water to 100° it is transformed into steam, which, in turn, is reconverted into water when it is cooled and condensed ; in this case the water has not undergone any essential modification. If we heat in a bulb a fragment of a substance of metallic aspect called iodine, we obtain violet vapours, which recondense on cooling on the sides of the bulb in scales of iodine, lustrous as before, showing that the iodine has not lost its intrinsic qualities by changing its form and state. A platinum wire, when heated, becomes red and glowing, but is still always platinum, and is found to be unaltered on cooling. When sulphur is heated out of contact with the air it becomes liquid and of a reddish colour ; on raising the temperature it again becomes solid, and finally liquid again at a still higher temperature ; if it is then poured into water when in this condition it becomes solid, but is at first plastic and only becomes hard and friable, as it was originally, after some time ; now, during all these long and various transformations the substance has not been altered ; the sulphur always remains sulphur. If fine zinc filings and flowers of sulphur are mixed an apparently homogeneous mass is obtained, which differs in appearance from its components. But with a simple lens the constituents are easily distinguished, and on pouring the mass into water the zinc is easily separated from the sulphur, as the latter remains on the surface, whilst the former sinks to the bottom. Thus also from a mixture of iron filings and sulphur the two components are easily separated with a magnet.

The experiments which have just been enumerated all illustrate so-called *physical phenomena*.

If, on the other hand, we take the mixture of zinc and sulphur, made in certain definite proportions, and heat it in a dish, it catches fire, producing much heat and light, and we obtain a new white, voluminous substance which, when examined with a lens, poured into water, or examined in any other way, cannot be separated into particles of the two components. Thus a new substance has been formed which no longer has any of the specific properties of the two original substances. This is a chemical phenomenon, because the nature of the admixed substances has been changed in a stable manner,

producing a sulphide of zinc. So on heating sulphur and iron filings in a glass tube the mass glows and catches fire, and we obtain a new substance differing in a stable manner from the components, which we are not able to separate by ordinary means, such as by a magnet. On mixing together powdered tartaric acid and sodium bicarbonate an apparently homogeneous substance is obtained, though with a lens this is seen to be a mixture of crystals of the two components; but on throwing this mixture into water a strong evolution of gas occurs, and the two substances are intimately combined, so that on evaporating almost all the water a product remains which is quite distinct, and nothing remains of the two components from which it has been formed.

If red mercuric oxide is heated in a test-tube a metallic mirror of mercury is formed on the walls, a gas is evolved (oxygen), which revives the combustion of a glowing splint of wood, and the mercuric oxide is completely decomposed.

If sulphur is heated in a tube without access of air, it changes its physical state, but the intimate character of the material is unaltered. If, on the other hand, sulphur is heated in a spoon, with access of air, it catches fire with a blue flame, emitting a colourless gas; the sulphur disappears, and in its place we have a colourless gas, soluble in water, which shows special reactions and reddens blue litmus paper.

On burning magnesium wire a very vivid light and a white powder of magnesium oxide are produced. On bringing ammonia vapours into contact with those of hydrochloric acid white fumes of ammonium chloride are produced.

These are all chemical phenomena.

Now that we have seen how substances are modified and transformed in many various ways we will endeavour to understand their constitution more exactly in order to be able to explain all these phenomena and many others, by passing from the more simple to the more complex.

Are substances formed of a continuous, uninterrupted mass, or are they constituted of many particles, which unite in various forms? Chemistry and physics have answered this question by rejecting the first hypothesis and accepting the second, because by its means chemical phenomena are more easily explained, and reasons are found for the expansibility and elasticity of bodies, and for the diffusion of gases which cannot be explained on the hypothesis of continuous matter.

Matter, then, must be considered as an aggregation of very small particles, extremely close together, but entirely distinct from one another. The finest particles of the most impalpable powder are enormously larger than those imagined in physics and chemistry.

A very simple experiment which will give an approximate idea of the smallness of these chemical particles is the following: 1 mgm. of Rhodamine Extra (a red artificial dyestuff) is dissolved in a few c.c. of alcohol and then poured into a bottle containing 10 litres of water, which is coloured red in a very evident manner. If we take a drop of this liquid, or, to be more exact, one milligramme, and observe it microscopically under a magnification of 1000 diameters we find that it is still coloured red, but that there is no differentiation into coloured and colourless particles. Now 10 litres of water, that is, 10,000,000 mgms., contain 0·001 grms. of rhodamine, so that each milligramme of the solution contains $\frac{0{\cdot}001}{10{,}000{,}000}$, that is, 0·000,000,000,1 grm. of rhodamine (one ten-thousand-millionth of a gramme).

But if this solution is diluted 1000 times, that is, 1 c.c. diluted to one litre, and if a glass tube some metres long is then filled with the liquid, then on illuminating the solution and looking through some depth of it, it will still appear to be homogeneously coloured,

and if each milligramme of this new solution contains at least one particle of dyestuff this will weigh less than 0·000,000,000,000,1 gramme, that is, less than one ten-billionth of a gramme. We may also confirm this result in another manner: If we take one milligramme of concentrated attar of roses, dissolve it in a little alcohol or ether, pour it over a strip of filter-paper placed on a warm plate and move about the room, this will be perfumed with the essence in a few minutes. If we take a large room of a capacity of 3000 cubic metres (35 × 12 × 7 metres), this is 3,000,000 litres, that is, 3,000,000,000 c.c. or three billion (3,000,000,000,000) cu. mm., which together contain one milligramme of the perfume; thus 1 cu. mm. contains $\frac{0{\cdot}001}{3{,}000{,}000{,}000{,}000}$, that is, ·000,000,000,000,000,333 grms. of perfume, so that each particle of attar of roses will certainly weigh less than one-third of a thousand-billionth of a gramme. In this case the sense of smell is more sensitive than that of sight in the case of coloured solutions.

In 1905, by illuminating solutions of fluorescein with a powerful electric arc, Spring deduced that the weight of the atom of hydrogen must be less than $2{\cdot}5 \times 10^{-21}$ grms.

It is precisely with these hypothetical infinitesimal particles that chemistry is concerned, and these are the particles which we will study in the various aspects which they present to us, in their most interesting properties, forming a marvellous world, regulated by positive and eternal laws.

THE CONSERVATION OF ENERGY

The principle of the conservation of energy, or equivalence of the various forms of energy, is the *first law of thermodynamics*. We have mechanical *energy* (of distance, volume, surface, and movement), and *non-mechanical energy* (chemical, thermal, electric, and radiant energy, &c.).

The value of each form of energy, as we have already seen in the case of chemical energy, is always expressed by the product of the factors of intensity and of capacity; mechanical energy is expressed by the product of mass and velocity $\left(\frac{m v^2}{2}\right.$ or *kinetic energy*$\left.\right)$; in the case of thermal energy the factor of capacity is measured by the quantity of heat expressed in calories and the factor of intensity (or thermal potential) by the temperature; for energy of distance the factors are the distance in metres and the force in kilogramme-metres; for energy of volume we have volume and pressure, &c.

For each form of energy the equivalent in other forms has been established; thus we have the mechanical equivalent of heat, the electrical equivalent of mechanical energy and of heat, &c.

In many practical cases we are able to follow the equivalent transformation of the various forms of energy, but especially in the case of mechanical energy, which is present in the two reversible forms of potential energy and kinetic energy; the first is dependent on the position occupied by a body, and when its position is changed this energy is converted into kinetic energy.

If, for example, a heavy object is on the ground and we wish to raise it to a height of one metre by placing it on a support, we must perform a certain amount of work. But this work is not lost, but passes into, or accumulates in, the raised body in that form of energy which we call potential energy. We may soon prove that this energy is not lost by connecting the heavy body by means of a wire with another body of equal weight, and passing the wire over an ideal frictionless pulley, also avoiding the friction of the air. On removing the support of the upper body a minimal impulse causes the upper body to descend, but in descending it carries the lower body upwards by the pull on the wire. The first body has lost potential energy, which is transformed into energy of motion, that is, kinetic energy, which has served to raise exactly the same weight as had previously been raised by our hands. Thus we see that work has been performed by transformation of energy, which energy has not been lost but has been transformed from potential energy, that is, energy of position, into actual or kinetic energy (energy of motion).

Examples of potential energy and of its transformation into kinetic energy are very abundant.

The movement and position of the planetary systems are the most perfect examples of continuous and incessant transformation of potential and kinetic energy. A large meteorite falling and giving up all its potential energy will acquire such a velocity that on reaching the earth's surface it will collide with it in a formidable and disastrous manner. This does not ordinarily happen, because a part of the energy is given up to the atmosphere through which the meteorite is obliged to pass, with a large amount of friction, before reaching the earth's surface, and a large part of the potential energy is thus transformed into thermal energy and reduces the velocity, so that the meteorite is heated and becomes red-hot. Even the hail which forms at high altitudes would be broken by the more resistant roofs of the houses on which it falls if it did not impart some of its energy to the atmosphere. The potential energy of falling water produces kinetic energy in a useful and evident manner on passing between the blades of a turbine.

But in the small world of the chemical particles the cases of potential energy are extraordinarily impressive, because in chemical systems enormous quantities of potential energy, or energy of position, take part.

If the configuration of our hypothetical system of chemical particles constituting a given substance is modified and the particles change their position, giving rise to another system (another substance), when, in short, the particles at any given point under certain conditions approach one another in such a manner as to form a new substance, then the amount of potential energy which is transformed into kinetic energy is so large and powerful as to astonish the most fantastic thinker.

The particles of hydrogen gas have a velocity of about two kilometres per second, and when they approach those of oxygen under certain external influences—impelled by their great velocity—in such a manner as to attract and combine with them, the potential energy is transformed into kinetic energy giving rise to heat, light, and detonation, with formation of water, a new substance. (*Translator's note.*—The kinetic energy due to the velocity of the hydrogen and oxygen molecules is quite distinct from their potential chemical energy, which is evidenced in the combination.)

A few grammes of dynamite or nitroglycerine enclosed in the interior of a rock, in changing the position of their particles during a chemical reaction produce such a quantity of kinetic energy that the most resistant rock is shattered ; in a few seconds an amount of work is accomplished which hundreds of workmen could not achieve in twenty-four hours.

Kinetic energy is of much interest to us, especially in its various transformations.

Matter, which we consider as divided into very small particles, manifests itself to us by means of its energy, which may be explained as an oscillatory movement of these particles, in the form of continuous, uninterrupted attractions and repulsions, which reach our senses in the form of vibrations transmitted by the ether, which is extremely attenuated and imponderable, and fills the entire universe.[1]

Let us suppose for a moment, with Crookes, a long thin plate of steel, fixed in the middle of a dark room ; on causing the plate to oscillate gently all its particles will vibrate,

[1] In order to explain chemical phenomena, matter has been imagined to be divided into very minute particles having a definite weight and volume. In order to explain certain physical phenomena scientists have had to make use of a hypothetical substance very much less dense than the chemical particles, so much so as to be imponderable, a substance which extends throughout the universe and penetrates all bodies, including the walls of glass vessels, &c. This substance is called the *vibratory ether* or *cosmic ether*, and is the medium by means of which the more important physical phenomena, light, electricity, &c., are manifested. When one remembers that solar light reaches us through space with a velocity of 300,000 kilometres per second, traversing regions where there is no air or other ponderable matter, it would be impossible to imagine such a rapid transmission without supposing the existence of the vibratory ether, diffused throughout the universe and penetrating all bodies and all space. (*See below :* Unity of Energy and Matter.)

Sound is transmitted by the vibrations of the air, and if an electric bell is placed under an evacuated receiver the sound no longer reaches our ear, whilst, on the contrary, the light of an electric lamp under the same evacuated receiver reaches our eye. The transmission of the light cannot be comprehended, except by the hypothesis of the cosmic ether. Previous to this hypothesis it was supposed that the propagation of heat was due to the detachment and expulsion of minute particles from the hot object, and that heat was in fact a sort of material, as was believed by Laplace (1749–1827) ; this notion caused great confusion in chemistry and physics, and retarded progress. In 1758 Le Sage had ventured the hypothesis that heat was due to rapid vibrations of small particles of matter, as had previously been imagined by Bacon (1600). In 1799 B. Thomson (Count Rumford) considered heat to be a form of motion, and already ascertained with certainty that heat did not affect the weight of bodies. In 1800 Nicholson further defined the hypothesis of heat, attributing it to the vibration of the particles of matter

and if these vibrations exceed sixteen per second we will observe a slight note ; as the vibrations are gradually increased in frequency up to 40,000 per second, we will ascend the scale of all notes from the lowest to the highest and shrillest ; we have thus obtained energy of sound. If the number of vibrations is further increased they are no longer perceived by the ear, but on approaching the plate with the hand it will be observed that it is warm ; we are obtaining thermal energy. If the frequency increases still further the temperature rises, and when the vibrations have attained a frequency of 400 billions per second the plate becomes red-hot and gradually more luminous ; we have now luminous energy. If the frequency of the vibrations exceeds 800 billions per second our eyes are no longer able to perceive them, but if a photographic plate containing silver salts is exposed to these rays, it is affected ; we have reached chemical energy, and by proceeding further it is theoretically possible to arrive at electrical energy, &c.

The transformations of kinetic energy are to-day of the greatest importance, and we see every day thousands of practical examples of the manner in which it may pass from one form to another.

Another experiment which gives some idea of the transformation of mechanical energy into thermal and luminous energy is the following: On throwing a piece of sodium into water it floats and travels rapidly over the surface, developing hydrogen gas, but if a piece of filter-paper is placed on the surface of the water and the sodium is placed on this, its motion is prevented ; the energy produced, which was in the previous case manifested as energy of motion, is now transformed into thermal energy, and the sodium is heated and catches fire, giving a luminous flame and then an explosion On striking a match the mechanical energy is transformed into thermal energy and the match is lit, transforming thermal and chemical energy into luminous energy.

But we are able to observe the most beautiful and marvellous examples of the transformations and indestructibility of energy every day in the case of the solar heat. This inexhaustible source of energy, which is given off by the sun without sensible diminution, is not lost. The heat which reaches the earth and is distributed over seas and continents, causing temperature disturbances at various points, also creates the aerial currents of the terrestrial atmosphere, and the energy thus formed is utilised in the sails of ships and of windmills. This beneficent heat also evaporates the water of seas, lakes, and rivers, transporting the water particles to greater altitudes and thus accumulating potential energy, which is again liberated when the vapour condenses to form rain or snow, and then descends in watercourses from higher to lower regions and the sea, returning the potential energy to nature in the form of mechanical, electrical, and thermal energy, moving the wheels of mills and turbines, which actuate dynamos giving motion, light, heat, and electricity in such a manner that the balance of nature is uninterruptedly maintained. This extends to all life, mineral, vegetable, and animal, in a marvellous harmony of simple and complicated transformations, to the nutrition of plants and animals, to human vitality, to that of the thinker and the genius.

In the entire universe, whatever changes it is undergoing, has undergone, or will undergo n the future, there will always at each instant be found exactly the same unaltered sum of kinetic and potential energy. Helmholtz calculated that of the potential and mechanical energy which originally existed in our own solar system only the four hundred and fifty-fourth part still remains, the rest having been dispersed and transformed into heat, light, &c., during the passage from the nebulous stage to that of consistent nuclei ; but none of this energy is lost to the universe.

which were the more intense and rapid the higher the temperature. The undulatory theory had already been upheld by Hooke (1650), Huyghens, and Euler (1707–1783) in order to explain luminous phenomena ; but until 1800 the opposite theory of Newton, that is, the emanation theory, was generally upheld. In 1810 Davy himself had accepted Rumford's theory of heat, but in the case of light he declared himself a follower of Newton's hypothesis of emission (1642–1727). In the meantime T. Young and Wollaston found themselves obliged to abandon the emission theory ; but Fresnel was first able to show that the emission theory was erroneous by replacing it by his own very brilliant hypothesis, which more satisfactorily explained these important physical phenomena, namely, the hypothesis of a continuous elastic medium which penetrated all bodies and the entire universe. Poisson (1781–1840) gave concrete and rigorous form to this hypothesis, imagining the elastic medium to be composed of very small ethereal particles, vibrating intensely, by which means he was able to explain, and mathematically demonstrate, many physical phenomena which were otherwise inexplicable. Afterwards it was possible for Clausius (1857) to mathematically lay the foundation of his brilliant mechanical theory of heat. It is convenient to record here that to-day, after further study of electrical phenomena, the idea of an ether subdivided into minimal particles has been abandoned, that is, the theory of its discontinuity is now excluded ; the study of cathode rays and of radio-activity has led to a species of return to the theory of material emanation, which has not yet found a clear explanation, by the general laws accepted to-day.

However, it is not possible to suppose a complete inversion of the process of transformation of kinetic into thermal energy, because of the *degradation* which accompanies this change, that is, the impossibility of reconverting the entire thermal energy into kinetic energy on account of the fact that part of the heat remains inherent in matter.

In fact, if all the absolute heat of bodies were converted into motion one would arrive at matter deprived of heat and energy, which is unattainable and absurd because it is impossible to imagine matter without energy, as this would be equivalent to the disappearance of that matter. This explains the constant evolution which forces the entire universe to always form itself anew ; retrogression in nature is absurd ; thus we are unavoidably impelled towards ever more various transformations, towards continuous evolution.

We are able to apply with mathematical rigour this first law of thermodynamics or the equivalence of the various forms of energy, in order to demonstrate the practical impossibility of perpetual motion (*perpetuum mobile*). If we follow the cycle of changes produced in any material system by the displacement of energy (addition or subtraction of heat) in such a manner as to return to the starting conditions, we will find that the work (A) produced by the system during the cycle will be proportional to the quantities of heat (W) imparted to the system, that is $A = J.W$, where J represents the factor of proportionality or the mechanical equivalent of heat (*see below*), and is independent of the nature of the system under consideration. With any change in the system the following changes of energy are connected : absorption or development of a certain quantity of heat, production of positive or negative work, and increase or diminution of the total amount of energy in the system. If dQ be the quantity of heat imparted, dU the portion of that heat which performs internal work and causes rise of temperature, and $J.dL$ that portion of the heat which is transformed into external work, dL, by increase of the volume or by overcoming pressure, then from the equivalence of heat and energy the mathematical expression of the first law of thermodynamics will be :

$$dQ = dU + J.dL$$

If U be the total quantity of energy contained in the original system, then the system will be modified if we subtract a given quantity of energy, say, $U - U_1$; and we will be able to return to the original system by restoring to the second system the exact quantity of energy ($U - U_1$) which it had lost ; if a lesser quantity of energy suffices for this restoration, then by continuing this process in one sense or the other we would arrive at a creation of energy or perpetual motion.

The quantity of energy yielded up in the passage from the one state to the other is rigorously determined by the difference in the energy contained by the two systems ; thus we cannot create energy without a corresponding amount of energy disappearing ; the transformation of one form of energy into another occurs in each case according to a well-determined numerical relationship ; and more especially in all cases a given amount of work is produced by means of heat, causing the latter to disappear, and inversely if work is transformed into heat.

This law of the conservation of energy was intuitively propounded in various branches of science in past centuries, by Galileo, Newton, Bernouilli, Rumford, and Davy, but was only enunciated in a precise manner by the Swabian medical man, Julius Robert Mayer, in 1842, whilst in 1847 Hermann v. Helmholtz, in his celebrated article on "The Conservation of Energy," collected all the evidence of general importance and applied it to all known phenomena ; the rigorous, quantitative experimental evidence was given by Joule in 1850, in his immortal researches on the mechanical equivalent of heat.

Not all the energy possessed by a system can be transformed, but only a part of it, called the free energy, which is utilisable, and to which the first law of thermodynamics refers ; the energy of motion, external work, &c., of a system may be transformed into other forms of energy, for example, into heat, but the thermal energy cannot be completely retransformed into work. Later, in discussing the second law of thermodynamics, we will study the limitations of the convertibility of one form of energy into another.

In the study of the transformations of energy, the law of the conservation of mass or of weight (or law of the conservation of, or indestructibility of matter as it was formerly less correctly called) is of special importance in chemistry.

Mass is one of the invariable properties of bodies, in virtue of which these bodies acquire

a definite velocity under the influence of a definite quantity of kinetic energy. If two objects of the same nature but of different size, that is, containing different quantities of mass, move with the same velocity, they contain varying amounts of kinetic energy which are proportional to their masses, and, in general, the quantity of energy in a moving body is equal to the product of the mass and the square of the velocity. The mass of a body is simply its capacity for kinetic energy. A projectile with a mass of 8 kilos thrown with a velocity of 400 metres per minute produces the same effect (shock) on an impenetrable target as one four times smaller (2 kilos) with double the velocity (800 metres) for

$$8 \times 400^2 = 2 \times 800^2.$$

Mass is measured by taking as unit the mass of 1 c.c. of distilled water at a temperature of 4° and at 760 mm. pressure. But this unit of mass is also the unit of weight, as the mass of a body is proportional to its weight ; it is called a *gramme*. Various bodies which have the same weight acquire equal velocities under the impulse of equal amounts of energy, that is, they have also the same mass. And for this reason the two words are commonly used interchangeably, and for ordinary purposes mass and weight are equivalent words.

More precisely the weight of a body is simply the force with which it tends to approach the centre of the earth, and as the earth is not a perfect sphere, and its movement does not take place equally in every direction, the weight of a given body varies with the latitude and with the altitude, whilst its mass remains unaltered. But this variation of weight occurs to an equal extent for all bodies placed under the same conditions, so that actually two different bodies which are equal in weight at any given point on the earth will still be of equal weight at any other point.

A century ago, before the classical researches of Lavoisier, who brought the balance into general use for the study of chemical phenomena, it was believed (and is still believed to-day by some ignorant people) that in certain cases matter is partially lost or consumed during its changes. A candle, a piece of wood or paper, &c., appear to continuously diminish in weight when burning until nothing finally remains but a very little ash ; from which it is supposed that the candle, wood, and paper are destroyed. In reality not only is the mass of these substances not destroyed during combustion, but if all the gaseous products of combustion are collected it is found that these weigh more than the combustible substance itself, because the materials of which the wood, candle, paper, &c., are composed have combined with the oxygen of the air, in the absence of which combustion does not occur. If we actually place on one pan of a balance a candle and a glass tube filled with caustic soda so arranged as to collect the products of combustion, then, on balancing these with weights in the other pan and lighting the candle, the pan containing this latter will gradually descend as the candle burns, demonstrating and confirming the increase of weight. An opposite impression to the apparent one produced by the burning candle is obtained by burning a very small amount of black gunpowder, which forms an enormous volume of smoke, giving the appearance of a true increase in the mass. On heating mercury sulphocyanide (Pharaoh's serpents) a large increase of volume takes place which gives rise to the illusion of a large increase in the amount of material, but in reality, with the balance, it can be shown that the gain is only apparent. A very minute turnip or beetroot seed buried in the earth reappears after some months in the form of a very large tuber, sometimes 500,000 times larger and heavier, some seeds weighing some centigrammes giving tubers weighing five or six kilos. But in this case also the weight and volume have been gained by the abstraction of various substances from the earth and the air.

Also among the more complex phenomena of physiology, all based on chemical and physical reactions, we meet again with the true indestructibility of mass. By weighing the materials excreted and food absorbed by any vegetable or plant whatever, we find that nothing is lost and that the part which is not assimilated is all found in the excretions of the organism. The vital phenomena of both animals and plants, from the most complex, such as those connected with human vitality, in which a man consumes about one-fiftieth of his weight in food daily, down to the most simple, such as those connected with the most elementary types of living beings, such as amœba or certain micro-organisms composed of one cell or of a few cells, which are able to consume up to three hundred times their own weight of food per day with prodigious reproductive powers, a bacterium being able to generate thousands and millions of similar organisms in a few hours, all these vital

phenomena are based on continuous chemical transformations, and these are always founded on the absolute indestructibility of matter.

In all the immense universe, in the infinite transformations which matter continually undergoes, not a single particle is lost, and a few grammes of matter will exist unchanged in the universe a million years later, and will weigh exactly as much to-day as they have weighed for a million years.[1]

HISTORY OF CHEMISTRY

Now that we have sought to explain by rational hypotheses the essence of Nature in her various forms and transformations, we will glance at past ages in order to gradually follow the investigations of our predecessors on this important question. We will thus have an idea of the development of human thought in the interpretation of nature and of the principal phenomena which affect the human senses, in order to then give an explanation of the manner in which the rational conceptions of modern chemical science arose.

THE EARLIEST CIVILISATION. We will turn backwards in the story of mankind, back to the commencement of historic documents and positive descriptions, and stop when the ancient legends no longer permit true history to become apparent. We will go beyond the Middle Ages, the Roman epoch, that of ancient Greece, 500 years B.C., and further back still to the first Egyptian civilisation. . . . But even then we must in fairness and justice pass beyond this to the ancient Chinese civilisation and the Assyrio-Babylonian civilisation, to a civilisation which is irrefutably recorded, and which would have been still greater if, for their warlike and religious undertakings, the rulers had thought fit to demand conscientious and honest scientists.

Whilst in the rest of the world barbarism was still supreme, in China, 3000 years B.C. and in Assyria and Babylonia 5000 years B.C., there was already a civilisation much superior to that of the other nations who were still groping in the primitive chaos of the rudimentary formation of human organisations. Agriculture flourished, and industry, which even many centuries later was in its infancy in other continents, had risen to important development in these parts of Asia.

We stand astonished before the art of our greatest artists, before the pictures of the period of Giotto and the Byzantine epoch ; but what shall we say of the truly admirable works of art which the yellow man produced 2000 and 3000 years previously ?

When we admire the very beautiful works of Michelangelo, who reproduced nature so ably and studied plastic anatomy by dissecting parts of animals and plants in order to study them more closely, what shall we say of the surprising reproductions in pictures, sculptures, and carvings made by Chinese about 2000 years previously and by the most ancient Egyptians 4000 years before ?

Faithful and marvellously exact reproductions of nature alive and dead on linen, bronze, in copper, stone, and silk, and with such harmonious and simple artistic feeling that they are capable of inspiring the artists of to-day ! Already 1000 years B.C. the walls of the Chinese palaces were painted and decorated ; and 200 years B C. the art of portrait painting flourished.

Whilst the powerful Romans in their frenzied luxury, which led to corruption of their morals and total decadence, used rich silken fabrics imported from Asia, in China the

[1] The law of the conservation of mass has not found any exceptions, and all the exact sciences accept as an undiscussed axiom the results of a century of varied researches and innumerable experiments. All the same, the experimental control of a law of such importance is always interesting, just as much so to-day, when science has at its disposal such perfect and rigorous apparatus, as in times past, from Lavoisier until now. Landolt and Heydweiller took up this question (1893, 1900, 1905) with the most exact experiments requiring a large amount of work. In two arms of a U-tube they placed two mutually reactive substances ; the tube was then sealed in the blowpipe and the whole weighed on a most exact balance (weighing to 0·03 mgrm.) ; after agitating and mixing the two substances, and when the chemical reaction was completed, the whole apparatus was reweighed. Of seventy-five reactions, produced with hundreds of grammes of materials, sixty-one showed a very slight diminution of weight, which in the case of silver sulphate and ferrous sulphate rose to 0·3 mgms. per 100 grms. of silver. It has been argued from these facts that in the shock of the atoms producing the new chemical reaction minimal traces are split off from these atoms (they appear not to be electrons—*see* Electrons *below*) and are dispersed by passing through the walls of the glass vessel. As a matter of fact, on coating the walls of the reaction chamber with paraffin the diminution of weight disappeared, even in the case of ferrous and silver sulphates. In the last series of experiments carried out by Landolt until 1908 the small differences previously observed are explained ; the small diminutions in weight are also obtained before the reaction if the substances are heated up to the temperature of reaction before they are mixed.

manipulation of silk was already well understood 2200 years B.C. under the Ju dynasty, and was in fact rapidly approaching perfection. Only 150 years B.C. the daughter of a Chinese emperor introduced silk manufacture into Japan, and from there it slowly extended throughout Asia; only in the third century of our era was it imported into Italy, and the culture of the silkworm only commenced in that country in the year 600.[1]

The manufacture of paper only commenced to be known in Europe at about A.D. 1200 whilst in China paper made from hemp and bamboo fibre was already known in 360 B.C. and in 105 B.C. a Chinese, Tsai-lun, taught the manufacture of paper from silk and linen rags.

Gunpowder, which was first used in Europe about A.D. 1200, was prepared in various ways in China many years before the Christian era, and was introduced into Europe by the Arabs.

The Chinese were real adepts in the smelting of minerals and of bronze 1800 years B.C. In the Imperial Museum in Pekin there are collected the historic treasures of the Chang dynasty (1766 B.C.) which testify to the delicacy and perfection of the sculpture and carving, equal, if not superior, to the best art of Greece and Tuscany; our modern Western civilisation, in its comparatively recent vandalic invasion of the City of Heaven, might at least have refrained from laying its hands on these artistic and historic treasures.

The working of wood and leather and the preparation of varnishes are also extremely old in China. The production of porcelain, which dates from the eighteenth century in Europe, was already known in China ten centuries previously.

But the Chinese have precedence not only in ancient, but also in comparatively modern, chemistry. We admire Priestley, who discovered and isolated the important element oxygen in 1774, and we admire the work of the celebrated Lavoisier and of Cavendish in connection with the discovery of the composition of water in or about the year 1783, but it has now been shown by Duckworth (*Chem. News*, 53, 1887, p. 250) that the Chinese knew of oxygen and the composition of water much earlier than Priestley and Lavoisier.

The Chinese were very well aware of the hygienic and domestic importance of water, and were the first, already in very remote historic times, to drill numerous wells of the kind now known as artesian wells in order to obtain good water from the subsoil, whilst even to-day many Italian towns and country places are without potable water.

Even in their philosophic disquisitions on the essence of nature and of the universe we find amongst this people ideas and conceptions inspired by very pure justice and morals; conceptions much clearer than those of the Greek philosophers who lived several centuries later. When Confucius, the founder of the philosophic religion of China, conceived the essence of nature to be "matter inseparably united to a virtue of matter itself, and to the continuous interchange of matter and of this virtue" he had realised the origin, essence, and rule of life.

EGYPTIAN CIVILISATION. After that of the Chinese the oldest civilisation is that of the Egyptians, especially in reference to the origin of chemistry and to the large number of experimental observations made and ingeniously utilised in order to increase the comforts of life. During the last ten years important discoveries have been made on the ancient Egyptian civilisation which show that even 4000 years B.C. it had in many points almost excelled the civilisation of China.

If we turn to the works of art of this period (even 2000 B.C.) we find that the Egyptians knew how to prepare various metals and alloys; they were well acquainted with dyeing, glass manufacture, and also the preparation and employment of pharmaceutical products and antiseptics.

Chemistry was considered a sacred art; it was exercised by priests and was only accessible to the elect. The temples were connected with laboratories in which every kind of chemical operation was conducted.

Even the origin of the name "chemistry," now so much discussed and debated, must almost certainly be sought in the name which the Egyptians gave to their country, Chemia,

[1] The Chinese were well acquainted with the dyeing of fabrics. The use of indigo also originated with the old Chinese civilisation, as the indigo-blue fabrics found in Europe, even at the time of the decadence of Rome, all came from the East; this was proved by an analysis of the remains of the mantle of St. Ambrose by Prof. Frapoli (1872) and by Prof. Carnelutti (1884) at the Society for the Encouragement of Arts and Manufactures of Milan.

on account of the black colour of the soil (they called the pupil of the eye by the same name). Therefore the first ideas of chemistry in Europe came from Egypt, imported by the Greeks and Romans, and later by the Arabs, so that it is probable that by "chemistry" they understood the science and art of the country of the Egyptians (Chemia).[1]

The Egyptians were fully aware of the putrefactive action of the air on corpses, and, therefore, preserved their dead out of contact with the air. Everybody knows how the Egyptian mummies have been preserved unaltered down to our own times.

The Egyptians were the first to construct wells lined with masonry in order to obtain good and wholesome water, whilst the other early peoples made use of the water of springs or tanks (except the Chinese, who already used artesian wells).

All the objects of art of the early Egyptians (statues, ornaments, temples, &c.) in wood or stone, were painted in various colours. Paintings produced 1600 B.C. show distinctly the use of fifteen different colours. White paint was prepared from gypsum mixed with white of egg or honey; yellow was obtained with natural arsenic sulphide or ochre, red with ochre or cinnabar, blue with lapis lazuli (an aqueous phosphate of aluminium, magnesium and ferrous iron) or with powdered copper sulphate, black with animal charcoal; a little gum tragacanth was added to the water used in mixing these colours.

The art of design in Egypt dates from prehistoric times. It became bizarre because it did not consider the perspective of the human body. It is found that in design, as a general rule the legs and feet are drawn from the side, the bust from the front, the head in profile, and the eye from the front. The manufacture of glass vessels among the ancient Egyptians was very noteworthy. They knew and used soda, potash, alum, nitre, iron, copper, tin, lead, gold, and silver.

The scientific activity of the Egyptians was concentrated in Alexandria, which was the most important city in the world apart from Rome. In Alexandria the best scientific and philosophical institutions existed together with the world's largest library, containing 700,000 volumes; but this was completely destroyed in the year 641 after the Arab invasion.

INDIAN AND GREEK CIVILISATION. The Egyptian civilisation was closely connected with that of the Greeks, who obtained much of their knowledge of nature and philosophy from Egypt. We will only refer to those matters related to the history of chemistry.

But for the sake of historic accuracy it is well to remark that the fundamental conceptions on the nature of the universe, attributed by almost all historians to the first Greek philosophers, have their real origin in India. The Indian civilisation was in some of its manifestations, especially in the realm of art, superior to that of Egypt. It is maintained in various Indian writings that the whole world is composed of four elements, water, earth, wind, and fire, and that everything is produced by their union; to these the philosophy of the sect of the Djainas added a fifth element, the ether, whilst Buddha (623–543 B.C.) introduced a sixth, namely, consciousness; the Buddhists believed in Nirvana, that is, the end of all beings and return to nullity, to universal emptiness, to unformed nature, and forestalling Schopenhauer and many modern positivists they confusedly denied the existence of matter, maintaining that everything which exists is nothing more than a collection of subjective impressions.

In the Greek civilisation we find, 600 years B.C., Thales, one of the seven wise men of Greece, a contemporary of Solon, who considered the whole of the universe to be derived from one single substance, water. Very soon afterwards we have Anaximenes, who considered air to be the primary material, with the property of infinite movement; Heraclitus (500 B.C.) maintained and pretended to demonstrate that the essence and origin of nature was *fire*. Anaxagoras (500 B.C.), on the contrary, believed that nature was formed from a single, continuous, and uninterrupted material, infinitely divisible without any interspace (the hypothesis of *homeomeria*), and not endowed with a movement of its own, but with movements imparted to it by an immaterial, supernatural intelligence.

All these are vague rudimentary conceptions of the unity of matter to which, after many

[1] The word "chimica" was already used in writing in the time of Constantine the Great (A.D. 325) in a book of Julius Firmicus Maternus, a writer of that epoch, in which, writing on astronomy, he declares that the position of the moon, relatively to a given planet, influences the fate of those born at the time, and thus when the moon is near Saturn those born at that time are destined to study "chemistry." But it can be safely maintained that the word chemistry was well known to the Emperor Diocletian (A.D. 300), who stated with pride that he had caused to be burnt all the Egyptian books which spoke of the chemistry of gold and silver.

centuries, we try to return to-day encouraged by the latest deductions of positive science.

About the year 430 B.C. a more brilliant philosopher, Leucippus (born at Elea), disheartened by the "numbers" and obscure philosophy of Pythagoras and the sophisms of his master Zeno, devoted himself to the study of nature. By considering the already preconceived ideas, he came to the conclusion that the universe is infinite and that the filled, ponderable part of it is composed of extremely small particles or imperceptible atoms of determinate form varying from substance to substance; these infinitely numerous atoms move in empty space, collide with one another and occasionally unite with similar atoms.

We have here the real origin of the atomic theory, the foundation of modern chemistry, which remained buried for about twenty-four centuries.

After the death of Leucippus he was followed by Democritus (born about 400 B.C.) whose memory will last in the history of philosophy. He continued to teach the opinions of his master on the essential character of nature, adding that all the atoms are composed of a single substance, differing only in their form, by means of which they give rise to the various bodies and to their properties. He taught also that the atoms are endowed with continuous motion, and that matter is eternal.

The only followers of Democritus were Epicurus, 350 B.C., and Lucretius, 90 B.C. It seems incomprehensible to-day that such a brilliant hypothesis should have been disregarded for so many centuries, as it contributed so largely later to the formation of modern chemical theory.

A philosopher of Sicilian origin (from Agrigentum) but who had lived for long in Greece, named Empedocles (490–430 B.C.) united to a brilliant intelligence the most impudent quackery, arrogating to himself almost Divine qualities. He believed in the atomistic theory in order to explain the intimate nature of matter, but maintained on the other hand that matter manifests itself to us through four fundamental elements, namely, water, air (that is, the "wind" of the East Indians), fire, and earth. This subdivision, which lasted through many centuries, is certainly much less brilliant than the theories of Leucippus and Democritus, and was evidently taken from the Indian philosophers.

Then comes Aristotle (380–322 B.C.), a pupil of Plato, to whom many historians erroneously attribute the theory of Empedocles on the four elements. Whilst Aristotle had undoubtedly brilliant conceptions in abstract philosophy, since he dared to affirm for the first time that the human mind is like a blank tablet on which experience writes that which is perceived by the senses, in the observation of natural phenomena on the other hand, he increased the confusion due to Empedocles, and starting from the manifestations of the four elements, he deduced four essences of nature, namely, heat, cold, humidity, and dryness. According to him, water was composed of cold and humidity; earth of cold and dryness; air of heat and humidity; and fire of heat and dryness. As these four elements were insufficient to explain all natural phenomena, he imagined a fifth of a superior order, which he called the fifth essence (*quinta essenza*), which was, however, of an ethereal character, more or less spiritual and diffused through the universe. Here also we find an adaptation from the Indian philosophy. We owe to Aristotle the first attempts to apply the experimental method in science. Wishing to discover whether air possessed weight, he placed an inflated bladder on the balance and then deflated it. As he found no difference in weight, after deflation, he concluded that air had no weight. Continuing his studies on the nature of air he was led to deny the possibility of a vacuum, and the aphorism, "Nature abhors a vacuum" is due to Aristotle. This idea was maintained for many centuries until the time of Galileo.

In the time of the Greeks seven metals were already well known: gold, silver, copper, iron, lead, and tin; and the treatment of various ores was also known. Dioscorides (A.D. 50) prepared mercury from cinnabar.

ROMAN CIVILISATION. The evolution of experimental methods as applied to science received a great impulse from Archimedes (280 B.C.), who by measuring specific gravity was able to determine how much silver was contained in the crown of King Hiero. This same Archimedes fell a victim to the Roman soldiers, more eager for booty than for science. Roman civilisation had little influence on the progress of chemical knowledge and the study of nature. Civil legislation, art, and the desire for conquest and warlike rapine did not leave much time for such studies, but we may recall the marvellous and

colossal hydraulic works of the Romans which furnished Rome with abundant supplies of good water. Rome had fifteen aqueducts, and the three which remain to-day alone suffice to supply water to the whole of the city. From this one sees that water was then used abundantly for baths and other purposes.

We must also note Pliny, born at Como A.D. 23, who died in the year 79, in the neighbourhood of Vesuvius during the famous eruption which buried Pompeii. He collected, in a species of enclycopædia of thirty-seven volumes, which has survived to our times, the "Historia Naturalis," all the natural knowledge which existed at his epoch, and in this work, often confused and contradictory, many facts were assembled without control, but purely for reference, which are a valuable record of the chemical knowledge of the time.

At the time of Pliny chemical theory was still based on the four Aristotelian properties of matter, and Pliny himself stated in all sincerity and certainty that rock crystal was nothing else than powerfully frozen water, frozen much more than ice. According to Pliny cold had the natural property of solidifying and hardening. Pliny indicates in his *Historia Naturalis* that the air forms clouds—that these are changed into water, and that this is again transformed into air by evaporation.

For many centuries afterwards chemistry remained under the domination of the Aristotelian conceptions. These conceptions on the transformations of matter gave rise to the belief of the possible transformation of other metals into the noble metals ; and thus the chemistry of the Middle Ages became a sort of magical speculation, and was limited to attempts to manufacture gold from other metals.

ARAB CIVILISATION. Egypt gave a strong impulse to the development of chemistry and of philosophy. It was from Egypt that chemical science was rapidly diffused by means of the Arabs. The Arabs invaded Egypt in 640, conquered the whole of North Africa, and finally even Spain. They continued researches for the manufacture of gold and silver. The word *chimica*, which they found in Egypt, was by them modified by adding the Arab definite article, and they thus formed the word "alchimia" (alchemy).

The greatest and most famous Arab alchemist was Gebir, whose fame was universal and whose writings were generally consulted and afterwards translated into Latin. He lived about A.D. 800, and being a follower of the principles of Aristotle, he undertook a series of chemical experiments in order to discover the preparation of gold. He also described in detail furnaces, retorts, and much other apparatus. He succeeded in purifying many substances by means of solution, crystallisation, filtration, distillation, and sublimation. He was acquainted with alum, green iron vitriol, saltpetre, and sal ammoniac. He describes for the first time nitric acid and aqua regia ; he prepared many derivatives of mercury, and it is not impossible that he already knew of sulphuric acid.

Starting from the Grecian philosophy and whilst investigating the possibility of preparing gold from other metals, Gebir propounded a new chemical theory, according to which all the metals always contained two substances in variable proportions according to their nature. He believed these two substances to be mercury and sulphur. The first of these produces fusibility, ductility, and the metallic lustre ; sulphur, on the other hand, produces the various modifications which the metals undergo when heated. By varying the proportions of these two elements, we should be able to pass from one metal to another. Gold and silver, according to Gebir, contain much mercury ; therefore they are very lustrous ; but gold also contains yellow sulphur, whilst silver contains white sulphur.

This phase of chemistry, called alchemy, lasted until the thirteenth century under the influence of the Arabs, and then extended rapidly from Spain throughout Europe ; thus we find Lull in Spain in 1200 ; Villanova in France in 1300 ; Magnus in Germany in 1250, and Thomas of Aquinas (the saint) in Italy in 1250—for he also was an alchemist and studied many minerals.

The alchemists of this period are represented with long hair and a beard, as persons clothed in ample vestments and locked up in impenetrable laboratories, completely intent and absorbed in the search for gold. Later, Basil Valentine (a German monk of whom the true family name is not known) dedicated himself about the year 1500 to the search for the philosopher's stone, by means of which all metals and other objects would be converted on contact into precious metals. Then other things followed. It was believed that it would be possible by means of the philosopher's stone to restore youth to the aged.

Certain facts supported these alchemists in their pretensions to manufacture gold from other metals. These consisted in the fact that during prolonged treatment of certain ores traces of gold resulted. It is no longer doubted that this gold is simply present as an impurity in the ores employed.

An alchemist of Hamburg named Brandt searched for the philosopher's stone in urine in 1669. He heated and slowly evaporated enormous quantities of urine in large alembics, hoping to finally discover the famous stone. As it happened, to his extreme surprise and the intense amazement of his contemporaries, he actually obtained a new substance which evolved light in the dark, namely, phosphorus.

To the two components of metals, mercury and sulphur, Basil Valentine added a third, namely, salt, and from that time the study of the metallic salts commenced.

IATROCHEMISTRY. With Paracelsus, a Swiss (1493–1541), a new phase of alchemy commences, called iatrochemistry, that is, the chemistry of medicines to prolong the life of mankind. Paracelsus combated the theories of the celebrated medical men Galen (131 B.C.) and Avicenna, an Arab (800 B.C.). He considered man as a chemical combination, and stated that illnesses occurred because this combination was altered, consequently illness could only be cured by chemical means. The purpose of chemistry, according to him, was not to search for gold but to prepare medicines, and this search led him to important discoveries. He travelled throughout Europe, Egypt, and Turkey, was Professor of Medicine at Basle and died at Salzburg in very great poverty. This was the bitter reward for his honesty, as he always fought against the quackery and stupidity of the self-styled manufacturers of gold, by whom he was persecuted, directly or indirectly, until his death. The contemporaries and successors of Paracelsus were Agricola in Germany (1490–1553), who carefully studied the smelting of metals, and Libavius, also in Germany (1540–1616), who wrote the first text-book of alchemy, in which he collected all the chemical knowledge of the time; Van Helmont of Brussels (1577–1644), who was a medical man of world-wide celebrity, studied alchemy in the same sense as Paracelsus, distinguished for the first time various kinds of gases, and identified the gas produced in fermentation with that from the Grotto of Dogs (near Naples).

He believed vaguely that the first cause of all things was water and something supernatural which was combined with it.[1]

The first to openly attack the Aristotelian hypothesis on the constituents of nature, heat, cold, humidity, and dryness, were: the brilliant but not always sincere English philosopher, Francis Bacon (1562–1626), who revived the atomic hypothesis of Democritus, maintained that matter was indestructible, and who intuitively guessed by means of philosophical speculation the existence of universal gravitation; he clarified ideas on the inductive method applied to science, basing natural laws on known facts and on experience, in a manner first started by Palissy, Leonardo da Vinci, and Paracelsus. He may be considered as the first founder of the inductive method (*see below*).

Bacon already defined heat as the effect of a motion, extension, and undulation of the

[1] To form an idea of the extravagant conceptions held even by the Iatrochemists with regard to medicines and the cause of diseases, it is necessary to read the writings of Van Helmont (1626) on "The Causes and Nature of Fever." We will confine ourselves here to translating the recipe of his celebrated ointment which was supposed to cure any fever, especially quartan-fever: "One heats in a brass pan 1½ oz. of turpentine of Cyprus and then introduces fifteen live spiders and mixes until the spiders have disappeared; one then places the whole on the fire and continues to stir, introducing as many cobwebs as the spiders would presumably have spun, or, if cobwebs are lacking, one adds nine other small spiders and agitates further; one then adds 1½ oz. of good asphalte and 1 oz. of white sal ammoniac, and allows to cool until one obtains a paste which is allowed to stand for fifteen days. Meanwhile one prepares a special oil in the following manner: One mixes oil of fresh water-lily flowers, one year old, with oil of bitter almonds; nine live scorpions are then introduced and the whole is exposed to the sun when this is in the constellation of the Virgin or of the Crab, and it is left thus until the scorpions are dead; 1 oz. of pastel of female vipers is then added and it is left in the sun for a further fifteen days. The oil is then ready. The paste is then softened on the fire and worked up by means of the hands with the oil already prepared in such a manner that a paste is obtained, which is spread out on a skin, which is then cut into pieces as large as a dollar. And now follows the method of application: An hour before the fever appears one ties two of these ointment preparations to the wrists of the patient and leaves them for exactly nine days (nine were the small spiders and nine the scorpions!), takes them off at the same hour at which they were applied and throws them into running water. Whatever be the nature of the fever, after this cure it will disappear."

Who would suppose that after four centuries, even in Italy amongst the ignorant mass of the cities, similar recipes are still largely used? Still more remarkable are the ideas of Paracelsus. His sudorific with a mercury base was celebrated for a long time, and was supposed to cure an extraordinary number of maladies.

In 1894 two interesting documents saw the light (*Chem. Zeitg.*, 18, p. 1998) which showed that alchemy survives even in our own time. These are two letters of a modern German alchemist who offers himself to the owner of a copper mine to place at his disposal his secret for extracting £12 worth of gold from each 50 kilos of old copper, whatever may be its origin, and demands a fee of 10,000 thaler, about £1600, for revealing the said secret, which had cost him thirty years of work.

smallest particles of substances. Then Glauber (1660), cleared up the composition of salts, especially of sodium sulphate, which still bears his name (Glauber's salt), and commenced already to develop technical chemistry, although he always remained a follower of iatrochemistry.

Lemery (Rouen, 1645–1717) extended the conceptions of chemistry, and in his book "Cours de Chimie," published in 1675, divided this science into the study of organic substances (animals and vegetables) and of inorganic substances (minerals). In a few years thirteen editions of his book were published. Before this time the greatest confusion reigned in the classification of substances. It will suffice if we cite a single example. Antimonious chloride was called butter of antimony on account of its white, pasty appearance, and for this reason was classed side by side with ordinary butter from milk.

PNEUMATIC CHEMISTRY. Whilst alchemy and iatrochemistry were gradually losing ground, Robert Boyle (1627–1691) founded a new era in chemistry, namely, that of pneumatic chemistry, which was specially concerned with the study of gases. He defined more exactly the nature of elementary bodies and of chemical compounds, and showed that chemistry should not mainly serve for alchemistic or therapeutic purposes, but should form a study apart, constituting one of the natural sciences.

Boyle was the first in England to erect a chemical laboratory for experimental research, at the University of Oxford, and was supported in this by all the other professors. He obtained nitric acid by distilling nitre with sulphuric acid ; he discovered the characteristic reaction of copper with ammonia, of chlorides with silver nitrate, and of iron with tannic acid ; he perfected the air-pump, and studied combustion in a vacuum ; he found that sulphur will not burn in a vacuum, and that the flames of hydrogen and of a candle die out, whereas gunpowder ignites in a vacuum if heated on an iron plate, and fulminate of gold explodes in a vacuum under the influence of concentrated light rays from a lens. He deduced thus that the substance which supports combustion in air is analogous to that contained in the nitre which is a constituent of the gunpowder.

Boyle was the first to state that on burning or heating metals in a furnace these show an increase in weight after cooling ; thus on heating mercury another substance is formed because the mercury absorbs or combines with some part of the products composing the flame.

CHEMISTRY OF PHLOGISTON. The study of combustion occupied the chemists of this epoch for another century, commencing with Hooke (1635, the inventor of the pocket-watch) and Mayow (1645), pupils of Boyle, who demonstrated that the gas which is formed on heating nitre is the same which is found in air and which maintains combustion of a fire and the vitality of animals. Mayow showed that there is also a gas in air which does not maintain combustion. Becher (1635–1682) brought forward a new hypothesis on combustion, which was defined and developed by Stahl (1660–1734), according to which all combustible bodies are formed of at least two components, one of which is evolved during combustion, the other remaining. On calcining a metal in a furnace one of the components, called phlogiston, escapes, and the calx of the metal, which we to-day call the oxide, remains. Thus a metal is composed of phlogiston and of the calx of the metal (oxide). On heating a metallic calx with carbon the metal is re-formed, that is, the carbon has restored phlogiston to the calx, forming the metal. As a result of this theory it followed that the metals were compound bodies, the weight of which should diminish on heating, because they lost one of their components, the phlogiston. But in practice this is found not to be true, for on the contrary metals increase when heated in the air as Boyle had already observed. The supporters of the phlogiston theory explained this evident contradiction of their hypothesis by supposing that the increase of weight was due to the increase of density (according to which reasoning on compressing a bundle of straw its absolute weight would be increased).

The phlogiston hypothesis, however erroneous, contributed very much indirectly to the development of chemistry, because by generalising and applying it to numerous substances discoveries of new bodies and studies of very varying phenomena were made.

Various gases formed during combustion were studied and knowledge of the behaviour of metals in general was increased.

The first formidable attack on the phlogiston hypothesis was made by Black (1728–1793),

who showed in 1755 that on heating magnesia alba to redness a constant quantity of fixed air (carbon dioxide), and not of phlogiston, was evolved, and that the weight of the remaining magnesia was less.[1]

Black may thus be considered to be the founder of quantitative gravimetric chemistry, although the control of chemical phenomena by taking the weight into account had already in some cases been exercised by Boyle. Black discovered carbon dioxide, which he called "fixed air," and identified in many varied cases: on heating magnesia to redness or treating it with acids, on burning carbon, on breathing, &c.

He also discovered the specific heat and latent heat of bodies.

Pneumatic chemistry, which had its origin in the experiments of Van Helmont (1540), who was already vaguely acquainted with carbon dioxide and other gases, and which was developed by the work of Boyle, Hooke, and Mayow, was greatly extended by the work of Black.

But the greatest contribution was due to Priestley (1735–1804), who also studied the gases of combustion, and from the respiration of animals and plants. He discovered nitrogen, carbon monoxide, nitric and nitrous oxides, and the still more important gas, oxygen, by heating mercuric oxide (August 1, 1774) in a vacuum with a strong lens, and was the first to determine with exactness the specific gravity of gases. He always remained a faithful and tenacious supporter of the phlogiston theory.

Cavendish (1731–1810) was a more exact experimentalist than Priestley. He discovered hydrogen by treating metals with dilute acids, 1766. He showed that by combustion of hydrogen, water alone was formed (1781, together with Watt). He also discovered that air is a simple mixture of two gases, oxygen and nitrogen, which are mixed in well-defined and constant proportions.

Contemporaneously, but independently, the Swede, Scheele (1742–1786), also arrived by other means at the same discovery, and apart from oxygen, he discovered nitrogen, chlorine, many organic and inorganic acids, glycerine, &c.

The history of the period of the older chemistry now ceases, because with Lavoisier, that is, with the end of the eighteenth century, we commence the history of modern chemistry, which has been the carrier of such abundant benefits to progress and civilisation, surpassing in a single century all which had been produced during the previous forty centuries. Boyle had already stated that chemistry should be considered as a science apart, as a distinct branch of the natural sciences. Stahl had defined chemistry as the science which has for its scope the resolution of compound substances into their constituent elements and the reconstruction from them of other substances.

Summarising the state of chemical theory and knowledge towards the middle of the eighteenth century, we find that seventeen elements were known at that time and that the metals were subdivided into: Perfect metals, such as gold and silver; imperfect metals, such as copper, iron, tin, lead, and mercury (because this latter could be frozen!); semi-metals (*i.e.* those which were less ductile), such as arsenic, antimony, bismuth, zinc (discovered in 1735), cobalt (in 1751), nickel (in 1774), manganese (about 1780), molybdenum and tungsten; platinum (1750) was considered as a special metal. Sulphur, phosphorus, and carbon were considered to be combinations of phlogiston with the acids corresponding to these substances. The alkalies, the alkaline earths, and the earths themselves (alumina, silica, &c.) were considered to be allied to the metallic calces. It was known that metals reacted with acids. The simple gases which were known were inflammable air (hydrogen), also called pure phlogiston, oxygen, nitrogen, and chlorine.

About the year 1772 Lavoisier devoted himself to the study of combustion, and came to the conclusion that the phlogiston theory of Stahl was completely erroneous and did not correspond to the facts. He showed by means of the balance that when sulphur or phosphorus is burnt there is no loss, but on

[1] We can to-day justify the phlogiston theory if for the word "phlogiston" we substitute the word "energy" (heat); we would then understand that on heating a metal which oxidises there has not been a loss or development of phlogiston but of energy.

the contrary an increase in weight, due to the union of the sulphur or phosphorus vapours with the air.

In 1773 Lavoisier investigated the character of the air (or gas) evolved in respiration, combustion, and fermentation.

In 1774 he found that on heating tin and lead in a closed flask no increase in weight occurred, whilst when the flask was open the weight increased through combination with a portion of the air in the flask, and that the air which remained was different from the ordinary air and from the air which was fixed by, and combined with, these metals.

In 1778 he found that on heating red mercuric oxide a very active gas is evolved which intensifies combustion and is concerned in the calcination of metals. He at first called this gas *pure air* (Condorcet called it *vital* air), but at a later date he named it *oxygen* (*i.e.*, generator of acids).

The discovery of oxygen is ordinarily attributed to Lavoisier, but it has now been shown that Priestley had already prepared it by the same method and had studied its properties (August 1, 1774), and that Scheele knew this gas at a still earlier date, namely, in 1771.

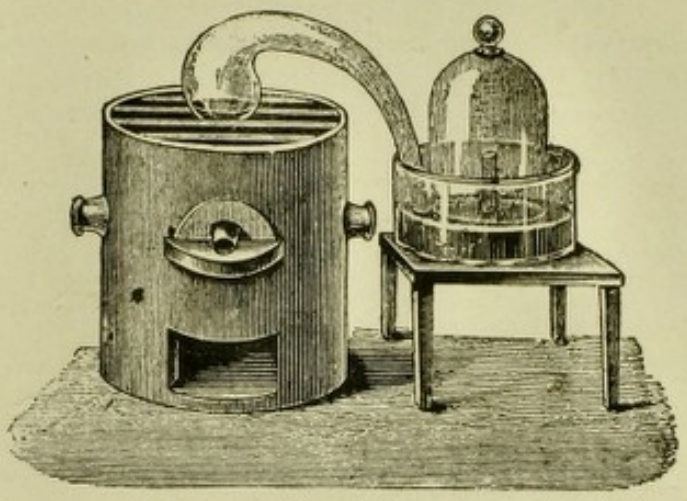


Fig. 1.

The composition of air was not clearly known at this time, but Lavoisier showed that on heating mercury for eleven days in a retort connected with a bell-jar filled with air the volume of the latter is diminished and the weight of the mercury increases, whilst the gas which remains is incapable of supporting life (Fig. 1). This gas was nothing else than nitrogen, and in this manner air was shown to be a mixture of oxygen and nitrogen.

In 1781 Lavoisier discovered the composition of water, showing that it was formed by the combination of oxygen with inflammable air (hydrogen), and in the years 1781 to 1783 he decomposed water in various ways into its components hydrogen and oxygen (action of steam on red-hot iron, &c.).

The composition of water, which had been considered to be a simple substance until that time, was thus elucidated clearly. But we now know that in 1781 Cavendish had already showed experimentally, shortly before Lavoisier's experiments, that water is formed by burning hydrogen owing to the combination of this gas with the atmospheric oxygen.

We may consider Lavoisier to be the founder of more definite quantitative analysis, and to him has been attributed the introduction of the balance as applied to the study of chemical phenomena. But Boyle had already found that mercury increases in weight on heating; and the gravimetric experiments of Black in 1755 show that the balance was then already used in chemistry.

The true merit of Lavoisier lies in his generalisation of the use of the balance in the study of chemical phenomena and his experimental demonstration of the indestructibility of matter: nothing is created and nothing destroyed in the universe.

At his epoch the possibility of transforming water into earths by prolonged boiling was much discussed. He boiled water in a weighed and closed glass flask for one hundred and one consecutive days and found that the weight of flask with contents remained unchanged; on emptying the water and reweighing the empty flask he found that it had

lost 17·4 grms. in weight, whilst on evaporating the water originally contained in it to dryness he obtained a residue of 20·4 grms. ; he was thus able to demonstrate (apart from errors in weighing) that the water had dissolved a portion of the glass. Indeed, when the residue was analysed by Scheele he found it to consist of silica and alkali. The Aristotelian theory was thus definitely buried for all time.

The old and renowned chemists of Lavoisier's epoch did not accept the new theory, especially on combustion, and died faithful followers of and supporters of the phlogiston theory, although this had been inexorably condemned by the numerous and rigorous experiments of Lavoisier.

On the other hand, the whole newer generation of European chemists at once embraced and accepted Lavoisier's theory with enthusiasm, and from that time chemistry developed in a marvellous manner, which has never been equalled in the history of any other science.[1]

THE FUNDAMENTAL LAWS OF MODERN CHEMISTRY

About 1650 Glauber made an important observation which was of much consequence later when chemistry had disentangled itself from the fetters of alchemy. He was trying to discover how the decomposition of certain salts by means of acids occurred, and he observed that when two neutral salts

[1] *Biographical note.*—Lavoisier (Antoine Laurent) was born in Paris on August 26, 1743. His family was rich, his father being an advocate, and Lavoisier studied mathematics, physics, astronomy, mineralogy, and botany at the Mazarin College ; with this vast scientific patrimony he turned, whilst still a youth, to the study of chemistry, in which he accomplished a real revolution and initiated a new era which is still animated to-day by the effects of his brilliant discoveries.

In spite of his great services it is impossible to overlook the sins of Lavoisier in appropriating to himself discoveries made by chemists who were his contemporaries or predecessors. Oxygen was first discovered by Hales in 1727, but had already been prepared from mercuric oxide by Priestley in 1774, by Bayen in the same year, and still earlier by Scheele in 1771. It was at a dinner at Lavoisier's house that Priestley confidentially communicated his discovery to Lavoisier, in 1774 ; in 1778 Lavoisier then claimed the discovery for himself, whereas in reality he had merely given the name of oxygen to the new gas.

In a similar manner Lavoisier claimed for himself the discovery of the composition of water, whilst, as is now known, Blagden, a friend of Cavendish, when visiting Paris in 1781, told Lavoisier that Cavendish had discovered the composition of water in a very simple manner by burning inflammable air (hydrogen) as water only was formed during this combustion.

Lavoisier and Laplace immediately repeated the experiment and then communicated the discovery to the French Academy in 1783.

These facts certainly do not obscure the fame of the great scientist when we remember his eminent services, but in the interests of historic accuracy and justice it is impossible to pass them over in silence.

In December 1793, before the end of the revolutionary Reign of Terror, Lavoisier was accused of conspiracy against the new Government and fraud against the people by preparing snuff containing much water and noxious substances, was arrested, together with twenty-seven other *fermiers généraux*, and condemned to death. It was in vain that he asked for a few weeks of liberty in order to conclude certain important experiments on respiration which would benefit the whole of humanity. This was denied to him, and Lavoisier was beheaded on May 8, 1794.

The severity of the Revolutionary tribunal was due to the profound and intense hatred amongst the people towards the *fermiers généraux*, who exercised an excessive taxation, ruthlessly exasperating the already miserable condition of those who contributed to support the weight of the triple domination of State, nobles, and clergy. The population of France, of 26,000,000 inhabitants, had to provide £19,000,000 a year towards the revenue of the king, and had to submit to vexatious taxation on the part of 140,000 nobles and of 130,000 clergy.

The *fermiers généraux* were entrusted with the collection of the most odious of these taxes, the monopoly of tobacco, the tax on beverages, and more especially the tax on salt. Each year 300 contrabandists were condemned to hard labour.

Renauldon, at the beginning of the revolution, wrote as follows : " The *fermier général* is a rapacious wolf, who impoverishes the earth, draws the last halfpenny from it, oppresses the labourers, reduces them to beggary, lays waste the fields, and renders odious the master who is obliged to submit to this taxation."

It is said that Lavoisier accumulated 1,200,000 lire in profits in a few years from his office as *fermier général*. This was fatal to him.

His chemical friends—and he had influential ones such as Guyton de Morveau, Monge, Laplace, Berthollet, and especially Fourcroy—did nothing to save him.

It is said that this same Fourcroy voted for the death sentence.

Only Loysel, Cadet, Baumé, and Hallé dared to do anything. The latter sent a memorandum to the Lyceum of Arts on all the work completed by Lavoisier and on the utility which would result from it. This memorandum was read during the trial but was of no use. It is said also by many historians and by most chemists that the ruthless tribunal which judged Lavoisier came under the influence of Marat, who had motives of hatred towards Lavoisier on account of the critique which he had written on his chemical works, especially on one entitled " Recherches physiques sur le Feu " of 1780 ; but this accusation is calumnious and absurd when one remembers that Marat was assassinated and died in July 1793, and Lavoisier was arrested in December 1793 and beheaded in May 1794 at the age of fifty years only.

The death of Lavoisier was a disaster for the progress of science, and Lagrange said that " a single instant sufficed to make that head fall, but many centuries will not suffice to reproduce a similar one."

Lavoisier's wife, who was married a second time to Count Rumford, collected and published the scientific memoirs of the great chemist in 1805.

react upon one another their components are reciprocally interchanged, giving rise to two new salts, saturated and neutral like the first (mercury chloride with antimony sulphide).

In 1700 Homberg also made an important experiment on the various quantities of basic (alkaline) substances which are needed to saturate a certain constant quantity of a given acid.

The first positive law arose from the immortal work of Lavoisier, who, by the universal and rigorous use of the balance in the study of chemical phenomena, showed that "the sum of the weights of two substances which combine is equal to the sum of the weights of the new combinations which are formed," and thus, for instance, on combining 8 grms. of oxygen with 1 grm. of hydrogen, the quantity of water which is formed is exactly 9 grms. "Nothing is lost and nothing is created," said Lavoisier, thus stating a most important law of nature, that of the conservation of matter.

On the other hand, Wenzel in 1777 published his important "Study on the Affinities of Substances," in which, based on an enormous number of analyses, carried out with great exactness, he demonstrated that the acid and basic substances combine with one another in constant quantities, then confirming and amplifying his studies by means of reactions which occurred between neutral salts.[1]

More extensive and important work and exact experiments were published by Richter in 1792 to 1794 with the title "Elements of Stoichiometry, or Mensuration of the Chemical Elements." Apart from the accurate determination of the quantities of various bases which saturated the same quantity of an acid and the quantities of various acids which saturated a constant quantity of a base, he also studied gravimetrically the reciprocal action of numerous neutral salts which react with formation of other neutral salts.

For the first time in history we encounter an attempt to apply mathematics to the elucidation of chemical reactions, and from the beginning of his chemical career (1789) Richter devoted his whole activity to the discovery of the mathematical laws which regulate chemical reactions. He considered chemistry as a part of applied mathematics, and endeavoured to establish so-called arithmetical and geometrical series from which to find such laws. We owe to him a clear conception of chemical equivalents, which he stated concisely for salts, in the following law. *In various salts derived from the same acid, the weight of the various metals corresponding to an equal and constant quantity of the acid is represented by values which are chemically equivalent and which are constantly found again unaltered* (*or in multiples*) *in the formation of other salts*; *thus also in various salts of the same metal, the quantities of the various acids corresponding to a definite weight of metal are constantly found again* (*or in multiples*) *in other salts.*

For example, the quantities of hydrochloric acid (c), of nitric acid (n), and of sulphuric acid (s), which are required to exactly saturate a constant quantity A of silver, are the same as are required to exactly saturate a constant quantity A' of another metal, for example, sodium :

$$\left.\begin{array}{l} A+c=\text{chloride} \\ A+n=\text{nitrate} \\ A+s=\text{sulphate} \end{array}\right\} \text{of silver} \qquad \left.\begin{array}{l} A'+c=\text{chloride} \\ A'+n=\text{nitrate} \\ A'+s=\text{sulphate} \end{array}\right\} \text{of sodium}$$

[1] Later on we will explain the significance of the words base, acid, and salt more exactly. For the present it will suffice to say that bases are ordinarily substances obtained by the oxidisation and subsequent hydration of a metal, and having the property of uniting with acids with reciprocal saturation forming salts. The bases have a so-called alkaline reaction, that is, they are able to turn red litmus paper blue in distinction to the reaction of the acids which turn blue litmus paper red.

Or *vice versa*, the quantities A, A', and A'' of various metals which are combined with a constant quantity (c) of hydrochloric acid to give the corresponding chlorides are the same as are combined with the constant quantity (n) of nitric acid to form the corresponding nitrates.[1]

In 1803 Berthollet published a classic work entitled "Chemical Statics," in which he endeavoured to demonstrate that the variety of chemical combinations and phenomena was due to a certain fundamental and immutable property of matter, and supposed that between the particles of matter there was a certain attractive force, a certain affinity, which existed, of the same character as gravity, and thus chemical phenomena, according to him, followed well-determined mechanical laws under the exclusive influence of mass and of affinity, and not as Richter declared in definite proportions of constant weights.

According to Berthollet, then, the quantity of one substance which combined with another varied with variations in the quantity by which one or the other preponderated, in such a manner that two substances would be able to combine in very varying proportions by varying the quantity of the substances, that is, of the amount of the one or other component, but in harmony with the affinities. He believed that a mathematical explanation had not yet been found, such as existed for gravitation between the stars, because the distance between the particles was so small and their forms so various, that the necessary mathematical calculation would be very difficult.

Proust (1801–1806) arrived by another method at the same results as Richter, and showed that there really existed a constant proportion between two elements in a compound, thus formulating for the first time the law of constant proportions. He also found that two elements are able to combine in more than one proportion, but that these proportions are always well determined and constant; for example, in the case of a metal which forms two oxides. This last observation should have led Proust to the law of multiple proportions, but this was only discovered and experimentally proved later on by Dalton, because Proust did not succeed in making the demonstration precise on account of the well-known inexactitude of his experiments and quantitative determinations.

The enormous number of analyses which led Proust with certainty to the law of constant proportions were repeated with the greatest accuracy and exactness by Berzelius, and later also by Stas. These results exactly confirmed the law of Proust.

Thus on decomposing and analysing

100 grms. of	water	one obtains	11·12	grms. of	hydrogen	and 88·88	grms. of	oxygen
,,	hydrochloric acid	,,	2·8	,,	,,	,, 97·2	,,	chlorine
,,	hydrogen sulphide	,,	5·9	,,	,,	,, 97·2	,,	sulphur
,,	lead sulphide	,,	13·4	,,	sulphur	,, 86·6	,,	lead
,,	lead chloride	,,	25·54	,,	chlorine	,, 74·46	,,	,,
,,	lead oxide	,,	92·825	,,	lead	,, 7·175	,,	oxygen
,,	ammonia	,,	17·7	,,	hydrogen	,, 82·3	,,	nitrogen

These are the direct results of the analyses, which did not apparently

[1] These most interesting studies of Richter were not considered to be of much importance at that time, although he himself introduced them into his principal work in eleven volumes, published in the years 1797–1802, and although G. E. Fischer in his German translation of Berthollet's work on "Affinity" introduced the table of equivalents and the ideas deduced by Richter—ideas and values which the same Berthollet had introduced in his principal work, "Chemical Statics," in 1803. It is difficult to understand how Berzelius himself could attribute the origin of these studies to Wenzel. Richter himself remained neglected by others for forty years until Hess brought his work to light again in his writings in 1840. Hess himself was forgotten in his turn by his contemporaries, but his work was recalled by Ostwald in 1886, who proclaimed him to be the true founder of thermochemistry. The work of Richter did not find followers because the attention of the chemists of that time was riveted entirely on the interesting dispute which was prolonged for many years between Berthollet in France and Proust in Spain.

represent anything further, but these figures acquire a surprising eloquence if they are compared with one another, after referring them to a definite quantity of one of the components, taken as unity ; thus if we refer all these weights to an equal unit quantity of hydrogen and then compare these new relations, we find that one part of weight of hydrogen corresponds to :

In water	to	8	parts of oxygen
,, hydrochloric acid	,,	35·5	,, chlorine
,, hydrogen sulphide	,,	16	,, sulphur
,, lead sulphide, 16 parts of sulphur (=1 hydrogen) .	,,	103	,, lead
,, lead chloride, 103 parts of lead (=16 sulphur=1 hydrogen)	,,	35·5	,, chlorine
,, lead oxide, 103 parts of lead	,,	8	,, oxygen
,, ammonia, 1 part of hydrogen	,,	4·67	,, nitrogen

Now we see that the oxygen in water and in lead oxide has the same value of 8 (referred to the weight of hydrogen as one) and that the sulphur occurs in the proportions of 16 parts by weight, both in hydrogen sulphide and in lead sulphide ; chlorine occurs in 35·5 parts by weight in hydrochloric acid and in lead chloride ; and lead occurs in the proportion of 103 parts by weight in both the oxide and chloride of lead.

These values were called combining weights or chemical equivalents or stoichiometric values. They represented the quantities by weight of each element which corresponded or were equivalent to hydrogen taken as unity.

It is evident from these results that the principle of the law of constant proportions of Proust is exact, that is, that the elements combine with one another in constant proportions or weights as Richter had perceived, and thus 16 grms. of sulphur combine chemically with 103 grms. only of lead, even though this latter may be present in much greater quantity. The excess over and above 103 grms. remains unaltered as lead and is not transformed into sulphide.

Thus there is no influence of mass, as was declared by Berthollet.[1]

Whilst the dispute between Berthollet and Proust still raged, Dalton succeeded in explaining by a brilliant conception (1800–1803–1808) in a simple and luminous manner the constant composition of chemical combinations. Starting from the hypothesis of the ancient Greek philosophers (Leucippus, Democritus, Epicurus, and Lucretius, *see* p. 12), who considered matter to be constituted of small particles, distinct from one another, he developed this hypothesis by supposing that the particles constituting a given simple substance which he called *atoms* were equal to one another in weight and in volume, but different from those of any other simple body ; the properties of qualities of these atoms are those which determine the qualities of the substance, and this will vary as the quality of the atoms varies. By mathematical speculations and chemical determinations and experiments he was able to show that chemical compounds result from the union of two or more atoms of varying kinds. On the foundation of experiments made by him, he succeeded also in determining the relative weight of these atoms with respect to one another, and was then able to demonstrate experimentally a fundamental law of modern chemistry, namely, the law of multiple proportions, which had already been suggested, but not proved, by Proust.

According to this law the atom of a given element (simple substance)

[1] The hypothesis of Berthollet did not meet with success at that time, mainly because it was antagonistic to the fundamental laws discovered by Proust and Dalton and by Gay-Lussac, but eventually its application was found much later, becoming a fundamental law for the exact interpretation of all chemical reactions. The Norwegians Guldberg and Waage found a mathematical expression for chemical systems in reaction which replaced the conception of chemical mass of Berthollet by a more rational conception of active mass, as will be explained later.

can combine with 1, 2, 3, 4, &c., atoms of another element, that is, with a multiple number of other atoms. Dalton deduced this important law experimentally by analysing numerous chemical compounds, and we may illustrate it by taking the combinations of nitrogen with oxygen, which give on analysis the following results :

I.	Nitrogen oxide	contains	63·6	per cent.	of nitrogen	and	36·4	per cent.	of oxygen
II.	Nitric oxide	„	46·7	„	„	„	53·3	„	„
III.	„ trioxide	„	36·8	„	„	„	63·2	„	„
IV.	„ tetraoxide	„	30·5	„	„	„	69·5	„	„
V.	„ pentoxide	„	25·9	„	„	„	74·1	„	„

On recalculating these results and referring then to the stoichiometric values or weights of combined oxygen, which we have already seen to be 8, we find that in the first compound the stoichiometric value of oxygen corresponds to 14 parts of nitrogen, that is, to three times its stoichiometric value, which we know to be 4·67.

If we now constantly retain the 14 parts of nitrogen for the other compounds, we find

In	I.	14 parts of nitrogen	combine	with	8	parts	of	oxygen
„	II.	„	„	„	16	„	„	
„	III.	„	„	„	24	„	„	
„	IV.	„	„	„	32	„	„	
„	V.	„	„	„	40	„	„	

It is evident from these results that a given constant quantity of one element, which may be one atom, combines with a given quantity of another element (for example, one atom) or with a double, triple, or quadruple, &c., quantity, and that actually these quantities are in the proportions of the stoichiometric values or combining weights. Thus complete atoms and not fractions of atoms or arbitrary quantities combine with one another. In this way the atomic hypothesis became more definite and concrete, and became necessary in the contemporary state of science in order to explain chemical phenomenon.

The brilliant hypothesis of Dalton was at once accepted by all the more authoritative scientists of other nations, who could only confirm its utility and importance both for chemistry and other sciences. This hypothesis has aided the interpretation of all phenomena to such an extent that by most chemists it is considered as a true positive theory and as the basis of chemical philosophy which has been developed in the last century.[1]

LAWS WHICH GOVERN MATTER IN THE STATE OF GAS

(1) **THE LAW OF BOYLE AND MARIOTTE.** It was the exact study of gaseous matter which first led to the discovery of the more important laws of chemistry and physics. Galileo (1564–1642), one of the founders of the inductive and experimental method, already succeeded in showing that the air possessed weight, by the use of sufficiently exact instruments, and thus shattered at one blow the statement of Aristotle, who believed the air to be imponderable ; all experiments up to that time had been made by weighing

[1] During the last few years the atomic hypothesis has become insufficient to explain certain new phenomena, and perhaps we are at present passing through a transitory period which will certainly lead to new and still vaster horizons, because the atom contains behind and within it a whole new world of marvels (*see below*, " Unity of Matter and Energy," and the chapter on Radium).

a bladder inflated with air and weighing it again when empty, by which means no difference in weight was found.

Torricelli (1608–1647) deduced by means of the barometer the weight of a long column of air, the atmosphere. Black studied the evaporation of liquids and deduced laws, showing that in such evaporation heat is absorbed (latent heat). Priestley, who was a strenuous worker, was one of the first to introduce exact instruments for the measurement of gases, but already before this time Boyle in 1662, and Mariotte in 1679, by studying dry air in vessels which allowed the volume to be measured and by always keeping the temperature constant whilst they altered the pressure, arrived at an important law, namely, that the volume of a gas varies in inverse proportion to the pressure, that is to say, that the volume of a gas diminishes proportionately to the increase of pressure.

This law can be represented by a mathematical formula in which v indicates the volume of a gas at pressure p, and v' the volume of the same gas at a different temperature, p'. As the volume of the gas is inversely proportionate to the pressure, we thus have $v : v' = p : p'$, or we arrive at another simple formula deduced from the above, $pv = p'v'$, which signifies that the product of the pressure and the volume of the same quantities of gas is always equal at any moment, so long as the changes of pressure or of volume are not accompanied by changes of temperature or of the quantity by weight of the gas.

If, for example, we have a volume of gas $v = 10$ litres at a pressure $p = 2$ atmospheres, then we have $p.v = 2 \times 10 = 20$. If we now subject the same 10 litres to the double pressure, $p' = 4$ atmospheres, the volume becomes halved, that is, 5 litres. Thus in this case also the product of the volume and the pressure is equal to 20 as in the first case, as $p'.v' = 4 \times 5 = 20$. Thus the product of the volume of a gas by the pressure (the temperature remaining invariable) is always constant at any pressure at any instant.

Boyle made his experiments up to pressures of four atmospheres only, but the law of Boyle and Mariotte has been confirmed by all who controlled it at a later date.[1]

We have seen that in a given quantity by weight of a gas, under varying pressures, the product of pressure and volume remains constant.

In the formula $p.v = C$ (constant), which represents Boyle's law, p is a function of v, and *vice versa* v is a function of p, because in general when two variable quantities are reciprocally dependent, if we know the value of the one the value of the other is determined. Thus, if for a constant value of C, namely, 100, the values of p are determined as 1, 2, 4, 10, 25, and 100, then the corresponding values of v, which is a function of p, will be 100, 50, 25, 10, 4, 2, and 1 respectively. That is, we have a *function of the second degree*

[1] Very small variations from the formula above expressed mathematically always occur, and were studied exactly by van Marum at the end of the eighteenth century in the case of ammonia gas.

Orstedt also found small differences in the case of sulphur dioxide, and in 1827 Despretz, in a numerous series of experiments, showed that the law of Boyle and Mariotte is not rigorously true in the case of vapours or of gases at a temperature or pressure near to their point of liquefaction, whilst the so-called perfect gases such as oxygen, which are not easily liquefied, follow the said law exactly at a pressure of 15 atmospheres. Dulong and Arago showed in 1829 that up to pressures of 27 atmospheres air follows the law of Boyle very exactly. Later on, about 1850, Regnault conducted a series of most important experiments carried out with the very greatest care and with the greatest facilities, and showed that no gas rigorously follows Boyle's law, but that they can all be compressed slightly more than they should be according to theory, excepting hydrogen, which is less compressible. In 1852 Natterer found that other gases also behave like hydrogen when they are strongly compressed. In 1870, 1877, and 1879, Cailletet made extensive experiments of this kind defining still more carefully the general law and its variations.

In 1880 Amagat undertook important experiments, exposing gases to extremely powerful pressures up to 430 atmospheres, by using a steel tube 327 metres long curved into a closed U at the lower end and filled with mercury and penetrating below into a deep mine (at Meons, near St. Etienne). He fully confirmed the results of Regnault and of Natterer for highly compressed gases, and also confirmed the exceptional behaviour of hydrogen.

But Amagat also found in the course of his work that the exceptions and variations from Boyle's law become less as the temperature increases, and that for every gas a different temperature must exist at which it behaves exactly according to Boyle's law. In 1883 Amagat studied the behaviour of gases with regard to Boyle's law at small pressures, less than one atmosphere, that is, he studied rarefied gases, and found that these also follow the said law exactly, thus coming to conclusions opposed to those which had been arrived at some years before by Mendelejew and Kirpitschoff.

We will later on explain all these small variations of Boyle's law, and they will serve as a basis for most important new laws which we will then study.

We will also give the graphic representation of this important law in order to demonstrate for once how advantageous this method is for rendering the mathematical expressions of such laws evident, enabling us in many cases to rapidly form an exact idea of the course of a physical or chemical phenomenon even at moments or under conditions which cannot be attained or which are difficult to arrive at by mathematical calculation.

which contains the product of the two quantities, and thus we arrive geometrically at a *linear function* which will be represented graphically by a curve. If then we take two *orthogonal axes* (that is, axes which intersect at right angles) OV and OP (Fig. 2), and mark off points along the axis OV, the distances of which from the point O correspond to the various volumes (having once for all fixed the relation between lengths and volumes (*e.g.* 1 mm. corresponding to 1 litre), and if we similarly mark off the corresponding pressures along the vertical axis (the axis of the ordinates) OP, then, supposing that we start with 50 litres of gas at a pressure of two atmospheres, we have a fixed point e in the plane of the paper, and the surface $OV\ e\ 2'$ represents geometrically the constant C of Boyle's formula ($2 \times 50 = 100$); a volume of 20 litres of gas will be exposed to a pressure of 5 atmospheres, which we represent by the ordinate d, and we have now fixed another point d, the surface O, 20, d, $5'$ again representing the constant C ($5 \times 20 = 100$); under a pressure of 10 atmospheres the volume becomes 10 litres and we have fixed the point c, the constant remaining always the same ($10 \times 10 = 100$); similarly we are able to fix the point b, where the pressure is 20 atmospheres and the volume 5 litres. If we establish a sufficient number of points in this manner, and then unite them with one another we obtain a curve which will in fact be a rectangular hyperbola, the extremities of which tend to approach indefinitely near to the respective axes, but without coming into contact with them (except at infinity); for that reason the axes are called *asymptotes* to the curve, and indicate that the volume of the gas will become zero when the pressure is infinite, and will become infinite when the pressure becomes zero. This would naturally only apply to an ideal gas (and we may consider nitrogen, oxygen, hydrogen, &c., to be practically though not absolutely ideal gases); but as we have seen, the law of Boyle has limitations, and is noticeably inaccurate in the case of vapours or of gases near their condensation point, such as ammonia, sulphur dioxide, &c. Since the formula which represents Boyle's law only holds when the temperature remains constant throughout the variations of pressure and volume, we will obtain other hyperbolas for other temperatures and each of these is called an *isothermal* curve and corresponds to a definite temperature. In Fig. 2 two other isothermals, corresponding to two other temperatures, are also shown.

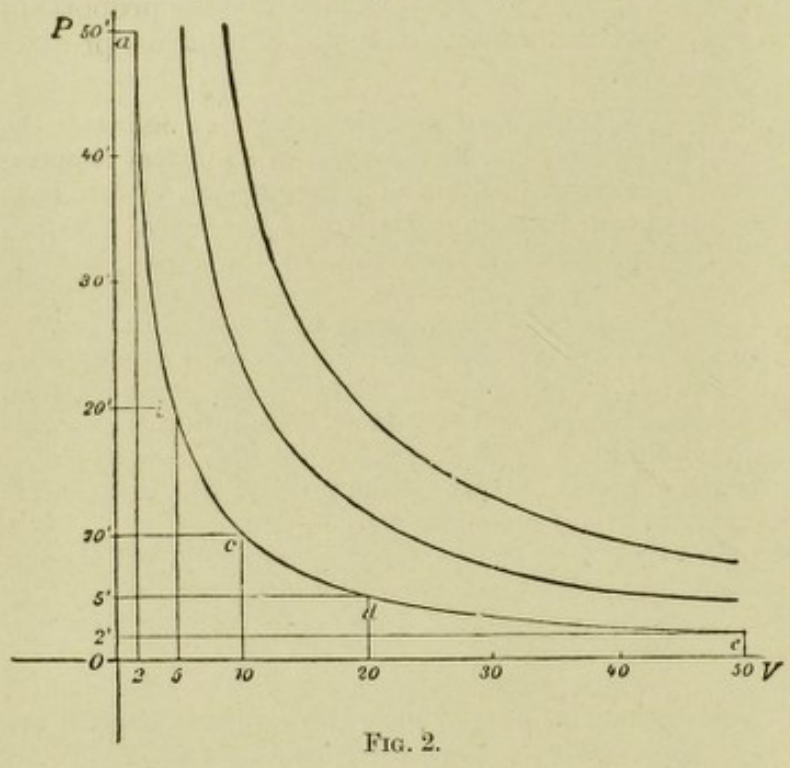


FIG. 2.

(2) **LAW OF GAY-LUSSAC AND DALTON.** The study of the behaviour of gases is very interesting under variation of other conditions than that of pressure. Already about the year 1805 Gay-Lussac and Dalton almost simultaneously discovered that all gases dilate to an equal extent when heated, and that this dilatation was proportional to the rise of temperature. Gay-Lussac and Dalton also measured the coefficient of expansion of air which they found to be 0·00375, but the more exact experiments of Rudberg, of Magnus, and of Regnault showed that the true coefficient of expansion of gases was 0·00367. This figure, when expressed as a fraction, is equal to $\frac{1}{273}$ and signifies that every gas increases or diminishes its volume by 1-273rd part of its volume at 0° for every degree of rise or fall of temperature. Thus if we imagine a volume of gas enclosed in a cylinder with an ideal friction-

less and weightless piston, at 0°, and if we divide the cylinder into 273 parts, then on lowering the temperature to 273° below zero the gas will diminish in volume by $\frac{1}{273}$ of its original volume (at 0°) for each degree and will not finally occupy any volume whatever, that is, will be deprived of every form of energy or matter, which is absurd ; we may say more correctly that below this temperature the energy of its material will remain constant. (If temperatures below absolute zero have any meaning.—*Translator's note.*) This limiting temperature, with regard to which the common zero point of thermometers would be + 273°, is called the *absolute zero*. Thus at 272° below zero a gas would really occupy $\frac{1}{273}$ of its volume at 0°. On raising the temperature the volume will constantly increase and at 273° above absolute zero, that is, at the ordinary zero temperature, it will occupy its original volume, which is 273 times larger than the volume which it occupied at 273° below zero. Thus the volume of a gas is proportional to its absolute temperature, and thus at 273° above the ordinary zero point a gas will acquire double the volume which it occupies at the ordinary zero, or 546 times its volume at − 272°.

The conception of absolute temperature is also interesting because it enables one to understand why it is impossible to completely transform thermal into mechanical energy. The actual mechanical work which can be produced by the interchange of heat between two substances is proportional to the temperature difference through which the transformation of heat into work occurs. The greater the difference in temperature between the two substances the greater will be the yield of mechanical work ; but it follows that in order to transform all the heat in a body into mechanical work it would be necessary to lower its temperature to absolute zero, which is practically impossible (*see also below*, and p. 7, " Degradation of Energy ").

The law of Gay-Lussac and Dalton may also be represented by a mathematical formula in which V indicates the volume of a gas at the temperature T, and V' the volume of the same quantity of gas by weight at the temperature T' ; the volumes being proportional to the absolute temperatures we have :

$$V : V' = T : T', \text{ or } V'.T = V.T', \text{ that is, } V' = \frac{V\,T'}{T}.$$

If, for example, a gas occupies a volume V of 4 litres at the temperature, T, of 300° absolute, that is, at 27° above the ordinary thermometric zero, it will occupy a volume V' of 8 litres at the temperature, T', of 600° absolute, that is, 327° above the ordinary zero ; controlling this by the above formula we have :

$$4 \times 600 = 8 \times 300$$
$$V.T' = V'.T$$

If we denote the coefficient of dilatation of a gas by α, and its volume measured at the temperature $t°$ of the ordinary scale by v, then the volume of a gas at 0° will be v_0, and at $t°$ it will be v_t ; then we have the equation : $v_t = v_0 (1 + \alpha t)$, always under the condition that the pressure remains constant.

If we take the volume at 0° as 1, then at 10° it will be 1·0367, at 20° v_t = 1·073 at 50° v_t = 1·184, and at 100° v_t = 1·367, &c.

The graphic representation will be a curve of the first degree, since the two variables are always present in the first power and are not multiplied by one another, and will lead to a linear function, so that the law of Gay-Lussac and Dalton will be represented by a straight line. If we actually take the temperatures t as abscissæ and the volumes v as ordinates (Fig. 3) then on drawing a curve through the points corresponding to the various pressures and corresponding volumes we obtain a straight line, which, if prolonged in the direction of the temperatures below 0° shows a zero volume at −273°.

We have seen that the formula of Gay-Lussac's law applies if the pressure of the gas remains constant during heating ; if, on the other hand, the volume of the gas is kept constant whilst it is heated its pressure will necessarily rise and then the pressure p_t at $t°$, expressed as a function of the pressure p_o at 0°, will be $p_t = p_o (1 + \alpha t)$.

By combining into a single equation the two expressions which represent the laws of Boyle and of Gay-Lussac, for a gas of volume v at pressure p, and a temperature of t on the ordinary scale, we obtain the *general equation for gases*: $p.v = p_o.v_o\ (1 + \alpha t)$, or, since $\alpha = \frac{1}{273}$, we may write $p.v = p_o.v_o\left(1 + \frac{t}{273}\right)$ and this corresponds equally to $p.v = \frac{p_o.v_o}{273}(273 + t)$ but the factor $273 + t$ indicates the absolute temperature T, so that we may write $p.v = \frac{p_o.v_o}{273}.\ T$.

The factor $\frac{p_o.v_o}{273}$ has a constant value R, which is equal for all gases whatever their chemical nature may be, if for the value v_o we select the molecular volume, that is, the volume in cubic centimetres at 0° and 760 mm. pressure, which a quantity of gas would occupy, the weight of which was equal to its molecular weight expressed in grammes (gramme - molecule, abbreviated to *Mol.*); then the final and *general formula for gases* becomes: $p.v = R.T$.

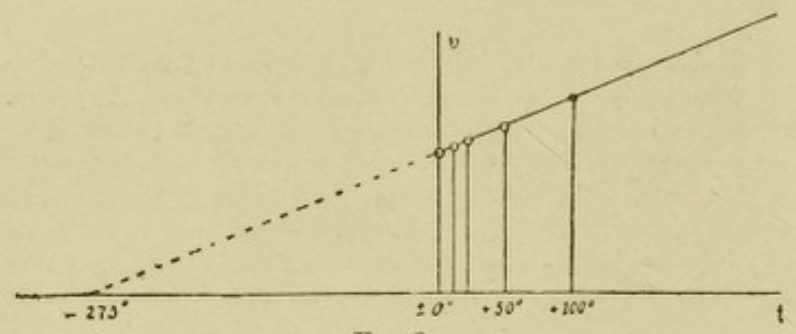


Fig. 3.

According to Avogadro's law the molecular volume of all perfect gases at 0° and 760 mm. pressure is always 22,412 c.c., that is, 2 grms. of hydrogen or 32 grms. of oxygen, and so on, occupy 22,412 c.c., and may then be represented by R.

The figure which represents the value R is, as we have said, independent of the nature of the gas, but varies with the units of measurement which we select to represent the magnitude p and the molecular volume; if we measure the pressure in units of one atmosphere ($p_o = 1$) and the molecular volume in litres (that is, 22·412 litres), then

$$R = \frac{22{\cdot}412}{273} = 0{\cdot}0821 \quad \text{and thus } p.v = 0{\cdot}0821\ T.$$

If instead of the pressure p, that is, one atmosphere, we express it in corresponding grammes of mercury (76 c.c. of mercury = 1033·3 grms.), and the molecular volume in c.c. (22,412), then the value of the *gas constant* becomes:

$$R = \frac{1033{\cdot}3 \times 22412}{273} = 84{,}780 \text{ and thus } p.v = 84{,}780\ T.$$

In the general formula for gases $pv = RT$, we know that pv represents a quantity of energy, namely, the energy of volume, which is independent of the volume and the pressure for any gas whatever and is only determined by the absolute temperature T. That is to say, that pv represents the quantity of energy (in absolute units)[1] necessary for the conversion of a gramme-

[1] *Absolute pressures* are pressures expressed in absolute units of the international system, the centimetre-gramme-second (C.G.S.) system. The *dyne* is the unit of force which causes an acceleration of 1 cm. per sec. per sec. on 1 grm. of matter at the sea-level at a latitude of 45°. It is known that gravitation produces an acceleration of 981 cm. per sec. per sec. on 1 grm. of matter, and thus a weight of 1 grm. expressed in absolute units of force corresponds to 981 dynes. The pressure of 1 atmosphere corresponds to a column of mercury 76 cm. high with a cross-section of 1 sq. cm. per sq. cm., that is, to a weight of 1033 grms. and therefore to 981 × 1033 dynes, *i.e.* about one million dynes or 10^6 dynes. And as the work corresponding to the unit of force (the dyne) is called the erg (the absolute unit of work), the pressure of an atmosphere expressed in absolute units of work will be 10 *ergs*, or, more exactly, 1,033,300 ergs. (*Translator's note.*—This should read "work done against atmospheric pressure through a distance of 1 centimetre.")

molecule of any liquid or solid substance whatever into gas (22,412 c.c.), in order to overcome the atmospheric pressure. We will show below that the work expressed in calorific units becomes $pv = 1{\cdot}985\ T$ calories, because a calorie corresponds to 42720 absolute units (ergs, *see below*), and thus

$$\frac{84780}{42720} = \text{about two calories.}$$

Or since the work necessary to increase the volume of any gas by one litre, overcoming the pressure of one atmosphere, is 1,033,300 absolute units[1] and since a calorie corresponds to 42,720 absolute units, the number of calories corresponding to the work of one litre-atmosphere will be :

$$\frac{1{,}033{,}300}{42720} = 24{\cdot}19 \text{ calories.}$$

If now in the general formula for gases (I), instead of representing p_o by unity, we represent it by the corresponding value in calories (of one litre-atmosphere) we will have :

$$p.v = 0{\cdot}0821 \times 24{\cdot}19\ T = 1{\cdot}985\ T.$$

CRITICAL TEMPERATURES AND PRESSURES OF GASES

On compressing or cooling a gas this is ordinarily transformed into a liquid, because the molecules approach one another through the pressure, or lowering of the temperature, until they reciprocally attract one another in a stable manner. In spite of this some gases resist liquefaction even under the strongest pressures, amounting to thousands of atmospheres, as was proved by Natterer.

At the close of 1823 Faraday found a general method of liquefying many gases and especially chlorine ; into a glass tube bent into an angle and closed at one end he introduced chlorine hydrate, and then closed the other end of the tube in the blow-pipe (Fig. 4). By immersing the end of the tube containing the crystals in a water-bath chlorine was already evolved at 30°, and on immersing the other end in a beaker containing ice the chlorine was liquefied through the strong pressure which the gas itself exerted as it was developed.

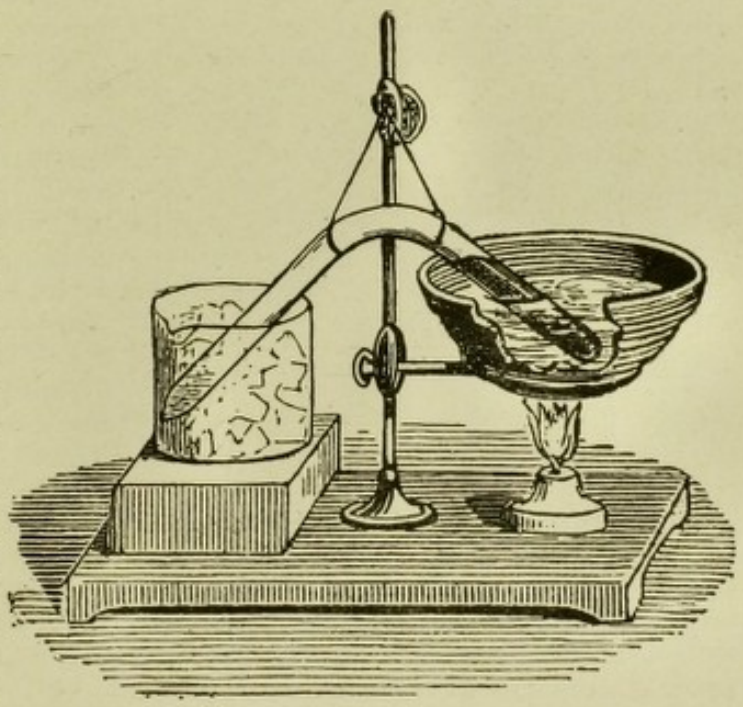


Fig. 4.

In this way Faraday succeeded in liquefying carbon dioxide, hydrogen sulphide, gaseous hydrochloric acid, sulphur dioxide, ammonia, and chlorine.

In 1835 Thilorier prepared large quantities of liquid and solid carbon dioxide. On mixing the latter with ether he obtained a temperature of 100° below zero and even of −110° by evaporating the mixture *in vacuo*. But until 1877 it had not been found possible

[1] If we imagine a cylinder of 1 sq. decimetre cross-section in which is a piston supporting a pressure of 1 atmosphere, then to raise the piston by 1 decimetre, that is, to increase the volume inside the cylinder by 1 litre, we must do work corresponding to the raising of 103·33 kilos through a height of 1 dm. (since the pressure of one atmosphere corresponds to 1033·3 grms. per sq. cm. and to 103·33 kilos per sq. decimetre) ; the work necessary to raise 103·33 kilos through a height of 1 dm. is equal to that required to raise 1 grm. through a height of 1,033,300 cms.

to liquefy hydrogen, oxygen, nitrogen, carbon monoxide, air, methane, or nitric oxide, and for this reason these gases were called the *permanent gases*. In 1869 and 1872 Andrews showed by important and numerous experiments that for gases in general a temperature exists above which they cannot be liquefied whatever the pressure may be. Thus at 0° carbon dioxide is liquefied at 35·4 atmospheres pressure, at 30° at 73 atmospheres, whilst at 31° it cannot be liquefied whatever the pressure may be. Its volume then diminishes until it corresponds to the liquid condition (critical volume) but the substance still remains gaseous. This limiting temperature, above which the liquefaction of a gas is impossible, is called its *critical temperature* (T), whilst the pressure which is necessary to liquefy it at the critical temperature is called the *critical pressure* (P).

Natanson, and, still more completely, van der Waals, obtained an equation of the third degree based on the deviations from the law of Boyle, by means of which they were able to calculate theoretically the critical temperatures and pressures of the various gases in advance, and experience has confirmed their deductions. On the opposite page we give the critical temperatures and pressures of a few gases.

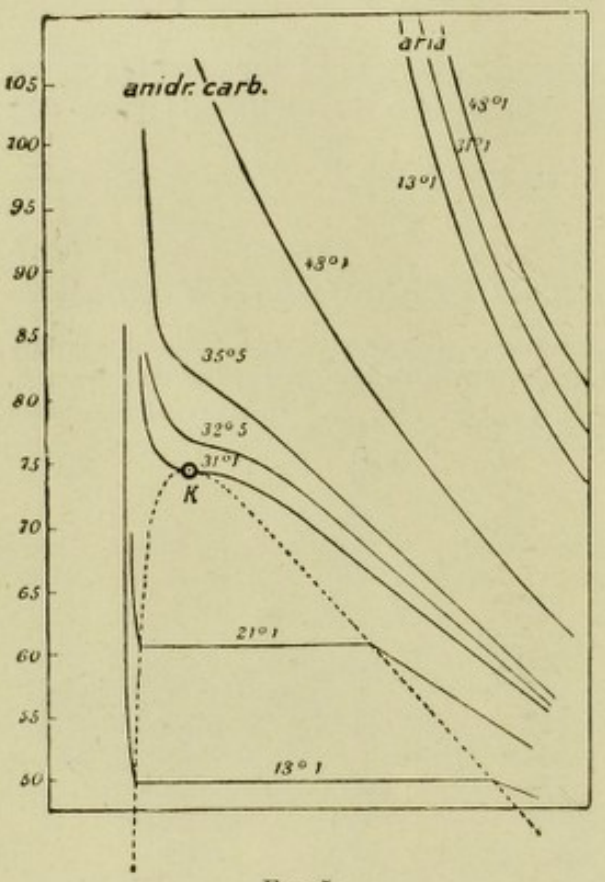


Fig. 5.

The phenomena of the critical temperature are graphically illustrated in Fig. 5, which refers to the behaviour of carbon dioxide. If we start with a given weight of carbon dioxide and plot as abscissæ on the horizontal axis the volumes which it assumes at varying pressures and plot the corresponding pressures as ordinates on the vertical axis, then we obtain for each temperature a different isothermic curve. In the first isothermal, corresponding to a temperature of 13·1°, we see that, starting from the base on the right hand, the curve rises for a short distance, because as the pressure rises the volume diminishes correspondingly; the curve then becomes rectilinear and horizontal, which indicates that the pressure remains constant whilst the volume rapidly diminishes; in this portion we have the gradual liquefaction of the carbon dioxide. During this transformation of vapour into liquid it is impossible to raise the pressure, as any attempt to do so simply increases the rate of liquefaction; when all the vapour is transformed into liquid we see that the volume scarcely diminishes any further, as liquids are only very slightly compressible, and thus the isothermal rises rapidly in an almost vertical direction up to the highest pressures. The next isothermal, corresponding to a temperature of 21·1° is analogous to the preceding one, but the horizontal portion, where vapour and liquid carbon dioxide coexist, is shorter and continues to diminish in the isothermals corresponding to higher temperatures until it is reduced to a point, K, in the isothermal corresponding to 31·1°, and at a pressure of about 76 atmospheres. The point K is called the critical point and corresponds to the critical temperature, critical pressure and critical volume (that is, the volume corresponding to K on the axis of the abscissæ.

At temperatures above 31·1° it is not possible to liquefy carbon dioxide and the isothermals corresponding to the temperatures of 32·5°, 35·5°, and 48·1° show that the curves no longer have a horizontal portion but show, on the other hand, the passage of vapour into the state of a more perfect gas. In the right-hand top corner of the diagram three isothermals of an almost perfect gas, namely, air, which has a critical point of − 140° (*see* Table), are drawn.

Gas	Critical temperature	Critical pressure: atm.	Boiling-point	Solidifying-point
Ammonia	+130°	115	− 33°	− 77°
Ethylene	+ 10°	52	−102°	−169°
Carbon dioxide	+ 31°	77	− 78·2°	− 57°
Nitrous oxide	+ 35·4°	75	− 89°	—
Nitric oxide	− 93·5°	71	−153·6°	−167°
Oxygen	−118°	50	−182·5°	−227°
Carbon monoxide	−139·5°	35·5	−190°	−212°
Air	−140°	39	−191°	—
Nitrogen	−146°	35	−196·4°	−214°
Hydrogen	−241°	20	−252·6°	−258·9°

LIQUEFACTION OF PERMANENT GASES

After the work of Andrews, Pictet at Geneva (December 2, 1877), and Cailletet at Paris (December 30, 1877), succeeded, independently of one another, in liquefying oxygen and almost all the other permanent gases. Pictet first liquefied an easily condensible gas by pressure and refrigeration; into this liquefied gas he then immersed a tube containing another compressed and refrigerated gas, and finally caused the first gas to evaporate rapidly by strongly diminishing the pressure. In this way he lowered the temperature sufficiently to produce liquefaction of the second compressed gas. Into this new liquid he then immersed another strongly compressed and cooled gas, more difficult to liquefy than the preceding one, and caused this to liquefy in turn by causing the other liquefied gas, in which it was immersed, to evaporate rapidly. In this way he gradually succeeded in liquefying almost all the permanent gases.

Cailletet, on the other hand, strongly compressed any cooled gas and then allowed it to expand rapidly until it attained the ordinary pressure; he succeeded in this way in cooling it very considerably. He then compressed it again and allowed it to expand, and repeated these operations of cooling by means of expansion until he finally obtained the liquid.

In 1884 Wroblewsky and Olszewsky, and later Dewar in London, with an ingenious apparatus based on Cailletet's principle, but which allowed the compressed gas at twenty atmospheres to expand, easily prepared liquid air and oxygen, at a temperature of only −190°. In 1898 Dewar prepared considerable quantities of liquid hydrogen and helium, which had not been prepared before, attaining a temperature of −258° and then obtained solid hydrogen at a temperature of −259°.[1]

In 1897 Linde constructed a simple and ingenious machine, based on the cooling produced by the expansion of compressed gases, for liquefying large quantities of air (*see* Liquid Air).

The behaviour of substances, and the chemical, physical, and vital phenomena, animal and vegetable, at such low temperatures, are interesting and often strange. Certain microbes, for instance, resist temperatures of −190° very well and merely cease to multiply, but when brought back to the ordinary temperature resume all their vital functions. Electrical phenomena at low temperatures are also very interesting (*see* Liquid Air).

LAWS OF GAY-LUSSAC ON GASEOUS COMBINATION. The brilliant hypothesis of Dalton was confirmed, and its importance increased, by the valuable experiments of Gay-Lussac and Humboldt which quickly followed in 1805; these scientists succeeded in showing that one volume of oxygen

[1] In order to measure such low temperatures Dewar used hydrogen thermometers at constant volume, or thermo-electric couples, or electrical resistance thermometers of various metals and alloys; the latter are not exact at temperatures below −200°, whilst the first are the best. For temperatures between −183° and −200° oxygen thermometers based on the vapour tension of this gas when liquefied served very well. For ordinary measurements down to −200° pentane thermometers served sufficiently well; pentane, C_5H_{12}, obtained from the more volatile petroleum fractions, is already liquid at ordinary temperatures and remains liquid down to about −200°.

gas combines with exactly two volumes of hydrogen gas to form water. In 1808 Gay-Lussac alone, continuing these experiments on the combination of gases, found that a constant and simple relation existed not only between the volumes of gases (or vapours) which combined, but also between the total volume of the gases entering into combination and the volume of the resulting mixture of gas or vapour.

We may illustrate these important laws discovered by Gay-Lussac by a few experiments.

In order to show that water is composed of hydrogen and oxygen, it is sufficient to decompose it with an electric current in a Hofmann U-tube (Fig. 6). One end of this tube is closed, and if connected with the negative (zinc) pole of an electric battery, hydrogen will collect there whilst oxygen is developed in the open arm at the positive pole. If the current is reversed, oxygen will collect at the positive pole and hydrogen at the negative.

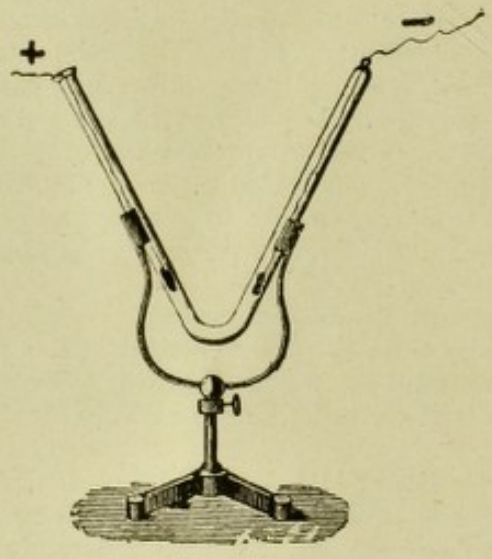


Fig. 6.

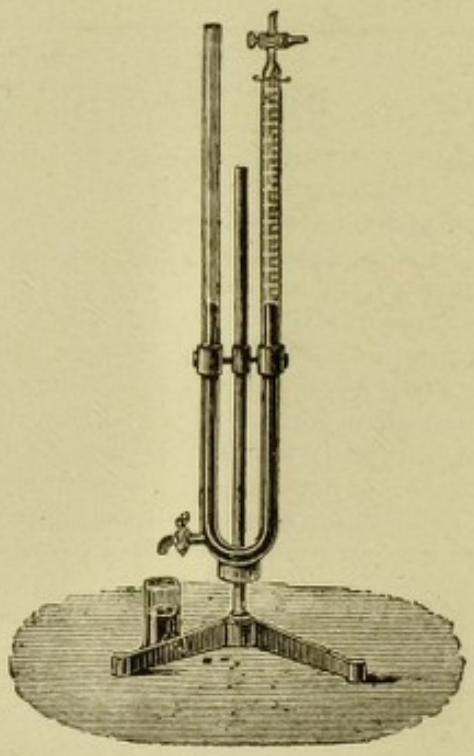


Fig. 7.

In order to demonstrate the nature of the two gases which are formed, the open end of the tube is filled with water, closed with the hand, and reversed in such a manner as to pass the gas into the open arm. Hydrogen is then recognised by burning when lighted with a match, whilst oxygen revives the combustion of a glowing splint of wood.

Gay-Lussac's demonstration of the fact that one volume of oxygen combines with two volumes of hydrogen may be shown in the apparatus (Fig. 7).

This is a U-shaped eudiometer filled with mercury, one arm of which is closed above with a tap and contains two platinum poles. By running out mercury through the lower tap a measured volume of oxygen, for example, 5 c.c., is allowed to enter through the top tap, and is then mixed with a measured excess of hydrogen, for example, 20 c.c. After reading the total volume of the mixed gases when the mercury in both arms of the eudiometer is at the same level, the excess of mercury is poured into the open arm in order to counterbalance the pressure which is produced on passing an electric spark between the platinum terminals by means of four Bunsen cells and a Ruhmkorff coil.

The electric discharge causes the hydrogen and oxygen to react with momentary dilation of the excess of gas and of the water-vapour which is formed.

After the reaction, and when the apparatus has cooled, the mercury is again brought to the same level in the two arms of the eudiometer, when the remaining quantity of hydrogen is found to be 10 c.c. Therefore, 5 c.c. of oxygen and 10 c.c. of hydrogen have disappeared, that is, have been transformed into liquid water. Thus the combination has taken place

in the proportion of one volume of oxygen with two volumes of hydrogen, and if the water thus formed were transformed into vapour by immersing the eudiometer into a medium with a temperature above 100°, it would occupy two volumes compared to the three complete volumes of gas from which it is derived (two of hydrogen and one of oxygen, measured at the same temperature). The second consequence of the law of Gay-Lussac has thus been demonstrated, which is that the total volume of gas formed is in a simple relation to the total volume of the component gases (two volumes of water vapour compared with three complete volumes of oxygen and hydrogen).

If we deduce the consequences of this experiment, we arrive at the interesting conclusion that if two volumes of hydrogen gas combine with one volume of oxygen gas in order to form water, the water must be formed according to the proportions by weight of the two components, hydrogen and oxygen, which would be equal to the proportion of the weight of one volume of oxygen gas with the weight of two volumes of hydrogen gas.

We have already found by means of various chemical analyses the weight of combination or stoichiometric values of this element, that is, we already know that in water one part by weight of hydrogen is combined with eight parts by weight of oxygen. On the other hand, we find with the balance that two litres of hydrogen (two volumes) weigh 0·18018 gr. and that one litre of oxygen (one volume) weighs 1·430 gr. The relation between these two weights is precisely 1 to 8, that is, the weight of one volume of oxygen is eight times greater than two volumes of hydrogen, or sixteen times greater than a single volume of hydrogen.

Since gases so diverse in physical and chemical properties (both simple and compound) all follow the laws of Boyle and of Gay-Lussac, we must suppose that this behaviour is due to some factor common to all gases independently of their chemical nature. If we actually suppose that in equal volumes of various gases there is an equal number of particles, and if we know that one volume of oxygen weighs sixteen times one volume of hydrogen, then it will follow that the particles or atoms of oxygen must weigh sixteen times as much as hydrogen particles. One litre of oxygen weighs 1·43 gr. and one litre of hydrogen 0·09 gr. The relation between these two weights is as 16 to 1, and since equal volumes will contain equal numbers of atoms, then the atomic weight of hydrogen being 1, that of oxygen will be 16. And if this reasoning suffices for all gases, it will be possible to determine the relative weight of the particles of any gaseous substance by a very simple method. It will be necessary, that is, to weigh a given volume of the gas to be studied and to see by how many times this weight is greater than that of an equal volume of hydrogen, taken as unity.

This conclusion was, however, not deduced by Dalton, who was not even willing to accept it, but by Berzelius about the year 1810, who felt himself authorised to deduce from the laws of Gay-Lussac and of Boyle on gases, and from the experiments of Proust and of Dalton, that in equal volumes of gas under equal conditions of temperature and pressure, equal numbers of *atoms* exist ; but when Berzelius came to control by practical experiments this daring and brilliant deduction, he at once found that numerous facts were in apparent and inexplicable contradiction with his hypothesis. Thus he says that if one combines one volume of hydrogen gas with one volume of chlorine gas, one volume of the new gas, hydrochloric acid should logically result, because the new volume of hydrochloric acid so formed should be constituted of one particle of hydrogen and one particle of chlorine, so that the two reacting particles should form one single particle of hydrochloric acid, and thus the two volumes of particles, for example, 1000 + 1000 particles, should give one volume only or 1000 particles of hydrochloric acid (particles formed of hydrogen and chlorine). But practical experiment

showed that two volumes of hydrochloric acid gas were formed. Thus also on combining two volumes of hydrogen with one of oxygen, a single volume of water vapour should result, because each particle of water necessarily requires three particles of the constituent elements, that is, one particle of hydrogen unites with another particle of hydrogen and one particle or volume of oxygen to give a single particle of water, so that three volumes should form a single volume, but it is actually found that two volumes result.

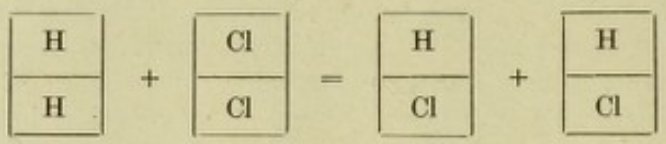
Confronted with this abnormality, Berzelius wavered, and not being able to explain the enigma, finished by partly renouncing his hypothesis and limiting it to the simple gases, and no longer applying it to gases formed of different elements or atoms.

Nevertheless, an Italian physicist, Count Amedeo Avogadro (1776–1856), in 1811 brilliantly explained this apparent contradiction by means of an ingenious hypothesis which he amplified and confirmed in 1814. He supposed that the particles which we imagine to constitute matter are composed of still smaller particles, and called the first *molecules* and the second *atoms*. These latter are not free, but are united in pairs or larger numbers with one another in order to form molecules, which, on the other hand, exist uncombined in the gas.

When chemical combination occurs under the influence of special circumstances, the molecules split and momentarily liberate atoms, by which means it becomes possible for these to combine with other atoms of different character, so creating new molecules of a new compound.

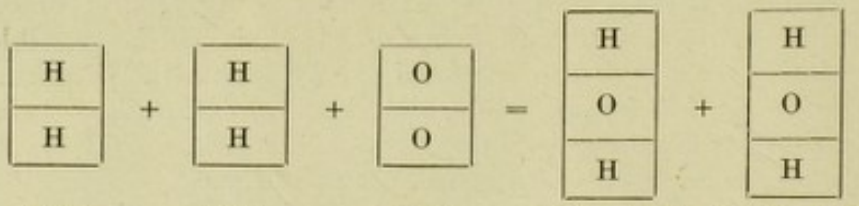
If we represent these molecules graphically, divided into two parts (the atoms), then the chemical reaction in respect to the volumes of gas and to the number of small and large particles (atoms and molecules) may be imagined with the help of the following figures, which indicate the atoms of hydrogen with the letter H, those of chlorine with the letters Cl, of oxygen with the letter O, hydrochloric acid with HCl, and water with H_2O.

I.



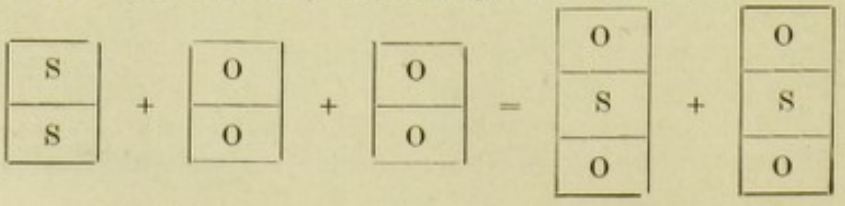
1 Vol. 1 Vol. 1 Vol. HCl 1 Vol. HCl

II.



1 Vol. 1 Vol. 1 Vol. 1 Vol. H_2O 1 Vol. H_2O

In this way the reactions which occur in practice are explained without any anomaly and in full conformity with the law of Gay-Lussac. We can now state with the greatest exactitude that in equal volumes of gas equal numbers of molecules (not of atoms) are contained. And with this conception it is also possible to foresee and establish *a priori* in the greater number of cases how many volumes of the gaseous compound will result from the action of given volumes of simple gases, and thus, for example, one knows that if one volume of sulphur combines with two volumes of oxygen to give sulphur dioxide, the volume occupied by this new gas should be two volumes. Thus :



Avogadro[1] thus clearly deduced from the available evidence the idea that *in equal volumes of gas under equal conditions of temperature and pressure, equal numbers of molecules exist,* and knowing also that the relation between the combining weights (stoichiometric values) is equal to the relation between the volumes of gases which combine, the conclusion is arrived at that the relation between the weight of one volume of any gas and the weight of an equal volume of hydrogen gas will be the same as that which exists between the weight of one molecule of the gas and that of a molecule of hydrogen.

Thus, in order to know the molecular weight of any gas, it is sufficient to know the weight of a given volume of hydrogen gas and that of an equal volume of the gas under consideration.

And thus the laws of Boyle and of Gay-Lussac also found their most beautiful and simple expression in the postulate of Avogadro.

The principal laws obeyed by gases being then known, it was easy to arrive at the molecular weights of all gaseous substances, or of such as could be evaporated, by determining the density of the gas or vapours, that is, by comparing the weight of the gas with that of an equal weight of hydrogen, taken as unity.

We will summarise briefly the various methods which have been devised for determining the densities of vapours and gases, because these have contributed greatly to the development of modern chemistry.

[1] We think it will be interesting to give a biographical note of this Italian scientist, who was for a long time unrecognised and who did so much for the progress of chemistry. Count Amedeo Avogadro was born at Turin on August 9, 1776, and died at Turin on July 9, 1856. In 1796 he was a doctor of law, and in 1806 was a teacher of physics in a college at Turin. From 1808 until 1820 he was professor of physics at the gymnasium at Vercelli, and later was nominated professor of mathematical physics in the University of Turin. His chair was suppressed after the revolutionary movement of 1821, and he devoted himself to the magistracy in order to soon return in 1833 to the study of physics in the same university. He was little known in Italy and still less abroad.

His important work appeared on July 14, 1811, in the *Journal de Physique*, and the second part in 1814 in the same journal under the title " Essai d'une maniere de déterminer les masses relatives des molécules élémentaires des corps et les proportions selon lesquelles elles entrent dans les combinaisons." From the law of Boyle and of Gay-Lussac he deduced that in equal volumes of any gas whatsoever equal numbers of particles are contained which are present at such a distance from one another that they no longer attract one another, and he called them *constituent molecules* or *integrants*. These molecules were formed in their turn of still smaller indivisible particles called *elementary molecules* (atoms).

Avogadro's hypothesis was not accepted at that time on account of the apparent difficulties of imagining particles of simple gases equal to those of compound gases, whilst according to Avogadro himself a difference existed between the molecules of simple gases and those of gaseous compounds. The former were in their turn constituted of two other indivisible particles of the same nature, of the " elementary molecules " (atoms) which held one another united to form the free molecules, whilst the molecules of other combinations were also formed of two atoms but of different nature. He demonstrated that no case was known in which, starting from one volume of a gas B, one volume of a gas AB was formed, as one would expect on the hypothesis of the indivisibility of molecules (to-day some cases of monatomic molecules are known), but in reality a volume results which is always at least double that of one of the components, so that it is necessary that such a component should be divided into at least two particles in order to enter into a double number of new particles. He thus explained how one volume of H and one volume of Cl could form two volumes of HCl, thus explaining brilliantly all the gaseous combinations known in his time.

In 1812 Davy made a vague note on the probability of the atoms first uniting into groups which constituted the chemical particles of a substance; in 1814 Ampère clarified and amplified Davy's conception, approaching considerably to the conception already clearly explained by Avogadro.

But there were individual facts which could only be explained by Avogadro's hypothesis, although these facts were not sufficiently numerous to make the need of the new hypothesis felt by all, and it remained neglected and obscured for about fifty years, although Berzelius noted it in his treatise on chemistry. Avogadro's hypothesis received full recognition about the year 1850 through the new and important work in organic chemistry initiated by Gerhardt and Laurent. Gerhardt even considered it as a scientific necessity in order to explain all chemical phenomena. In 1856, whilst the dispute on this hypothesis still raged, Clausius, starting from purely physical considerations, developed the mechanical theory of heat by using Avogadro's hypothesis.

It was also the great merit of Cannizzaro to have co-operated with enthusiasm since 1858 in the propagation in Italy of Avogadro's important postulate, and to have placed the atomic theory on a fundamental basis and given a brilliant and synthetic explanation of it in a modest and most valuable monograph entitled " Sunto di un corso di filosofia chimica " (" Synopsis of a Course of Chemical Philosophy ").

DETERMINATION OF THE DENSITIES OF VAPOURS AND GASES

The density of gases is given by the relation between the weight of a given volume of gas and that of an equal volume of air, measured under the same conditions and taken as the unit of comparison. It would be more rational to refer the density of gases to that of hydrogen.

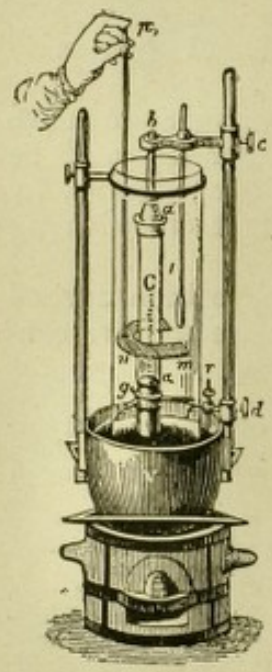


Fig. 8.

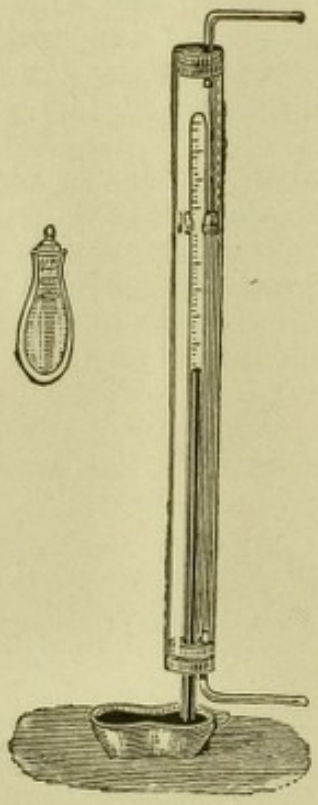


Fig. 9.

The gases must be compared at the same temperature and pressure, and it is convenient to compare all gas volumes, V_o at zero temperature and at the normal pressure of 760 mm. Then by combining the two formulæ representing the laws of Boyle and of Gay-Lussac respectively (*see* pp. 23–24) and noting the coefficient of dilatation of gases, we arrive at a single general formula for any temperature:

$$V_o = \frac{V\,(p - h)}{760\,(1 + 0{\cdot}00367\,t)}$$

where V indicates the volume of gas at the temperature t and pressure p observed in mm. by the mercury barometer. But it is necessary to take into account the vapour tension of the liquids over which the gases are measured; the tensions, h, for water are indicated in the table which is given in the chapter on Water.

There are various methods of determining the densities or specific weights of gases and vapours, but in all these it is necessary to take into account the observation of Amagat, that gases and vapours follow the laws of Boyle and of Gay-Lussac the more exactly the further the vapour is removed from the temperature of condensation or liquefaction, that is, the hotter it is.

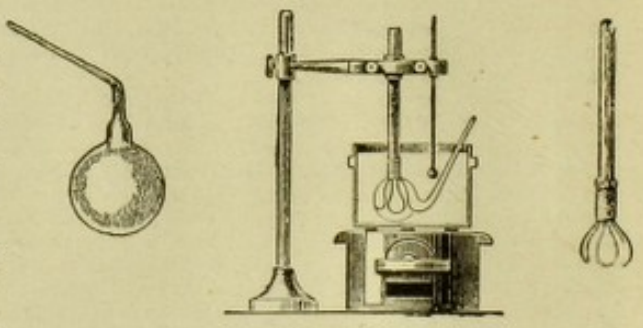


Fig. 10.

Gay-Lussac's Method (1816). A weighed quantity of a liquid or solid substance is introduced into a graduated glass tube (*see* Fig. 8) full of mercury and standing in a bath of mercury. The tube is surrounded by a large glass cylinder in which a liquid is placed (water, oil, &c.), which boils at a more elevated temperature than the point of ebullition of the substance under examination. The outer liquid is then boiled by raising the mercury to a sufficiently high temperature and the amount of vapour formed by the substance under examination is then measured, the temperature and pressure to which it is subjected being also noted.

A. W. Hofmann's Method (1868). This is an improvement upon Gay-Lussac's method, because the graduated tube containing the mercury is 1 m. high (Fig. 9), and the substance

can thus be evaporated in a barometric vacuum. We are thus able to study, undecomposed and in a state of vapour, those substances which decompose on boiling at the ordinary pressure. The substance is heated by the vapour of substances boiling at a considerably higher temperature than the product under examination in the outer tube.

Dumas' Method (1827). A weighed closed bulb of about 500 c.c. capacity furnished with a capillary neck is heated and the capillary immersed in the liquid or molten solid substance which is to be studied. On cooling, about 5 to 10 grms. of the substance are allowed to enter the bulb. The bulb is then immersed in a bath heated to a temperature higher than that of the boiling-point of the substance under examination. This then gradually evaporates, driving all the air out of the bulb, and when it is completely evaporated and no further vapour issues from the point of the capillary this is sealed in the blow-pipe and the temperature of the bath (which should be equal to that of the vapour filling the bulb) is measured, and also the height of the barometer. The bulb is well cleaned, carefully weighed, and the point then immersed in a vessel of mercury; on breaking the closed point the mercury enters and fills the bulb completely, as a vacuum has been formed by the condensation of the vapour. This mercury is then poured into a graduated cylinder where it is exactly measured, or it is weighed. We have thus all the data for calculating: (1) the weight of the bulb full of air at a certain pressure and temperature; (2) the volume of the bulb at that same temperature (by deducting the volume of the mercury); (3) the volume of the air and its corresponding weight (found from a suitable table); (4) the volume of the air at the temperature of the heated vapour (calculated by means of the coefficient of the dilatation of gases, 0·00367), and thus also the volume of the vapour at the same temperature; (5) the weight of the evacuated bulb without air (obtained by deducting from the weight of the bulb with mercury the weight of the mercury); and (6) the weight of vapour contained in the heated bulb (found from the weight of the bulb full of vapour by subtracting the weight of the evacuated bulb).

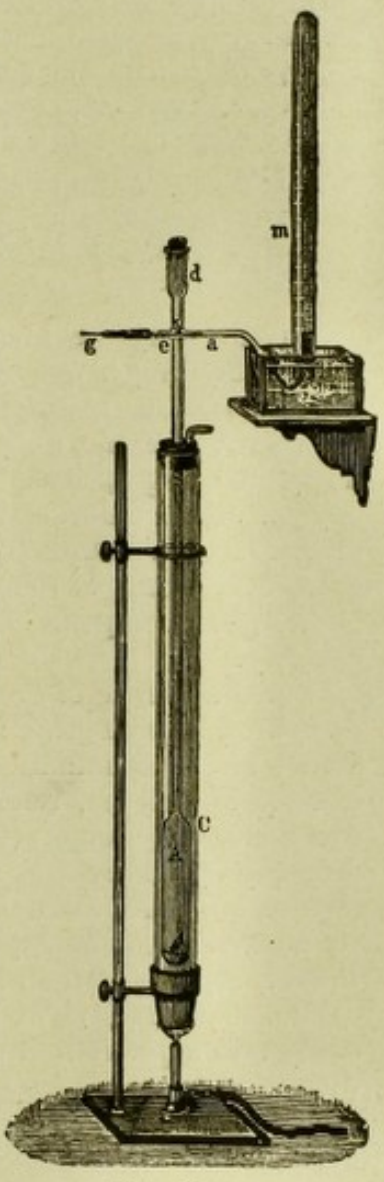


Fig. 11.

Victor Meyer's Method (1878). The volume of air which is displaced by the vapour of a given weight of substance is measured. The weighed substance under examination is placed in a very small tube and is dropped into a vertical glass tube provided with a delivery tube which is heated to a constant temperature by hot vapours produced in an external mantle. It is there immediately evaporated, giving a certain quantity of vapour which displaces the same volume of air. This is collected in a graduated tube as is indicated in Fig. 11.

The temperature of the vapour is given by the boiling-point of the substance which produces the vapours in the outer mantle by heating the apparatus from outside.

This simple, rapid, and exact method is one of the most widely diffused in chemical laboratories. In the case of substances which evaporate at high temperatures vessels of porcelain or of platinum are employed which are heated in furnaces or in some other manner. Exact determinations can be made with as little as 0·1 grm. of substance.

In some cases various other methods of determining molecular weights are used, but none of them are in current use in laboratories, although they sometimes serve as methods of control.

We will refer amongst these to the methods of Wrede Svanberg (1846), Buff (1831), Marchand (1848), Pfaundler (1879), Malfatti-Schoop (1886), &c.

Some substances or elements cannot be transformed into vapour, and the molecular weight must then be determined indirectly by determining that of some volatile derivative.

For instance, chloride of iron can be evaporated and from its density the atomic weights of the components can be calculated, correcting in some cases the inevitable errors by means of the stoichiometric values which, as we have seen, stand in simple relationship to the atomic weights. Thus, if in a given compound we find the resulting molecular value of oxygen to be 32·7 we must correct it, as it must be an exact multiple of the stoichiometric value of 8, and therefore 32.

We will now consider some simple examples of the calculation of molecular weights. We know from the work of Gay-Lussac that one volume of oxygen combines with two volumes of hydrogen, and that this volume of oxygen weighs eight times the two volumes of hydrogen, that is to say, a single volume of hydrogen weighs sixteen times less than the same volume of oxygen. Hence, if we take the atomic weight of hydrogen as unity, an atom of oxygen will weigh 16 because in equal volumes of gas there are equal numbers of particles, which in this case are diatomic molecules :

1 litre of hydrogen weighs 0·09009 grms., and if we take the weight of hydrogen as unity, then 1 litre of chlorine weighs 3·175 grms., that is, 35·5 times as much as hydrogen ;
1 litre of oxygen weighs 1·430 grms., that is, 16 times as much as hydrogen ;
1 litre of nitrogen weighs 1·257 grms. that is, 14 times as much as hydrogen.

In this way we know that for elementary or simple substances if the atom of hydrogen weighs 1, then that of chlorine weighs 35·5, that of oxygen 16, and that of nitrogen 14, &c. If, on the other hand, we wish to know the relative atomic weight of the molecules, as it is really these which move freely in the gas, then the diatomic molecules of hydrogen will weigh 2, of oxygen 32, of chlorine 71, of nitrogen 28, that is to say, double the weight of the atoms. Ordinarily, for convenience and exactness, the density of gases or vapours is referred to that of air. That is, the weight of one litre of the gas or vapour is compared with the weight of one litre of air, taken as unity.

Since one litre of air (1·294 grms.) weighs 14·44 times as much as one litre of hydrogen (0·09 grms.), then if we would have the atomic weight of the substance under examination referred to hydrogen as unity, we must multiply the density of the gas, referred to air as unity, by 14·44, and if we would have the molecular weight (where there are two atoms in a molecule) we must multiply by 28·88.

For example, the density of sulphur dioxide compared with air was found to be 2·21. On multiplying this number by 28·88, one obtains 64, which, in fact, represents the molecular weight of sulphur dioxide.

Consequently, if we know the molecular weight of a substance we can easily and *a priori* find the density of its vapours referred to air, by dividing the molecular weight by 28·88.

KINETIC THEORY OF GASES

As soon as the molecular weights were first studied, it was observed that some substances did not give results concordant with their vapour densities. For example, ammonium carbonate, ammonium chloride, and phosphorus pentachloride (PCl_5), give vapour densities, compared with hydrogen, which lead to a value for the molecular weight which is one-half of that deduced from analyses and other determinations. For many years these substances were considered as true exceptions to Avogadro's law, since being compound substances it appeared absurd to imagine them as monatomic molecules (*see below*).

In order to explain these important exceptions, it became necessary to study the intimate nature of gases and of the particles which composed them still more attentively, and from first principles. It was actually the kinetic theory of gases which indirectly and by means of quite different

considerations gave a new mathematical explanation of the laws of Boyle and of Gay-Lussac.

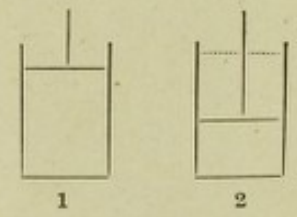
It was the work of Bernouilli (1738) the physicist of Basle, of Herapath (1821), of Joule (1851), and to a still greater degree of Krönig in 1856, and more especially of Clausius in 1857, which led to the explanation of these exceptions by means of a rational mathematical theory on the nature of the pressure exercised by gases.

On what does the pressure which compressed gases exercise on the containing vessel depend, and to what is it due ?

Newton believed that the pressure which is produced or exercised by compressed gases on the walls of the containing vessel was due to the action of repulsive forces which the gaseous particles exercised on one another. Bernouilli and his successors demonstrated that this hypothesis was erroneous and untenable, and it is untenable because if the gaseous particles were endowed with this repulsive force, then in expanding freely without doing any work this force should be transformed into heat, and thus on expanding a gas should become hot.[1] In practice the exact opposite occurs, that is, a gas which expands greatly is strongly cooled, as was shown by Joule and Thomson.

Bernouilli and his successors supposed, on the other hand, that the particles of gases are endowed with rectilinear motion, and that they collide with one another and more especially with the walls of the containing vessel. The sum of these impacts with the walls of the containing vessel causes the pressure. The number of these impacts is proportional to the velocity of the particles and is inversely proportional to the distance between the walls, and the result of the impacts is in direct proportion to the mass.

If then the particles contained in a given volume collide a given number of times in unit of time with the walls of the containing vessel 1, and if we now compress the gas to half the volume (vessel 2), the velocity remaining constant, then the particles will collide twice the number of times against the walls in unit of time because they now have half the distance to traverse. Thus, they will exercise twice the pressure. This fully confirms Boyle's law. Actually, if in a cube with the side l, n molecules are contained, in order to determine the pressure which all these molecules exercise on the walls per unit of time, we must multiply the effect produced by the impact of one molecule by the number of impacts and by the total number of molecules. The molecules of mass m and of velocity c will collide in various ways and at different inclinations with the several walls of the cube, and therefore, by one of the laws of mechanics, we may resolve the velocity of each single molecule, whatever may be its direction, into three components, u, v, z, perpendicularly and parallel to the sides of the cube, and we may then imagine that of all the n molecules, one-third move with a uniform velocity in one of these three senses, and two-thirds in the other two senses, colliding perpendicularly with the walls of the cube. The time taken by one molecule to travel from one wall to the other through the distance l and to return to its point of departure will be $\frac{2l}{u}$, and thus the number of impacts in one second which result will be $\frac{u}{2l}$. The effect produced on the walls by each impact is represented by twice the quantity of motion mu, because the molecule first collides with the wall and then turns back (we suppose the wall to be perfectly elastic and able to reverse the direction of the velocity) ; thus we have for each impact $2\,mu$ per second, and the effect produced on the wall by one molecule will be $\frac{u}{2l}\,2mu = \frac{mu^2}{l}$. Since on each wall we have one-third of the impacts of the molecules, the effect of this third will be $\frac{1}{3}\,n\,\frac{mu^2}{l}$. In order to find the pressure exercised on a unit surface, we must divide by the surface of the wall (l^2), and we then have $p = \frac{1}{3}\,n\,\frac{mu^2}{l^3}$, and taking the same expression for the other molecules which move in the direction of the other components, we arrive at equal values for the velocities v^2 and z^2, and we must substitute the sum of these squares of the components



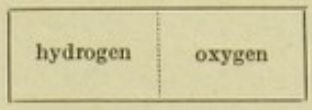
[1] *Translator's note.*—There is some lack of clearness here. Actually the work done would absorb heat from the gas itself and render it *cooler*.

$u^2+v^2+z^2$ by c^2, and since, on the other hand, l^3 is simply the volume, the final expression will be $p = \frac{1}{3}\, n \frac{mc^2}{v}$ or $p.v = \frac{1}{3}\, nmc^2$. This conclusion, which was deduced by Clausius and Krönig, represents another expression of Boyle's law. In many cases it is convenient to use another expression corresponding to the kinetic energy: as $p.v = \frac{2}{3}\, n\frac{mc^2}{2}$, and $n\,\frac{mc^2}{2}$ is the kinetic energy, we may say that *the pressure produced in a given volume of the gas is equal to two-thirds of the kinetic energy of its molecules.* By comparing this with the general gas formula $p.v = RT$ (p. 26) we have $RT = \frac{2}{3}\, n\,\frac{mc^2}{2}$, and the kinetic energy $n\,\frac{mc^2}{2} = \frac{3}{2}\, RT$, and therefore we may say that the absolute temperature T is proportional to the kinetic energy (molecular translation). When $T = 0$ (absolute zero) then the kinetic energy of the molecules will become zero, that is, at 273° below zero we have no longer any motion or any heat.

If we represent equal volumes of two different gases under the same condition of temperature and pressure by the general gas formula, which we have deduced above, and which comprises the laws of Boyle and of Gay-Lussac, we have in the one case $pv = \frac{2}{3}\, n\,\frac{mc^2}{2}$ and in the other case $p'v' = \frac{2}{3} n' \frac{m'c'^2}{2}$ where n, n', m, m' are the numbers and mass respectively of the molecules of the two gases which are under the same conditions of temperature, pressure, and volume. We therefore have $pv = p'v'$ and $\frac{2}{3}\, n' \frac{m'c'^2}{2} = \frac{2}{3}\, n\,\frac{mc^2}{2}$ or $n' \frac{m'c'^2}{2} = n\,\frac{mc^2}{2}$. When the temperature of a gas decreases, the kinetic energy $\frac{mc^2}{2}$ alone changes, but not the number of the molecules. Since these two gases have the same temperature and pressure their respective kinetic energies will be equal, that is, $\frac{m'c'^2}{2} = \frac{mc^2}{2}$, and eliminating these in the preceding equation we obtain the result $n = n'$. But this is nothing else than a demonstration of Avogadro's law according to which equal volumes of two gases under the same conditions of temperature and pressure contain equal numbers of molecules.

We have seen that the kinetic energy of the molecules of two gases under the same conditions is equal, that is, $\frac{mc^2}{2} = \frac{m'c'^2}{2}$. From this equation we can deduce this other, $mc^2 = m'c'^2$, that is to say, $c^2 : c'^2 = m' : m$, or the *squares of the velocities of the molecules of a gas are in inverse ratio to their masses* (the greater the mass the less the velocity), or again: $c : c' = \sqrt{m'} : \sqrt{m}$, which is to say that *the molecular velocities of gases are in the inverse ratio of the square roots of the masses of their molecules* (or molecular weights). Since on increasing the temperature the number n of the molecules is constant and the mass m or m' is also constant, then in order to increase the kinetic energy of a gas, we cannot do otherwise than increase the value of c, that is, increase the velocity of the particles by means of an elevation of the temperature. On heating a gas the velocity of its particles increases, and if the volume is maintained constant, these will collide a larger number of times with the walls of the containing vessel, and thus the pressure will be increased, which exactly confirms the law of Gay-Lussac.

We have seen that if the gas particles move more rapidly they weigh less. Now, if we imagine two closed vessels, one containing hydrogen and the other oxygen, divided by a porous partition with pores sufficiently large to allow the molecules to pass through



them since the hydrogen molecule is the lighter it moves more rapidly and will thus collide a larger number of times than the oxygen molecule with the porous partition, and will pass through the pores very easily; and more hydrogen molecules will pass into the vessel containing oxygen than oxygen molecules into the vessel of hydrogen.

Now as the volume of the vessel containing oxygen remains constant, if at a certain moment a larger number of molecules is present in it, the pressure should be increased on account of the more rapid diffusion of the hydrogen. This phenomenon actually occurs, as may be shown with the following apparatus.

A two-necked Woulf's bottle contains water into which a tube dips, passing through a stopper and terminating above in a capillary tube. The other neck carries through the stopper a long glass tube which does not dip into the liquid, and the top extremity of which terminates in a closed porous cell of porcelain (porous cell of a battery). If this cylinder, which is full of air, is covered with a bell-jar into which hydrogen is allowed to pass, the pressure inside the porous cell immediately increases and is transmitted to the liquid by means of the glass tube, driving the water up the capillary tube and producing a little fountain, as is seen in Fig. 12. There are also small pieces of apparatus which sound a bell (Ansell's apparatus) which illustrate the phenomena of diffusion (*see below*, Carbon Dioxide).

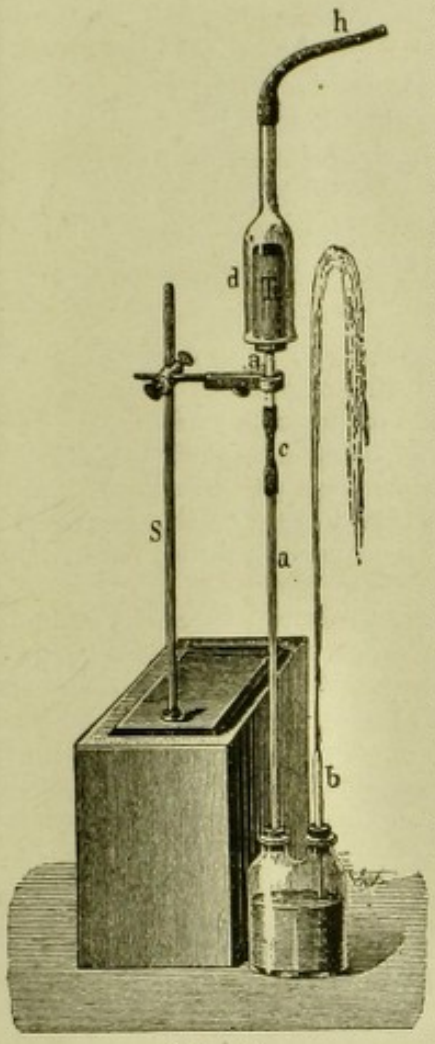


Fig. 12.

We have also deduced from the kinetic theory of gases by means of a simple mathematical formula that the velocity of the molecules is inversely proportional to the square root of their weight: $c : c' = \sqrt{m'} : \sqrt{m}$: if, for example, we suppose the molecular weight of hydrogen (H_2) to be 2 and that of oxygen (O_2) to be 32, we find that the velocity of the hydrogen molecule will be four times greater than that of the oxygen molecule, because as $c\,(H_2) : c'\,(O_2) = \sqrt{32} : \sqrt{2}$ $c\,(H_2) : c'\,(O_2) = 5{\cdot}65 : 1{\cdot}414$.

Graham also showed practically the truth of this deduction, and in 1857 Bunsen applied it to the determination of molecular weights of various gaseous substances, using minimum quantities and simply measuring the time taken by two equal volumes of gas under the same conditions of temperature and pressure in passing through a very small perforation, scarcely perceptible to the naked eye, in a platinum plate.

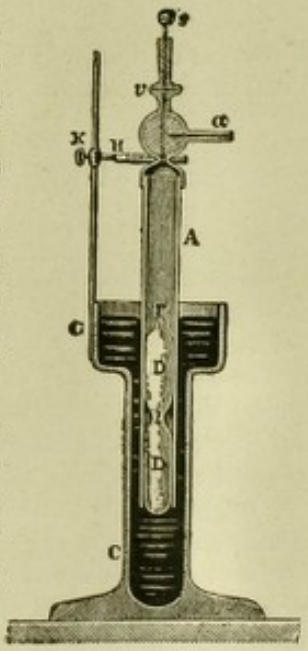


Fig. 13.

The gas under experiment is enclosed in a tube inverted over mercury. This contains above a platinum plate with a small hole which permits the gas to escape under the pressure of the external column of mercury. By means of a glass float, one is able to read from a distance the exact volume of gas which escapes in a given time. This effusiometer of Bunsen is illustrated in Fig. 13. By introducing the factor of time into the general formula, together with the velocity, and taking into account that the lighter the gas the less will be the time taken in escaping, it is easy to deduce the molecular weight. The velocity of the oxygen molecule has been calculated to be 461 metres per second, that of hydrogen 1844 metres per second, of chlorine 392 metres per second, &c.

Bearing in mind these new ideas on the behaviour of gases, we return to the determination of molecular weights by means of vapour densities in order to explain those important exceptions, such as ammonium chloride, &c., which led to half the true molecular weight.

In 1857 St. Claire Deville first made important experiments on certain

decompositions which occurred in some substances at high temperatures, and observed that the degree of dissociation is always the same for a given temperature and pressure. He applied the laws of thermodynamics to the study of these chemical equilibria, thus anticipating by thirty years the deductions arrived at by modern chemistry. In this same year, 1857, Cannizzaro and, immediately afterwards, Kopp and Kekulé (1858) showed that a molecule of ammonium chloride (NH_4Cl) dissociates at high temperatures into two new molecules, namely, into ammonia (NH_3) and hydrochloric acid (HCl), and the reason why the molecular weight became halved was thus explained. For some years the discussion continued as to whether this theoretical deduction was really possible, that is, whether two such substances as ammonia and hydrochloric acid, which have very great affinity for one another, are able to exist together at high temperatures without combination.

The question was experimentally solved in an elegant manner by Pebal in 1862 and by Than in 1864, by demonstrating the dissociation of ammonium chloride by means of the varying velocities of the molecules of hydrochloric acid and of ammonia on diffusion.

Thus, on heating a portion of ammonium chloride in a long open inclined tube, which is divided towards the middle by a plug of asbestos, the ammonia particles diffuse more rapidly and are able to turn red litmus paper blue if it is placed at the further extremity of the tube, whilst in the lower portion of the tube blue litmus paper is turned red by the action of the heavier molecules of hydrochloric acid.

After this demonstration that the molecules of compounds can be dissociated at high temperatures, and knowing that monatomic molecules of simple substances exist (metal, in the state of vapour, argon, &c.), the question arose whether the diatomic molecules of simple substances could be dissociated into free atoms. Victor Meyer and others have actually demonstrated that bromine is constituted of diatomic molecules at 228°, whilst at 1260° its dissociation into monatomic molecules is almost complete ; elementary iodine is formed of diatomic molecules at 253°, whilst at 1500° it is almost exclusively formed of monatomic molecules.

EXCEPTIONS TO BOYLE'S LAW—NEW EQUATIONS OF VAN DER WAALS—SIZE OF THE MOLECULES

Having thus explained in a plausible manner the apparent exceptions to Avogadro's law, we will now study the deviations from Boyle's law which occur when gases are highly compressed.

In 1852 Natterer exposed oxygen and air to pressures up to 3600 atmospheres, and found that the compressibility at increased pressures is somewhat less than that required by Boyle's law, as Regnault had also observed in 1850 in the case of hydrogen even under normal conditions.

By means of the kinetic theory of gases we are able to easily explain this apparent abnormality. In calculating the compression of gases by the mathematical formulæ, we do not consider the space occupied by the molecules themselves, consisting of their sphere of action or of vibration, into which another molecule is unable to penetrate. The distance traversed by each molecule of gas in order to collide with the walls of the vessel in which it is enclosed must be diminished by the radius of the molecule and its sphere of action. When considering ordinary pressures, these radii are negligible compared with the distance between the molecules, and Boyle's law remains uninfluenced. But when gases are strongly compressed and thus occupy relatively small volumes, the volumes of the molecules exert an influence and produce the small deflections from Boyle's law observed in compressed gases.

It has actually been proved that with pressures from 30 to 125 atmospheres, the gases are generally compressed a little more than is required by Boyle's law, and that above these pressures they are compressed a little less than the ordinary theory requires. Hydrogen, on the other hand, approaches more nearly than the other gases to the behaviour of an ideal gas. The first phase of greater compressibility is explained by the fact that as

the molecules approach one another they also attract one another a little, and thus the pressure which we read on the manometer is less than that which it would have been if this attraction did not exist, and the true pressure would, therefore, be $p + \frac{a}{v^2}$, where a represents a constant which measures the reciprocal attraction of the molecules, which attraction is directly proportional to the square root of the density of the gas, and, therefore, inversely proportional to the square root of the volume. In strongly compressed gases on the other hand, for example, at above 200 atmospheres, it is necessary to take account, as we have said above, of the volume occupied by the mass of the molecules themselves, and thus the true free volume is a little less than that which is measured (that is, $v - b$). The general formula for the gaseous state, $p.v = RT$, must therefore be corrected, according to Van der Waals, in the following manner : $\left(p + \frac{a}{v^2}\right)\left(v - b\right) = RT$.

Van der Waals and Clausius, taking the above data into account, calculated the value of the magnitude b of this formula from the specific volumes,[1] absolute pressures, &c. The diameter of a molecule of hydrogen resulting from these calculations was $1{\cdot}6 \times 10^{-8}$ cm., and thus the number of hydrogen molecules contained in 1 c.c. would amount to 5×10^{19}, which is to say that in a spherule of $\frac{1}{100}$ mm. diameter there would be contained fifty million molecules of hydrogen.

SYMBOLS AND CHEMICAL FORMULÆ

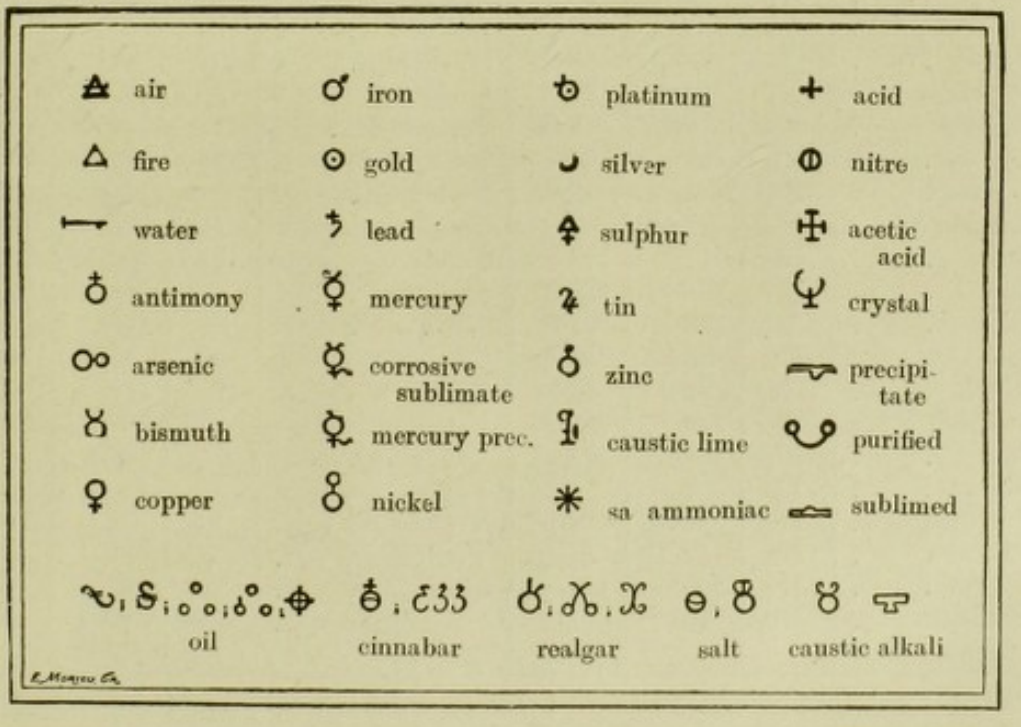
In order to represent the elements present as such or in chemical reactions, it was found useful to abbreviate graphic expressions by employing symbols.

The ancients, and still more the alchemists, had already adopted special and extravagant signs to represent certain substances.[2]

But Dalton, who had clarified the conception of elementary substances and had given a concrete idea of the elements by means of his atomic hypothesis, imagining them to be formed of simple atoms, was the first to propose the use of symbols to represent the atoms of the various elementary substances. The so-called non-metals, a special group of elements with non-metallic aspect, such as hydrogen, oxygen, chlorine, iodine, &c., were represented by conventional signs, for example, oxygen = ○, hydrogen ⊙, nitrogen ⊕,

[1] The specific volume is the volume occupied by a gramme of any substance in the gaseous state measured at 0° and 760 mm. pressure. If, for example, one litre of air weighs 1·294 grms., a gramme of air will have the specific volume of 773 c.c. The volume occupied by 1 grm. of hydrogen is 11,162 c.c., that is, 14·44 times more than that of air. The specific volume of oxygen is 699 c.c.

[2]



water ○⊙, ammonia ⊙◐. For metals, on the other hand, he proposed to employ as a symbol the first letter of the corresponding Latin name, for example, mercury with Hg, from the Latin *Hydrargirium*; iron, Fe (*ferrum*), &c.

Berzelius, who studied numerous substances and discovered new elements confirming all the conclusions of Dalton's hypothesis, proposed a little later (1813) to also represent the non-metals by the first letters of the Latin names. It is this nomenclature which has survived until to-day, and is accepted everywhere. Dalton wrote the stoichiometric value (combining weight or equivalent) at the side of the symbol, taking hydrogen as unity. Later on

TABLE OF ATOMIC WEIGHTS (1910)[1]

Name of the Element	Symbol	Atomic weight		Name of the Element	Symbol	Atomic weight	
		O=16	H=1			O=16	H=1
Aluminium	Al	27·1	26·9	Neodymium	Nd	144·3	143·15
Antimony	Sb	120·2	119·3	Neon	Ne	20	19·9
Argon	Ar	39·9	39·6	Nickel	Ni	58·68	58·3
Arsenic	As	74·96	74·36	Nitrogen	N	14·01	13·89
Barium	Ba	137·37	136·27	Osmium	Os	190·9	189·37
Bismuth	Bi	208·0	206·34	Oxygen	O	16	15·88
Boron	B	11	10·9	Palladium	Pd	106·7	105·85
Bromine	Br	79·92	79·28	Phosphorus	P	31	30·77
Cadmium	Cd	112·4	111·6	Platinum	Pt	195	193·45
Cæsium	Cs	132·81	131·75	Potassium	K	39·10	38·79
Calcium	Ca	40·09	39·77	Praseodymium	Pr	140·6	139·4
Carbon	C	12	11·91	Radium	Ra	226·4	224·6
Cerium	Ce	140·25	139·2	Rhodium	Rh	102·9	102·08
Chlorine	Cl	35·46	35·17	Rubidium	Rb	85·45	84·77
Chromium	Cr	52	51·58	Ruthenium	Ru	101·7	100·9
Cobalt	Co	58·97	58·50	Samarium	Sa	150·4	149·2
Columbium	Nb	93·5	92·75	Scandium	Sc	44·1	43·8
Copper	Cu	63·57	63·06	Selenium	Se	79·2	78·6
Erbium	Er	167·4	166·07	Silicon	Si	28·3	28·07
Fluorine	F	19	18·9	Silver	Ag	107·88	107·02
Gadolinium	Gd	157·3	156·05	Sodium	Na	23	22·81
Gallium	Ga	69·9	69·34	Strontium	Sr	87·6	86·94
Germanium	Ge	72·5	71·9	Sulphur	S	32·07	31·81
Glucinum	Be	9·1	9·03	Tantalum	Ta	181	179·56
Gold	Au	197·2	195·7	Tellurium	Te	127·5	126·48
Helium	He	4	3·96	Terbium	Tb	159·2	157·93
Hydrogen	H	1·008	1	Thallium	Tl	204	202·38
Indium	In	114·8	113·88	Thorium	Th	232·42	230·57
Iodine	I	126·92	125·9	Thulium	Tu	168·5	166·16
Iridium	Ir	193·1	191·5	Tin	Sn	119	118·1
Iron	Fe	55·85	55·5	Titanium	Ti	48·1	47·7
Krypton	Kr	83	82·34	Tungsten	W	184	182·6
Lanthanum	La	139	137·9	Uranium	U	238·5	236·7
Lead	Pb	207·1	205·45	Vanadium	V	51·2	50·8
Lithium	Li	7	6·94	Xenon	Xe	130·7	129·66
Magnesium	Mg	24·32	24·15	Ytterbium	Yb	172	170·63
Manganese	Mn	54·93	54·49	Yttrium	Y	89	88·3
Mercury	Hg	200	198·5	Zinc	Zn	65·37	64·85
Molybdenum	Mo	96	95·3	Zirconium	Zr	90·6	89·9

[1] *Translator's note.*—This differs slightly from the International Table.

Berzelius proposed to take oxygen as unity, but all the chemists very soon returned to hydrogen, and this remained until a few years ago. To-day the atomic weights of the elements are referred to oxygen, which is taken as equal to 16, because it is easier to prepare very pure oxygen than very pure hydrogen, and also because the atomic weights of the other elements are thus obtained more exactly. On the previous page we give a table of the symbols of all the elements with atomic weights referred to hydrogen = 1 and to oxygen = 16.

CHEMICAL FORMULÆ. By means of symbols we are also able to indicate very simply and clearly the molecules of various substances and of the elements themselves, by also indicating the number of atoms contained in the molecules. Thus, for example, the molecule of hydrogen, which is formed of two atoms, is represented by the symbol H_2, the molecule of oxygen by O_2, that of chlorine by Cl_2, &c.; that is, the symbol is written down and a number which indicates how many atoms enter into the molecule is written to the right of it, below, as proposed by Poggendorf, or above, as proposed by Berzelius, and still used by a few people to-day.

The molecular formula of hydrochloric acid is HCl, that of water, which contains two atoms of hydrogen and one of oxygen, is H_2O, whilst that of ammonia is NH_3. These formulæ also show that one volume of hydrogen gas combines with one volume of chlorine to give hydrochloric acid, and that two volumes of hydrogen gas are combined with one volume of oxygen gas to give water, as was demonstrated by Gay-Lussac, &c.

If the symbols constitute the chemical alphabet, the formulæ must be considered as the words of the chemical language. It is a language formed by equations which express the various reactions which occur between various molecules, thus forming a kind of chemical algebra.

The molecular formulæ also show the molecular weight of each chemical element or compound; thus the molecule of hydrogen, H_2, shows that the molecular weight is 2 (H = 1); the molecule of oxygen shows that the molecular weight is 32, that is twice the atomic weight of oxygen (16 × 2); the molecule of hydrochloric acid also shows the molecular weight, which is 36·5, that is, the weight of an atom of hydrogen 1 + the weight of an atom of chlorine, 35·5, showing also that in 36·5 kilos of pure hydrochloric acid gas, 53·5 kilos of chlorine and 1 kilo of hydrogen are contained. In 18 kilos of water, 2 kilos of hydrogen and 16 kilos of oxygen are contained, the molecular weight of water being 18.

The formula of any substance shows its molecular weight, and thence the percentage composition can be deducted in a simple manner, that is, we can find the quantity of each element which is contained in 100 parts by weight of the substance by means of simple arithmetical operations. For water, for example, we have:

$H_2 = 2$	$18\ (H_2O) : 2\ (H_2) = 100 : x$	$x =$ 11·12 % of H
$O = 16$	$18\ (H_2O) : 16\ (O) = 100 : x'$	$x' =$ 88·88 % of O
molecular weight 18		per 100 parts of water

We thus find that on electrolytically decomposing 100 kg. of water (as is industrially done to-day on a large scale) we obtain 88·88 kg. of oxygen and 11·12 kg. of hydrogen.

In the case of sulphuric acid, which has the formula H_2SO_4, we have:

$H_2 = 2$	$98 : 2\ (H_2) = 100 : x$	$x =$ 2·04 % of hydrogen
$S = 32$	$98 : 32\ (S) = 100 : x'$	$x' =$ 32·65 % of sulphur
$O_4 = 64$	$98 : 64\ (O_4) = 100 : x''$	$x'' =$ 65·31 % of oxygen
molecular weight 98		per 100 of total sulphuric acid

We are thus able to deduce that in a sulphuric acid factory, if there is no loss, 100 kilos of sulphuric acid should be obtained per 32·65 kilos of sulphur employed, and every manufacturing process will be the more perfect and regular the nearer the practical yields approximate to those demanded by theory.

From the percentage composition of a substance which is determined by means of ordinary chemical analysis,[1] together with the determination of its vapour density or of some other method for determining its molecular weight, its formula can be deduced.

If, for example, we wish to determine the formula of water, we commence by making a quantitative analysis (*see later*, chapter on Water), which allows us to deduce the percentage composition: H = 11·12 per cent., O = 88·8 per cent. If we now determine the density of water vapour compared with that of air, we find that it is 0·626, and multiplying this by 28·88, we have the molecular weight compared with hydrogen, which is $28{\cdot}88 \times 0{\cdot}626 = 18$. In order to now discover in what proportion by weight oxygen and hydrogen enter into 18 parts of water (molecular weight), it will be necessary to establish some simple proportion, taking into account the percentage composition:

$$100 : 11{\cdot}12\ (\mathrm{H}) = 18 : x \qquad x = 2$$
$$100 : 88{\cdot}88\ (\mathrm{O}) = 18 : x' \qquad x' = 16$$

The quantities by weight of the individual elements contained in the molecule correspond to the atomic weights of these elements or the multiples of these, in cases where several atoms are present. Thus by dividing these values, x and x', by the atomic weights, we will obtain the number of atoms of these elements contained in a molecule of water.

$$2 : 1\ (\text{atomic weight of H}) = 2 = \mathrm{H_2}$$
$$16 : 16\ (\text{atomic weight of O}) = 1 = \mathrm{O}$$

The chemical formula of water is, therefore, $\mathrm{H_2O}$. The formulæ of numerous other inorganic and organic substances are found in the same way.

This is the simplest method of calculating the formulæ of substances, but it cannot be employed when the molecular weight is not known, and this is then arrived at by indirect methods which are often employed in organic chemistry, for example, by the formation of various salts or other derivatives.

DUALISTIC FORMULÆ. Lavoisier believed that when a base and an acid combine to form a salt they retain their primitive constitution in the new molecule. From this idea Lavoisier derived his system of dualistic formulæ, which represented molecules of salts. Thus, he wrote the formula of calcium carbonate as $\mathrm{CaO.CO_2}$, because he supposed the components calcium, CaO (base) and carbon dioxide, $\mathrm{CO_2}$ (acid), to exist side by side within the molecule. Sulphuric acid was represented by the dualistic formula $\mathrm{SO_3.H_2O}$, because it was supposed to contain the separate components $\mathrm{SO_3}$ (sulphur trioxide) and $\mathrm{H_2O}$ (water).

In 1819 Berzelius in his studies on the intimate nature of chemical combinations, based on the conceptions of Lavoisier and the work of Davy, enunciated an electrolytical theory of dualistic formulæ, according to which all compound substances were composed of two parts with different electric charges, negative and positive, namely, the acid residue —negative—(oxy-acids were alone well known at that time, but not the halogen acids) and the basic residue—positive—namely, the metallic oxides, for example:

$$\overset{+}{\frown}\ \overset{-}{\frown}\qquad\qquad \overset{+}{\frown}\ \overset{-}{\frown}$$
$$\mathrm{BaO}\ .\ \mathrm{SO_3} \qquad\qquad \mathrm{ZnO}\ .\ \mathrm{CO_2},\ \&c.$$
Barium sulphate — Zinc carbonate

[1] By *analysis* in general is understood the operation of splitting a given substance into any or all of its components in order to determine its composition; whilst by synthesis is understood that chemical process by means of which a complex substance is obtained, starting from other simple substances. Thus analysis is the demolition whilst synthesis is the reconstruction of one or more chemical structures. Synthesis is often used in order to test the exactitude of analysis, and *vice versa*.

By electrolytic decomposition of these salts, the components of the molecule were supposed to separate, and confirmation of this idea was sought in the appearance of the two substances at the two poles of a cell (voltameter). The classic experiment of this epoch was the electrolytic decomposition of a solution of sodium sulphate ($SO_3.Na_2O$).

At the positive pole, where the acid residue should have been formed, litmus solution did actually become red, and at the negative pole, where the basic residue should have been obtained, the litmus was coloured blue. But Daniell already perceived that the results which are apparently obtained by electrolysis really occur in another manner, and that it is not sodium oxide which separates at the negative pole as had always been supposed, but metallic sodium, which by combining with the water of the solution at the instant of its formation, forms the base which colours the litmus blue ; but if we take mercury as the negative pole, this at once fixes a part of the metallic sodium which is liberated as it is formed, giving sodium amalgam, and he thus showed that in the electrolytic decomposition of sodium sulphate, metallic sodium and not sodium oxide is obtained at the negative pole. It was in this very manner that Davy discovered and isolated sodium and potassium.

It was observed, on the other hand, that a gas was developed at the positive pole, which was identified as oxygen. Thus on electrolysing copper sulphate, copper oxide (CuO) should be obtained at the negative pole, and the sulphuric acid residue (SO_3) at the positive pole, according to the dualistic theory ; but actually, on the other hand, metallic copper was obtained at the negative pole and oxygen was developed at the positive pole, apart from the formation of sulphuric acid.

Liebig, who at first opposed the unitary formula of Davy, finished by abandoning the dualistic theory of Berzelius, which had also been shaken to its foundations by the important work of Dumas, Laurent, and Gerhardt.

Salts are to-day considered to be composed of a metallic (positive) residue and of an acid (negative) residue ; this latter may be an oxidised or non-oxidised halogen (the latter in the case of the halogen salts, such as sodium chloride, &c.). According to this conception, then, the fact that metallic copper separates at the negative pole and oxygen at the positive pole in the case of copper sulphate ($CuSO_4$) is explained, because the acid residue of copper sulphate being SO_4, this is unstable and at once decomposes, giving oxygen and sulphur trioxide (SO_3), which yields sulphuric acid with water. The error committed by Berzelius was that he did not take into account the oxygen which is developed, but only the acid reaction.

The theory of Berzelius was completely abandoned many years ago, because the residues of the halogen acids which are not oxygenated and of the polybasic acids, were studied and these could not be explained by means of the dualistic theory.

VALENCY

By studying the various compounds represented by chemical formulæ more closely and intimately, we are able to indicate the manner in which the atoms are united with one another in the molecule, and to explain why, in the case of chemical reactions, certain atoms are constantly found united with one or more atoms of other elements. Given that there is an attraction or affinity between atoms of various kinds, it is interesting to know in what manner they saturate one another reciprocally.

Glauber already in the Middle Ages, Wenzel and Richter later, determined the proportions of saturation of a certain quantity of an acid by various quantities of different bases, or *vice versa*.

In 1811, Berzelius clarified this conception by finding a simple and constant relation between the oxygen of a base and that of an acid which constituted a salt. It was found that a molecule of potassium nitrate contained a quantity of nitric acid corresponding to one molecule of this acid, whilst a molecule of ferric nitrate contained a quantity of nitric acid corresponding to three molecules of the acid, that is to say, that potassium oxide—which is the base combined to the nitric acid in potassium nitrate KNO_3—represents a mono-

acid base, whilst oxide of iron in ferric nitrate $Fe(NO_3)_3$, is a tri-acid base. Numerous bases are known which have a different valency or power of saturation for this acid.

In 1835 Graham demonstrated the polybasicity of phosphoric acid, and in 1845–1850 Kolbe, by means of his classic studies on the radicals of organic compounds, prepared the ground for Frankland and his fertile and brilliant conception of the theory of valency (1853), which was extended to inorganic compounds and to all the elements. Wurtz showed later by a notable series of experimental researches, that a reciprocal power of saturation also exists between elementary substances, and this threw light on the relation between the theory of variable valency and Dalton's law of multiple proportions.

The *constant* valency of the elements generally found confirmation in organic compounds, whilst various examples of *variable* valency were found in inorganic compounds, and thus the conception of valency grew and acquired a wider horizon.

We may easily grasp the simple conception of valency if we arrange a certain number of substances according to their chemical composition in a small table, according to a definite plan :

HCl	$HgCl_2$	PCl_3	CCl_4	$NbCl_5$
HBr	OCl_2	$AsCl_3$	$SiCl_4$	$TaCl_5$
HI	$BaCl_2$	$SbCl_3$	$SnCl_4$	
HF	$ZnCl_2$	$BiCl_3$	CH_4	
KCl	$CuCl_2$	BCl_3	SiH_4	
$NaCl$	SH_2	NH_3		
$AgCl$	OH_2	AsH_3		

In the first vertical column four halogen acids are collected, the molecules of which are all formed of one atom of hydrogen, combined or saturated with one atom of Cl, or Br, I, F, so that one may say of these elements that they are monovalent with respect to hydrogen. We next find in the same column three salts, the molecules of which contain one atom of Cl, which is monovalent, that is, has the power of saturating one atom of H, now combined with one atom of K, Na, or Ag. Thus we may also consider K, Na, and Ag as monovalent elements, because one atom of these saturates a single atom of chlorine, which in turn saturates a single atom of hydrogen. In the second column we find elements the atoms of which are saturated with two atoms of monovalent chlorine ; thus these elements, Hg, O, Ba, Zn, S are divalent, that is, have a power of saturation corresponding to two atoms of chlorine or to two atoms of hydrogen.

In the third column we have trivalent, in the fourth column tetravalent, and in the fifth column pentavalent elements.

The elements, which have the same capacity for saturation, are able to substitute one another reciprocally in their various combinations, giving products of analogous composition. Thus we can practically carry out the following series of reactions and successive substitutions:

(*a*)	$2\,NO_3H$	$+\,Ag_2$	$=\,H_2$	$+\,2\,NO_3Ag$
(*b*)	$2\,NO_3Ag$	$+\,Hg$	$=\,Ag_2$	$+\,(NO_3)_2Hg$
(*c*)	$(NO_3)_2Hg$	$+\,Cu$	$=\,Hg$	$+\,(NO_3)_2Cu$
(*d*)	$(NO_3)_2Cu$	$+\,Zn$	$=\,Cu$	$+\,(NO_3)_2Zn$
(*e*)	$(NO_3)_2Mg$	$+\,Na_2O$	$=\,MgO$	$+\,2\,NO_3Na$

As we see here, two atoms of monovalent silver replace two atoms of H (*a*), and are in turn replaced by one atom of divalent mercury (*b*), and this by one atom of divalent copper (*c*) ; the copper is replaced by one atom of divalent zinc (*d*), and one atom of divalent magnesium replaces two atoms of monovalent sodium (*e*), thus this atom has the power of saturation by two atoms of H and can also replace two atoms which have the capacity for saturating one atom of H, for example, Hg corresponds to Ag_2.

Now the elements which have the same *capacity for saturation* by H have also the same *capacity of combination*, that is, in a iven chemical compound

they may substitute or replace one another reciprocally, always giving rise to *saturated* molecules which no longer have any disposable affinity which may enable them to combine with further quantities of that element which they contain. We may thus define the capacity of combination also as the *capacity for saturation* or VALENCY of the elements, and this is actually expressed and indicated by small indices or by Roman numerals which are placed above the symbol of the element on the right.

The monovalent elements then are those which have the capacity for being saturated by a single atom of H, as Cl′, I′, Br′, F′, &c.

The divalent elements are capable of saturation by two atoms of H, or a monovalent element, for example, Cu″, Ba″, Zn″, S″, O″, &c.

The trivalent elements saturate three atoms of H or three monovalent atoms or one monovalent and one divalent atom, for example, N‴, Sb‴, As‴.

The tetravalent elements saturate 4 H, or four monovalent atoms, or two divalent atoms, &c., for example, C^{iv}, Si^{iv}.

And the same thing applies to the pentavalent elements, columbium and tantalum, Nb^{v}, Ta^{v}.

Care must be taken to remember that valency is a property entirely distinct and different from chemical affinity. Thus hydrogen and fluorine, which are only monovalent, have an extraordinary reciprocal chemical affinity, whilst nitrogen, which is trivalent, has very little affinity for hydrogen and for the other elements.

The valency of an element is measured by the number of atoms of hydrogen or of monovalent elements with which it can be saturated; whilst, on the other hand, affinity is measured by the quantity of energy which the substance develops during combination. There is no connection between valency and affinity, just as there is no connection between the height or the weight of a person and his muscular or intellectual power. We will later explain more rationally the conceptions of affinity and valency (*see* Valency of the Ions and Affinity).

We have now studied and discussed the significance of the equivalents, that is, of the stoichiometric or combining weights of the elements, referred to unit weight of hydrogen, values deduced from percentage analyses.

We know, in fact, that on analysing water we find the percentage composition of 88·88 per cent. of oxygen and 11·12 per cent. of hydrogen; that is to say, that 1 of H corresponds to 8 of oxygen. This figure 8 is the stoichiometric value or equivalent of oxygen, that is, the quantity which combines with 1 of H.

In the same manner on analysing ammonia, we find 82 per cent. N and 18 per cent. H; the stoichiometric value or equivalent of nitrogen is thus equal to 4·67, which is the quantity which corresponds to 1 of H.

If we now compare these equivalents of oxygen and of nitrogen with their relative atomic weights, we have:

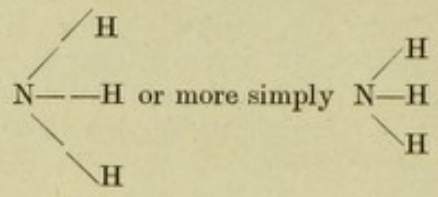
	O	N
Equivalent	8	4·67
Atomic weight . . .	16	14

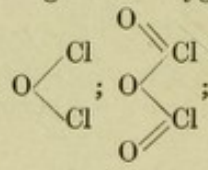
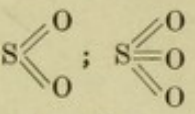
and we at once see that a simple relationship exists between the equivalents and the atomic weights. For oxygen the atomic weight is twice the equivalent. For nitrogen it is three times the equivalent; but we have already found that oxygen is divalent and nitrogen trivalent. Thus the valency is a function of the combining weights or stoichiometric values. These latter are thus fractions of atoms corresponding in each case to one valency or to one atom of hydrogen. Thus the valency, or capacity for saturation, of the elements is easily found or determined when the atomic weight, which can be

determined in various ways, is known, and when the stoichiometric value, which may easily be found by analysing a given compound, is also known. On then dividing the atomic weight by the equivalent, the valency is obtained.

Formulæ in which the manner in which the atoms are combined and distributed in each molecule are shown, and in which the valencies are represented by small lines, are called *constitutional formulæ*, while those in which merely the complete number of the atoms of each element composing the molecule is shown, are called *empirical formulæ*.

Thus the empirical formula of ammonia is NH_3, and nitrogen being trivalent, its constitutional formula will be :

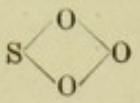


But the valency of a given element is not a constant property, but varies with the substance upon which it is exerted. For example, chlorine is always monovalent with regard to hydrogen, whilst with regard to oxygen it may be divalent, trivalent, tetra-, penta-, and heptavalent : HCl ;  ; similarly sulphur is divalent with respect to hydrogen, but tetravalent and also hexavalent with respect to oxygen 

The valency of metals with respect to oxygen sometimes varies with variation of the temperature, and if this is high, we have the minimum valency, and if low, the maximum valency, that is, the compound of maximum oxidation. If the temperature is very high the affinity of oxygen may be altogether overcome by the so-called tension of the oxygen and the free metal is then formed as can be seen in the following table :

CuO at 1110° yields Cu_2O, and at 1800° yields Cu.
Tl_2O_3 at 875° yields Tl_2O, and at 1865° yields Tl.
PbO_2 at 390° yields Pb_3O_4, at 615° yields PbO, and at 2240° yields Pb.
Sb_2O_5 at 450° yields SbO_2, at 1060° yields Sb_2O_3, and at 2490° yields Sb.
MnO_2 at 570° yields Mn_2O_3, at 1090° yields Mn_3O_4, at 2500° yields MnO, and at 4050° yields Mn.
Fe_2O_3 at 1970° yields Fe_3O_4, and at 3025° yields Fe.
Co_2O_3 at 895° yields CoO, and at 2860° yields Co.
PdO_2 at 180° yields PdO, and at 875° yields Pd.

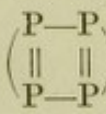
Until a few years ago, the older generation of chemists, and there are some even now, did not accept the conception of variable valency of the elements and in the case of abnormal compounds supposed that there were free valencies as in carbon monoxide C≡O : or a reciprocal saturation between elements of the same nature linking them together with one another, as in chlorine oxide : Cl—O—O—O—Cl, or sulphur trioxide



But to-day a numerous series of organic and inorganic compounds show that when an element appears to be saturated with respect to its ordinary valencies, it will always possess affinities for other atoms or molecules of other substances, so that one is forced to admit another form of valency which is regularly exercised under certain conditions.

There are also various thermochemical data which are not in accordance with the conception of constant valency, and also various other facts, such as the behaviour of the ions, which we will study later.

Now that we are acquainted with valency and its signification, we are also able to explain generally why the elements themselves are not composed of atoms in the free state, but why these are always regrouped into molecules. In these latter the valencies or affinities of the atoms remain saturated and the molecules may be represented thus : (H – H), (S = S), (N ≡ N), (Cl – Cl) ; phosphorus is trivalent, but we know from its vapour density that its molecules are composed of four atoms, and may be represented thus :



MONATOMIC MOLECULES. We already know how the molecular weight of a substance is found from its vapour density, and we have also seen that the greater number of simple substances are formed of diatomic molecules.

But on determining the vapour density of certain simple substances, such as mercury, zinc, and certain of the new gaseous elements, such as argon, &c., it is found that the molecules of these substances are not formed of two atoms, but of a single atom only ; these substances are therefore composed of free atoms, that is, of monatomic molecules.

Obviously these substances cannot be proved to be monatomic by direct deduction from the vapour density because this simply determines the relative weight of the free particles of a gas or vapour, compared with that of the free diatomic particles of hydrogen, without indicating whether the former are composed of 1, 2, 3, or more atoms. If mercury, with a vapour density of 200, consisted of diatomic molecules, its atomic weight would be $\frac{200}{2}$, that is, 100 ; but by studying other gaseous mercury derivatives we are always able to deduce an atomic weight of 200 for mercury, that is, one which is equal to the molecular weight as indicated by the vapour density ; we must therefore admit that mercury particles in the state of vapour are monatomic and that the value 200, derived from the vapour density compared with hydrogen, directly indicates the atomic weight of mercury. The same remarks apply to zinc and all the other metals.

The presence of monatomic molecules cannot be confirmed (by ordinary means) in the case of simple substances which do not enter into chemical combinations ; in such cases other indirect methods are employed. Thus the size of the molecules of certain recently discovered elementary gases, argon, helium, xenon, neon, and krypton, has been determined by means of their specific heats at constant pressure and at constant volume. It was not found possible to obtain any compounds of these substances, and it was therefore not known with certainty whether their density compared with that of hydrogen indicated the size of monatomic or of diatomic molecules, and, therefore, whether the atomic weight was equal to, or one-half of, that indicated by the density of the gas. Lord Rayleigh has recently been able to show that these gases are composed of monatomic molecules by means of investigations of their specific heats (as we will explain below) and thus demonstrated that the molecular weights of these gases are identical with their atomic weight. (There is an error in the original.—*Translator.*)

THERMAL CAPACITY AND SPECIFIC HEAT OF GASES PRINCIPLES OF THERMODYNAMICS

If a gas is heated its temperature is raised. The ratio between the heat which is added and the rise of temperature (expressed in degrees Centigrade) is called the *thermal capacity* of the gas, and varies with the nature of the gas, with the temperature, and with the pressure, whereas in the case of liquids and solids, pressure has no influence on this property. A *calorie* is the quantity of heat required to raise 1 grm. of water from 0° to 1°.

The expression thermal capacity arose in the epoch during which it was still believed that heat was composed of some kind of material substance (Newton).

The term *specific heat* (c) indicates the thermal capacity of unit weight of a gas, that is, the amount of heat necessary to raise the temperature of 1 grm. of the substance by one degree; on the other hand, the thermal capacity of a gramme-molecule of the gas is called the *molecular heat* (C). At high temperatures, such as 1000° or 2000°, or over, the specific heat of gases is rather higher.

The specific heat of a gas may be determined at *constant pressure* (c_p), or at *constant volume* (c_v); the former value is always larger than the latter, and for molecular heats the difference is about two calories: $C_p - C_v = 2$ cal. (*see* Table, *below*). These two calories represent the heat which is absorbed by the gas to supply the work done during dilatation, and we are thus able to calculate, from the difference between these specific heats, the amount of heat which is evolved when a gas decreases in volume, and also when it passes from the gaseous into the liquid or solid state (*see* p. 27).

We may deduce these results from the following considerations, which lead to the **first law of thermodynamics**, by means of which the equivalence between heat and mechanical work (*see also* p. 52) is established. The heat required to raise by one degree of temperature 1 grm. of air (that is, 773 c.c.) at constant pressure, is given by the specific heat c_p, which is 0·2375 cals.; the heat required to raise its temperature by the same amount at constant volume is given by the specific heat c_p, which is 0·1683 cals. The difference, $c_p - c_v = 0{\cdot}0692$ cals., indicates that portion of the heat which is converted into work, and this is expressed by the product of the pressure p, and the increase of volume dv, that is, by $p.dv$. Since the volume of any gas, according to the law of Gay-Lussac, increases by $\frac{1}{273}$ for each degree rise of temperature, dv will in this case be $\frac{773}{273} = 2{\cdot}83$ c.c., and the pressure exerted by the atmosphere on each sq. cm. of surface being 1033·3 grms. we have: $p.dv = 1033{\cdot}3 \times 2{\cdot}83 = 2924{\cdot}24$ grm.-cms., which represents the mechanical equivalent of the quantity of heat, $c_p - c_v$, that is, 0·0692 cals.

We are now able to deduce the mechanical equivalent of heat by comparing the heat absorbed with the resulting work, and thus find: $\frac{2924{\cdot}24}{0{\cdot}0692} = 42{,}260$ gramme-centimetres (or ergs, *i.e.* absolute units of energy),[1] which represent the work equivalent to a small calorie (0·0692 cal. : 2924·24 = 1 : x; $x = 42{,}260$);[2] and for a large calorie (that is, for 1000 small calories) we have 422·6 kilogramme-metres, which is the value of the mechanical equivalent of heat (*see* Note).

On introducing this equivalent (A) in order to calculate the work produced we have: $A\ (C_p - C_v) = p.dv = p\ (v_2 - v_1) = pv$, where v_1 and v_2 are the volumes of the gas before and after heating, and v the difference between them. From the general gas equation, taking a temperature difference of 1 degree, so that $(T_2 - T_1 = 1)$, we obtain $A\ (C_p - C_v) = R$ (T being equal to 1), and it is then possible to also deduce in this manner the value of the gas constant, R, which must always be referred to a gramme-molecule of the gaseous substance. We already know that the value of R is 84,780 (*see* p. 26), and if we wish to express this in thermal units by giving to C_p and C_v the values of the molecular heats we have: $C_p - C_v = \frac{R}{A}$, that is, $\frac{84780}{42260}$ = about 2 calories, if A denotes the thermal equivalent of a small calorie expressed in gramme-centimetres. *The difference between the specific heats at constant pressure and at constant volume is thus equal to about two calories* for each gramme-molecule.

It has also been found that the relation between specific heats at constant pressure and

[1] *Translator's Note.*—An error has here crept into the original text. The erg, which is the absolute unit of energy on the C.G.S. system, is the work accomplished by a movement through 1 cm. against a resisting force of 1 dyne (*see* p. 26).

[2] The absolutely correct value for this is 42720 (*see* p. 27); it is the quantity of energy expressed in absolute (?) (*see* Translator's Note above) units, each of which suffices to raise 1 grm. of matter against gravity through a distance of 1 cm. The equivalent of the large calorie (1000 small calories) is 42,720,000 grm.-cms., or 427·2 kilogramme-metres (each of which suffices to raise 1000 grms. through a height of 100 cms. against the action of gravity); this is the mechanical equivalent of the large calorie, which is simply called the mechanical equivalent of heat. The difference $Cp - Cv$ in correct values is 1·985 cal.

at constant volume $\left(\frac{Cp}{Cv}\right)$ diminishes with the increase in the number of atoms in the molecule.

Gaseous substance	Specific heat [1]		Molecular heat molecule of hydrogen = 2		Difference $Cp - Cv$	Ratio $\frac{Cp}{Cv}$	Number of atoms in the molecule
	at constant pressure Cp	at constant volume Cv	at constant pressure $= Cp$	at constant volume $= Cv$			
Oxygen . .	$O_2 = 0{\cdot}2175$	0·1551	6·96	4·96	2	1·40	2
Nitrogen . .	$N_2 = 0{\cdot}2438$	0·1727	6·83	4·83	2	1·41	2
Hydrogen . .	$H_2 = 3{\cdot}4090$	2·411	6·82	4·82	2	1·41	2
Carbon dioxide .	$CO_2 = 0{\cdot}2169$	0·172	9·55	7·55	2	1·33	3
Ammonia . .	$NH_3 = 0{\cdot}5284$	0·391	8·64	6·64	2	1·37	4
Methane . .	$CH_4 = 0{\cdot}5929$	0·468	9·49	7·49	2	1·27	5
Ethyl ether .	$C_4H_{10}O = 0{\cdot}4797$	0·453	35·50	33·50	2	1·06	15

As has already been stated, mercury in the state of vapour contains monatomic molecules, and the relation between its molecular heat $\frac{Cp}{Cv} = 1{\cdot}666$. Now by means of the kinetic theory of gases, one is able to demonstrate mathematically that for free atoms or monatomic molecules, the relation $\frac{Cp}{Cv}$ must be 1·666 (*see* p. 52). The fact that mercury vapour consists of monatomic molecules is thus confirmed. The ratio $\frac{Cp}{Cv}$ varies between 1 for very large molecules, that is, such as contain many atoms, and 1·4 for diatomic molecules, whilst for monatomic molecules it approaches 1·667.

The determination of the ratio between the specific heat of gases at constant pressure and at constant volume has led, as has already been stated, to the demonstration that the molecules of the gases, argon, helium, crypton, xenon, and neon are formed even at ordinary temperatures of monatomic molecules, and since these gases are very indifferent and give no combinations with other elements, it was impossible to control it from the density of these gases. The density of these gases represents nothing but a relative value, that is, a maximum limit, and shows that the free particles of these gases have a given weight

[1] For various practical purposes the specific heats of gases and vapours at constant pressure (water = 1) are often required :

Substance	Temperature of experiment	Specific heat	Substance	Temperature of experiment	Specific heat
Air . . .	from −100° to +200°	0·2374	Carbon dioxide .	10°–214°	0·2169
,, at 40 atm. .	at −120°	0·4700	Nitric oxide . .	13°–170°	0·2317
,, ,, 70 ,, .	at −120°	0·7770	Nitrogen peroxide .	27°– 67°	1·625
Oxygen . .	from 10° to 200°	0·2175		27°–150°	1·115
,, liquid .	−200° to −183°	0·3470		27°–280°	0·650
Hydrogen . .	−30° to +200°	3·410	Ammonia . .	20°–200°	0·52
,, at 30 atm.	—	3·7882	Sulphur dioxide .	16°–200°	0·1544
Nitrogen . .	0°–200°	0·2438	Hydrogen sulphide .	20°–200°	0·2451
,, liquid .	—	0·430	Carbon disulphide .	86°–190°	0·1596
Argon . . .	20°– 90°	0·1233	Water vapour . .	100°	0·421
Chlorine . .	10°–202°	0·1241	,, ,, . .	180°	0·510
Bromine . .	20°–388°	0·0554	Methane . .	18°–208°	0·5930
Iodine . . .	206°–377°	0·0336	Ethyl alcohol .	108°–220°	0·4534
Hydrochloric acid .	10°–200°	0·190	Methyl ,, . .	101°–223°	0·4580
Hydrobromic ,, .	10°–100°	0·0820	Ethyl ether . .	27°–190°	0·4618
Hydriodic ,, .	20°–100°	0·0550	Benzene, C_6H_6 .	116°–218°	0·3754
Carbon monoxide .	20°–200°	0·2425	Acetone . .	129°–233°	0·4125
,, dioxide .	15°–100°	0·2025	Chloroform . .	28°–189°	0·1489

relatively to those of hydrogen; but this does not decide whether this weight represents diatomic molecules or free atoms. Only by means of the ratio of the specific heats $\frac{C_p}{C_v} = 1{\cdot}667$ was Lord Rayleigh able to demonstrate that monatomic molecules were present.

By the kinetic theory of gases we are also able to explain the relation which exists between the specific heats of a gas and the number of atoms contained in its molecule.

We know (*see* p. 7) that on heating a gas its *internal energy* is increased by an amount dU resulting from an increase of its *molecular kinetic energy*, dU_m, or *internal kinetic energy*, or energy of motion due to the rise of temperature, and to the increase of the *internal potential energy* (or energy of position, *see* p. 5). In order to determine this latter, that is, the quantity of energy necessary to alter the positions of the atoms in the molecule of the gas, we require to know the difference, $dU - dU_m$. But in the case of the monatomic molecules this difference becomes equal to zero, because no part of the energy, dU, is consumed by increasing the distance between the atoms of the molecule, and it is all employed on the contrary in increasing the molecular kinetic energy, that is, the increase of temperature, and therefore we have, $dU = dU_m$ or $\frac{dU_m}{dU} = 1$.

If we wish to express the total increase of energy dU as a function of the temperature for a mass of gas, M, and for an increase of temperature, dT, then for the specific heat at constant volume, C_v, we will have the following equation:

$$dU = M.C_v.dT.$$

Then the equation of Clausius and Krönig, deduced from the kinetic theory of gases (p. 37) for the mass, $M\ (= n.m)$ becomes $\frac{3}{2}\ MRT = \frac{Mc^2}{2}$. The increase in the molecular kinetic energy $\frac{Mc^2}{2}$, which we have expressed by dU_m, thus corresponds to the increase of temperature, dT, and we arrive at the equation $dU_m = \frac{3}{2}\ MRdT$. But we are able to replace the gas constant R by the corresponding expression in thermal units resulting from the difference $C_p - C_v$ (*see above*), and we thus have: $dU_m = \frac{3}{2}\ M\ (C_p - C_v)\ dT$. Dividing this increase of the molecular kinetic energy by the total increase of internal energy, $dU = MC_v\,dT$, we obtain: $\frac{dU_m}{dU} = \frac{3}{2}\ \frac{C_p - C_v}{C_v}$, and in the case of monatomic molecules $\frac{3}{2}\ .\ \frac{C_p - C_v}{C_v} = 1$, that is, $\frac{C_p}{C_v} = \frac{5}{3} = 1{\cdot}667$.

We have thus shown that for monatomic substances, the ratio between the specific heats $\frac{C_p}{C_v}$ must be equal to or approximate to 1·667, and will always depart from this value towards unity as the molecules become more complicated by increasing the number of their atoms. It is precisely by this method that Rayleigh has shown that the new gases of the atmosphere, argon, helium, &c., are composed of monatomic molecules.

SECOND LAW OF THERMODYNAMICS. This was theoretically deduced by Carnot (1824). By this means the amount of work was established which can be obtained from a given quantity of heat. We may explain this principle graphically by supposing that a given quantity of gas enclosed in an ideal cylinder provided with a piston and which can receive or emit heat only through its base, is subjected to a closed cycle of transformations. If this gas, the conditions of temperature and pressure of which, and therefore also its absolute temperature, T_1, are determined by the point A respectively to the two orthogonal axes of pressure, OP, and of volume, OV (Fig. 15), is placed over an inexhaustible source of heat, it tends to dilate up to the point B, and as the heat-supply prevents any cooling (in consequence of the dilatation) it is maintained at a constant temperature, so that we have an isothermal transformation, and the absorbed heat may be denoted by Q_1. The work done during expansion is represented by the surface $a\ b\ B\ A$. If the gas were to expand without being in contact with the heat-supply, it would be cooled down to T_2, because the expansion occurs at the expense of the internal kinetic energy. This cooling is equal to the mechanical work done during expansion, and in this case we

have an adiabatic transformation, because there is no exchange of heat with the external medium.

Now on compressing the gas adiabatically, that is, without addition, or abstraction of heat, down to the volume c, we increase not only the pressure but also the temperature up to T_2. On then compressing the gas in an isothermal manner, that is, on placing the gas over an ideal refrigerator which abstracts heat developed during compression, from the volume c to the volume d, the quantity of heat abstracted will be Q_2. On finally allowing the gas to expand adiabatically up to the original volume a, it will then acquire the original pressure and temperature T_1 at the point of departure A. On recommencing the experiment one can repeat the same closed cycle of transformations which always reconduct the gas to the original conditions of volume, temperature, and pressure, ultimately passing through two adiabatic and two isothermal transformations.

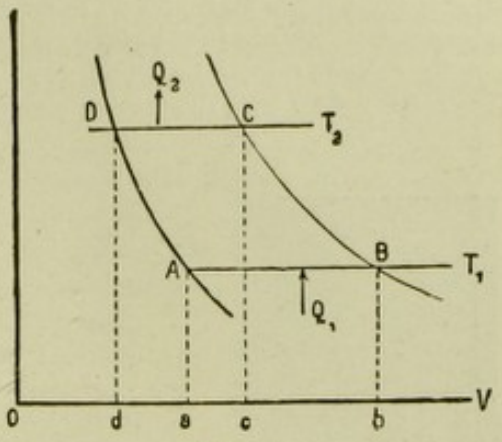


FIG. 15.

The surface $A\ B\ C\ D$ enclosed in the cycle represents the total useful work produced by the entire quantity of heat, $Q_1 - Q_2$. By a calculation which we will not reproduce an important final equation is deduced:

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$

which says that the ratio between the quantities of heat abstracted from and supplied to the gas is equal to the ratio between the absolute temperatures of the refrigerator and of the source of heat.

The ratio between the quantities of heat transformed into work and the quantity furnished to the gas, which is given by Carnot's cycle, may be deduced by writing the last equation thus:

$$1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1} \quad \text{or} \quad \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

Thus the yield depends upon the temperature interval, $T_1 - T_2$, and it is evident that it is impossible to transform all the heat into work, becuase in that case it would be necessary in the original equation to make the fraction $\frac{T_2}{T_1} = 0$, that is to make T_2, which is the temperature of the refrigerator employed, equal to absolute zero, which is not possible in practice [1] for reasons which we have often explained (pp. 7 and 25).

OPTICAL PROPERTIES OF GASES

SPECTROSCOPY. If the rays of the sun are allowed to enter a dark chamber through a hole, these may be directly collected on to a sheet of cardboard perpendicular to the rays, a large spot of light being thus obtained. If these luminous rays are first passed through a prism, then a streak of light of many colours is obtained on the cardboard ranging from violet to red, passing gradually through blue, green, yellow, and orange. The white light has been dispersed, and since the various waves composing white light are unequally refracted by the prism, the violet rays of smaller wave-length being most refracted and the red rays of greater wave-length least refracted, there will be found on the screen separate from one another, the colours corresponding to various waves and forming together a continuous coloured spectrum. If the white light before entering the prism is passed through a red glass, this absorbs all the other

[1] If in the equation showing the efficiency of Carnot's cycle we take an infinitely small temperature dT and express the work in thermal units, using the product of the infinitely small pressure dp and the infinitely small increment of volume dv, then we obtain it in the following form: $\frac{dp - dv}{Q} = \frac{dT}{T}$ and consequently $\frac{dT}{dp} = \frac{Tdv}{Q}$. This is Clapeyron's equation, which thus expresses quantitatively the *mobile equilibrium*, and may also be applied to changes of state (fusion, &c.), and generally to all cases where there is a supply or evolution of heat, differences of temperature, of pressure, and of work.

coloured rays and allows the red rays only to pass. If these are then refracted by a second prism, they simply produce a red spot on the cardboard in the precise position where the red coloration was found in the preceding complete spectrum. If green rays pass into the prism a green spot and no other colour is obtained in the proper position where the green coloration was in the complete spectrum of the white light, and so on.

This shows that the ethereal waves of various lengths corresponding to various colours are refracted through different angles, and that, in fact, the minimum refraction is given by the red light and the maximum by the violet light. Bearing in mind this fundamental idea of the refraction of light, we may study how gases behave when rendered incandescent and luminous by strong heating, using for this purpose the spectroscope which is illustrated on p. 56 (Fig. 18).

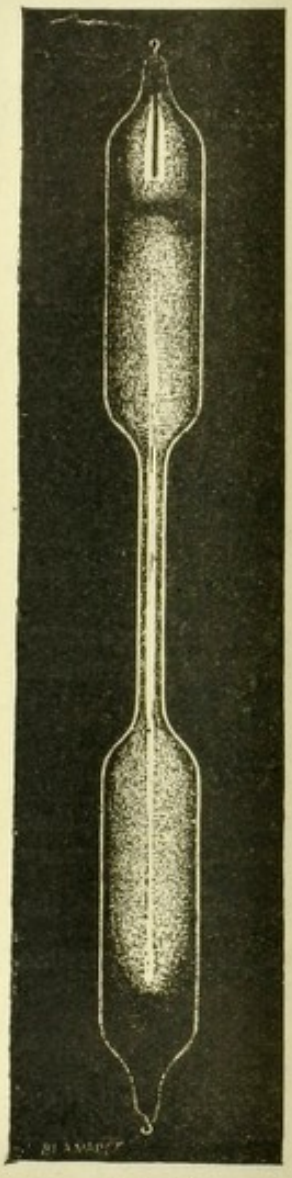


Fig. 16.

The light emitted by incandescent gases is different from that produced by liquid and solid substances or by the same gas when liquefied or solidified. The latter emit luminous rays of all wave-lengths and thus give a continuous spectrum. The light emitted by incandescent gases is formed of a few rays of definite wave-length, which, after passing through the prism of the spectroscope, give a direct spectrum with a few luminous coloured lines, characteristic for each gas or substance. They give, that is, *emission spectra*. These lines appear in the spectroscope when a minimal trace of the substance to be studied is placed in a Bunsen flame. The incandescent and luminous gases which are immediately formed produce the emission spectra.

We are thus able to discover and distinguish various substances even when mixed together without the necessity for previous separation.

Spectroscopic studies were first rationally conducted by Foucault, Talbot, Wheatstone, &c., but systematic spectral analysis was initiated by Kirchhoff and Bunsen in 1859, by studying and identifying the spectra characteristic of various substances heated to high temperatures. In 1865 Plücker and Hittorf found for the first time that the same gas is able to give different spectra according to the temperature. At relatively low temperatures, the gases actually give continuous spectra ; on raising the temperature characteristic emission spectra are obtained for each gas ; on raising the temperature still further, spectra are obtained with many coloured lines collected into groups, which are no longer characteristic. Helmholtz, Moser, Ciamician, and Wiedemann found that chemical compounds give a spectrum with coloured lines in groups which have nothing in common with the spectra of their elementary components.

Nevertheless Bunsen and Kirchhoff observed that various chemical compounds of the same alkalies or alkaline earth metals (*e.g.* chloride, carbonate, and oxide of barium, &c.) all gave the same spectrum corresponding to that of the metal (barium), and were not able to explain this behaviour, which was not in harmony with the observations of Helmholtz, which were that chemical compounds did not give emission spectra with isolated characteristic lines.

In 1864 Mitscherlich showed that this fact observed by Bunsen was due to the decomposition which takes place in the flame of the various compounds of the same metal. Thus the various salts of barium decompose or dissociate, and all give the spectrum of barium oxide or of barium itself.

An explanation or theory of spectroscopic phenomenon was first given in 1865 by Lecocq Boisbaudran,[1] but his hypothesis was erroneous; whist in 1878 Maxwell published a more rational hypothesis in harmony with the kinetic theory of gases. The atoms which collide in the interior of the molecule produce vibrations of the cosmic ether, but the molecules also collide with one another at considerably longer intervals, influencing the oscillations produced by the atoms. In this latter case, however, in addition to the striations or lines of the spectrum due to the vibrations of the colliding atoms, we have also luminous groups of lines or continuous portions of the spectrum due to the collision of the molecules. Further, if the gas is rarefied in a suitable tube (Plücker-Geissler tube) such as is indicated in Fig. 16, so that the electric discharge is formed in a capillary tube, where a few molecules are present, then the molecular impacts are much fewer and the spectrum of the atoms formed of striations or isolated luminous lines is better seen. In Fig. 17 is shown the arrangement of a Plücker tube on a suitable support for passing the electric discharge.

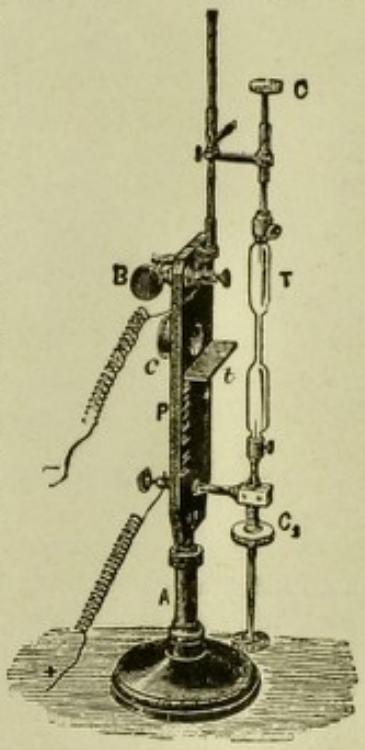


Fig. 17.

Kayser attempted to show that the number of lines of emission spectra of the elements were functions of their atomic weights, but there are many gaps in his conclusions. Certain regularities were only found in harmony with the first groups of the *periodic system* of the elements, and in each group it was actually found that with the increase of the atomic weights of the elements, the spectroscopic lines were displaced from the violet towards the red. From one group to another, on the other hand, the displacement took place in a marked manner towards the shorter undulations, that is, towards the violet, and the lines approached one another and became more numerous, so that the maximum accumulation of lines was found in the ultra-violet portion of the spectrum. According to Reinganum (1904), the regularities are more evident if instead of the atomic weights we take into consideration the atomic volumes, that is, the volumes in c.c. occupied by a quantity in grammes of a solid element, corresponding to the atomic weight.

The emission spectrum is solely composed of lines or groups of lines corresponding to given elements. There are, however, other spectra called *absorption spectra*, which are continuous spectra in which non-luminous lines of the emission spectra are found. White light gives a continuous spectrum, but if it is passed through an incandescent gas, then those waves only of the spectrum will pass which are not isochronous with those of the gaseous incandescent element; whilst those which are isochronous (in the white light passing through the incandescent gas) will interfere, and in the positions corresponding to such wave-lengths black lines will be observed in the spectrum.

There are also other absorption spectra which are characteristic of solutions of various coloured organic substances. (*Translator's Note.*—And also of certain inorganic solutions.)

In order to study these questions in the laboratory, the spectroscope (Fig. 18), which was invented by Bunsen and Kirchhoff, is employed. On a table carried by a pedestal there is placed a prism of flint glass with angles of 60°. On to one face of the prism the observation tube *B* converges, and collects the spectrum formed from the luminous rays which enter through the collimeter *A* and also the light from the millimetre scale which is reflected from the same face of the prism and proceeds from the tube *C*.

[1] He imagined that the atoms had projections, which on impact against the sides of the vessel or against a plane produced waves of determinate length, and thus in the case of an atom with several projections there would be waves of more than one wave-length, which would be characteristic and different for different gases. This hypothesis, however, could not be maintained because the wave-lengths producing such characteristic luminous lines are independent of variations of temperature, whilst according to this hypothesis they would depend upon the variation of the rotation and undulation of the atoms, which variation could not be independent of the temperature.

The substance under examination is rendered incandescent by a non-luminous flame F, and the emitted light enters the tube A through a vertical adjustable slit. The rays are rendered parallel by a collimating lens placed in the tube A near to the prism and at such a distance from the slit that the rays are exactly at the focus of the lens. The rays which are now parallel meet one face of the prism at the angle of minimum refraction, in which way the spectrum is rendered sharper. The spectrum is observed through the observation tube B, which is so adjusted horizontally that the rays of the spectrum are in the centre of the visual field. In order to determine the position of the spectral lines, a tube C is

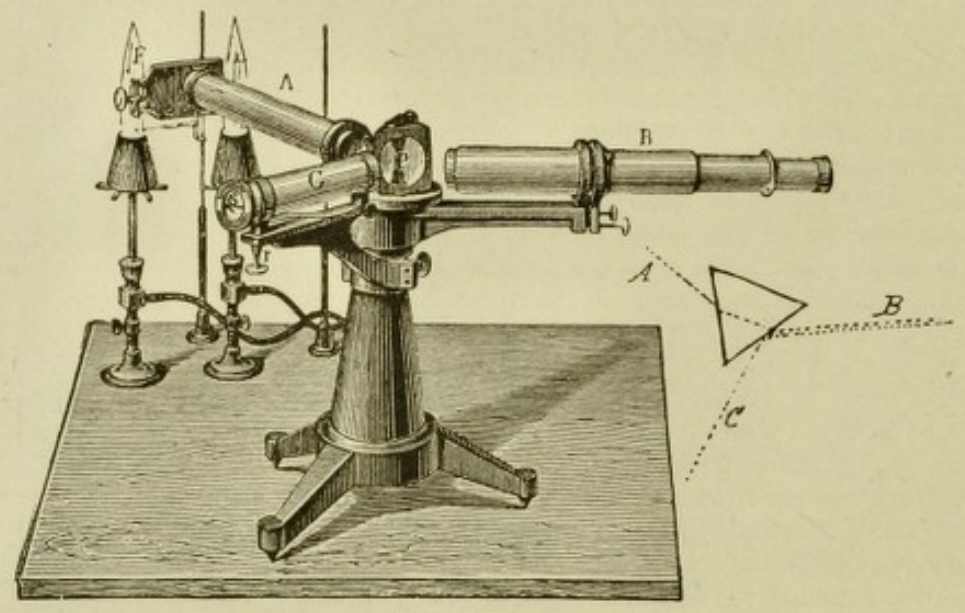


Fig. 18.

used which carries at its extremity *S*, a horizontal slit through which the rays of a luminous flame enter and immediately impinge on a millimetre scale photographed on to a glass plate. The divisions of this scale are reflected from the face of the prism and can be observed through the telescope B, together with the spectrum. In order to compare the position of the spectral lines of different substances, the scale in the tube C is adjusted in such a manner that the division marked 50 corresponds to the yellow line of the emission spectrum of sodium. The scale remains definitely fixed at this point, and the positions of the spectral lines of other substances can thus be determined.

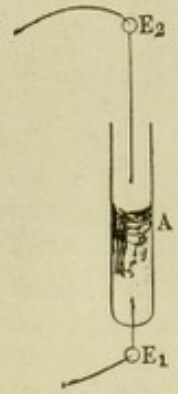


Fig. 19.

In order to obtain the spectra of liquid or dissolved substances, these are placed in a test-tube provided with a platinum point in its base (Fig. 19) which is united to one pole of a Ruhmkorff coil. Another platinum wire is carried close to the surface of the liquid and united with the other pole of the coil, so that sparks pass which give the spectrum corresponding to the liquid or dissolved substances in the spray which is formed.

If the white light of a luminous body, such as the sun, electric arc, &c., is passed through a gas heated to a high temperature (incandescent gas), we obtain characteristic lines of absorption of the continuous spectrum of the white light, black lines which correspond in the scale of the spectroscope exactly in position to those of the emission spectra of the same incandescent gas. The experiment is practically carried out by placing the substance to be studied above one of the carbons of an arc lamp.

In this manner the fact is explained that the white light of the incandescent solar nucleus by passing through the solar atmosphere formed of many strongly heated gases, gives a continuous spectrum divided by numerous black lines. These were first observed by Wollaston and correspond to the gaseous elements which are found in the solar photosphere. These were then studied by Fraunhofer, who assigned letters of the alphabet to the principal lines, the sodium light being denoted by D. Bunsen and Kirchhoff then

studied many more of them. The following elements, which we will denote by their symbols only (*see* Table, p. 43), were thus found with certainty in the sun: Na, Fe, Ca, Cr, Ni, Ba, Zn, Co, H, Mn, Ti, Al, Sr, Pb, Cd, Ce, U, W, Pd, Mo; the following are also probably present: In, Li, Rb, Bi, Sn, Ag, Be, La, Y. The presence of carbon, oxygen, and nitrogen is, on the other hand, largely contested, but most probably at such elevated temperatures (supposed by Moissan in 1906 to be 4000–6500°) the characteristic lines of these elements due to the impacts of the simple atoms are no longer obtained, and it may be supposed that under such conditions these atoms are finally split into still smaller particles. The above-mentioned single yellow line of sodium is, in fact, formed of two lines very close together, and similarly other atoms give multiple lines, which perhaps denote the impacts of still smaller particles. By means of spectral analysis we are able to identify minimal quantities of substances. Thus the spectrum will reveal $\frac{1}{50,000,000,000}$ of a gramme of sodium.

CHEMICAL EQUATIONS

The chemical reactions which occur between various substances, simple or compound, may be represented by means of equations, which are just as rigorous as algebraic equations. The reactions always occur between chemical particles, and therefore between definite weights of the reacting substances. Since no matter is lost in any reaction, the chemical equation must also quantitatively represent the equality between the weights of the reacting substances and of the new substances which are formed.

Thus, for example, the reaction which occurs between one molecule of chlorine and one molecule of hydrogen, giving hydrochloric acid, may be represented by the following equation: $H_2 + Cl_2 = HCl + HCl = 2\,(HCl)$.

All the atoms of the first member of this equation are found again differently grouped in the second member, and the complete weight of the molecules of the first is equal to the weight of the molecules of the second. Thus these equations express to us in a simple and exact manner one of the most important laws of chemistry and of nature in general, which says that in all transformations of matter nothing is created and nothing is lost. Thus:

$$\begin{array}{rcl} & H_2 + Cl_2 & = 2HCl \\ \text{weight} & 2 + 71 & = 2 \times 36{\cdot}5 \\ & \underbrace{\qquad}_{73} & \underbrace{\qquad}_{73} \end{array} \qquad \begin{array}{rcl} & H_2SO_4 + Zn & = ZnSO_4 + H_2 \\ \text{weight} & 98 + 65 & = 161\ (\text{zinc sulphate}) + 2 \\ & \underbrace{\qquad}_{163} & \underbrace{\qquad}_{163} \end{array}$$

From this equation we clearly see that in order to prepare 161 grms. of zinc sulphate and 2 grms. of hydrogen, 98 grms. of sulphuric acid and 65 grms. of zinc are required.

In other cases chemical equations serve to solve important practical problems. Thus, for example, in order to determine in advance whether sodium chloride or potassium chloride is more suitable for the manufacture of hydrochloric acid (supposing that the prices of these two salts are equal), we find for the chemical reaction between the salt and sulphuric acid the following equation:

$$\begin{array}{rcl} NaCl + H_2SO_4 & = & NaHSO_4 + HCl \\ 58{\cdot}5 + 98 & = & 120 + 36{\cdot}5 \end{array} \quad \text{or} \quad \begin{array}{rcl} KCl + H_2SO_4 & = & KHSO_4 + HCl \\ 74{\cdot}5 + 98 & = & 136 + 36{\cdot}5 \end{array}$$

Now we see that with the same quantity (98) of sulphuric acid, in one case 58·5 parts by weight of sodium chloride and in the other case 74·5 parts by weight of potassium chloride are needed in order to obtain the same quantity, 36·5 parts, of hydrochloric acid. It will thus be better to employ sodium chloride even if this costs as much as potassium chloride; the practical advantage is, however, still greater because sodium chloride costs much less.

FUNDAMENTAL PRINCIPLES OF THERMOCHEMISTRY

When we write a chemical equation, we do not completely express the chemical phenomenon. Though the equation evidently expresses a transformation of matter, we have still no idea of the changes which occur in the inherent energy of the same substances, and which are closely connected with chemical phenomena.

The chemical energy or internal energy of the substance, being indestructible, will be found in equal quantities, though partly under different forms, both before and after a given chemical reaction has occurred.[1]

Modifications in the chemical state of one or more substances are always accompanied by development or absorption of energy, which is easily measurable in the form of heat. Hence the name thermochemistry given to the study of chemical reactions with the measurement of the thermal changes.

Lavoisier and Laplace argued without experimental demonstration that in order to decompose a substance into its components, there would be required the same quantity of heat as was developed in its formation. The experimental demonstration of this important conception was not undertaken until the work of G. H. Hess was carried out in about the year 1840, and thus at an epoch anterior to the discovery of the law of the conservation of energy by R. Mayer in 1842.

Hess demonstrated experimentally, by studying the formation of ammonium sulphate, that the total heat which is developed in a chemical process is always the same however the reaction occurs, whether in one step or in many phases. Hess may be considered to be the founder of thermochemistry.[2]

The work of Andrews (1841–1848), of Graham (1843–1845), and of Grassi (1845) did not advance the progress of thermochemistry very much. In France, however, for some years from 1844 to 1850, the extensive and important thermochemical researches of Favre and Silbermann were undertaken and proved that there are also chemical reactions in the course of which heat is absorbed, whilst until that time it had been believed that chemical combination was always accompanied by evolution of heat. Those reactions which occur with evolution of heat were then called *exothermic* reactions, whilst those which occurred with absorption of heat were called *endothermic*.

In 1853 to 1854 J. Thomsen established the foundations of a thermochemical system by applying for the first time the principles of the mechanical theory of heat. He showed that the thermochemical equivalent of a substance (or internal energy, supposing this all to be transformed into heat) under the same conditions has always the same value.

If heat is developed during a chemical combination with or without increase of volume (external work), the internal energy must diminish by the corresponding amount. The thermal tonality, that is, the evolution or absorption of heat, and the heat corresponding to the external work (increase of volume) of a chemical process must then be equal to the internal energy of the reacting substances, diminished by the internal energy which remains in the products of the reaction. The thermal tonality is proportional to the quantities of the substances which react.

In 1851–1852 Woods carried out similar work independently of that of Thomsen, leading to the same results.

When solid and liquid substances react with production of a gas, the external work is increased by 24·19 calories for every litre of increase of volume (*see* p. 27).

The true founder of thermochemistry in France was Berthelot. From 1865 up to the last few years, together with his numerous pupils, who are disseminated throughout Europe, he has enriched this branch of chemistry by numerous and important experiments which have led to a complete system from which the fundamental laws of thermochemistry have been deduced, which Berthelot collected, together with his more important work, in

[1] Chemical energy is of the greatest importance throughout the large economy of nature. Firstly, because it is durable: thus, a piece of coal provided by a plant which accumulated radiant energy from the sun is conserved for thousands of years in the depths of the earth without losing any of its energy, which may be utilised in combustion. Secondly, because chemical energy is ordinarily found in very concentrated forms; in fact, if one were able, for example, to completely transform into mechanical work the heat of combustion of a single gramme of hydrogen, one would be able to raise a weight of 1400 kilos to a height of one metre. It is thus evident that mechanical energy is found in a form which is very convenient for transportation, because it is greatly concentrated. Boyle, Lavoisier, and Laplace already carried out chemical experiments in which the heat was measured which is developed by animal organisms, and similar experiments were also made in 1779 by Crawford, in 1822 by Dulong, and in 1824 by Despretz. Furthermore, Davy in 1813 and Rumford in 1817 determined directly the calorific power of solid, liquid, and gaseous combustibles.

[2] By a strange fatality and historic coincidence, Hess, who in 1840 had rediscovered the valuable work of Richter which leads to the first fundamental laws of chemistry (equivalents, &c.) and which were unjustly attributed by Berzelius to Wenzel, was in his turn the true founder of thermochemistry and was forgotten by his contemporaries, whilst the great importance of his work was only recalled and pointed out by Ostwald in 1886.

two volumes published in 1876. He enunciated the three following general laws : (1) *The heat developed in a chemical process is the measure of the chemical and physical work produced*[1] ; (2) *the thermal effect of a chemical process depends only upon the difference between the thermal state before and after the reaction whatever may be the intermediate reactions which have occurred* (law of Hess) ; (3) *every chemical transformation which occurs without the intervention of energy from outside, tends towards the formation of those compounds or systems of compounds in which the largest quantity of heat is evolved* (principle of greatest work). This last principle, which was enunciated by Thomsen in 1853, was then developed by Berthelot, but in the last few years it has proved to be in contradiction to many reactions (reversible actions, actions of catalysts, chemical equilibria, &c., *see below*), and van't Hoff, Nernst, and others have shown that it is insufficient or have accepted it as exact only when departing from absolute zero for solid reactions, that is, when the product of the reaction separates as an insoluble solid and when the thermal tonality is independent of the temperature (*see below*, chapter on Affinity.)

From 1869 to 1882 Thomsen carried out further very numerous experiments, which are collected into four volumes published in 1882–1884, and which all confirm these fundamental laws.

Stohmann, in Germany, after a large number of experiments on thermochemistry applied to physiological chemistry, obtained results in perfect harmony with the above-mentioned laws.

Important improvements in the apparatus used in more rigorous thermochemical research are due to Thomsen and more especially to Berthelot. Berthelot's calorimeter or bomb is used in all laboratories and has also been of use in the study of numerous organic compounds. We give a description of it in the chapter on carbon and combustibles. The chemical reactions are

[1] The calorific unit which serves as the basis of all thermochemical measurements is the *small calorie* (cal.) which indicates the heat required to raise the temperature of 1 grm. of water from 0° to 1°, or the *large Calorie* (Cal.) of Berthelot, which expresses the heat required to raise the temperature of 1 kilo of water from 0° to 1°, and is equal to 1000 cals. Finally, Ostwald has advised the acceptance of the rational calorie proposed by Schuller and Wartha in 1877, which expresses the quantity of heat necessary to raise 1 grm. of water from 0° to 100°, and is denoted by the letter K, which distinguishes it from the others. This is equal to 100 small calories.

It was more especially the work of Joule which led to the exact determination of the mechanical equivalent of heat. It was then generally confirmed that 1 Calorie could accomplish the work of 427 kilogrammetres (1 kilogrammetre is the work necessary to raise 1 kilo to a height of 1 metre) ; and, *vice versa*, the mechanical work of 427 kilogrammetres corresponds to exactly 1 Cal. of heat.

More rationally, the *joule* (j) is used to-day and refers to the fundamental unit of work, the erg, or, better still, the kilojoule is used, which is equal to 1000 j and corresponds to 239 cals.

We have already seen (p. 38), in considering the kinetic theory of gases, that the kinetic energy (E) of a body $= \frac{1}{2}\, m.c^2$, and thus the whole energy may be represented by or referred to this formula. If we wish to deduce from this formula the rational unit of energy, we must substitute for the value m 1 grm., that is, the one-thousandth part of the unit of weight preserved at Paris, and constituted by a block of platinum, the weight of which is fixed at 1 kilo ; velocity (c) is deduced from a simple formula $c = \frac{L}{T}$, where L is the length of the path measured in centimetres, and T the time, measured in seconds. Then for 1 grm. moving with a velocity of 1 cm. per second, we have $E = \frac{1}{2} . 1 . 1^2 = \frac{1}{2}$. Transforming into units the value of the energy resulting from this formula $\left(\frac{1}{2} \times 2 = 1\right)$ we will find that the unit of energy is double the amount of energy contained in 1 grm. of any substance, moving with the velocity of 1 cm. per second. The unit of force is called the *dyne* (*see* p. 26), and the work which corresponds to one dyne is called the *erg* (unit of work), which has a very small value. In order to form an idea of the erg, it will suffice to imagine a mass of 100 grms. projected with a velocity of 1000 cm. per second, which corresponds to 50,000,000 ergs. For practical convenience, calculations are made with units of 10,000,000 ergs (= 107), and this quantity or practical unit is called the *joule* and denoted by *j*.

The work of Mayer and of Joule determined the relationship between work and heat, and this relationship was corrected later by the most exact determinations, so that we know to-day that one small calorie (referred to 1 grm. of water at 18°) corresponds to 41,890,000 ergs, that is, 1 calorie = 4·18 j ; or the rational (centesimal) calorie K = 418 j. This is the most exact expression for the mechanical equivalent of heat measured with the fundamental unit of work, that is, the erg, or with the joule, j. Since the kilojoule (Kj) = 1000 j, then 1 cal. = 0·00418 Kj., or 1 cal. = $\frac{1}{239}$ Kj., that is, 1 Kj. = 239 cal. On the other hand, 1 cal. corresponds to 427 kilogrammetres of work.

One horse-power (h.p.) corresponds to 75 kilogrammetres per second (= 270,000 kgrm. per hour), and thus 1 Cal. corresponds to 5·69 horse-power seconds (= 427 kgrm. 75), and a horse-power hour corresponds to 630 Cal. With a good steam-engine a horse-power hour is obtained with about 3–4 kilos of coal, according to the size of the engine, so that this will cost from 1·2*d*. to 1·5*d*. in Italy. With gas motors a horse-power hour costs less than 0·3*d*. to 0·4*d*. The price of an electrical horse-power (with transport of energy) varies very much from ½*d*. up to 1·2*d*., and one may remember that a horse-power corresponds to 734 watts or 0·734 kilowatts.

made to occur in a closed metallic receiver which is immersed in a measured quantity of water, the temperature of which is measured both before and after the reaction.

There is a general agreement to-day to refer the thermal tonality of a substance or of a chemical reaction to gramme-molecules of the substances in question (*see mol.*, p. 26), or in the case of metals to gramme-atoms ; they may also be referred to gramme-equivalents.

We will now follow some reactions thermochemically :

$$Pb + I_2 = PbI_2 + 39{,}800 \text{ cal.}$$

This equation signifies that the internal energy of 207 grms. of Pb (atomic weight 207) + the internal energy of 2 × 127 grms. of iodine (atomic weight 127) = the internal energy of 460·6 grms. of PbI_2 (molecular weight) + 39,800 calories developed in the reaction. Thus $PbI_2 = -39{,}800$ cals., that is, PbI contains 39,800 calories less than the free components and, in order to regain Pb and I from it, it would be necessary to employ 39,800 cals. which were evolved during its formation.

In the formation of 18 grms. (mol. wt.) of water at 0° starting from 2 grms. of hydrogen and 16 grms. of oxygen, 68,400 cals. are developed, and thus H_2O liquid $= -68{,}400$ cals. (or 286 Kj. ; as 1 Kj. = 239 cals.). If, on the other hand, 18 grms. of water vapour at 100° is under consideration it is necessary to deduct 100 calories which are developed for each gramme of water when cooled from 100° to 0° and also the heat of evaporation which is 537 cals. for each gramme of water, and the expression now becomes :

H_2O vapour $= -57{,}000$ cals. [*i.e.*, $68{,}400 - (637 \times 18)$] also referred to 18 grms.

But this result, and also that obtained in the case of liquid water, must be still further corrected to allow for the fact that, starting from gaseous substances, and in fact from one mol. (22,412 litres = 1 grm.) of hydrogen and ½ mol. of oxygen (11,206 litres), we obtain liquid water, so that there has been a diminution of volume of 1½ mols., that is, 33·618 litres, and the corresponding quantity of heat has thus been developed and can be calculated because we know that 1 litre-atmosphere corresponds to 24·19 cals. (*see* p. 27). Thus the true thermal tonality of the formation of H_2O liquid will be :

$$68{,}400 - (24{\cdot}10 \times 33{\cdot}618) = 68{,}400 - 814 = 67{,}586 \text{ cals.}$$

The accurate thermal tonality for H_2O vapour will be 57,000 cals. diminished by the heat corresponding to ½ mol. by volume, because 1 mol. of water vapour finally results from 1½ mols. of hydrogen and oxygen.

When a gas reacts on a liquid it is sometimes necessary to take the heat of solution of the gas in the liquid into account.

Thus if we allow aqueous solutions of potassium hydroxide and HCl to react we will have the following equation, the thermal tonality of which in this case expresses the heat of neutralisation :

$$KOH \text{ aq} + HCl \text{ aq} = KCl \text{ aq} + H_2O + 57{\cdot}35 \text{ Kj. } (= 13{,}700 \text{ cals.})$$

If an aqueous solution of KOH reacts directly with HCl gas the equation will be :

$$KOH \text{ aq} + HCl \text{ gas} = KCl \text{ aq} + H_2O + 129{\cdot}91 \text{ Kj. } (= 31{\cdot}060 \text{ cals.})$$

According to this second equation we have a development of 72·38 Kj. (= 17,360 cals.) more heat, and this expresses the heat of solution of HCl gas in water. In the thermal effect which results from these reactions the work of dissociation of the reacting molecules into the corresponding simple atoms, a process which requires considerable quantities of heat, is also included.

Thus, the heat which is actually measured represents the difference between the heats of combination of the reacting atoms and the heats of dissociation of the reacting molecules.

The second law of thermochemistry (of Hess) is also called the law of the constant sum of the heat effects, and says that the final thermal effect of a complete reaction is equal to that obtained if the reaction occurs in one phase, whatever the number of phases through which it actually passes, that is, the difference of energy between two states of a chemical system is independent of the cycle through which it has passed from the one state to the other. If, for example, we add to an aqueous solution of 1 grm.-molecule

of phosphoric acid, H_3PO_4 (tribasic acid), an aqueous solution of 3 grm.-molecules of sodium hydroxide, 3NaOH, trisodium phosphate is formed with development of 142·4 Kj. (= 34,030 cals.):

$$3NaOH\ aq. + H_3PO_4\ aq. = Na_3PO_4\ aq. + 3H_2O + 142{\cdot}4\ Kj.$$

If, on the other hand, we add the three molecules of NaOH one at a time we have the following three phases of the reaction, which, however, lead to the same final thermal result:

$$NaOH\ aq. + H_3PO_4\ aq. = NaH_2PO_4\ aq. + H_2O + 14{,}829\ cals.$$
$$NaOH\ aq. + NaH_2PO_4\ aq. = Na_2HPO_4\ aq. + H_2O + 12{,}251\ cals.$$
$$NaOH\ aq. + Na_2HPO_4 aq. = Na_3PO_4\ aq. + H_2O + 6950\ cals.$$

The sum of the amounts of heat liberated by the three intermediate reactions is 34,030 cals. and corresponds to the heat produced when the reaction takes place in a single phase.

The heat of formation of the intermediate compounds of a given reaction can be deduced by an *indirect method* from the original thermochemical system and the final reaction. For example: though the heat of formation of carbon monoxide, C + O = CO, cannot be determined directly, yet it can be indirectly deduced from the knowledge that $C + O_2 = CO_2 + 97{,}000$ cals. (405·8 Kj.) and that $CO + O = CO_2 + 67{,}850$ cals. (284·5 Kj.); by subtracting the one phase from the other we have the other phase:

$$C + O = CO + 29{,}150\ cals.\ (i.e.\ 97{,}000 - 67{,}850).$$

This indirect method is exact and is often employed for complicated chemical systems, and especially for the indirect determination of the thermal effect of reactions which cannot be directly obtained, or in special cases in which it is not practically possible to measure the effect of such reactions.

Berthelot maintained that the heat developed during the combination of two substances is proportional to their affinity, but this is not always correct, as was shown by Le Chatelier, who elucidated the bearing of the principle of the resistance to reaction, which he had deduced thermodynamically, on chemical reactions. This principle is closely connected with the principle of mobile equilibrium enunciated by van't Hoff in the case of the various physical states of matter.

This rule says that by every change of one of the factors which regulate a chemical-physical system in equilibrium, there are produced, by the transformation in the system, actions which are opposed to the modifying factor. Thus, for example, by altering the temperature of a liquid, for instance, by heating it, evaporation occurs, that is a phenomenon which tends to absorb heat. Two substances which combine with evolution of heat have a tendency to dissociate when reheated, that is, to be transformed into their components with absorption of heat, and since the greater portion of the number of known substances are formed with evolution of heat, therefore at temperatures more or less elevated they are decomposed, whilst, on the other hand, substances which absorb heat during combination (endothermic substances) are not dissociated by elevation of temperature (in fact they are generally formed at high temperatures), but on the contrary become more stable as the temperature is raised. We thus see that the belief of many, that at very high temperatures, for instance, in the sun, all substances have a tendency to dissociate into their respective elements, is erroneous; this being only true for substances which are formed with development of heat, but not for those which absorb it during formation.

Rhombic sulphur is transformed into the monoclinic variety with absorption of heat; therefore on heating rhombic sulphur it is transformed into the monoclinic form (*see also* chapter on Sulphur).

By Le Chatelier's principle and with the aid of thermodynamics, one can always foresee in which sense a chemical reaction will proceed, or whether such a reaction is possible or not. One cannot, however, always bring about a reaction which is theoretically possible, because of the so-called passive resistances (friction, capillarity, ionisation, &c.), which often cannot be calculated by means of thermodynamics. Thus alcohol does not burn in oxygen at the temperature of liquid air (− 190°), and under the same conditions sodium does not react with alcohol nor chlorine with hydrogen, &c., and it is well that it is so, because if all theoretically possible reactions were to

occur in nature, than all combustible or oxidisable substances would burn, even at ordinary temperatures, and our planet would become a veritable inferno, uninhabitable for vegetables and animals.

Temperature has much influence on chemical reactions and the velocity of reaction is in general much smaller when the temperature is lowered. Whilst the temperature rises according to an arithmetical series the velocity rises according to a geometrical series. On raising the temperature by 10°, the velocity of reaction increases to double or treble its former amount (*see below*).

CHEMICAL EQUILIBRIA AND VELOCITIES OF REACTION

In chemical reactions we have many evident examples, and also others which are less evident, in which the reacting substances do not combine completely, but only partially (*partial reactions* which are in contradiction to the third principle of thermodynamics enunciated by Berthelot). It is supposed that in such cases under given conditions a part of the product of reaction is again dissociated into its components, thus establishing a chemical equilibrium between the reaction which proceeds in one sense and that which proceeds in the opposite sense, hence in all such phenomena one can no longer speak of a static equilibrium, but rather of an equilibrium of kinetic character.

The Swedes, Guldberg and Waage, inspired by the conceptions of Berthollet, published in 1867 an important work ("Études sur les affinités chimiques"), in which they placed the equilibrium of chemical reactions on a mathematical basis. This work passed unobserved, and in 1873 an Englishman, Jellet, came to an analogous conclusion. It was only in 1877 that van't Hoff pointed out the great importance of these studies to chemistry.

In the study of chemical equilibrium it is necesssary to clearly fix the conception of concentration of substances which come into play during reactions. It is not the absolute quantities of the mass of reacting substances which are of interest, but rather their relative mass, per unit of volume. The rational method of expressing concentration is by the number of gramme-molecules (*see* p. 26) contained in a unit of volume (ordinarily one litre).

One mol. of any gas at 0° and 760 mm. pressure occupies a volume of 22·412 litres (*see* p. 26), and its concentration A is given by

$$C = \frac{1}{22{\cdot}412} = 0{\cdot}044619$$

Since, by the laws of Boyle and Gay-Lussac (*see* p.26) the volume v of a gas at temperature T and pressure p is given by $v = \frac{V_0 p_0 T}{p \,.\, 273}$, then these 22·412 litres at pressure p and absolute temperature T, will be:

$$v = \frac{22{\cdot}412\ p_0 T}{p\ .\ 273}$$

and consequently the concentration $C = \frac{273\ .\ p}{22{\cdot}412\ p_0 T}$. When gaseous mixtures are under consideration in which one of the components has the percentage value, V, and partial pressure, p, whilst the total pressure is P, we have $p = \frac{V\,.\,P}{100}$, and thus the concentration of that component will be:

$$C = \frac{273\ PV}{100\ \times 22{\cdot}412\ T} = \frac{0{\cdot}12181\ PV}{T}$$

If the gas formula, $p\,v = R\,T$ (*see* p. 26) refers to 1 mol. of a substance, that is, to

22·412 litres, then in all those cases in which n mols. of a substance are contained in that volume, we have $pv = n.RT$, and the concentration becomes :

$$C = \frac{n}{v} = \frac{p}{RT}$$

that is to say, that the *concentration of a given quantity of a substance is directly proportional to the pressure to which it is exposed, and inversely proportional to the absolute temperature, and also to the volume*, that is :

$$\frac{C}{C_1} = \frac{p}{p_1} = \frac{T'}{T} = \frac{v_1}{v}$$

In a mixture of gases in which the total pressure is P and the partial pressure of one of the components p, we have $pv = nRT$, and $Pv = NRT$, where n and N indicate the number of mols. ; and since both for the mixture and for each of the component gases the volume and the temperature are common and equal, we deduce the equation : $\frac{p}{P} = \frac{n}{N}$; that is to say, *the partial pressure p_1 of one component is in the same ratio to the total pressure P of the mixture, as that of the number of mols. n contained in volume v, and corresponding to p, to the total number of mols. N, or*

$$\frac{p}{P} = \frac{\frac{n}{v}}{\frac{N}{v}} = \frac{C}{\Sigma C}$$

which is to say, that the *partial pressure of one component of a gaseous mixture is in the same ratio to the total pressure as its concentration is to that of the sum of the concentrations of the components.*

We may also write $C = \frac{p}{P} \Sigma C$, that is to say, *that the concentration of one of the components of a gaseous mixture is equal to the sum of the concentrations of all the components multiplied by the ratio between the partial pressure and the total pressure.*

We will have occasion to refer back to these considerations of concentration not only for the following general considerations of chemical equilibria, but also when we study systematically certain important chemical reactions. (*see* Sulphur Trioxide, &c.)

REVERSIBLE REACTIONS. Wenzel already in 1777, and Berthollet in 1799 agreed that in some cases certain reactions are not completed, but a rigorous study of such chemical equilibria was only undertaken much later by Berthelot and Péan de Saint-Gilles in the case of the formation of ethers, where it may easily be observed that a reaction may proceed in opposite directions. In such reversible reactions we replace the sign of equality in the equation by $\rightleftharpoons$ or even more simply by $\longrightarrow$, in order to indicate that the reaction may take place in two senses. At certain temperatures hydrogen and iodine combine *in part* to form hydriodic acid (HI), but hydriodic acid dissociates in part at the same temperature into H and I. This reversible reaction may be represented by the equation $H_2 + I_2 \rightleftharpoons 2HI$.

In the study of chemical equilibria, it is necessary to distinguish cases in which the system is called a one-phase system and forms a homogeneous equilibrium, from those in which there are several phases (*see below*, Theory of Phases), that is, when there are various states of aggregation or non-miscible liquids constituting a *heterogeneous equilibrium.*

In order to establish chemical equilibrium various factors contribute, and more precisely three *external factors*, temperature, pressure and electromotive force, and three *internal factors*, physical state, chemical nature and concentration of the substances. When even a single one of these factors is changed the state of equilibrium of the system becomes modified, and therefore if two or more *equivalent factors* are altered at the same time, the equilibrium of the system may even remain unchanged. Catalytic action is not

considered as one of the factors of equilibrium, because a reaction can occur even without the presence of a catalyst (*see below*), and even if this is present, the equilibrium is not displaced except in the case of a consequent modification of temperature.

The factors of equilibrium need not always be studied quantitatively in order to fix the conditions of equilibrium. A qualitative test which indicates in which sense the change of equilibrium is taking place, is often sufficient, and may be deduced by the principle of *mobile equilibrium* (*see* pp. 53 and 61) studied by van't Hoff for temperatures, and generalised by Le Chatelier for all the other factors of equilibrium.

We will add a few other examples to those already recorded in order to better illustrate this important *rule of the antitheses*. On raising, for example, the temperature, the equilibrium is displaced in a sense favourable to the reaction which absorbs heat. Substances which dissolve with absorption of heat are the more soluble the more they are heated. On the other hand, those which dissolve with evolution of heat are less soluble when hot than in the cold (anhydrous sodium sulphate, calcium hydroxide, &c., *see* Part II., Freezing Mixtures). If the heat of solution of a salt is zero or very small, then the solubility is constant even when the temperature varies. This is the case for sodium chloride. Substances which are formed with evolution of heat are less stable when hot than in the cold, and above a certain temperature tend to dissociate into their components. This is the case for water, carbon dioxide ($CO_2 = CO + O$), calcium carbonate ($CaCO_3 = CaO + CO_2$), &c. Substances, on the other hand, which are formed with absorption of heat are more stable when hot than at low temperatures (for example, calcium carbide, acetylene, nitrogen peroxide, &c., *see* p. 61).

Increase of pressure displaces chemical equilibrium in that sense which conduces to a system requiring less pressure. Ice melts more easily under pressure, because on passing from the solid to the liquid state, it diminishes in volume. Dissociations which lead to an increase of volume ($CaCO_3$ solid = CaO solid + CO_2 gas) are retarded or prevented by increase of pressure and facilitated by diminution of pressure. The reaction 2CO gas = CO_2 gas + C solid, which leads to a diminution of volume, is facilitated by increase of pressure and rendered more difficult by reduction of pressure. Reactions which occur without change of volume are not influenced by the pressure (2HI gas when heated = H_2 gas + I_2 gas).

Increase of *concentration* of one of the components of a system displaces the equilibrium in the direction of that system which diminishes the concentration of that component which is increased in concentration. Thus, in the system $H_2 + I_2 \rightleftharpoons 2HI$, on increasing the concentration of H_2 or of I_2, there will be a greater formation of HI ; this phenomenon is also called *mass action*. The reaction is still further facilitated if the concentration of the reaction products is diminished, that is, by eliminating the HI as fast as it is formed. This also explains why, in a liquid system, on causing a solution of sulphuric acid to react with one of barium chloride, complete transformation into barium sulphate occurs, because this latter is insoluble and separates. In the chapter on catalytic sulphur trioxide, we will see what industrial importance the study of such chemical equilibria has, and we will also see how in the system

$$2SO_2 + O_2 \longrightarrow 2SO_3,$$

it has not been possible to apply the laws of equilibrium to their full extent.

Secondary reactions have a varied and often complex influence on the chemical equilibrium of a system, because in this way several systems of equilibria are present contemporarily. We will have occasion later (Theory of Ions) to also consider such cases.

A knowledge of *velocity of reaction* is also of great importance in the study of chemical equilibrium, and we may illustrate it by an example which was very exactly studied by Lemoine in 1877. This is the action of hydrogen on iodine, with formation of hydriodic acid (HI). At 270° the partial

reaction only occurs after some months; at 300° after fifteen days, but at 440°, on heating equimolecular quantities of hydrogen and oxygen ($H_2 + I_2$), the maximum quantity of hydriodic acid which is already formed in three or four hours, and is 79 per cent. of the reacting substances, whilst 21 per cent. remains apparently unaltered (kinetic equilibrium). At high temperatures, the HI diminishes steadily and every temperature corresponds to a certain relation between HI, H, and I. It is evident that on raising the temperature a dissociation of HI into its components occurs, and we may thus suppose that this dissociation takes place even at temperatures lower than 440°, but up to that temperature the quantity of HI which is formed is greater than the amount dissociated, whilst above 440° the quantity of HI which dissociates is more than that which is formed.

The degree of reaction and of dissociation is constant for a given temperature. Thus, on heating pure hydriodic acid in a closed tube at a temperature of 440°, after some hours 21 per cent. of it is found to be dissociated into H and I. Now the state of equilibrium for a given temperature and pressure between two systems, that is, $H_2 + I_2 = 2HI$ and $2HI = H_2 + I_2$, or $H_2 + I_2 \rightleftharpoons 2HI$, is reached, when in unit of time equal parts of the one system are transformed into the other, and *vice versa*.

For each temperature the quantity of the product of reaction is a function of the time. Thus we may call velocity of reaction v, the change of concentration of one of the components of the system per unit of time C, and we may represent it thus : $v = \frac{dC}{dT}$.

The velocity of reaction depends upon the nature of the substances and upon their concentration (or active mass) because the greater the latter the more frequently do the molecules collide and combine. The number of impacts between the molecules is not merely proportional to the concentration, but also to the velocity of the molecules and therefore to the temperature.

If we suppose the temperature to be constant in the reaction between one molecule of H_2 and one molecule of I_2 (= 2HI), and denote their concentration in a given volume by C_{H_2} and C_{I_2}, then the velocity of reaction, v, will be proportional to the concentration and to a certain constant factor, k, or coefficient of velocity which varies for each reaction; we have thus: $v = k.C_{H_2}.C_{I_2}$. For the more complex reaction

$$H_2O + NO_2 + NO + O_2 = 2NO_3H, \text{ we have } v = k.C_{H_2O}.C_{NO_2}.C_{NO}.C_{O_2},$$

that is to say, the velocity of reaction is equal to the product of the concentrations multiplied by the coefficient of velocity. If one of the components of a reaction takes part by means of a greater number of molecules, we have, for example, $2H_2 + O_2 = 2H_2O$, and, therefore, $v = k.C_{H_2}.C_{H_2}C_{O_2}$ or $v = k.(C_{H_2})^2.C_{O_2}$.

We may always represent a general chemical reaction between the substances A, A', A'' . . . , apart from questions of energy, by the following equation :

$$n_1 A + n_1' A' + n_1'' A'' + \ldots = n_2 B + n_2' B' + n_2'' B'' + \ldots$$

and the velocity will be expressed by : $v = k_1 (C_A)^{n_1'}.(C_A')^{n_1'}.(C_A'')^{n_1''} \ldots$

If we call $(C)^n$ the *active mass* or concentration of the given substance and suppose it to be equal to 1 in the preceding equation, then v becomes k. That is, k would be the velocity of reaction in the case in which the product of the active masses, or the single concentration, would be 1.

In the case of reversible reactions, equilibrium occurs when the velocity of reaction v of a system is equal to the velocity v' of the system which represents the opposite reaction, that is, $v = v'$, or :

$$k_1.(C_A)^{n_1}.(C_A')^{n_1'}.(C_A'')^{n_1''} \ldots = k_2(C_B)^{n_2}.(C_B')^{n_2'}.(C_B'')^{n_2''}$$

and thus: $$\frac{(C_B)^{n_2} \cdot (C_{B'})^{n_{2'}} \cdot (C_{B''})^{n_{2''}} \cdot \ldots}{(C_A)^{n_1'} \cdot (C_{A'})^{n_1'} \cdot (C_{A''})^{n_1''} \cdot \ldots} = \frac{k_1}{k_2} = K$$

the logarithmic solution of which becomes $\Sigma n_2 \log C_2 - \Sigma n_1 \log C_1 = \log k_1 - \log k_2$, and combining the first members we have the following general, simpler expression: $\Sigma n \log C = \log K$, at which we may also arrive from thermodynamical considerations; in each case K represents the constant of the *law of mass* or of the *isothermic equilibrium.*

We are now able, without penetrating into the mystery of the intimate nature of matter and without, therefore, being able to really define the affinity of substances, to mathematically represent their behaviour in all their varied transformations by making use of this general equation of the law of mass.

From this equation we at once see that if the concentration of one of the reacting bodies increases, for example, C_A, then the product of the reaction must also consequently increase, for example, C_B, whilst K remains constant. Thus the action of the mass is mathematically regulated, and the equilibrium of chemical reactions depends upon the concentration of the reacting substances, that is, upon the relative quantity contained in unit of volume and not on the absolute quantity present in the system.

In the case of the reaction between $H_2 + I_2$, we have seen that a limit is reached in the direction of the reaction $H_2 + I_2 \rightarrow 2HI$, when at 400° about four-fifths of the molecules of H_2 and I_2 are transformed into HI; and for a given temperature equilibrium of a homogeneous system (all gases) occurs when the molecules of H_2, I_2, and 2HI are present in a definite proportion. But if we now use a chemical reagent to fix the HI in such a manner as to separate it in the solid or liquid state, then the equilibrium ceases and a further number of molecules of H and I are transformed into HI in order to re-establish the equilibrium. But we may obtain the same effect of transforming more than four-fifths of the H and I into HI, by displacing the equilibrium in another sense, namely, if in the same volume which contains the molecules of the preceding system we introduce, for example, double the number of molecules of hydrogen (that is, if we increase the concentration of the hydrogen per unit of volume); the probability that molecules of H_2 will encounter those of I_2 then becomes double, and thus the limit of the reaction will be increased, whilst, however, the velocity of the reaction in unit of time will remain unaltered under the new conditions.

On applying the general formula of the law of mass to the reversible reaction $H_2 + I_2 \rightleftharpoons 2HI$, we have $K = \frac{(C_{HI})^2}{(C_{H_2}) \cdot (C_{I_2})}$, and thus we see that by increasing the concentration of the hydrogen or of the iodine, we must increase the quantity of HI, because the value of K remains constant.

In the study of chemical equilibria we may distinguish cases of *monomolecular* and *dimolecular reactions.* In the same case of hydriodic acid, if this is dissociated under the action of sunlight, then the action is monomolecular, $HI = H + I$; whilst if it dissociates under the action of heat, the reaction becomes dimolecular, $2HI = H_2 + I_2$. In many dimolecular reactions the reacting molecules are different from one another. In the case of monomolecular reactions, the velocity of reaction is proportional to the quantity of undecomposed substance, and if the number of molecules of the substance A at the beginning of the reaction is indicated by a, and the number of molecules decomposed in a very short time t by z, we find that the velocity of reaction $\frac{dz}{dt} = k(a - z)$ where k represents the reaction constant.

In the case of dimolecular reactions, we have a molecules of the substance A, and b molecules of the substance B, and then in a very short time the molecules which have reacted will be $a - z$ and $b - z$, and we arrive at the equation:

$$\frac{dz}{dt} = k_1 (a - z)(b - z)$$

where k_1 is the new reaction constant. In the case of a dimolecular reaction occurring between equal molecules, for example, $2HI = I_2 + H_2$, a becomes equal to b, and the equation becomes: $\frac{dz}{dt} = k_1 (a - z)^2$.

It thus becomes possible by means of this equation to discover whether a reaction is monomolecular or dimolecular. On integrating this equation and solving for values of k and k_1, the calculation results finally thus:

$$k = \frac{1}{t} \log \frac{a}{a - z} \quad \text{and} \quad k_1 = \frac{1}{t} \frac{z}{a(a - z)}$$

Thus, by bringing about a given reaction in successive measured times and determining the quantities of matter dissociated in a given time, then by trying to apply one or other equation one is able to establish whether the reaction is monomolecular or dimolecular.

If we consider the inverse reaction for hydrochloric acid, that is, its formation from hydrogen and iodine on heating, we have $H_2 + I_2 = 2HI$, and if z be the number of the molecules which are dissociated, there will result from this $\frac{z}{2}$ molecules of hydrogen and the same amount of iodine, and the reaction being dimolecular the reaction-velocity will be $k_2 \cdot \left(\frac{z}{2}\right)^2$ and for the general reversible reaction $H_2 + I_2 \rightleftharpoons 2HI$, we will have chemical equilibrium when the two reaction velocities in contrary senses are equal:

$$k_1 (a - z)^2 = k_2 \left(\frac{z}{2}\right)^2 \quad \text{or} \quad \left(\frac{z}{a - z}\right)^2 = \frac{4 k_1}{k_2} = K$$

Thus, when equilibrium is established, whatever may be the concentrations and temperatures, the relations between the square roots of the quantities of dissociated and non-dissociated substances remains constant.

We have already noted that the *velocity of reaction* depends upon the nature of the substances which react and on their concentration, but we have also noted the influence exerted by the temperature. This increases the velocity of the molecules, and thus of their mutual impacts, and the reaction velocity consequently increases. Van't Hoff has experimentally deduced for many substances the ratios between reaction velocities k_{t_1} and k_t for temperature differences $t_1 - t =$ about 10°, and has found that these values are generally between 1·9 and 3·5, that is to say, that on increasing the temperature by 10° the velocity of reaction becomes double or treble or even more for many chemical processes (*see* the considerations stated on p. 62).

CATALYTIC PHENOMENA

Now that we have studied chemical reactions qualitatively and quantitatively and know under what conditions, in what sense, and up to what point they occur, we will turn to an interesting category of phenomena already known in the time of Berzelius and utilised during the last few years in important industrial processes, but which even to-day remain without rigorous and exhaustive explanation.

For many years it has been known that hydrogen peroxide (H_2O_2) decomposes slightly and very slowly, when allowed to stand by itself, into $H_2O + O$, but Berzelius, Schönbein, and a few others had already noted that on adding very small quantities of subdivided platinum or magnesium dioxide, the decomposition of hydrogen peroxide occurred very rapidly, sometimes causing a tumultuous development of oxygen. The platinum remains unaltered and transforms an indefinite quantity of H_2O_2 into $H_2O + O$. The same phenomenon with H_2O_2 may also be induced by other substances, for example, by pumice-stone, by colloidal metallic solutions (*see below*), by blood, or more exactly by a ferment (enzyme) called catalase contained in it.[1]

[1] The blood of various animals may be distinguished by the degree of its catalytic action. On pouring 1 c.c. of various kinds of blood into 1 per cent. hydrogen peroxide solution, the following quantities of oxygen in c.c.

The case is the same for hydrogen and oxygen. These two gases do not combine at ordinary temperatures except in imperceptible quantities, and after 120 hours at 450° only 20 per cent. is combined. But in presence of very small amounts of platinum sponge, the reaction occurs rapidly even at ordinary temperatures with formation of water without alteration of the platinum. Similarly it has been found that the velocity of reaction also varies notably with simple variation of the vessels in which it is produced. The atmospheric oxygen does not react even on heating with hydrochloric acid gas, but in presence of small quantities of copper sulphate or chloride at about 400° reaction occurs quickly with formation of chlorine (industrial Deacon process). Sulphur dioxide (SO_2) does not react with the oxygen of the air under ordinary conditions, even on heating, to form sulphur trioxide (SO_3), but in presence of platinised asbestos at 450°, 99 per cent. of the SO_2 is transformed into SO_3 (industrial process for the manufacture of sulphur trioxide).

All these special substances which accelerate chemical reactions which would even take place spontaneously, but with extreme slowness (measureable perhaps only after many years), and which do not take any part in the reaction and are found unaltered at the finish, after having transformed a very large quantity of the substance, were called by Berzelius *catalysts ;* their action is called *catalytic* action, and the phenomenon *catalysis*.

Catalysts are not able to induce reactions which would not occur alone at all, but only to accelerate those which can occur even very slowly, without, however, being able to displace the conditions of equilibrium of a chemical process. If, for instance, at 440° the reaction between $H_2 + I_2$ occurs up to 79 per cent. in the sense of the formation of HI, at lowered or higher temperatures, at which, on the other hand, the opposite reaction, that is, the dissociation of HI into H and I, is more marked, the same catalyst will then accelerate this opposite reaction. At certain temperatures, ammonia and hydrochloric acid unite to give ammonium chloride, but only on condition that a trace of water vapour is present. But the opposite reaction, that is, the dissociation of ammonium chloride into NH_3 and HCl, can only also occur at high temperatures in presence of traces of water. In this reaction, as in some others, it is always water which acts as a catalyst.

It has been supposed that catalytic substances form very unstable intermediate compounds with the reacting substances, and that by their decomposition the catalytic substances result anew, together with the true final product of the reaction. But in many cases it has not been found possible to demonstrate the formation of such intermediate products and Ostwald prefers to compare the action of catalysts to that of lubricating oil in a rotating wheel, which turns slowly and with much friction when oil is lacking, but turns much more rapidly under the same impulse if the axis is lubricated, although the lubricant takes no part in the movement, and is not used up.

Those reactions in which it has been shown that small quantities of the supposed catalyst give rise to unstable intermediate compounds which decompose with great rapidity, such as have been recently proved to exist, even in the case of platinum (which gives very labile oxides), are called *pseudo-catalytic phenomena*.

So-called negative catalysts are also known, and these impede or prevent certain reactions which would otherwise take place easily. In 1898 Bigelow found, for example, that minimal traces of mannite or of certain other organic substances completely prevented the oxidisation of sodium sulphite by oxygen.

The hypothesis that the catalytic phenomenon depends on intermediate reactions which accelerate the phenomenon compared with the direct reaction, and the practical proof of the existence of intermediate reactions, do not suffice to give a general explanation of catalytic phenomena ; it is necessary, on the other hand, to show that under such conditions the intermediate

at 0° and 760 mm. are developed : Human blood, 710 c.c. ; apes, 706 c.c. ; horse, 288 c.c. (venous) and 438 c.c (arterial) ; ox, 136 c.c. ; goat, 58 c.c. ; pigeon, 4 c.c. The catalysts (catalases) in the blood of various animals vary, but those of man and of the apes are the same (L. van Itallie, 1906).

reaction proceeds more rapidly than the direct reaction, and even in that case we are not yet able to explain all catalytic phenomena, especially those which hinder the reaction, because in such cases if a reaction occurs more slowly by taking place by means of intermediate products, it is natural that this should tend by preference to take place in the direct manner, and thus we cannot speak of the catalytic influence of intermediate products as these are not formed.

Euler recently propounded the hypothesis that the velocity of reaction being dependent on the concentration of free ions, catalysts had the property of modifying this concentration. This hypothesis is capable of explaining many reactions, but not the fact that in certain cases, when two catalysts are present simultaneously, the reaction velocity increases in a much greater proportion than would be the case according to the sum of the actions of the individual catalysts.

All substances may, perhaps, be specific catalysts for certain reactions, and perhaps all reactions are more or less catalytic reactions, but a general and positive explanation of catalytic phenomena has not yet been given.

AFFINITY

By affinity is understood the force by means of which the atoms are united with one another in the molecule, but it is not always easy to determine this force in practice. Though it is possible to have sufficiently precise data in such cases as, for example, the dissociation on heating of molecular into atomic iodine $I_2 \longrightarrow I + I$, this is not the case in reactions which take place, firstly, by the dissociation of all the reacting molecules into atoms, followed by the union of these to produce new molecules. The reaction velocity does not serve to measure chemical affinity because it varies greatly with the temperature, and may be notably increased by the presence of a simple catalyst. Berthelot believed it to be possible to measure affinity by the heat developed in a chemical reaction. And although by the third principle of thermochemistry (*see* p. 59), those reactions take place by preference which give rise to the greatest development of heat, thus corresponding to the maximum work, this is only generally true on condition that the reaction occurs without the intervention of external energy, as otherwise it would not be possible to explain the formation of endothermic compounds which absorb heat during their formation. We can thus only obtain a determination of the affinity by measuring the change of free energy of combination,[1] that is, the heat and external work developed in the formation of a substance from its components.

The external work may be determined in an isothermic and reversible chemical transformation, bearing in mind the thermochemical law of Hess (p. 60). By establishing the relation which exists between the change of free energy and the temperature, one can show by calculations that *the diminution of total energy is only equal to the change of free energy at absolute zero*, because by lowering the temperature of a body from dT down to absolute zero, all the heat contained in it is transformed into other forms of energy [2] (*see* pp. 25 and 59).

[1] The *free energy* of a substance is that part of the total available energy which can be transformed into another form of energy (in our case into heat). The difference between the total and the free energy is the *combined energy* and the ratio between this and the absolute temperature is called the *entropy* (Clausius), which for every substance becomes larger as its temperature is further removed from absolute zero.

[2] If we denote the work exercised by A, and the thermal effect by q, we have $A_0 = q^0$, and in order to calculate q_0 it is sufficient to know the thermal effect qT of the reaction at the temperature T and the specific heat of the original system (C_I) and of the final system (C_{II}). We then have $q_T = q_0 + (C_I - C_{II})_T$. If we assume that the specific heat of the substance is equal at all temperatures, then we may consider the change of free energy as a linear function of the absolute temperature. Strictly, however, the specific heat is not independent of the temperature and may be represented by the empirical formula $C = \alpha + \beta T + \gamma T^2 + \ldots$

The change of free energy in a reaction represents the maximum work which may be absorbed by the system if all the work is transformed into chemical energy. But it is not necessary in practice that all the work should be used in every case. Thus to take an analogous case, we may cool a liquid below its freezing-point by taking certain precautions, in such a manner that it does not solidify and liberate the latent heat of fusion, having thus abstracted from the liquid merely the quantity of heat corresponding to its specific heat. Thus, in a chemical system we may so arrange matters that all the heat corresponding to the maximum work is not immediately developed, and thus intermediate labile chemical systems are formed.

Ostwald opposed to Berthelot's principle of maximum work the *law of successive reactions*, according to which, if a chemical system be transformed into various others, the less stable systems are first formed (with small changes of free energy, that is, with a minimum evolution of heat), which are successively transformed into systems more and more stable. Metastable equilibria are thus produced which, however, follow the common laws of chemical equilibrium. Thus, on reacting with chlorine on a solution of sodium hydroxide, we are able to obtain all the following successive reactions :

$$\overbrace{24\,NaOH + 12Cl_2}^{I} = \overbrace{12\,NaOCl + 12\,NaCl + (12\,H_2O)}^{II} =$$

(II: sodium hypochlorite, sodium chloride)

$$\overbrace{4\,NaClO_3 + 20\,NaCl}^{III} = \overbrace{3\,NaClO_4 + 21\,NaCl}^{IV} = \overbrace{24\,NaCl + 6O_2}^{V}$$

(III: sodium chlorate; IV: sodium perchlorate)

The maximum of free energy is contained in System I and the minimum amount in System V. In consequence of these successive reactions, it is possible in practice to prepare hypochlorites, chlorates, and perchlorates, even simultaneously ; for example, by electrolytic methods.

SOLUBILITY OF GASES IN LIQUIDS

All gases dissolve in liquids to a greater or less extent. It was found by Henry in 1803 and 1805 (and confirmed by Bunsen and his pupils much later, in 1855) that the quantity by weight of a gas absorbed or dissolved by a given quantity of liquid varies with the nature of the gas and of the liquid, but for a given gas and a given liquid *is proportional to the pressure to which the gas is exposed*. Since the volume of a gas is inversely proportional to the pressure, we may say that a *given quantity of liquid always absorbs the same volume* (not the same weight) *of a gas whatever may be the pressure*. If we call the quantity by weight of gas which is present in unit volume of the gas or of the liquid its concentration, we may then say that the concentration of the dissolved gas is proportional to the concentration of the compressed gas in the space above the liquid, and this proportion or ratio, called the *coefficient of solubility* of the gas, remains constant at all pressures and becomes smaller as the temperature is raised, that is to say, the solubility of gases diminishes with rise of temperature. This law is apparently only true for gases which do not combine chemically with the liquid, and in general for small concentrations and small pressures. But by making use of the phase rule, which will be explained later, we shall be able to include the apparent exceptions of gases which are partly combined with the liquid, and we shall see that Henry's law may be considered as a particular case of the phase rule, that is, when the gas in the gaseous phase and in the liquid has the same molecular weight.

In 1807, Dalton showed that this law is also true for gaseous mixtures,

and *that each component of the mixture is absorbed in proportion to the ratio in which it is present in the mixture, or, in other words, in the proportion in which it would be absorbed if the other components of the mixture were not present, and it were present alone in unaltered quantity occupying the whole of the volume,* in which case it would thus be present at a reduced pressure.

If, for example, in 100 litres of a gaseous mixture at a pressure of one atmosphere, we have 20 litres of carbon dioxide, the pressure due to the carbon dioxide (partial pressure) is $\frac{20}{100}$, that is, $\frac{1}{5}$ of an atmosphere, and the quantity of carbon dioxide dissolved in the water present in the same vessel as the gas is the same as would be dissolved if the other gases did not exist, and the volume of 100 litres were occupied exclusively by the 20 litres of carbon dioxide, in which case this would be present at a pressure of $\frac{1}{5}$ of an atmosphere. If in the 100 litres of the gaseous mixture, 50 litres of carbon dioxide were present at a total pressure of one atmosphere, the pressure of the carbon dioxide would be $\frac{1}{2}$, that is, $\frac{50}{100}$ of an atmosphere, that is, $\frac{1}{2}$ that of the total gaseous pressure. In this case the quantity of carbon dioxide absorbed is the same as would be absorbed if the carbon dioxide only were present throughout the same volume at a pressure of $\frac{1}{2}$ atmosphere. In every case then the quantity of carbon dioxide absorbed depends upon the partial pressure exercised by this gas in the mixture and its partial pressure is in the same ratio to the total pressure as the volume of the carbon dioxide is to the total volume of the gaseous mixture. Practical illustrations of this law will be found in the chapters on the industries of liquid carbon dioxide, and catalytic sulphur trioxide, &c.

Dalton believed that the absorption of gases occurred because their particles entered into the intermolecular spaces of the liquid, and this was in harmony with the fact that the absorption is proportional to the pressure, but in this case the various gases should be absorbed to the same amount by the same liquid, which is not the case ; but the hypothesis becomes still more absurd when one remembers that the absorption becomes less with elevation of the temperature, which increases the intermolecular spaces. To-day, on the other hand, it is admitted that a certain attraction takes place between the molecules of a gas and those of a liquid by means of which the particles of gas are at first partially drawn into the liquid, but that these attracted gas particles are in turn detached from the liquid surface and that equilibrium and saturation are established when the number of gas molecules attracted by the liquid is equal to the number which are detached in the same period of time in virtue of the kinetic energy which they possess, that is, when the gas in the liquid and above it is at the same pressure. The law of Henry is more rigorously explained by means of the phase rule and of mathematical expressions of the equilibrium of various chemical systems, as will be explained later.

Bunsen determined the coefficient of absorption of gases by liquids, that is, the volumes of gas reduced to 0° and to normal pressure absorbed by unit volume of the liquid under normal pressure.

All the gases dissolve with more or less evolution of heat and the solubility for a given gas is diminished when a solid substance is dissolved in the liquid.

Certain irregularities shown by certain gases at low temperatures disappear at high temperatures. It has also been observed that on diminishing the pressure on the gas above the liquid, the total quantity of the gas corresponding to Henry's law is not immediately liberated, but that a kind of supersaturation continues for some time, and is only removed by agitating the liquid or by introducing a porous body which carries down air in its pores.

The question whether the gas absorbed by a liquid is present as such or in the liquid state has not been settled, and although the gas and the liquid form a homogeneous mixture, the particles of gas appear to retain their gaseous character, provided that one does not descend below the critical temperature of any individual gas, in which case one would have to admit that the gas must be liquefied.

SOLUBILITY OF GASES IN SALT SOLUTIONS. This phenomenon has been studied from a biological standpoint in order to see in what manner carbon dioxide and oxygen are absorbed by the blood, which may be considered

as an aqueous solution of various salts, more particularly of sodium chloride. This work has been carried out more particularly by Fernet (1858), Heidenhaim, and L. Meyer (1857–1863).

When a chemical reaction occurs between the salt and the gas, Henry's law cannot be applied. In other cases it can. In this way the fact is explained that the eagle is able to live even in very high atmospheric regions where the air is rarefied, as the oxygen is not held according to Henry's law, but by means of chemical reactions.

MATTER IN THE LIQUID STATE

The difference between a gas and a liquid consists in the fact that the volume of a gas varies proportionately and without limit with increase or diminution of pressure, whilst the volume of a liquid only varies to a limited extent about a certain constant point.

Liquids, like gases, consist of very mobile particles which transmit pressure in all directions and adapt themselves completely to the form of the containing vessel. Whilst the attraction between the molecules of a gas is almost non-existant, in a liquid this attraction overcomes the kinetic energy of molecular motion and the molecules of a liquid are thus unable to escape ; but they are not firmly united to one another but travel over one another, the distance between individual molecules remaining constant, even though they travel about in this manner. Thus in liquids an indifferent equilibrium is established between the molecules.

Liquids are compressible to a minimal degree, and therefore do not follow regular laws as do gases with regard to temperature and pressure, as has been shown by the work of Amagat (1886) and also of Pagliani and Vicentini (1883).

The specific gravity or density of a liquid is given by the ratio between the weight of a given volume of the liquid and that of an equal volume of water, measured at a temperature of 4° (maximum density of water), or more simply the specific gravity S, is given by the relation between the weight (P) and the volume (V) of the same liquid (because the volume expressed in c.c. also expresses the weight in grammes of an equal volume of water) $\frac{P}{V} = S$. Since it is not convenient to work at temperatures of 4°, there is a general agreement to determine the specific gravity at temperatures of 15° referred to water at 4° as unity, and then the circumstances are indicated by the following symbols at the side of the specific gravity $\left(\frac{15°}{4°}\right)$. The reciprocal value of the specific gravity is called the specific volume (w), $\left(\text{thus } \frac{V}{P} = w\right)$, and indicates the volume occupied by unit weight of the given liquid.

The specific gravity is commonly determined with pyknometers and areometers, or with the Mohr-Westphal balance.

PYKNOMETERS. These are of various types. The simplest is that of Stohmann, and is formed of a glass flask of any size from 25 to 300 c.c., closed by a ground stopper, the centre of which is traversed by a capillary tube. The dry apparatus is exactly weighed to at least the nearest milligramme (= P), then filled with distilled water at 15°, and the stopper well closed, when the excess of liquid is displaced by the tap itself, and by means of the capillary tube which remains full. It is then well dried externally and accurately weighed (= P'). The pyknometer is then emptied, dried in an oven, or more quickly by washing with a little alcohol and then with ether, and is then filled in the same manner with the liquid under examination at the temperature of 15°. It is again dried outside and exactly weighed (= P''). Then $P' - P$ is the weight of the water and $P'' - P$

the weight of an equal volume of the liquid under examination. The specific gravity $S = \frac{P'' - P}{P' - P}$. When greater exactitude is required, this formula must be corrected by comparison with water at 4°, and for weights *in vacuo*, because the weights P'' and P are smaller than the reality, as the pyknometer full of liquid displaces a corresponding volume of air. If, therefore, we indicate by d the density of water at the temperature t, at which the weighings were made, and by λ the mean weight of 1 c.c. of air (0·0012 gr.), the corrected formula becomes: $S = \frac{P'' - P}{P' - P}(d - \lambda) + \lambda$.[1]

A pyknometer which is very convenient and exact because the temperature of the liquid at any instant is also given by means of the included thermometer, is that illustrated in Fig. 20. This is first weighed empty in the usual manner, then filled with water, and then with the liquid under examination, filled up to the mark, *m*, on the capillary tube at the side. If the liquid rises slightly above the mark, it is removed with a small piece of filter paper.

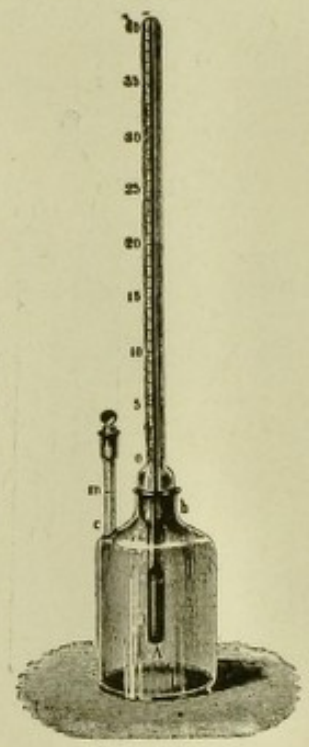


Fig. 20.

A simpler and more exact form, particularly for small quantities of liquid, is Sprengel's pyknometer (1873) formed of a simple U-tube (Fig. 21) with capillary ends, which is filled after weighing up to the mark, *m*, by sucking up the liquid from the one end in the method indicated in the lower portion of the figure.

MOHR'S BALANCE (1853) *modified by Westphal* (Fig. 22). This instrument is based on the *principle of Archimedes*, according to which a body immersed in a liquid apparently loses weight, that is, is impelled upwards, by an amount equal to the weight of the water displaced. If a glass body of constant volume is suspended by a very thin platinum wire and first weighed in the air and then again when immersed in distilled water at 15°, and again weighed when totally immersed (that is, up to the same point on the wire) in another liquid, the specific gravity of which is to be determined, the diminutions of weight found when immersed in water and in the liquid under examination indicate the weights of equal volumes of the two liquids. The ratio between these two weights gives the specific gravity as we have seen above.

In practice the work is carried out in the following manner. The glass body provided with a thermometer is first hung on to the hook at the right-hand end of the beam of the balance, after which it is adjusted horizontally by turning the screw, *S*, as much as is necessary, in such a way that the two points at *K* are in horizontal alignment. We have thus equilibrium in the air. When the glass body is immersed in distilled water at 15° it is necessary to hang the rider *A'* on the beam in order to bring it back to a horizontal position, as is seen in the figure, and thus we have the weight of water = 1. If, on the other hand, we immerse the glass body in a liquid heavier than water, then, in order to bring the beam to the same zero point, we must place other weights on the beam (the weights, *A*, *B*, *C*, give the first, second, and third decimals respectively) as may be clearly seen from the two examples in Fig. 23. In the case of liquids lighter than water, the weight *A* suffices, and thus we have the arrangement illustrated in the same Fig. 23 to the right. We may

[1] SPECIFIC GRAVITY OF WATER AT VARIOUS TEMPERATURES

Temperature	Specific gravity	Temperature	Specific gravity	Temperature	Specific gravity
0°	0·999 87	15°	0·999 12	30°	0·995 67
2°	0·999 97	16°	0·998 97	40°	0·992 24
4°	1·000 00	18°	0·998 62	50°	0·988 07
6°	0·999 97	20°	0·998 23	60°	0·983 24
8°	0·999 88	22°	0·997 80	70°	0·977 81
10°	0·999 73	24°	0·997 32	80°	0·971 83
12°	0·999 53	26°	0·996 81	90°	0·965 34
14°	0·999 27	28°	0·996 26	100°	0·958 38

even estimate the fourth decimal figure approximately if the weight C is placed on the beam between one number and the other. If the specific gravity at 15° is to be referred to water at 4°, it is necessary to multiply by 0·99912 (specific gravity of water at 15°, *see* the table on p. 73).

HYDROMETERS. Hydrometers are much used in commerce and also industrially, and their discovery was due to the philosopher Hypatia of Alexandria, about the year 400. There are hydrometers of constant volume (Nicholson) and hydrometers of constant weight. These latter are the most used.

Their employment for the determination of the specific gravity of liquids is based on the fact that a floating body of constant weight and of stable form if immersed in a liquid will displace a weight of the latter equal to its own. Hydrometers are ordinarily formed of small glass cylinders suitably graduated and weighted below by means of mercury or lead shot so that they float in a vertical position when immersed in the liquid. (*See below*, figure of Baumé's hydrometer.) The thinner the stem the more exact are the results. For exact determinations the scale is read by slightly immersing the dry hydrometer

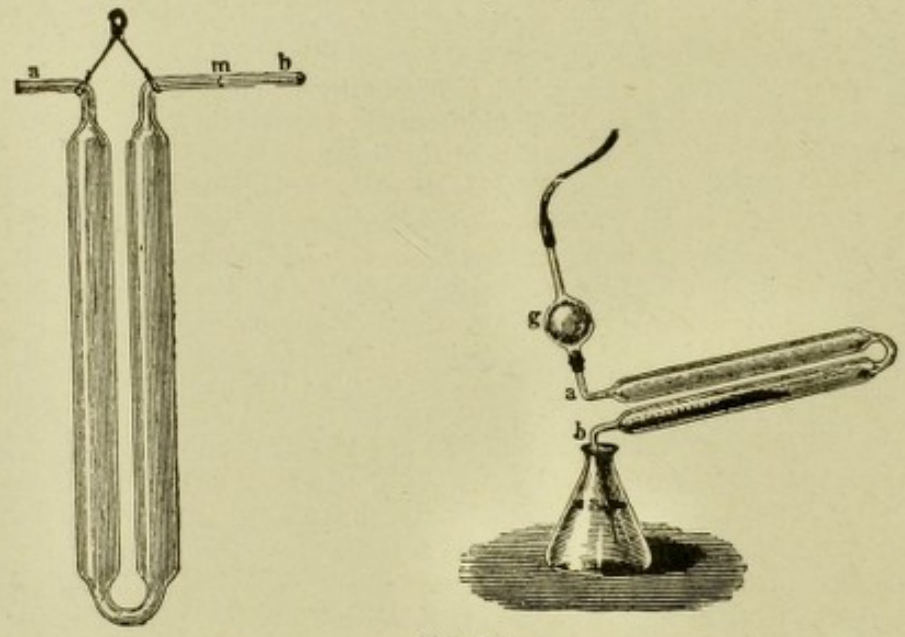


FIG. 21.

into the liquid in such a way that this is not moistened above the graduation corresponding to the correct specific gravity, or the liquid is carefully poured into the cylinder containing the hydrometer, in such a manner that the part of the stem which remains above the liquid is not moistened (if the stem of the hydrometer above the liquid is wetted, the instrument weighs more and the reading is inexact).

Hydrometers are constructed for liquids heavier than water and for liquids lighter than water, and the scale is *rational* when the indications are in direct accordance with the specific gravity (centesimal hydrometer of Gay-Lussac), or it is *empirical*, in which case the specific gravity has to be deduced from corresponding tables (hydrometers of Baumé, Beck, &c.), or calculated from formulæ. They are called densimeters when the specific gravity is directly indicated on the scale.

The centesimal hydrometer of Gay-Lussac gives the specific gravity of a liquid heavier or lighter than water by dividing by 100 the figure given on the stem at the point up to which it sinks.[1]

[1] The scale of Gay-Lussac's centesimal hydrometer is calibrated by immersing the instrument, the tubular stem of which is open at the top, in distilled water at 15° and weighting it to such an extent that it floats with about half the length of the stem immersed. This point is called 100°. The weight of water displaced at this moment is given by the weight of the glass apparatus r plus the weight of the mercury p. If we then add still more mercury p' to the hydrometer so that $r + P' = 2\ (r + p)$, we will have to indicate the point to which it sinks by 200°, because the volume or weight of water displaced will be doubled. The open end of the stem is then sealed in a blow-pipe. On now dividing the space between 100 and 200 into 100 parts, and also continuing the divisions in the opposite direction, that is, below the 100° mark, we will have a scale which will give the specific gravities of liquids heavier or lighter than water. If, for example, we immerse the hydrometer in a liquid which indicates 80°, we are able to say that the displaced liquid (80 parts by volume) weighs as much as 100 parts of water, because the weight of the hydrometer is constant; and if we indicate the weight of 1 part of water by 1, an equal volume of the liquid under consideration (that is, its specific gravity) will be $\frac{100}{80} = 1{\cdot}25$. If the

Special hydrometers are also constructed for particular liquids or solutions (sugar, glucose, glycerine, alcohol, &c.), which give direct readings on the scale of the percentage of the dissolved substance, and it is obvious that in such cases a special hydrometer is required for each particular kind of liquid.

The most generally used of these are the centesimal alcoholimeters of Gay-Lussac (1820–1824) and of Tralles (1811), which show directly on the scale the percentage by volume of alcohol contained in admixture with more or less water. The first is commonly used in France, Germany, and Italy, whilst that of Tralles, with a scale corrected by Brix, is officially used in Germany and by the Italian customs.[2]

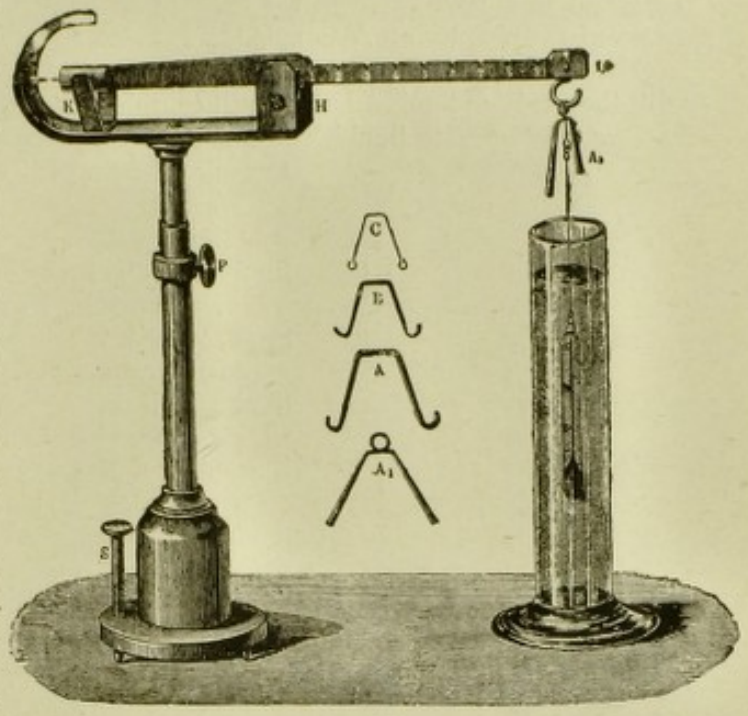


Fig. 22.

Hydrometers of constant weight and with an empirical scale are much used in practice for the determination of the density of solutions of acids, salts, &c., and the most commonly used of these to-day are those of Baumé (1768) and of Beck (1803), both for liquids heavier and lighter than water. In recording observations indicating degrees of these hydrometers it is necessary to state whether they refer to

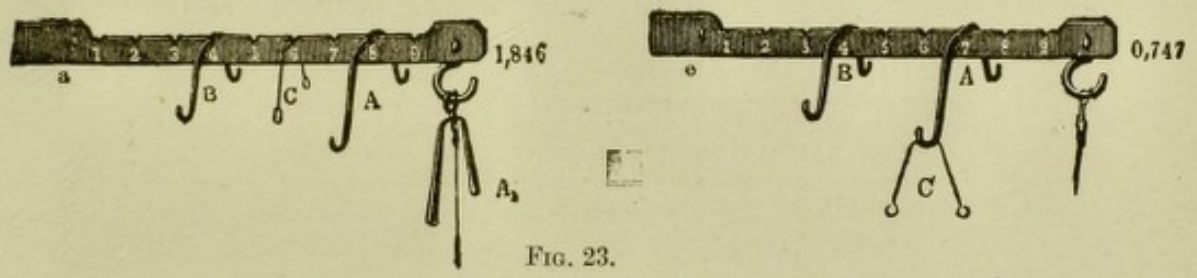


Fig. 23.

liquids lighter or heavier than water, because the same figures may refer to the one or to the other (Fig. 24). The graduation is made by starting from distilled water and from a salt solution of known specific gravity (*see note below*). The specific gravity is obtained

hydrometer floats in another liquid up to the 120° mark, the specific gravity of this liquid will be $\frac{100}{120} = 0{\cdot}833$.

In general the specific gravities of liquids, lighter or heavier than air, are deduced from the readings of Gay-Lussac's hydrometer, by dividing by 100 the degree indicated on the scale. In practice, in order to avoid the use of hydrometers with a very long scale, separate instruments are made for liquids heavier or lighter than water.

[2] The scale of centesimal alcoholimeters is graduated by immersing the instrument in various solutions of alcohol and water prepared with exact quantities of the components and indicating by 100° on the stem the point of immersion in absolute alcohol and by 0° at the base of the stem the point of immersion in distilled water. Each degree is then fixed by means of the corresponding solutions, because no simple proportion exists between the volumes of water and of alcohol in the mixture on account of the contraction of volume which is accompanied by evolution of heat. Thus, if 460 c.c. of water are added to 500 c.c. of absolute alcohol, the volume of the mixture is only 930 c.c. instead of 960 c.c., and 100 c.c. of this mixture contain 53·7 c.c. of pure alcohol. The alcoholimeter immersed in this liquid will give the reading 53·7. The differences between Tralles' and Gay-Lussac's degrees are small, and are due to the fact that Tralles determined the specific gravity of the alcoholic solutions at the normal temperature of 15·56°C. (= 60° F.), and then referred these to equal volumes of water at 4° ; or, according to the corrections of Brix (officially used in Germany and also by the Italian Customs for alcohol), the specific gravity is referred to that of water at the same temperature of 15·56°. Gay-Lussac's degrees, on the other hand, referred to the temperature of 15° and to water at 15°. Strictly speaking, the true specific gravity is found neither in the one case nor in the other, because 1 c.c. of water at 15° weighs 0·99912 gr., and Fischern (1872) prepared corrected tables by multiplying the centesimal degrees by 0·99912, but these have not been practically applied industrially.

Richter in Germany and Lejeune in France (1872) prepared centesimal alcoholimeters which gave the direct percentage weights of alcohol, but these have not met with success.

It need hardly be pointed out that alcoholimeters can only be used for mixtures of alcohol and water and not for alcoholic liquids such as wine, beer, and spirits, in which other substances are present which influence the specific gravity.

from the readings of these hydrometers by means of tables or very simple formulæ. The relationship between Baumé degrees (abbreviated Bé.) for liquids heavier than water will be found in a later table in the chapter on Sulphuric Acid, and for liquids lighter than water in the chapter on Ammonia.[1]

The boiling-point, evaporation, distillation, &c., are very important in connection with the study of liquids, but we will consider the laws of heat and the optical phenomena in their relation with liquids in connection with the study of organic substances (Vol. II., Organic Mixture).

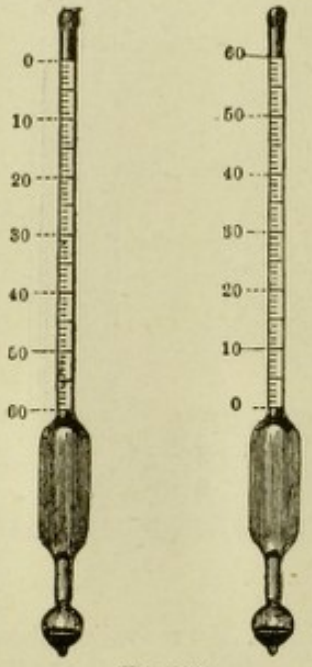


FIG. 24.

We will merely mention that while gases give spectra containing well-marked luminous lines, the corresponding liquids, on the other hand, give continuous spectra, which, however, contain dark lines in place of the luminous lines of the corresponding gas. Therefore, as the gas gradually approaches the liquid state the characteristic luminous lines of its spectrum become enlarged until they coalesce with one another, giving a complete spectrum containing dark absorption bands.

The action of polarised light passing through liquids is also characteristic of certain substances. It forms an extensive and important branch of physical chemistry which is of special importance for organic substances, and will be studied in the second volume of this work.

The capillary phenomena of liquids are in a certain relation with their chemical composition, but no sufficiently general laws have yet been found to enable one to deduce important results.

We will find out some important laws on studying the solutions of salts or other substances in liquids. We will thus arrive at new and simple methods for determining the molecular weight of many substances, even of such as cannot be converted into vapour.

It is sometimes useful to know the specific heat of liquids or solutions, and we therefore give the following convenient and practical table for this purpose:

SPECIFIC HEAT OF LIQUID SUBSTANCES AND SOLUTIONS

Substance	Temperature of observation	Specific gravity	Substance	Temperature of observation	Specific gravity
Ammonia liquid	0°	0·876	Nitric acid 3·4%	20°–50°	0·962
,, ,,	30°	1·218	Ethyl ether	0°	0·529
,, ,,	70°	1·233	,, ,,	30°	0·547
,, aqueous 3%	18°	0·997	,, ,,	180°	1·041
Potassium hydroxide 39%		0·697	,, alcohol	0°	0·547
,, ,, 8%		0·900	,, ,,	65°	0·699
Sodium ,, 73%	0.98°	0·960	,, ,, 10%	10°–16°	1·015
,, ,, 23%	18°	0·847	,, ,, 50%	0°–15°	0·992
Calcium chloride 41%	23°–80°	0·636	Formic acid	20°–80°	0·517
,, ,, 3%	20°–51°	0·955	Aniline	15°	0·514
Magnesium chloride 26%	22°–52°	0·682	,,	50°	0·529
,, ,, 2·6%	18°–52°	0·959	Benzene C_6H_6	10°	0·407
Sodium ,, 24%	18°	0·791	,,	50°	0·450
,, ,, 5%	19°–46°	0·944	Chloroform	0°	0·232
,, sulphate 30%	24°–100°	0·781	,,	60°	0·238
,, ,, 2%	14°	0·976	Hexane C_6H_{14}	0°–50°	0·527
Calcium nitrate 48%	20°–50°	0·625	Acetic acid	20°–50°	0·512
,, ,, 4·4%	20°–50°	0·951	,, ,, 50%	22°–62°	0·778
Sulphur dioxide liquid	0°	0·317	Glycerine	15°–50°	0·576
,, ,, ,,	40°	0·342	,, 50%	15°–50	0·813
,, ,, ,,	155°	2·200	Methyl alcohol	15°–20°	0·601
Sulphuric acid pure	20°	0·345	,, ,, 20%	7°–11°	1·073
,, ,, ,,	50°	0·359	Nitrobenzene	10°–15°	0·348
,, ,, 50%	5°–22°	0·332	Palmitic acid, liquid	65°–104°	0·653
,, ,, 5%	5° –22°	0·960	Carbon disulphide	30°	0·240
Hydrochloric acid 17%	18°	0·749	,, ,,	80°	0·260
,, ,, 2%	18°	0·965	Petroleum	21°–58°	0·511
Nitric acid 58%	20°–50°	0·655	Olive oil	6°	0·471

[1] The scale of Baumé's hydrometers for liquids lighter than water is obtained by indicating by the point 0° the immersion-point at the lower end of the stem when the hydrometer is immersed in a solution of 90 parts of

STUDY OF DILUTE SOLUTIONS

OSMOTIC PRESSURE. The study of liquids acquires new importance when extended in a special manner to dilute solutions.

About the year 1750 the Abbé Nollet observed that when a beaker filled with spirits is closed by an animal membrane and immersed in water, the membrane swells and sometimes bursts. This observation was forgotten by everybody and was rediscovered as a new thing by Parrot in 1815, by W. Fischer in 1822, and by Dutrochet in 1827. This fact was classified as an osmotic phenomenon, and Liebig in 1848 endeavoured to explain by this means the movement of the liquids in the animal organism.

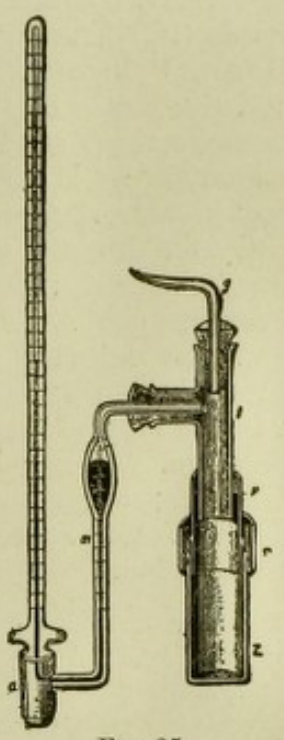


FIG. 25.

We will now interpret this phenomenon according to modern conceptions:

If water is poured on to the top of a strong solution of sugar, an internal movement of the liquid at once takes place, and the molecules of sugar pass from the concentrated solution into the superposed liquid until equilibrium is established, when the two solutions have the same concentration. If from the first a porous membrane only permeable by water and not by the sugar molecules is placed between the concentrated solution and the layer of water, then the sugar molecules which have a tendency to diffuse into the superposed liquid collide with the membrane, exercising a pressure. Since the phenomenon is an ordinary process of osmosis, this pressure is called *osmotic pressure*.

In 1867 Traube prepared artificial semi-permeable membranes of this kind by means of the films which form at the surface, limiting two superposed solutions, one of copper sulphate and the other of potassium ferrocyanide. In 1877 W. Pfeffer prepared rigid membranes by producing the precipitate of copper ferrocyanide directly in the pores of an unglazed porcelain cell (battery cell). These rigid osmometers perfected by Naccari in 1898, and provided with a manometer, serve for the study of this important phenomenon of osmotic pressure (Fig. 25).

On placing inside the porous cell of the osmometer a 1 per cent. solution of sugar, and immersing the whole in water, the manometer shows after a

water and 10 parts of sodium chloride, at the temperature of 17·5°, and by 10° the immersion-point in distilled water at the same temperature. The space from 0°–10° is divided into 10 equal parts and then continued up to the top of the stem, and this gives the maximum number of degrees for lighter liquids. In the scale of the hydrometer for liquids heavier than water, the immersion-point in distilled water is indicated by 0° at the top of the stem, and the immersion-point in a solution produced from 85 parts by weight of water and 15 parts of sodium chloride at a temperature of 17·5° is indicated at 15°. The space between 0° and 15° is divided into 15 parts, and these divisions are continued down the stem as far as about 70°.

With the first hydrometer water is indicated by 10° and with the second by 0°, and thus it is necessary to always indicate to which of these two hydrometers the degrees Bé. refer.

In Beck's hydrometer, on the other hand, the zero-point at about the middle of the stem indicates the specific gravity of distilled water at a temperature of 12·5° and 30° the point of immersion in a solution the specific gravity of which is 0·850. The space from 0° to 30° is divided into 30 parts, and the same divisions are continued both above and below the zero-point. Here also, if it is not clearly expressed, the same degree may refer to a liquid lighter or heavier than water.

In order to reduce the degrees (n) of these hydrometers to the corresponding specific gravity (S), the following formulæ must be used. For rational Bé. hydrometers for liquids heavier than water, $S = \frac{144{\cdot}3}{144{\cdot}3 - n}$, and for those lighter than water $S = \frac{144{\cdot}3}{134{\cdot}3 + n}$; in Beck's hydrometer for liquids heavier than water $S = \frac{170}{170 - n}$, and for those lighter than water $S = \frac{170}{170 + n}$.

Very occasionally another hydrometer is used in France for alcoholic liquids and extract, namely, Cartier's hydrometer, which differs very slightly from that of Bé.—the 10° points correspond on the two hydrometers, and 29° Cart. equal 31° Bé.

In England especially, for liquids heavier than water Twaddel's hydrometer (Tw.) is used, and the specific gravity S is converted into degree Tw., (n) by the formula $n\,(S - 1)\,.200$, or *vice versa*. Tw. degrees are obtained from the specific gravity by the formula $S = \frac{n + 200}{200}$. The following relationships exist between degrees Bé. and degrees Tw.: 0° Bé. = 0° Tw., 6° Bé. = 9° Tw., 16° Bé. = 25° Tw., 25° Bé. = 42° Tw., 35° Bé. = 64° Tw., 50 Bé. = 106° Tw., 60° Bé. = 142° Tw., 67° Bé. = 173° Tw.

little time a pressure of about two-thirds of an atmosphere (493 cms. of mercury). If, on the other hand, a 2 per cent. sugar solution is placed in the osmometer, the pressure is double, that is, it is $1\frac{1}{3}$ atmospheres; with a 3 per cent. sugar solution the pressure is treble, that is, it is 2 atmospheres, and in the same way with a 6 per cent. sugar solution, a pressure six times greater than that obtained with a 1 per cent. solution is obtained.

Various hypotheses have been proposed to explain this interesting behaviour, by van't Hoff (1885 to 1895), Ostwald (1891–93), Nernst (1883–93), Pupin (1889), Bredy (1889), Lothar Meyer (1890), and later by Nasini, Pickering (1890), Boltzmann (1890), Naccari (1893), Magnanini (1894), Moore (1895), and the writer in 1895. Some of these authors maintained that the osmotic pressure must be due to the particles of the dissolved substance, whilst the solvent which is able to enter and leave the osmometer freely could not exercise any pressure. Others, on the other hand, held the exactly opposite opinion and said that the osmotic pressure was entirely due to the solvent. Others finally accepted neither the one explanation nor the other, but said that even in open vessels there should be a large osmotic pressure of the solution and that the walls of the vessel ought necessarily to be broken (*Pupin*). All these doubts were cleared up later, and it was shown that even in open vessels many properties of solutions are in strict accordance with the osmotic pressure. A logical explanation of osmotic pressure may be found by the following argument, which unites the views of all the above-mentioned authors, and also explains the apparent exceptions or abnormalities of osmotic phenomena.

We will imagine a Pfeffer osmometer (porcelain cell, &c.), semi-permeable, of one litre capacity and full of a gas, A, which is not able to escape. If we now surround the cell by another gas, B, which is able to penetrate into the cell, the manometer will indicate two atmospheres' pressure (one from the gas A at ordinary pressure, and one from the gas B). We now suppose that the osmometer is varnished with an ideal substance which has the property of preventing the exit of the internal gases A and B, but permits the entrance of a third gas, C. The manometer will then indicate three atmospheres' pressure.

On varnishing the cell with another ideal substance which permits a fourth gas, D, to enter without allowing the three first gases to escape, a pressure of four atmospheres will be indicated. Equilibrium is established for the last gas, D, which has free access when as many molecules enter the osmometer as leave it. In order to understand under what conditions this last gas, D, is present in the interior of the osmometer, which indicates four atmospheres of pressure, although the gas D communicates with the outside where the same gas D is at one atmosphere's pressure only, we will imagine one litre of the gas D to be enclosed in an impermeable cylinder provided with a piston, at the ordinary atmospheric pressure. If we now reduce the volume to a quarter by means of the piston, the pressure will become four atmospheres. This gas is now under equal or analogous conditions to the gas D contained in the osmometer, together with the other gases. In fact the difference between the gas D in the cylinder at one atmosphere and the same gas in the osmometer at four atmospheres consists in this, that in a given volume, in 1 c.c. for example, four times as many molecules are present, and thus the average distance between the molecules is four times as small.

But in the osmometer, the gas D mixing with the other three gases is present under the same conditions, that is, it has only one-quarter of the total space at its disposal, whilst the other three-quarters are occupied by the other three gases. The distance between the molecules of the various gases taken together is only one-quarter, because in 1 c.c. in the interior of the osmometer the number of the molecules is four times greater than those in the gas D outside at a pressure of one atmosphere only. We also know that the pressure is due to the number of impacts which the molecules produce on the walls and also that the gas D has free entry and exit and that as many molecules enter as escape. In the interior these molecules collide with other molecules and are not always able to arrive at the pores whence they escape, and the difficulty from this cause is fourfold, because in

1 c.c. four times the number of molecules are present compared with 1 c.c. of the internal gas; and as equal numbers of molecules of the gas *D* are always escaping and entering at a pressure of four atmospheres, the gas *D* inside must of necessity be at four atmospheres' pressure, and thus as only a fourth part of the molecules is in a position to arrive at and collide with the walls in unit of time, they must, therefore, collide four times as many times with the walls because the distance between the molecules is four times smaller, and the possibility must exist to collide more often with the pores by means of which they escape.

Now, always remembering that the total internal pressure is due to the sum of the partial pressures exercised by the individual gases, it is a logical and justifiable hypothesis that the gas *D* inside is present at four atmospheres' pressure, together with the other gases, whilst outside it is at a pressure of one atmosphere. The same hypothetical experiment which we have made with gases, using the osmometer, will also explain very well the behaviour of solutions. Turning to the sugar solutions of 1 per cent., 2 per cent., 3 per cent. . . . 6 per cent., we may very well affirm that the osmotic pressure is due to the sugar molecules, but is exerted by the solvent, water, which penetrates into the interior of the osmometer.

It is now clear to us that we may consider the osmotic pressure as the sum of the impacts produced by the dissolved substance and by the solvent and that it is thus of a kinetic nature. The causes of the manifestation of osmotic pressure are to be found in the mechanical combination represented schematically by the osmometer, which may be replaced by a vegetable cell, &c., a combination constituted in its entirety of molecular particles of various sizes (solvent and dissolved substance) endowed with continuous movement, contained in a semi-permeable receptacle (permeable for the solvent only) and by the solvent which surrounds this receptacle.

Now wherever in nature a similar or analogous combination is present, we will obtain an osmotic pressure. It appears, in fact, that the rise of the sap to extraordinary heights in the most gigantic trees (the height of eucalyptus trees reaches 160 m.) is due to osmotic phenomena which occur between the vessels carrying the sap and the vegetable cells, as was shown by the brilliant experiments of the Dutch botanist de Vries in 1884. In 1909 Bigelow and Bartel determined the size of the pores of an unglazed porcelain plate by closing a non-porous vessel with this plate and then compressing water inside it until it issued from the pores. From the pressure necessary for this purpose with the aid of Jurin's law, they calculated the size of the pores. They were thus able to establish that a sugar solution shows the phenomena of osmotic pressure if the porcelain cell of the osmometer has pores of a diameter lower than 0·37 μ.

Solutions of different substances of equal concentration by weight produce different osmotic pressures. De Vries, however, succeeded in preparing isotonic solutions, that is, solutions which exerted the same osmotic pressure, by dissolving various quantities of solvent, and the importance of the discovery of de Vries consists of this, that isotonic solutions are always equimolecular, that is, solutions which contain the various substances dissolve in the proportion of their molecular weight in equal volumes of the solvent, that is, which contain the same number of molecules all exercise the same osmotic pressure.

But this is nothing else than the law of Avogadro as enunciated for gases in another form, as according to this law equal volumes of different gases under the same conditions of temperature and pressure contain equal numbers of molecules, and the weights of these gases are thus in the same ratio as their respective molecular weights (*see below*, the demonstration of the relation which exists between osmotic pressure and the pressure of gases).

It is thus evident that by means of the osmotic pressure we have in our hands a method of determining the molecular weight of substance. In fact,

if the osmotic pressure exercised by a solution containing the molecular weight in grammes of a known substance in a given volume is known, and if we then dilute or concentrate solutions of substances of unknown molecular weight in the same solvent until they exercise the same osmotic pressure, we will then know that equal volumes of these solutions contain the same number of molecules as are contained in equal volumes of the solution of the known substance.

For his determinations de Vries used vegetable cells by immersing them in solutions of various concentration, and thus obtained at will various osmotic pressures. The cells of *tradescantia discolor*, of *curcuma rubricaulis*, and even *blood corpuscles* (Hamburger), are well suited for this purpose. We may see under the microscope that if these cells are immersed in a saline solution more concentrated than the protoplasmic liquid, the hyaloplasm contracts. If, on the other hand, the saline solution is more dilute, the cell swells until its envelope sometimes even bursts. This phenomenon, called plasmolysis, was used by de Vries to determine the molecular weight of various substances.

In 1887 van't Hoff showed that isotonic (equimolecular) solutions remain isotonic even if the temperature is varied, and more precisely he found that the osmotic pressure is proportional to the absolute temperature. Thus to such isotonic solutions, when very dilute,[1] the general formula may be applied which expresses the laws of Boyle and Gay-Lussac, according to which the product of the pressure (P) and the volume (V) is equal to the product of a constant (R) and the absolute temperature (T), that is to say, $P\,V = R\,T$.

For all gases the constant R is equal to 84,780 (that is, $\mathrm{R} = \frac{PV}{T}$, *see* p. 26).

If in place of P in this formula we introduce the osmotic pressure of a 1 per cent. sugar solution at 0° (273° absolute), that is, the pressure of a column of mercury of 49·3 cms. equivalent to 671 gr. [that is, 49·3 × 13·6 (weight of 1 c.c. of mercury)] as was obtained by Pfeffer, we then know that the molecular weight of sugar expressed in grammes (342) at 1 per cent. dilution will occupy a volume, V, of 34,200 c.c. and the formula will become :

$$R = \frac{671 \times 34{,}200}{273} = 84{,}100.$$

Thus we see that the constant, R, deduced from the osmotic pressure may be considered equal to the gas constant, and that, in fact, the quantity of sugar in solution, if it could be transformed into a gas, would exercise a pressure equal to the osmotic pressure of that solution.

We may thus visualise this action of the solvent by supposing it to assist in the separation of the sugar molecules from one another by carrying them to such a distance apart that the same quantity of sugar will be found as would be present in the same volume of vapour if the solvent were absent. Or again, if we take one litre of alcohol vapour which weighs about 1½ grms., the molecules are present at a certain characteristic distance from one another, which is characteristic of alcohol in the gaseous condition. If we now take another 1½ grms. of alcohol, that is, the same number of molecules of alcohol as before, and dissolve them in a litre of water, the molecules of alcohol will be present at the same distance from one another as was the case in the gaseous state ; and we may say in general that the solvents, in the case of dilute solutions, produce a species of gassification of liquid and solid substances (as had already been suggested by Rosenstiehl in 1870).

The determination of molecular weights by means of osmotic pressure is very suitable for all indifferent substances, but gives abnormal results in the case of acids, bases, and salts, especially if these are dissolved in water. We will see below how these exceptions, which are due to the dissociation of the dissolved molecules, have been brilliantly explained.

SURFACE TENSION OF LIQUIDS. At their surface, liquids contain a layer of molecules which are present under different conditions from those in the interior of the mass, and give rise to various phenomena which we may

[1] We make the reservation that the solutions must be very dilute, because this law has also a limitation and is only true for great dilutions, just as the law for gases and vapours is only true when these are studied at temperatures far from their point of condensation.

explain provisionally by the following hypothesis. In the interior of a liquid the molecules are present in equilibrium, because they collide with one another in several directions (from above, from below, and from the sides), and therefore there must be an enormous latent internal pressure due to the impacts between the molecules of the liquid. This pressure is balanced by the attraction which exists between these same liquid molecules. The molecules at the surface only receive impacts from the molecules below and to a certain extent from the sides, but receive no impacts from above, and if they do not evaporate it is because of the molecular attraction by the molecules below (Fig. 26). These surface molecules are, however, transformed into vapour with about half as much work as the others, and therefore have a tendency to escape from the liquid with great facility, forming vapour. In any case they possess certain properties which are manifested in various ways.

This force at the surface of liquids shows itself as a tendency to diminish their surface area, and thus as a tendency to form spheres, and more precisely as a tendency to become concave when the liquid moistens the walls of the receptacle and convex when it does not moisten them. These special forces act on the surface as though the liquid itself were enclosed in a stretched elastic film which tended to contract.[1] In capillary phenomena this surface tension of liquids manifests itself by the rise of a column of the liquid in a capillary tube until the weight of this liquid column is in equilibrium with the surface tension at a certain height. Mendelejew (1860), Quincke and Duclaux Stephan (1886), and specially R. Schiff (1884), found that certain stoichiometric relations may be deduced between various substances, but they were not able to deduce a general law, although for certain groups of substances the rise of the liquids in capillary tubes is the same for equal molecular weights ; for example, isobutyl alcohol, ether, &c.

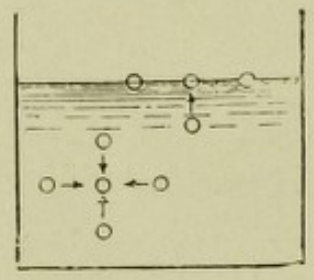


Fig. 26.

VAPOUR TENSION OF SOLUTIONS AND MOLECULAR WEIGHTS

Water boils and is transformed into steam when its vapour tension is equal to the atmospheric pressure. Water containing a salt in solution boils at a higher temperature, so that we find that the vapour tension is diminished by an amount which becomes greater as the amount of salt in solution increases, the rise in the boiling-point being proportional to the diminution of the vapour tension of the solution.

This fact already noted by Faraday (1822), by Griffith (1824), and by Legrand (1835) was, however, first methodically studied by Gay-Lussac and then by von Babo in 1849–1857, and by Wüllner in 1856–1860, and it was also found that the diminution of the tension is the same at whatever temperature the experiments are conducted.

The diminution of the vapour tension produced by 1 grm. of various substances on the solvent water was then determined.

In 1883–1884, Ostwald suggested that the diminution of the vapour tension should be referred to a weight of the substance representing the molecular weight, and that the diminution of the molecular tension would then have a constant value. In 1885 Tammann showed experimentally that the molecular

[1] Thus, if from the clean-ground end of the glass tube of a pipette held horizontally drops of a liquid are allowed to form, these assume a spherical form in falling, and also if a drop of a liquid is removed from the action of gravity by being dropped into another liquid of the same density with which it does not mix, the drop, instead of extending on the liquid surface, contracts and forms a floating spherical drop. Similarly, when mercury is thrown on to a flat solid it collects into small spherical drops on account of its surface tension.

decrease of the vapour tension is equal for analogous salts dissolved in water, but notable differences were found in the case of different salts.

In 1886 Raoult made numerous experiments in the barometric vacuum, employing other solvents instead of water, and he obtained results of very wide and general bearing which fully confirmed the prophecy of Ostwald (1883). In this way we have at our disposal another very convenient method of determining the molecular weight of a very large number of substances, simply by observing the decrease in the vapour tension of the solvents on dissolving such substances, by determining, that is, their relative boiling-points. This also is a limited law which is only true for very dilute solutions.

If we denote the vapour tension of the solvent by f and that of the solution of g grammes of the substance by f', then $f - f'$ indicates the *absolute decrease* of the vapour tension, whilst $\frac{f - f'}{f}$ indicates the *relative decrease* which remains constant at all temperatures as was shown experimentally by Raoult in 1886. If we then indicate by k a constant which represents the relative decrease for concentrations of 1 grm. of substance per unit volume, we will have for g grammes:

$$\frac{f - f'}{f} = k \cdot g.$$

We know that *equimolecular solutions have an equal vapour tension*, that is to say, the molecular lowering of the vapour tension of various substances dissolved in the same solvent is a constant quantity, or in order to obtain an equal decrease of the vapour tension it is necessary that a given quantity of a dissolved substance should be dissolved in quantities of different solvents which are in the same proportion to one another as the respective molecular weights of these substances. Now the lowering of the vapour tension is independent of the nature of the solvent and of the dissolved substance, and is a function of the number of molecules of the solvent (N) and of the substance (n) only. The ratio between the vapour tension of the solution and that of the solvent is the same as that which exists between the number of the molecules of the solvent (N) and the number of the molecules of the solution, $N + n$, that is, $\frac{f'}{f} = \frac{N}{N + n}$; and as the relative decrease of the vapour tension of a solution corresponds to the relative number of the molecules of the dissolved substance $\frac{n}{N + n}$, we have: $\frac{f - f'}{f} = \frac{n}{N + n}$, that is, the relative decrease of the vapour tension of a solution is equal to the ratio between the number of molecules of the dissolved substance and the total number of molecules in the solution. Since, however, we do not in practice know the absolute number of the molecules, we must introduce into this formula the corresponding relative number, which we can easily do, and can always find it by dividing the weight of the substance (g) and of the solvent (G) by the corresponding molecular weights (m and M), so that $\frac{g}{m} = n$ and $\frac{G}{M} = N$; on substituting these values for those really known in the preceding general formula, and taking, for simplicity's sake, a quantity of solvent in grammes expressed by the molecular weight so that $N = 1$, we obtain the formula:

$$\frac{f - f'}{f} = \frac{\frac{g}{m}}{1 + \frac{g}{m}} = \frac{g}{g + m}.$$

or inversely the ratio: $\frac{f}{f - f'} = \frac{g + m}{g}$, and we thus obtain the following value of m:

$$m = \frac{fg}{f - f'} - g = \frac{fg}{f - f'} - g\left(\frac{f - f'}{f - f'}\right) = \frac{f'g}{f - f'}$$

Now by means of this general formula $m = \frac{f'g}{f - f'}$ we can always determine the molecular weight of any substance.

Let us take an example : 11·346 grms. of turpentine oil were dissolved in 100 grms. of ether. Before the addition of the turpentine, the vapour tension, f, of the ether was 38·30 cm. of mercury, whilst that of the solution f' was 36·1 cm., and thus $f - f' = 2{\cdot}29$. We must now refer the weight of the dissolved substance not to 100 grms. of ether, but to the number of grammes indicated by the molecular weight of ether (= 74) ; and thus the value g will be obtained from the following proportion : $100 : 11{\cdot}346 = 74 : g$, and thus $g = 8{\cdot}396$. On introducing this value in the general formula, we have : $m = \frac{8{\cdot}396 \times 36{\cdot}1}{2{\cdot}29} = 132$, and this molecular weight is, in fact, very close to the theoretical molecular weight, which is 138.

EBULLIOSCOPIC METHOD OF DETERMINING MOLECULAR WEIGHTS. It is not convenient in practice to determine the vapour tensions of various solvents and solutions at the same temperature, whilst on the other hand it is much easier to determine at which temperature the solution and the solvent have the same vapour tension. The atmospheric pressure is taken as the constant vapour tension ; then the solvents and the solutions will have the same vapour tension when they overcome the atmospheric pressure, that is, when they boil. In this case the temperature is given by the boiling-point of the solvent and of the solution.

Raoult had already shown that the diminution of vapour tension of a solution, compared with that of the solvent, was proportional to the rise of its boiling-point, compared with that of the solvent, and thus in calculating the molecular weight from the diminution of vapour tension we may substitute for this the rise of boiling-point.

From the general formula $\frac{f - f'}{f} = \frac{n}{N \times n'}$, we may deduce that for a solution formed from 99 gramme-molecules of solvent and 1 gramme-molecule of the substance, the depression of the vapour tension of the solvent is equal to one-hundredth of the ordinary pressure, to which a certain rise of the boiling-point of the solvent corresponds, and if this rise, due to one molecule, is multiplied by 100, we obtain the so-called molecular increase of the boiling-point, which we indicate by S. This value is equal to 28·44° in the case of ether, that is, one molecule of any substance whatever dissolved in 99 molecules of ether raises the boiling-point of this liquid by 0·2844°. If g grammes of a substance are dissolved in the weight corresponding to 1 mol. of the solvent (74 grms. for ether), then if the increase of the boiling-point is Δ, and the molecular increase is S, we have : $S = \frac{\Delta}{g} m$, and from this we can deduce the molecular weight, m, of the unknown substance $m = S \frac{g}{\Delta}$. Each solvent has its own characteristic constant, S, which may easily be determined, once for all, by employing a substance of known molecular weight.

On the other hand, these constants (for ether = 28·45) instead of being referred to the molecular weight of the solvent (ether = 74), may for convenience be referred to 100 grms. of the solvent (and the value then diminishes as the dilution is increased). We have then for ether the inverse proportion : $28{\cdot}44 : 100 = x : 74$, and thus for ether, S becomes 21·2. On calculating the value of S in the same manner for various other solvents we find : aniline = 32·2 ; phenol = 30·4 ; water = 5·2 ; benzene = 26·7 ; alcohol = 11·5 ; chloroform = 36·6 ; acetic acid = 25·3 ; carbon disulphide = 23·7 ; ethylene bromide = 63·2 ; nitrobenzene = 50 ; ethyl acetate = 25·1 ; acetone = 16·7 ; cyclohexane = 27·5 (Mascarelli, 1908).

Thus if $\frac{g}{\Delta}$ is the specific rise per G grammes of solvent, we find that per one gramme of solvent the rise will be $\frac{g}{\Delta G}$, and for 100 grammes of solvent, it will be $\frac{g \cdot 100}{\Delta G}$, and we thus arrive at the general formula, $M = S \frac{g \cdot 100}{\Delta G}$, where all the values are known and determinable. In 1889 Arrhenius found from thermodynamical considerations that a

relation exists between this constant, S, the latent heat of evaporation of the solvent, and its absolute boiling-point.

In 1889 Beckmann devised a very practical apparatus for the determination of molecular weights according to the above formulæ.

For dilute solutions there are differences of 1° or 2° between the boiling-point of the solvent and of the solution, and very exact thermometers are thus necessary. As constructed to-day they are divided into fiftieths or hundredths of a degree, sometimes even into thousandths, with a scale 40 to 50 cms. long, which includes divisions corresponding to 4° or 5°. Since the same solvents are not used for all substances, Beckmann ingeniously modified the upper extremity of the capillary tube containing the mercury, in a manner indicated in Fig. 27, so that it was not necessary to construct such costly thermometers for each particular solvent, or to construct scales of immense length. In this way it is possible to measure the absolute difference of the boiling-point of the solvent and the solution with the same thermometer, whatever may be the solvent employed.

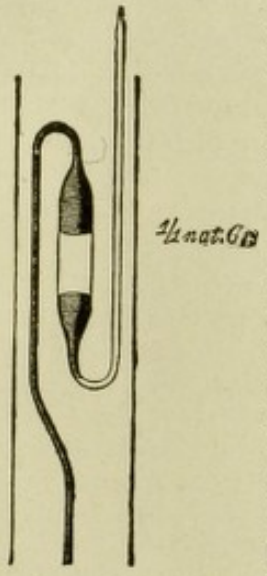


Fig. 27.

The scale of the thermometer indicates the relative boiling-points, that is, it indicates the point which the mercury column reaches when the solvent and the solution respectively boil. We will explain this more clearly by means of two examples.

1. If a thermometer has been used beforehand for a lower temperature and is then required for a solvent boiling at a higher temperature, it is immersed in a bath which is 3° or 4° hotter than the boiling-point of the new solvent. By this means the excess of mercury rises in the capillary tube into the small upper reservoir of the thermometer, forming a suspended droplet. If at this point a sudden shock is given to the thermometer, the droplet of mercury falls from the capillary column and collects at the bottom of the little reservoir. On now removing the thermometer from the bath, the capillary mercury column descends into the lower bulb of the thermometer. The relative boiling-point of the solvent will now be indicated by the mercury in one of the divisions of the lower part of the scale. It will then advance through a few divisions (3° to 4°) and indicate exactly the rise of boiling-point when the substance under examination has been dissolved.

2. In order to adjust the thermometer for a solvent which boils at a lower temperature, the instrument is inverted and subjected to a sudden shock, so that the drop of mercury contained in the small reservoir falls back on to the mouth of the capillary tube and adheres to this. At this point the thermometer is turned right side up and then heated until the mercury in the bulb rises into the capillary tube and unites with the upper droplet. The thermometer is then immediately immersed in a bath 3° or 4° lower in temperature than the boiling-point of the new solvent. The excess of mercury at the upper extremity of the capillary column is then made to fall by means of a sudden shock and the determination proceeded with as in the preceding example.

Since the same Beckmann thermometer is used for solvents which boil at very various temperatures, it is clear that the same quantity of mercury distributed in the capillary column indicates a different number of divisions when working at different temperatures.

For this reason, in the case of very exact experiments, the readings of these thermometers must always be corrected by means of special tables which refer to particular temperatures.

If we wish to determine the molecular weight of a substance, we first read on the scale the division which the capillary column of the mercury reaches when the thermometer is immersed in a given weight of the pure boiling solvent (for example, 1·57°). A given weight of the substance under examination is then dropped into the solvent and the point is noted which the capillary mercury column reaches when the solution boils (for example, 2·09°). The absolute rise of boiling-point which results is then 0·52° (that is, 2·09° − 1·57°), and this suffices for the calculation of the molecular weight as we already know the weight of the solvent and the weight of the dissolved substance.

The complete apparatus is shown in Fig. 28. In order that the heat may be uniformly

transmitted and the liquid may not be superheated, the vessel *e*, which has the form of a large test-tube with a side tube connected with a cooling coil in order to condense the vapours of the solvent, has fused into its base a piece of platinum wire which is surmounted with a polished garnet or glass bead, or with a small piece of platinum foil. This test-tube is surrounded by a cylinder of glass or porcelain with double walls, *c*, in which 20 to 30 c.c. of the solvent are strongly boiled in order to maintain this mantle at a constant temperature. The side tube of the mantle is also connected with a condensing coil or small condensing tube in order to condense the vapours. The thermometer dips into the solvent and almost touches the garnet.

This apparatus was again slightly modified by Beckmann in 1902 by causing the solvent to boil by means of internal circulation of the vapours of the external liquid. Later, in 1908, he also applied electrical heating, but the apparatus described above is still the one most commonly used.

The weighed substance, of which the molecular weight is to be determined, is introduced into the test-tube which contains the weighed solvent and of which the boiling-point has already been determined with the thermometer, by means of a capillary U-pipette, if the substance is a liquid, or in a glass capsule if it is viscous or solid, the coil *f* being momentarily removed.

In the case of solid substances small pastilles may also be formed by means of a steel mortar and are then easily weighed.

The apparatus rests on a table of solid asbestos plate provided with two small asbestos chimneys for the escape of the burner gases. 40 to 50 grms. of solvent and about 0·2 grms. of the substance are ordinarily employed. When the first determination is finished, a fresh quantity of the substance is added to the same solution and the new boiling-point determined. A third and fourth addition may also be made so that several results are obtained from which a more exact average may be deduced.

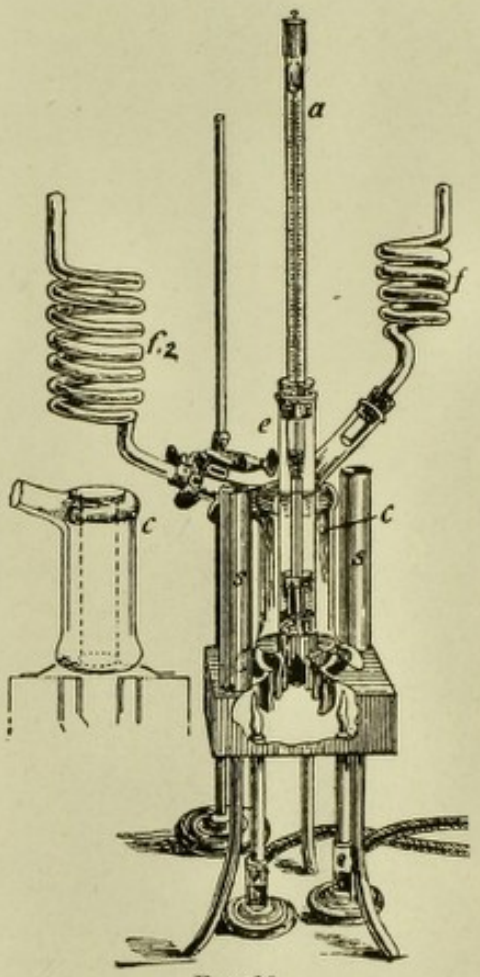


Fig. 28.

DETERMINATION OF THE FREEZING-POINT OF SOLUTIONS AND OF MOLECULAR WEIGHTS (CRYOSCOPY). Already in the year 1788 Blagden observed that the freezing-points of various aqueous solutions of the same substance are all more or less lowered as the quantity of dissolved substance is increased. This law was forgotten for many years, and in 1861 Rüdorff announced it as a new discovery, whilst in 1871 De Coppet, rediscovering the work of Blagden, pointed out its great importance.

It had been known since ancient times that the ice which separates from sea water is almost free from salt. This phenomenon was more carefully studied by Kries in 1814, and was discussed by Dufour, Rüdorff, and Fritsche about the year 1860. Many exceptions to Blagden's law are explained by the knowledge that various substances combine with the solvents. In 1871-1872 De Cappet determined the lowering of the freezing-point of various dissolved substances and water in relation to their molecular weight, and thus found that the molecular decrease of the freezing-point was almost equal for the whole of many different substances (with the exception of ammonium nitrate, which dissociates in dilute solutions, &c.).

In 1882 Raoult extended these researches to many organic substances, dissolved both in water and in the purest benzene or acetic acid, and

obtained for all of them molecular freezing-points which were equal and constant. With certain other solvents, he obtained double molecular values. These exceptions were, however, explained later. On dissolving any substance which does not dissociate in a litre of water in a quantity in grammes equal to the molecular weight, a lowering of the freezing-point of 1·85° is always found.

In 1885 Raoult proposed a very convenient method of determining the molecular weight of substances, based on his work on the lowering of the freezing-point of solutions. In 1886 Paternò and Nasini confirmed the value and practicability of the method proposed by Raoult, but the attention of chemists was only turned to it after the year 1890, when van't Hoff had already expounded, theoretically and mathematically, his brilliant theory of solutions (*see below*).

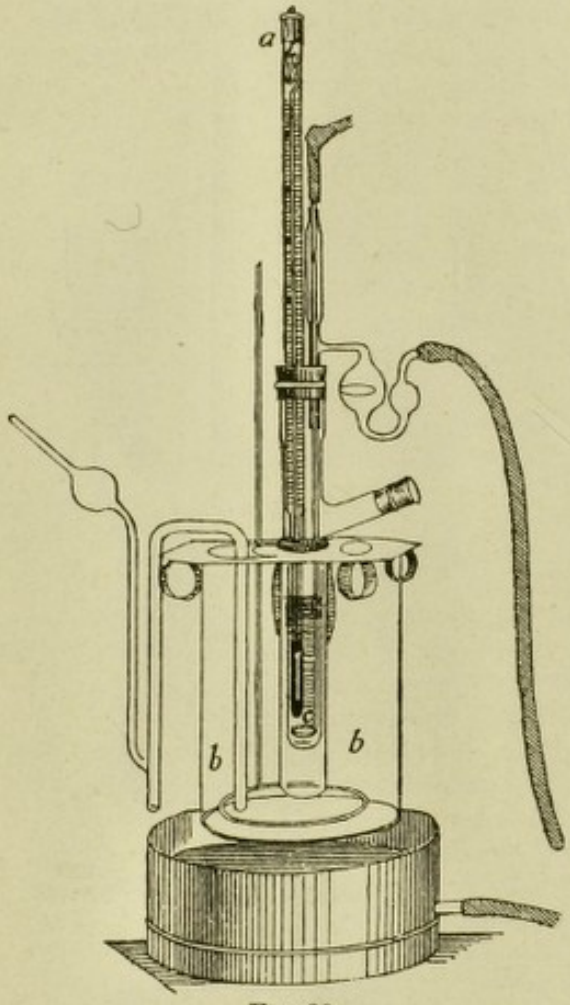


FIG. 29.

Various forms of apparatus are made for the practical application of this method, but the most convenient and the most used is that proposed by Beckmann in 1888.

The apparatus is constructed of glass and consists (as indicated in Fig. 29) of a large test-tube of 2½ to 3½ cm. diameter, with a side tube for the introduction of the substance. The stopper with which it is closed carries a thermometer graduated in hundredths of a degree and a special tube through which a glass or platinum stirrer works which communicates with a bulb-tube containing concentrated sulphuric acid in order to prevent the entrance of moisture.

This test-tube is surrounded by another large tube so that the heat may be transmitted regularly. The whole is immersed in a large beaker which contains a freezing mixture to induce the freezing of the solution.

An exact quantity (20 to 25 grms.) of solvent is placed in the test-tube so that it completely covers the bulb of the thermometer, and then freezing is effected, the apparatus being arranged as is indicated in the figure and the solvent stirred continually until it freezes.

When the ice commences to separate from the solvent (we will in this case call the solid substance which separates *ice*, whatever the solvent may be) the mercury in the thermometer, which has been descending and oscillating, suddenly rises to the temperature of freezing and remains very steady for some minutes. The highest temperature which is observed in two or three melting and freezing operations, carried out consecutively, is the true freezing-point of the solvent. When the ice is again melted a small quantity (0·1 to 0·2 grm.) of the substance under examination is introduced. Freezing is again induced until the ice separates and the freezing-point is noted. The ice is allowed to melt and again frozen, noting the temperature each time, and the mean of these two temperatures is taken. After the ice has thawed, a further quantity of the substance is added and the new freezing-point of this more concentrated solution is noted. Third and fourth quantities of the substance may then be introduced so that about 1 grm. of substance is present in solution altogether. The mean of the molecular weights found from these four determinations may be taken as the closest approximation, so long as these determinations are concordant with one another. Otherwise the mean must not be taken.

The method of calculating the molecular weight is analogous to that already employed for the ebullioscopic method. If g grammes of a substance dissolved in 100 grms. of solvent

produce a depression, d, of the freezing-point of the solvent itself; then $\frac{d}{g}$ is the specific depression of the freezing-point, and on referring this to the molecular weight, m, of the substance, we obtain the molecular depression : $\frac{dm}{g}$. In this case also, acids and strong bases in aqueous solutions give abnormal molecular depression of the freezing-point, because these substances are dissociated. The molecular weight, m, of any substance may be deduced by the following formula : $m = \frac{K}{A}$ where K is a constant depending only on the nature of the solvent (water = 18·5, acetic acid = 39, formic acid = 27·7, benzene = 49, phenol = 74, naphthalene = 71, and nitrobenzene = 70·7) ; A indicates the specific depression of the freezing-point, that is, the quotient of the depression observed, divided by the percentage contents of the solution.

If g grammes of substance are dissolved in G grammes of solvent, they produce a lowering, Δ, of the freezing-point of the solvent ; then if the percentage contents of the solution are x, we have : $x = \frac{100g}{G}$, and the specific depression A will be : $A = \frac{\Delta}{\frac{100g}{G}} = \frac{\Delta G}{100g}$; and knowing that $m = \frac{K}{A}$, we have : $m = \frac{K \,.\, 100g}{\Delta G}$. All these values being known or easily determined, the molecular weight can be calculated, and if with various solvents the same substance leads to various multiples it is necessary to select the smallest value as the most correct molecular weight.

Example. Determination of the molecular weight of naphthalene ($C_{10}H_8$) by employing benzene as the solvent ; 0·5507 grms. of naphthalene in 18·65 grms. of benzene produce a lowering of the freezing-point of 1·170° ; the constant K for benzene is 59 and thus the molecular weight $m = \frac{49 \times 100 \times 0{\cdot}5507}{1{\cdot}170 \times 18{\cdot}65} = 124$, a value very near to the theoretical value, which is 128.

ANOMALIES IN CRYOSCOPY AND EBULLIOSCOPY. It has been observed that the molecular weights obtained by these two methods increase slightly as the solvent becomes more concentrated, but the differences do not influence the results very much, because it is not a method for obtaining precise molecular weights, but simply for obtaining values a little lower or a little higher than the theoretical figures. In practice it is usually a question of deciding whether the substance under examination has a given molecular weight or one double or half as large.

The chemical nature of the solvent in relation to the chemical nature of the substance has, on the other hand, a considerable influence on molecular weight determination.

These anomalies are not due to the dissociating action (into free ions) of certain solvents, such as water, alcohol, &c., of which we will speak later on p. 91, but are due to the associating or polymerising action of certain solvents on the dissolved substance so that a lowering of the freezing-point or boiling-point is found and the molecular weights calculated by this means are thus larger (up to two or three times) than the real values. This associating action is large when hydrocarbons (benzene, &c.), are used as solvents for substances containing hydroxyl groups (such as acids, alcohols, phenols, oximes, &c.), and the association or polymerisation increases rapidly with increase of the concentration where cryoscopic and ebullioscopic methods are applied.

The abnormalities are avoided in these cases by using substances containing hydroxyl groups themselves as solvents, for instance, acetic acid, as these have a depolymerising action.

Abnormalities also occur when the dissolved substance separates together with the "ice" of the solvent, or when vapours of the dissolved substance form together with those of the solvent. This occurs in the freezing-point method when the solvent is of analogous chemical composition to the dissolved substance, for example, if bromoform ($CHBr_3$) is used as a solvent for the substances chloroform ($CHCl_3$) or iodoform (CHI_3), because then, as was pointed out by van't Hoff, mixed crystals separate (*see* p. 111) ; analogous ebullioscopic anomalies occur when the dissolved substance has also a certain vapour tension, so that the vapours of the dissolved substance are found mixed with those of the

solvent. In the first case the abnormality is avoided by choosing as the cryoscopic solvent a liquid the chemical composition of which is not analogous to that of the dissolved substance, and in the second case by using as the ebullioscopic solvent a liquid having a boiling-point much lower than that of the dissolved substance.

Hantzsch and also Oddo (1908–1909) have recently studied the behaviour of various substances when pure concentrated sulphuric acid, free from sulphur trioxide and from water, is used as a solvent. They found that some substances, especially inorganic substances (potassium, sodium, or ammonium disulphate, &c.), which do not actually react with sulphuric acid, behave as electrolytes, because, according to the oxonium or hydronium hypothesis of Hantzsch, the substance and water itself by uniting themselves loosely with sulphuric acid give complexes dissociating into the corresponding ions: $HSO_4H + H_2O = HSO_4'(H_3O)$, hydronium sulphate; $HSO_4H + NH_3 = HSO_4'(NH_4)'$, ammonium sulphate; $HSO_4H + O(C_2H_5)_2$ (ethyl ether) $= HSO_4'(HO(C_2H_5)_2)$, diethyl hydronium sulphate, &c.

RELATIONS BETWEEN RISE OF THE BOILING-POINT, DEPRESSION OF THE FREEZING-POINT, AND OSMOTIC PRESSURE OF DILUTE SOLUTIONS

In a very important treatise which has greatly helped the progress of chemical theory and practice during the last few years, and also obtained for him the first Nobel prize of £8000, assigned to him at the end of 1902, van't Hoff showed by means of thermodynamics that certain relations exist between the pressure of gases or vapours and the osmotic pressure, depression of the freezing-point and rise of the boiling-point of solutions.

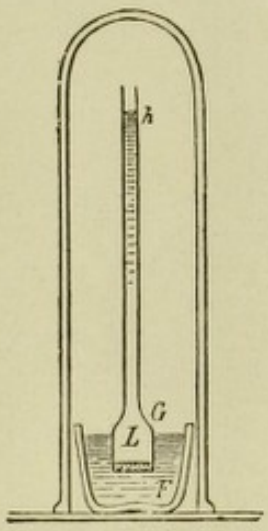


Fig. 30.

The scientific and industrial bearing of this work has already been manifested by various very important applications.

We have seen how Avogadro's law for gases recurs in all the new methods of molecular weight determination with the sole difference that osmotic pressure is substituted for gaseous pressure.

We have shown how the fundamental formula for these methods may be derived from the general gas formula ($pv = RT$) with the help of the constant R; we deduced this constant (R) from the osmotic pressure of a sugar solution (p. 80).

With the help of an ideal experiment due to Arrhenius in 1889, we are able to show from first principles the relation between osmotic pressure and the diminution in the vapour tension of solutions. We introduce a given solution, L, into a vessel shaped like an inverted thistle-funnel with a long neck, which is closed at the base by a semi-permeable membrane (Fig. 30). We then immerse the wide portion of this instrument in a vessel containing the pure solvent, F. The whole is covered by a tall bell-jar, which is evacuated. Osmotic action occurs between the solution, L, and the solvent, F, and the solution will rise in the tube of the funnel to a certain height, h. Equilibrium will be established when the pressure exerted by the column of liquid, Gh, is equal to the osmotic pressure of the solution.

In the interior of the bell-jar liquid evaporates both from the surface of the solvent, G, and from the surface, h, of the solution, and it is quite clear that the vapours which are evolved by h support the pressure of all the vapours which are formed below, and that the vapours which are formed in G must equalise the pressure of the vapours which are formed above, so that the vapours of the solvent at the height h support the same weight as the vapours of the solution at height h, that is, they have the same vapour tension.[1]

[1] No other supposition is possible. If, in fact, the vapours at the height h had a lesser vapour tension than the solution in h, then liquid would distil from the solution and these vapours would join those of the solvent to establish equilibrium; but, on the other hand, this distillation would increase the concentration of the solution in h

If one supposes that there are n molecules of the dissolved substance and N molecules of solvent in the solution, the osmotic pressure of the solution may be represented by the general gas formula, because we have seen that the dissolved substance will cause the same pressure, p, which it would cause if present in an equal volume as gas (*see* p. 80).

Now $pv = nRT$, that is, $p = \frac{nRT}{v}$; we know that $R = 84{,}700$ and T indicates the absolute temperature. In order to find the value of v we must remember that N molecules of the solvent have a weight MN; if M is the molecular weight, and S indicates the specific gravity of the solvent, then $v = \frac{MN}{S}$. Introducing this value of v into the general formula we obtain: $p = \frac{nRTS}{MN}$, if we suppose that the pure solvent and the very dilute solution have the same volume.

But the difference between the vapour tension of the solution (f') and that of the vapours of the solvent (f) is equal to a column of vapour of the height h, and of 1 sq. cm. cross-section (if we express the pressure in grammes per sq. cm.), and the density being d, we have for this value $f' = f - hd$. This value may also be obtained from the general formula given above by substituting the corresponding values, and we then arrive by suitable manipulation at the same formula as that of Raoult $\frac{f - f'}{f} = \frac{n}{N}$, where we have N instead of $N + n$, because we consider a very dilute solution in which the value of n is so small that it may be neglected in comparison with the value N. The close relation between the osmotic pressure and the vapour tension is now evident, as is, therefore, also the relation between the corresponding methods of determining molecular weights.

It is now easy to show that the method of molecular weight determination by means of the lowering of the freezing-point of solutions is founded on the same principle as that of the diminution of the vapour tension.

The relation between the vapour tension of the frozen solvent which separates from the solution and the vapour tension of the solution itself was stated empirically and proved experimentally by Raoult in 1878, but Guldberg deduced it mathematically in 1870.

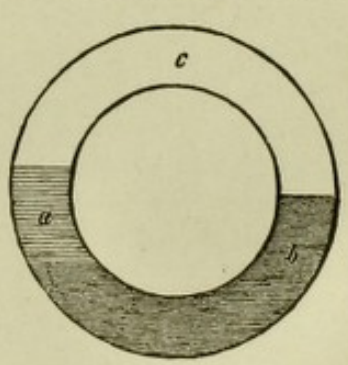


Fig. 31.

We will imagine a curved glass tube closed to form an anchor ring (Fig. 31) in the interior of which there is a dilute solution, b, of a solid substance in a liquid; the tube above the solution has been evacuated and is thus filled with the vapour of the solvent. If we now cool the tube so that a little of the frozen solvent separates in a and floats on the solution, then the vapour tension of the solution and of the frozen solvent at the temperature at which it commences to separate must necessarily be equal. If the vapour tension of the frozen solvent in a were actually greater than that of the solution in b, then part of the frozen solvent would distil over and condense in b, thus diluting the solution; but since on dilution the freezing-point is raised, new frozen solvent will separate in a and consequently a further portion of frozen solvent will distil as at first, so that we arrive at the absurdity of perpetual motion.

If we imagine the reverse case, that is, that the vapour tension of the solution is greater than that of the frozen solvent in a, then the solvent will distil from b and be condensed as frozen solvent in a; but the solution in b will then become more concentrated and its

and consequently the osmotic pressure, so that fresh solvent would penetrate into L through the membrane, and the new liquid would again be evaporated in h so that we would have a case of perpetual motion in contradiction to the second law of thermodynamics. If we take the reverse hypothesis, which is that the vapours of the solvent at the same height, h, have a larger vapour tension than those of the solution at the same height, then the vapours of the solvent would necessarily condense at the surface of the solution, which would then become dilute until its vapour was in equilibrium with that of the solvent in h, but this dilution would diminish the osmotic pressure of the solution, causing a part of the liquid to issue through the membrane at the base, and we again arrive at the absurdity of a perpetual motion being set up, because condensation of the vapours in h would recommence. Thus the only possible hypothesis is that which supposes the solvent and the solution at the height h to have the same vapour pressure. Then we have equilibrium and the phenomenon can be clearly explained.

freezing-point will be lowered. Consequently a part of the frozen solvent in a will dissolve and a new portion will be formed by condensation of the vapours of the solvent so that perpetual motion will again occur.

A plausible explanation of the phenomenon can thus only be made by supposing that at the temperature of freezing, the vapour tension of the frozen solvent and of the solution are equal, so that the equivalent of the cryoscopic and ebullioscopic methods of determining the molecular weights is proved.

We may also prove this fact by a graphic method in the following manner. We imagine a system of co-ordinates in which the abscissæ indicate the temperatures $-t$ to $+t$, and the ordinates the vapour tensions (Fig. 32).

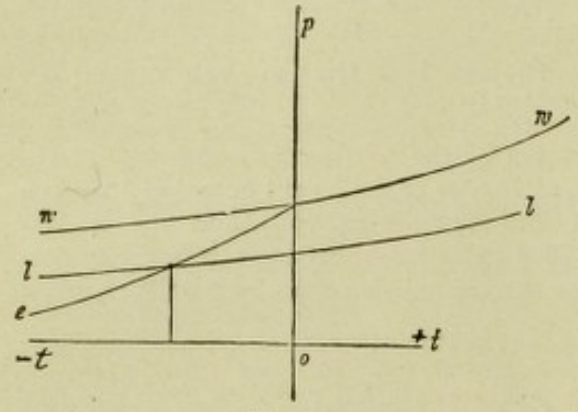


Fig. 32.

The curve n indicates the vapour tension of water at various temperatures even when the liquid is kept below 0° ; e is the curve of vapour tension of ice, for which Kirchhoff has shown that it coincides at 0° with that of water meeting it at a certain angle. If l is the vapour tension curve of a given solution at a different temperature, then the point where e meets l indicates the temperature at which experimentally the solution commences to separate ice, but also indicates that at the point of junction the vapour tensions of the solution and of the ice are equal.

The relation between osmotic pressure, vapour tension, lowering of the freezing-point and rise of the boiling-point of dilute solutions is thus evident.

THE DEDUCTION OF THE MOLECULAR WEIGHT FROM THE ACTION OF TWO SOLVENTS ON THE SAME SUBSTANCE

Already in 1872 Berthelot and Jungfleisch showed that there were certain regularities in the method of subdivision of a substance between two superposed solvents which do not mix. If one of the solvents, A, is slightly soluble in the other, B, the solubility being l, then the vapour tension of the latter will diminish and will correspond to a certain osmotic pressure. If n molecules of another substance are dissolved in N molecules of A, the solubility of A in B will diminish and will now be equal to l', and we then arrive at a formula analogous to that which has already been obtained for the determination of molecular weight by means of the vapour tension : $\frac{l - l'}{l'} = \frac{n}{N}$; we may express n by the weight, p, of the substance divided by the unknown molecular weight : $n = \frac{p}{m}$; we may now replace N by the known values, the weight of P and the molecular weight, M, that is, $N = \frac{P}{M}$, and we thus have all the data necessary to calculate the molecular weight.

In 1889–1890, Nernst actually dissolved a liquid, A, in another liquid, B, until this was saturated and then froze the solution. In the solid solvent which separated, A and B were found (and not the solvent B alone because the solution was saturated). He then added a substance soluble in A, and since the solubility of A in B was thus diminished, the freezing-point was raised by a quantity which was in a certain ratio to the amount of dissolved substance.

This method is not much used, but in certain cases has given very exact results.

ELECTROLYTIC DISSOCIATION OF SOLUTIONS AND IONIC THEORY

On determining molecular weights by means of the lowering of the vapour tension of solutions, Raoult observed that on dissolving 1 *mol.* of numerous substances in a litre of water, a lowering of the freezing-point of about 1·85° was obtained, but that dilute aqueous solutions of acids and strong bases or of their salts showed a lowering of the freezing-point or rise of the boiling-point, and also an osmotic pressure noticeably greater than that which corresponded to their true molecular weights. For dilute solutions of hydrochloric acid the displacements of the boiling and freezing points were approximately doubled ; for sulphuric acid they were trebled, &c. Thus, per litre of water, about 18·3 grms. of hydrochloric acid were needed instead of 36·6 grms. in order to depress the freezing-point by 1·85°.

Solutions giving these abnormal values also behave in an abnormal manner with regard to the refraction of light, magnetic rotation, optical properties, &c.

In 1887 the Swedish physicists, Svante Arrhenius and Planck, simultaneously explained all these apparent abnormalities by means of a simple and equally brilliant hypothesis which then became the indispensable foundation for explaining all electrolytic phenomena.

Arrhenius was, in fact, able to demonstrate that all these numerous exceptions were shown by solutions which conducted the electric current, that is, by electrolytes, to which various aqueous solutions of acids, bases, and salts belong. Water itself is not an electrolyte, but if an acid, a base, or a salt is added to water it then allows the electric current to pass and this causes the separation at the respective poles of the components of the dissolved substance. In order to explain all these facts, Arrhenius supposed that the molecules of such substances, on entering into solution, were dissociated into two or more parts which he called *ions*, a name already used by Faraday. These ions carry a strong electric charge (96540 coulombs, or a multiple of this quantity for each monovalent gramme-ion) ; those are called *anions*, which carry a negative electric charge and which move in a direction contrary to the electric current and collect at the *anode* (positive pole), where they give up their electric charge and separate in the atomic or molecular condition ; those are called *cations*, on the other hand, which carry an electropositive charge ; these move in the same direction as the current from the positive to the negative pole, and separate at the *cathode* (negative pole).

Those substances which in aqueous solutions give osmotic pressures or depressions of the vapour tension or freezing-point of the solution which are abnormal and which conduct the current, when dissolved in certain other substances no longer conduct the electric current, and then show normal osmotic pressure and depression of the vapour tension and freezing-point of such normal solutions.

We thus see that the electric conductivity is closely connected with the dissociation of the molecules into ions, and that with certain solvents this electric dissociation (so easily obtained with water) does not occur, and that the current does not then pass. A minimal and partial dissociation of the molecules into ions suffices, however, to cause electric conductivity which increases with the ionic dissociation.[1]

[1] We find in nature substances which conduct, and others which do not conduct electricity. Electric conductors may be divided into three classes. Conductors of the first class are those which conduct the electric current and are at the same time heated without altering chemically and without transportation of matter. Metals belong to this group, and their conductivity increases with diminution of the temperature. Conductors of the second class are aqueous solutions of salts, of acids or of bases, which allow the electric current to pass, but with simultaneous decomposition of the molecules of the dissolved substance into the corresponding ions which are carried to the poles of contrary sign. The electric conductivity of such conductors increases with

In dissociated, dissolved *salts*, the *cation* is usually formed of a metal and the *anion* of an acid residue. All dissolved and dissociated *acids* are, on the other hand, characterised by the hydrogen *cation* H, whatever may be the rest of the molecule forming the anion. All dissolved and dissociated *bases* are characterised by the *anion* OH, which is common to all of them whatever may be the cation forming the rest of the molecule.

The characteristic ions of acids (H) and of bases (OH) have the property of modifying the colour of *indicators* (*see below*) and of causing certain catalytic reactions (*see below*).

All hydrogenated substances are not acids; but all are acids, on the other hand, which dissociate in aqueous solution to a greater or less extent with production of hydrogen ions.

The hydrogen which is characteristic of any acid substance is freely evolved when this is mixed with magnesium powder, and often even with other metals, such as zinc, iron, &c. In order that electrolytic dissociation may occur, a solvent is required, which is ordinarily water.

Acids have, furthermore, a special taste, redden blue litmus solution, form salts by combining with basic substances or with metals (in the latter case hydrogen is developed) and also possess certain catalytic properties which we will study in connection with organic chemistry, such as the inversion of sugar, hydrolysis of maltose, &c.; but all these properties are manifested when dissociation of the molecules occurs, that is, when the hydrogen is present in the form of a cation, and its acid reactions are ordinarily observed in presence of water or moisture.

Even the most energetic acids, when absolutely deprived of water, no longer give any of the characteristic actions which we have enumerated. Thus, pure anhydrous hydrochloric acid, whether gaseous or liquefied, does not react with metals and no longer reddens dry blue litmus paper, whilst in the dilute condition it reacts energetically. Large quantities of the more energetic acids, such as sulphuric acid, are to-day transported with the greatest security in iron tanks, mounted on railway cars, because it is quite easy to obtain such acid free, or almost free, from water, and there is then no danger of the iron being corroded, because the molecules of sulphuric acid are not dissociated and the chemical reaction is only produced by the ions.

The characteristic properties of dissolved acids can be completely modified or neutralised by means of the action of basic substances. These bases are ordinarily substances which turn litmus solution, which has been reddened by acids, blue. They have a special taste, cause various catalytic reactions of organic compounds, saponify fats and ethers, &c. The greater number of

elevation of the temperature. Conductors of the third class are the gases especially at reduced pressure, and their conductivity diminishes with increase of the pressure. Gases at the ordinary pressure are not generally conductors of electricity, but they become so under the influence of certain ultra-violet radiations or cathodic or radio-active emanations. Gases with monatomic molecules (argon, helium, neon, &c.) are the best gaseous conductors of electricity.

Aqueous solutions of organic compounds, except the acids, bases, and typical salts, are not electrolytes. No organic or inorganic substance is an electrolyte when dissolved in benzene, carbon disulphide, ether, or similar solvents. Sugar does not conduct the electric current even when dissolved in water. In aqueous solution neutral salts are the most dissociated; at moderate concentration half their molecules are dissociated; in dilute solution the dissociation is almost complete. There are also other solvents than water, such as alcohol, hydrocyanic acid, &c., which in certain cases give dissociated solutions which are good conductors of the electric current.

Water is the best medium for producing ionic dissociation on account of its high dielectric constant. The *dielectric constant* is the ratio between the charges which can be maintained between the two armatures of an electric condenser when water and air respectively are interposed between them. Then if the charge which can be maintained in air is taken as unity, that which can be maintained in presence of water = 81, which is the dielectric constant of water. The constant varies with the nature of the dielectric (or insulator). It is relatively small for certain organic solvents, such as ether, carbon disulphide, &c., which, in fact, form solutions of electrolytes which are very little dissociated; whilst, on the other hand, there are other substances than water, even other substances of minimal electric conductivity but with a high dielectric constant, such as liquid sulphur dioxide, hydrocyanic acid, and liquid ammonia, which have considerable dissociating power. Pure liquefied hydrochloric acid has a very small dielectric constant, and this explains why, although it dissolves certain salts readily, these solutions are not good conductors of the electric current, because no ionic dissociation is produced. Alcohol, on the other hand, has a fairly high dielectric constant, and consequently a dissociating or ionising power which is about one-quarter that of water.

bases are obtained by dissolving oxides of metals in water and in aqueous solution they then form free characteristic ions consisting of the OH (hydroxyl) group. Potassium hydroxide, KOH, for example, is dissociated into the cation K and the anion OH. If to the solution of an acid which has been reddened by litmus we add a solution of a base, drop by drop, the H cations of the acid gradually unite with the OH anions of the base to form undissociated water, and we thus finally arrive at a point in which all the cations of the acid are transformed into water and then the solution has a neutral reaction. A single drop of the base in excess immediately changes the colour of the solution to blue, because free OH anions of the base are then present. In the case, for example, of solutions of HCl and of KOH, when the mixture is neutral, that is, when all the acid cations and basic anions have disappeared, Cl anions from the acid and K cations from the base will remain in solution as the ions of the salt (potassium chloride, KCl), which is thus formed by the exact saturation of the acid by the base. In general, salt formation always occurs when the characteristic hydrogen of an acid is replaced by a metal.

When we have a salt in dilute aqueous solution, we find it to be dissociated into the corresponding ions; for example, sodium chloride (NaCl) is dissociated into chlorine (Cl) anions and sodium (Na) cations. At first sight it may appear strange that sodium, which reacts so energetically with water and decomposes it at once when brought into contact with it, should exist in the free condition in aqueous solution without reacting, and also that chlorine, which we know as a greenish-yellow gas of suffocating odour, should exist free as an ion without making its presence known in the aqueous solution of sodium chloride. But this is because we are accustomed to characterise these substances Na and Cl in the free atomic or molecular state, but not in the state of dissociation as ions with an electric charge of 96,540 coulombs per gramme-ion, and thus in equilibrium with one another by means of equal charges of contrary sign. The properties of the ions are very different from those of the molecules, especially as regards the nature and quantity of the energy contained in them.

These properties of solutions are not those of the dissolved salts themselves, but are those of the free ions of the salt.

DOUBLE DECOMPOSITION OF SALTS. By means of the hypothesis of the electric dissociation of salts in solutions, the so-called double decomposition of salts is explained. It was at one time believed (by Berthollet in 1803 and by Guldberg and Waage later) that on mixing the solutions of two salts the new resultant solution would contain four salts formed by partial reciprocal decomposition, that is, supposing that no precipitation occurred. It was also believed that the quantity of the four salts varied according to the preponderance of one or other of the two salts primarily mixed, and thus on mixing, for instance, solutions of equimolecular quantities of NaCl and KI, it was believed that in the new solution portions of NaI and KCl were also present, and this was considered to be proved by the fact that on gradually evaporating the solution of the mixture, the new salts really separated. On mixing coloured salts, change of colour due to one or the other was also observed; thus on mixing $CuSO_4$ with NaCl, the solution acquired a greenish tint, and this was attributed to the formation of $CuCl_2$. When, however, the solubility relations in the solution are not altered, the formation of new salts should be accompanied by the development or absorption of heat (increase or diminution of energy) which would explain and justify the occurrence of a chemical reaction. In normal cases, however, no thermochemical alteration was observed, and this excludes the formation of new chemical compounds, that is, of new salts.

On the ionic theory this phenomenon can be completely explained. In the case, for instance, of two dilute solutions of NaCl and KI, these salts must be considered as mainly dissociated into the respective ions Na, Cl, K, and I, but the same occurs in a single solution of KCl and NaI, obtained directly from the two salts or by the mixture of their respective solutions, so that the same ions are always present, and therefore Na, K, Cl, and I are present without any chemical reaction occurring.

But, on the other hand, since the various characteristic chemical reactions of individual salts in solution are due to the free ions and not to undissociated molecules of the salts, we will have the same characteristic reactions in an equi-molecular solution of NaCl and KI, as in an equimolecular solution of KCl + NaI or any mixture of these two solutions. And therefore if the equilibrium between these ions is altered by the separation of part of the ions in the form of insoluble or less soluble salts, then a reaction will really occur, and thus in the ordinary way the reaction proceeds entirely in a given sense. Thus on concentrating the solution by evaporation, at a certain point those ions will unite and separate which form a less soluble salt (*see* preparation of potassium nitrate or conversion nitrate). Again on adding barium chloride to a solution of sodium sulphate, barium sulphate is formed and separates, because it is insoluble, and then all the sodium sulphate can be transformed and separated in the form of insoluble barium sulphate. These true chemical reactions are, however, accompanied by measurable thermal phenomena.

The same may be said when by mixing two electrolytes two of the four types of ions which are formed have great affinity to one another and unite to form a substance which has little tendency towards dissociation. In this case true combination of the ions, that is, true chemical combination, occurs. Thus on mixing two strongly dissociated substances, such as hydrochloric acid solution and sodium acetate, the formation of NaCl and acetic acid is possible, because NaCl has a great tendency to dissociation and is therefore not formed, whilst, on the other hand, acetic acid being a weak acid is only slightly dissociated and the affinity between the H ions and those of the acetic acid being very great, undissociated acetic acid is easily formed. This fact explains how in practice the strong acids readily liberate the weak acids from the corresponding salts, and how strong bases liberate weak bases from their salts, because the H cations of the acid have a great affinity for, and tend to unite with, the anions of the weak acid, whilst the OH anions of the base have great affinity for and tend to unite with the cations of the weak base ; thus caustic soda liberates ammonia from ammonium salts.

In 1908 Rosenstiehl stated that double decomposition between salts, as in the case of organic esters, is always preceded by hydrolysis, by means of an intermediate reaction with one or more molecules of water, for example : $MeCl + HOH = MeOH + HCl$; $[+ AgNO_3] = AgCl + Me.No_3 + H_2O$. He called the salts and ethers which are slowly hydrolised *bradolytes*, whilst those which are rapidly hydrolised he called *stenolytes*.

ANALYTICAL TESTS FOR THE IONS. The extraordinary simplicity of the tests used in analytical chemistry is explained by the ionic theory, because in a solution of many salts we do not require to recognise the properties of all the salts, but simply those of the respective ions, which possess properties common to many salts. If, for example, we have a solution which contains 50 anions and 50 cations, these would be theoretically able to form 2500 salts, and if all these salts possessed individual characteristic reactions, it would be necessary to verify the presence of 2500 substances. Since, on the other hand, salts in aqueous solution are dissociated into their ions, all that is necessary to completely analyse this solution is to confirm the presence of 100 ions (50 anions and 50 cations).

But certain apparent abnormalities in analytical chemistry can also be explained by the new theory of electrolytic dissociation. We know, for example, that silver nitrate is the safest reaction and an almost general one for the detection of chlorine, because the cation of silver (in the soluble nitrate) unites with the anion, chlorine (of any soluble chloride) with the separation of the white insoluble substance silver chloride. Now whilst this reaction occurs with hundreds of chlorinated compounds and with all soluble chlorides, certain other compounds which also contain chlorine, such as potassium chlorate, chloroform, chloroacetic acids, &c., give no precipitate with silver nitrate.

By the electrolytic dissociation theory we know, in fact, that the formation of silver chloride by means of soluble silver salts is a reaction characteristic of chlorine ions, but chloroform is not a salt and is not dissociated, and therefore cannot give this reaction. Potassium chlorate (ClO_3K) is a salt, but in aqueous solution it is dissociated into its ions, one of which is potassium (K) and the other the chloric acid residue (ClO_3), which is different from the chlorine ion and thus does not give the reaction with silver nitrate.

VALENCY OF THE IONS. Molecules dissociated into two ions also exercise double the normal osmotic pressure, and in the case of very dilute sulphuric acid, three times the osmotic pressure which would be deduced

from its formula if undissociated is obtained. This is easily explained by the theory of electrolytic dissociation. The sulphuric acid molecule H_2SO_4, is, in fact, dissociated into the divalent anion SO_4, and two monovalent cations (2H), that is, three ions altogether, which exercise an osmotic pressure three times that which would be due to the undissociated molecule. The osmotic pressure is thus strictly dependent on the number of free ions and not on their nature. This valency of the ions corresponds exactly to the valency which has already been studied and deduced from atomistic considerations and from analytical or stoichiometrical results.

The valency of cations is indicated by dots to the right of the symbol at the top, whilst that of the anions is indicated similarly by dashes, and we thus have the cations $K^{\cdot}$, $K^{\cdot}$, $Ba^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, &c., and the anions Cl', S'', &c. Apart from the simple ions, others are known of complex composition, such as SO_4'', NO_3', &c. The monovalent ions have all an equal electric charge of 96,540 coulombs. The valency of these ions may be deduced from the relations between the quantity of electricity with which the polyvalent ions are charged and the quantity carried by a monovalent ion. The divalent ions have a double electric charge, &c.

The electrolytic behaviour of sulphuric acid also explains why this acid is dibasic, that is, why it is able to saturate two basic monovalent radicals, or one divalent basic radical, and thus the basicity of an acid may also be deduced from the number of H cations corresponding to its anions.

In the dissocation of bases we always find the hydroxyl anion OH, which is monovalent, and thus for sodium hydroxyl we have :

$$\underset{}{NaOH} = \underset{+}{Na} + \underset{-}{OH'}$$

thus this base is monoacid, that is, the saturation of its anion requires a single cation of an acid, and thus one molecule of a monoacid base will be saturated by one molecule of a monobasic acid (for instance, hydrochloric acid, HCl). The molecule of barium hydroxide, on the other hand, forms three ions ; $Ba(OH)_2 = \underset{+}{Ba^{\cdot\cdot}} + \underset{-}{OH'} + \underset{-}{OH'}$; thus this base is diacidic, that is, its divalent cation corresponds to two monovalent ions, and one molecule will be saturated by one molecule of a dibasic acid or by two molecules of a monobasic acid.

It is important to note that the charge of the same ion may vary in various salts. Thus the ferrous-ion in ferrous sulphate ($FeSO_4$) is divalent : $FeSO_4 = Fe^{\cdot\cdot} + SO_4''$, whilst in ferric chloride ($FeCl_3$), on the other hand, iron is trivalent :

$$\underset{}{FeCl_3} = \underset{+}{Fe^{\cdot\cdot\cdot}} + \underset{-}{Cl'} + \underset{-}{Cl'} + \underset{-}{Cl'}.$$

When the polyvalent cation of a metal combines with several chlorine ions (monovalent) then the quantity of electricity corresponding to the metallic cation is a multiple of that corresponding to the monovalent chlorine-anion ; that is to say, it is equal per gramme-ion to as many times 96,540 coulombs as there are chlorine-ions corresponding to one ion of the metal, so that each valency corresponds to a definite quantity of electricity.

On electrolysing cupric chloride $Cu\begin{matrix}Cl\\Cl\end{matrix}$ a given quantity of electricity separates 31·8 grms. of copper for every 35·5 grms. of chlorine, or 63·6 grms. of copper (gramme-ion) per 71 grms. of chlorine (gramme-ions corresponding to two valencies).

On electrolysing cuprous chloride, $\begin{matrix}Cu—Cl\\|\\Cu—Cl\end{matrix}$, the same quantity of electricity

produces double the quantity of copper, that is, 63·6 grms. of copper for each 35·5 grms. of chlorine ; thus in cupric chloride we have a simple divalent copper cation $Cu^{\cdot\cdot}$, and 31·8 grms. of copper for every gramme-ion of monovalent chlorine Cl', whilst in cuprous chloride we have a compound divalent cation of copper $Cu_2^{\cdot\cdot}$ and 63·6 grms. of copper for each gramme-ion of monovalent Cl'. For this reason in practice salts with a minimum valency are electrolysed whenever practicable, because for equal consumption of energy a greater quantity of metal is separated in this way.

We have thus arrived at conceptions of ionic valency without any addition to the atomic hypothesis, simply basing our considerations on the electrolytic behaviour of many substances in dilute solution, and we see how in these phenomena also we obtain a proof of the existence of variable valency, in distinction to the constant valency which was supposed to exist until a short time ago, based on exclusively atomistic conceptions. We have also shown that valency is generally lower at high temperatures where compounds in a state of minimum oxidisation are often found, whilst at lower temperatures the compounds are more stable and are generally present in a more highly oxidised condition.

MOLS, NORMAL SOLUTIONS, AND VOLUMETRIC ANALYSIS. The behaviour of acids and bases in solution serves as the basis of a whole department of analytical chemistry, that of volumetric analysis.

Bases and acids saturate one another through the reciprocal saturation of their characteristic ions. A divalent ion is equivalent to two monovalent ions, and three of these latter are equivalent to one trivalent ion. The quantity of matter which corresponds to each valency of the ions is the same as that which we know under the name of combining weight or equivalent or stoichiometric value (*see* p. 21), and thus if we have a quantity of an acid or base corresponding to its equivalent expressed in grammes or gramme-equivalent, dissolved in one litre of an aqueous solution, this is the quantity corresponding to one valency, or finally, the quantity corresponding to a monovalent ion, and such a solution is called a *normal solution*. Such solutions are used for the determination of the strength or concentration of any acid or base, that is, for the determination of the quantities of pure acid or base contained in a given volume of their solutions whatever may be the dilution in which they are present.

For the sake of brevity in the discussion of electrolytic phenomena, the use of the word *mol* to express the quantity in grammes corresponding to the molecular weight of a substance has been proposed ; but it was then found more practicable to call the quantity in grammes corresponding to the ion, a *mol-ion* (gramme-ion), thus one mol-ion of Cl = 35·5 grms. ; one mol-ion of H = 1·01 grm. ; one mol-ion of SO_4 = 96 grms., &c.

Thus in order to obtain a normal solution of hydrochloric acid (HCl), we must dissolve the quantity of HCl corresponding to one mol-ion of hydrogen (that is, to 1·01 grm., or 36·46 grms. of pure HCl) in sufficient water to form one litre of solution.

In order to obtain a normal solution of sulphuric acid, which contains a divalent SO_4'' anion corresponding to two monovalent H' cations, we must dissolve the quantity corresponding to one mol-ion of H only, that is, $\frac{H_2SO_4}{2} = \frac{98}{2}$, = 49 grms. of the pure acid, in sufficient water to form one litre. In this case equal volumes of the normal solutions of HCl and of H_2SO_4 are equivalent and will saturate the same quantity of a basic substance.

The normal solutions of bases always refer to one gramme-ion of OH, and in the case of polybasic bases, a quantity in grammes is used corresponding to one OH anion, that is, to one mol-ion of OH. Equal volumes of normal solutions of an acid and of a base exactly neutralise one another, because the OH' anions of the base unite with the H' cations of the acid to form undissociated water, which is neutral. The point of neutrality is

rendered evident by the employment of indicators which indicate colorimetrically the acid or alkaline reaction of the acids or bases.[1]

By means of a normal solution of HCl we may always determine the quantity of sodium hydroxide contained in any solution whatever, because we know that 36·46 grms. of HCl saturate 17 grms. of the basic OH ion, or corresponding quantities of basic substances. In the case of sodium hydroxide, we have 23 grms. of sodium united to the anion OH, therefore 36·46 grms. of HCl correspond to 40 grms. of NaOH (23 + 17 = 40).

In the reverse case, with a normal solution of a base we are always able to determine the concentration of any acid solution ; 1 c.c. of normal NaOH solution corresponds to 0·03646 grms. of HCl and 0·049 grms. of H_2SO_4, &c.

The equivalence of the normal solutions which serve as standards in volumetric analysis is also easily demonstrated by the fact that on neutralising equivalent quantities of strong bases with a given quantity of strong acid, the same quantity of heat is always developed, this being the *heat of neutralisation* which is proportional to the number of ions which unite to form water, independently of the nature of the acid and the base.

$$Na^{\cdot}OH' + H^{\cdot}Cl' = Na^{\cdot}Cl' + H_2O + 13700 \text{ cal. (due to } H^{\cdot} + OH' = H_2O)$$

$$K^{\cdot}OH' + H^{\cdot}NO_3' = K^{\cdot}NO_3' + H_2O \ldots . + 13700 \text{ cal.}$$

$Ca^{\cdot\cdot}(OH)_2' + 2H^{\cdot}Cl' = Ca^{\cdot\cdot}Cl_2' + 2H_2O \ldots + 27400$ cal., that is, double the amount of heat, because $2H^{\cdot}$ cations unite with $2OH'$ anions.

We may also consider the ions of non-dissociated molecules to be held together by large amounts of chemical energy, whilst those of the greatly dissociated substances have less affinity with one another, their independent existence in solution being thus explained. The dissociation of water is extraordinarily small (its dissociation constant being estimated at about 10^{-14} at ordinary temperatures, whilst at 50° it is three times larger), because the $H^{\cdot}$ and OH' ions have a strong affinity for one another and always tend to combine to form undissociated water. We can thus easily explain why on mixing equal volumes of equivalent solutions of acids and bases, all the $H^{\cdot}$ and OH' ions unite to form neutral water until a new equilibrium is established corresponding to the minimum dissociation of water (10^{-14}). Therefore whatever may be the acids and bases which react, the heat which is developed is always due to the total transformation of the $H^{\cdot}$ and OH' ions into H_2O. When mixing dilute salt solutions, on the other hand, there is no evolution

[1] *Indicators* are weak organic acids or bases, and are therefore only very slightly dissociated. The non-dissociated portion has a varying colour corresponding to the free ions, and since the typical $H^{\cdot}$ and OH' ions are not coloured, the coloured portion of basic indicators will be the cation and the coloured portion of acid indicators the anion. Ordinarily acid indicators are used, and not salts, because these are more dissociated. When a strong acid is titrated with a base, employing an acid indicator, the numerous $H^{\cdot}$ cations of the strong acid completely suppress the dissociation of the indicator. As the base is gradually added during titration, the $H^{\cdot}$ cations of the strong acid gradually disappear, as they unite with the OH' anions of the base to form undissociated water. When, however, all the $H^{\cdot}$ cations are saturated, a single drop of the base in excess causes formation of salts of the indicator which easily dissociate, and we then have its free anion of characteristic colour which indicates the end of the titration (saturation).

The titration is complete even when the substance which is being titrated is not highly dissociated, because even if an acid is not highly dissociated and only a part of its cations $H^{\cdot}$ are in the free state (actual ions), these are in a certain equilibrium with the remaining acid hydrogen which is not dissociated (potential ions) ; and as the basic solution employed in the titration gradually reacts, the actual ions are used up in the formation of water ; and as they are destroyed the equilibrium between the actual and potential ions of the acid is disturbed and a part of the latter immediately dissociates, giving actual ions to restore the equilibrium. The titration process continues in this manner until all the $H^{\cdot}$ ions of the acid, including those which were not at first dissociated, have reacted with the hydroxyl of the base. Thus during titration in general *all the acid hydrogen reacts*, and not merely the hydrogen which is dissociated in the form of ions.

In order to measure the quantity of actual ions of an acid or a base, that is, in order to ascertain its degree of dissociation, it is necessary to measure, as we have already said, the electric conductivity of the solution.

If a very weak acid is to be titrated, its dissociation is small and the number of $H^{\cdot}$ cations is not sufficient to prevent a slight dissociation of the indicator. In these cases, therefore, there is not a sharp change of colour at the moment where the neutral point is passed, and the titration remains uncertain and inexact. In such cases this difficulty is avoided by using very weak indicators, such as phenolphthalein or litmus, and by titrating with a strong base. Weak bases should be titrated with a strong acid and a strong indicator, such as methyl orange. When dissociated this preserves its characteristic colour even at points very close to the neutral point, and therefore even when this is passed to the extent of one drop of strong acid, the $H^{\cdot}$ cations of the latter immediately repress all dissociation of the indicator completely and its colour is changed. In general, the titration of weak acids with weak bases and *vice versa* should be avoided. When a strong acid is titrated with a strong base, any indicator whatever can be used ; but even if a salt with a weak cation, such as ammonium chloride, is also present, a strong indicator should be employed and not phenolphthalein, because the $NH_4^{\cdot}$ cations of the dissociated ammonium salts fix a portion of the OH' anions of the strong base with which they unite even after the neutral point has been passed, ammonia and undissociated water being formed ; and thus when using weak indicators, such as phenolphthalein, many OH' anions are required in order to repress dissociation, so that one obtains an uncertain titration, whilst strong indicators react immediately from the beginning as soon as the neutral point is passed. If, on the other hand, the salt which is present contains a weak anion, then it is advisable to use a weak indicator.

of heat, because the ions are free both before and after mixing, and no combination occurs though the contrary was believed at one time.

HEAT OF FORMATION OF THE IONS. After the above considerations we are also able to deduce the heat of formation of the ions. The heat evolved in reactions between acids and bases, as shown by the above equations, is simply due to the formation of water by the union of $H^{\cdot}$ and OH' ions.

But it is evident that whatever may be the acid and the base which react to form a salt, the same quantity of heat will always be developed per molecule of water which is formed, on condition that the reacting substances and the salt which is transformed are completely dissociated. Otherwise it will be necessary to remove or supply heat to affect the ionic dissociation or to account for the combination of ions which unite to form molecules.

The energy contained in the actual ions (*see* preceding footnote) is less than that contained in the potential ions (non-ionised substances). The molecules of chlorine gas contain much more energy than ionised chlorine, whilst, on the other hand, the difference in energy between $H^{\cdot}$ ions and the H_2 gaseous molecule is almost zero. We may also consider the chlorine ion and the molecule of chlorine gas as allotropic forms of the same element, and therefore they should actually contain different quantities of energy. The heat of ionisation may be deduced in the following manner. It is found from various considerations, which we will not record here, that gaseous H_2 on passing into the ionised condition in solution would develop no heat; H_2 + aq. = $2H^{\cdot}$ aq. + zero calories; the heat of formation of one molecule of hydrochloric acid in aqueous solution is 42,200 calories, that is, $H_2 + Cl_2$ + aq. = $2H^{\cdot}Cl'$ aq. + 42,200 cals. × 2, and since the HCl is dissociated into its ions $2Cl'$ and $2H^{\cdot}$, and since we also know that the ionic dissociation of hydrogen takes place without evolution of heat, therefore the 42,200 cals. must be exclusively devoted to the ionic dissociation of chlorine: Cl_2 + aq. = $2Cl'$ aq. + 42,200 cals. As we see, the heat of formation of chlorine ions in solution must be equal to the heat of formation of HCl in solution. And we may say in general that *the heat of formation of any acid in dilute solution is equal to the heat of formation of its anions.* From the heat of formation of their salts, we may deduce the heat of formation of the metallic cations. On dissolving Na in HCl, NaCl is formed with evolution of H and of 57,100 cals. for each molecule of NaCl:

$$Na_2 + 2H^{\cdot}Cl' \text{ aq.} = 2Na^{\cdot}Cl' \text{ aq.} + H_2 + 2 \times 57100 \text{ cals.}$$

Since the $H^{\cdot}$ ions of the HCl on conversion into gaseous H_2 do not develop heat, and the other new products of the reaction are only the $2Na^{\cdot}$ ions (for the chlorine ions already existed in the aqueous HCl), the 57100 × 2 cals. are entirely due to the formation of the $2Na^{\cdot}$ ions. We may generalise and say that *when a metal reacts with an acid to form a salt and free hydrogen,* the heat developed depends only on the character of the metal and not on that of the acid, and corresponds to the heat of formation of the metallic cation.

DEGREE OF DISSOCIATION, EQUIVALENT AND SPECIFIC CONDUCTIVITY. Dissociation becomes more complete as the solution is diluted, and varies with the nature of the substance itself. Since the electric conductivity increases with the number of ions, that is, with the number of dissociated molecules, we may measure the degree of dissociation of a substance in aqueous solution by measuring the electric conductivity, also taking the mobility of the ions into account.

The energy of acids and bases is also the greater the more these substances are dissociated into the corresponding ions, and we may always determine it by means of the electric conductivity. HCl is actually more energetic than H_2SO_4, and this latter is more energetic than acetic acid, because if we take equal volumes of normal solutions of hydrochloric, sulphuric, and acetic acids, and mix them with the same weight of zinc, on collecting and measuring the hydrogen which is developed, it is observed that in equal times much more hydrogen is formed with the HCl, less with the H_2SO_4, and still less with acetic acid.

The velocity of reaction is different for these three acids, and we see that HCl reacts much more energetically than the other two and that different times are required for the evolution of all the hydrogen characteristic of these acids. If we measure the electric conductivities of normal solutions of these three acids, we find that it is much greater in the case of HCl, less for H_2SO_4 and still less for acetic acid, and that the relation between

the electric conductivities of these acids is exactly equal to the relation between their velocities of reaction. But we also know that a solution conducts the electric current the more easily the greater the number of free ions, and the greater energy of reaction of HCl which has a larger number of free ions or of dissociated molecules is thus explained. The strength of bases may also be determined by the electric conductivity of equivalent normal solutions.

In the case of polybasic acids, the dissociation is gradual in the same molecule, thus H_2SO_4 first dissociates into the two monovalent ions $H^{\cdot}$ and HSO_4', and the anion HSO_4' is then dissociated at a later stage into $H^{\cdot}$ and SO_4''.

The degree of dissociation (a) of various electrolytes, for equivalent solutions, is given by the ratio between the molecules which are dissociated into ions and those which are undissociated, and may be deduced in two ways, namely, from the osmotic pressure and from the electric conductivity. We know that acids, bases, and salts in aqueous solution give abnormal osmotic pressures with respect to their molecular weights, deduced by other methods, and we have seen that these abnormalities are due to the dissociation of molecules into ions. Van't Hoff indicated the coefficient which expresses how many times the molecular concentration resulting from osmotic determinations is greater than that theoretically deduced from the chemical formula, by the symbol i. If we now indicate the fraction of dissociated molecules in 1 mol. of a given salt by a, and the non-dissociated portion of the molecules by $(1 - a)$, and if we also know the number, n, of the ions which are able to produce the completely dissociated molecule, then we have $n-a$ free ions, and thus the complete number of molecules and ions together, that is, i, will be : $i = 1 - a + na = 1 + (n - 1)a$, and thus we may also deduce the degree of dissociation, $a = \dfrac{i - 1}{n - 1}$.

Arrhenius, on the other hand, arrived at the degree of dissociation by deducing it from the electric conductivity. He called the *specific conductivity*, k, of an electrolyte the current intensity which is produced when two electrodes of surface 1 sq. cm. are immersed in the electrolyte 1 cm. apart at a potential difference of one volt, and he compared this for different electrolytes, always referred to the same concentration, n, in equivalents per c.c. (normal solutions). (*See* the chapter on Electro-Chemistry for definition of the electrical units.) Then the *equivalent conductivity*, L, is given by the formula $L = \dfrac{k}{n}$. This equivalent conductivity increases on dilution and it tends towards the maximum conductivity, L_0, which corresponds to the complete dissociation of the molecule into ions, that is, when all the ions take part in the transport of the current. It only reaches this value for infinitely dilute solutions, whilst for solutions of certain salts (KCl, NaCl, &c.), this conductivity is reached even for dilutions which are not very large and easily measurable. In these cases the degree of dissociation, a, is given by $a = \dfrac{L}{L_0}$.

On determining the value of a from the osmotic pressure or the corresponding cryoscopic methods and from the electric conductivity, perfectly concordant values are obtained in practice. It has thus been possible to group the various electrolytes according to their degrees of dissociation into *strong electrolytes*, which are more than half dissociated, even in solutions of considerable strength, such as the alkali salts, the acids HCl, HBr, HI, HNO_3, HF, and H_2SO_4, the alkali and alkaline earth bases, the quaternary organic bases (but not ammonia), and into weak electrolytes which are very slightly dissociated, such as the various salts of heavy metals with weak acids, ammonia, the non-quaternary amino-organic bases, and many weak acids, such as sulphydric, hydrocyanic, boric, carbonic, sulphurous, nitrous, hydrochlorous, iodic, and phosphoric acids, and the organic acids.

It is then also found that the conductivity of solutions varies in proportion to the square root of their dilution. Thus, if a solution is diluted four times, its conductivity is reduced by half ; if it is diluted ten times, the conductivity becomes 3·16 times less.

ISOHYDRISM AND IONIC EQUILIBRIUM. The ionic equilibrium in solutions of electrolytes may be influenced by various means and as in the dissociation of gases, for example, of the vapours of PCl_5 into $PCl_3 + Cl_2$, the dissociation is repressed by addition of Cl_2 or PCl_3, so by the addition of an electrolyte to another electrolyte, having a common ion, the dissociation is influenced in a manner which is also regulated by the law of mass action (*see* p. 65).

When two electrolytes having a common ion are mixed, then if the concentration of these ions is equal in the two solutions (*isohydric solutions*), no variation of the degree of concentration will take place even after mixing. But on mixing two acids the degrees of concentration of which are different, the degree of dissociation of both the acids will be lowered, but that of the weaker acid will be influenced much more greatly. The same remarks apply to bases and all weak electrolytes. In general, the further removed two solutions of electrolytes are from being isohydric, the greater will be the conductivity of the mixture compared with that of the original solutions.

In normal solutions of ammonia and acetic acid, the degrees of dissociation are 0·5 and 0·4 per cent. respectively. On adding to the first of these a normal solution of an ammonium salt and to the second a normal solution of an acetate, these values are reduced to 0·0022 and 0·0018 per cent. respectively. We see from this that it is possible to diminish the acid or basic properties of solutions of acids and bases very greatly, and we may thus explain how in presence of much ammonium chloride magnesium salts are not precipitated by ammonia as magnesium hydroxide, and why the precipitation of zinc by means of hydrogen sulphide is prevented if a strong acid is added to the solution of the zinc salt, so that the concentration of the $H^{\cdot}$ ions is increased and consequently the concentration of the sulphur ions of the weak precipitating acid H_2S is decreased. When wool is dyed industrially in a bath acidified with sulphuric acid, the fixation of the dyestuff may be moderated by diminishing the acidity; this diminution of acidity and consequent retardation of the dyeing process is obtained by adding sodium sulphate, which decreases the dissociation of the sulphuric acid, because it augments the concentration of the SO_4'' anions.

MOBILITY OF THE IONS AND TRANSPORT NUMBERS. If we indicate the velocity which a cation acquires for a potential difference of one volt per cm. by u, and the corresponding relative velocity of an anion moving in the positive direction by v, then knowing that the charge of an equivalent ion is always the same, F coulombs (96,540 coulombs per gramme-ion), it is clear that between the electrodes $u.F$ coulombs of positive electricity move each second with the cations and $v.F$ coulombs of negative electricity with the anions, and therefore the total current L_0 which is established will be $L_0 = (u + v).F$ coulomb-seconds or amperes. During this movement of the ions a certain number of cations will depart from the anode, and a certain number of anions from the cathode, so that in the proximity of the electrodes there will be a diminution of concentration by measuring which, per unit of time, we will obtain an expression for the ratio of the velocities of the ions themselves. The ratio of the diminutions of concentration of the ions in the neighbourhood of the two electrodes also represents the ratio $\frac{u}{v}$. If from the variation of concentration of one of the ions which is found in a given time we calculate how many coulombs have been transported by it, and if we compare this number of coulombs with the total number which pass through the electrolyte in the same time, we obtain the so-called *transport numbers*, which may be represented by the fractions $\frac{u}{u + v}$ and $\frac{v}{u + v}$.

For many salts in dilute solution the transport number is found to be about 0·5 (for KCl, for example, 0·497), and this signifies that half of the electric current is transported by the cation and the other half by the anion, and thus the two have the same mobility. The transport number 1 would indicate that the whole of the current was transported by the anion or by the cation only, and this is never actually the case.

Kohlrausch calculated the equivalent conductivity L_0 for dilute solutions of KCl, $L_0 = (u + v)\ 96540 = 130{\cdot}1$, and since we also know that for KCl the transport number $\frac{u}{u + v} = 0{\cdot}497$, it is possible to also calculate the values of u and v, and from these, by taking into account the (maximum) conductivity equivalent, we may deduce the mobility of the ions of other salts.

The mobility of the $H^{\cdot}$ ions, characteristic of acids, is about five times that of the OH' ions, characteristic of bases, and about three times that of the more mobile ions of any other substance, and this explains why on comparing the strong electrolytes the acids and the bases are much better conductors than the neutral salts, even if these latter are largely dissociated, when equivalent solutions are compared. In the case of electrolytes with polyvalent ions, the relations are more complicated, but for elementary

ions in general the mobility is a periodic function of the atomic weight, whilst for complex ions it diminishes more or less regularly with increase of the number of the components of the ion.

At low temperatures all ions tend to acquire the same mobility.

COLOUR OF THE IONS. The metallic cations are those which determine the colour of the solutions of various substances. Thus, for example, the divalent ferrous cation is green, and the solutions of all salts containing divalent iron are also green (ferrous sulphate and chloride, &c.); the trivalent ferric cation is yellow, and all solutions of salts containing trivalent ion are also yellow (ferric chloride, nitrate, &c.).

Ostwald found that the absorption spectra of the various permanganates ($MnO_4'X^{\cdot}$) in equivalent solutions are always the same, and thus this spectrum is due to the anion MnO_4', whatever may be the metallic cation ($X^{\cdot}$) with which it is combined. On the other hand, all ions which are found in colourless solutions have no colour of their own. Such ions are $H^{\cdot}$, $Na^{\cdot}$, $K^{\cdot}$, $Ca^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, SO_4'', ClO_3'', NO_3', F', Cl', Br', I', &c. The ionic constituents of electrolytes do not generally influence one another reciprocally, and their specific characteristics are found in the most varied combinations. Thus Valson has found that the difference of specific gravity between equivalent solutions of NaCl and KCl always remains the same even if the chlorine of the two salts is substituted by other acid residues, and in this way he confirmed that the ions of an electrolyte do not influence one another reciprocally.

IONS AND ELECTRONS. The ions are the so-called vehicles of the electric current and move without expenditure of energy (Clausius and Helmholtz), so that the negative current which transports the anions (Cl', SO_4'', &c.) moves from the negative to the positive pole, that is, from the cathode towards the anode, whilst, on the other hand, the positive current passes from the positive pole (anode) to the negative pole (cathode).

The ions may be considered as minimal quantities of simple or compound substances corresponding to parts or fractions of molecules, and for each gramme-ion and for each valency of these ions, a positive or negative electric charge of 96540 coulombs is present. In the electrolysis of silver salts, we know that for each coulomb 1·1181 mgrms. of silver are separated, and from the recent studies of Plank on the new law of radiation it has been found that one gramme-ion of any substance contains a number of ions equal to $0{\cdot}617 \times 10^{24}$, that is, about half of a quadrillion; that is to say, an ion of hydrogen weighs $1{\cdot}617 \times 10^{-24}$ grm. We can deduce from this that the quantity of electricity accompanying a free monovalent ion is $\frac{96540}{0{\cdot}617 \times 10^{24}}$, that is, $15{\cdot}63 \times 10^{-20}$ coulombs, whilst a divalent ion would have a double charge, a trivalent ion a triple charge, &c. This smallest quantity of electricitiy which is known in the free state and accompanies the smallest quantity of matter (the monovalent free ion) is called the *electron*.

We thus have *negative electrons* which are represented by the symbol $\ominus$ and *positive electrons* represented by the symbol (+), corresponding to the anion and cation of any dissociated substance, whilst in non-dissociated substances the two ions with their opposite charges are united and form the *neutron* $\ominus$ (+). The degree of electrical conductivity of substances is thus dependent on the degree of dissociation of the neutrons. The neutrons of metals, for example, will be strongly dissociated, and this will explain why they are such good conductors, and their rise in temperature during the passage of the current is due to friction between the electrons, because in the solid metal the solvent, which should serve as a sort of lubricant for the movements of the electrons themselves, as is the case in solutions, is lacking.

During electrolysis the ions which arrive at the electrodes separate neutral matter and the electrons which formed the electric charge of the ions are liberated and continue their course, disunited from the matter with which they were at first joined, through the metallic wire of the circuit of the cell. It is not necessary, however, to deny that the last word has not been said on the ultimate nature of electrons.

COLLOIDAL SOLUTIONS ("SOLS" AND "GELS")

We have already seen what important laws may be deduced from the study of *true dilute solutions*, and how van't Hoff established interesting relations between the osmotic pressure, molecular weight, and pressure of the dissolved substances in the gaseous state. We have seen how dissolved substances diffuse easily through the solvent, through other substances which are also in solution, and also through partitions formed of various substances, and more precisely of substances which do not follow the laws of van't Hoff and which are not electrolytes in the ordinary sense, such as we have studied. There are, in fact, substances which yield aqueous solutions but do not exercise any, or scarcely any, osmotic pressure, and thus have a minimal or zero power of diffusion, especially through membranes formed of substances of this same category. On mixing solutions of these two different kinds, they may be easily separated again by introducing the mixture into a dialyser (*see below*), and then that substance only which has a strong power of diffusion will pass through the porous parchment membrane which is immersed in water.[1]

The classical studies of Thomas Graham (1862), which remained forgotten for a long time, have opened up a new horizon in connection with *dialysis* during these later years, by the explanation of certain industrial processes and by new applications which have recently been made and which we will record later. Substances which diffuse through the dialyser often remain behind in the crystalline condition when the solvent is evaporated and re-form the original solution when mixed with the solvent. This process is, therefore, *reversible* and these substances are called *crystalloids;* those which do not diffuse are amorphous when the solvent is separated ; they are analogous to glue and rarely re-form the original solution when mixed with the solvent. This is, therefore, an *irreversible process*, and these substances are called *colloids.*

As the osmotic pressure observed in colloidal solutions is extremely small we may infer that colloids have an extremely large molecular weight, or at least we must admit that they do not form true solutions, but *pseudo-solutions*, or suspensions of finely divided solids or liquids in another liquid. Graham called these pseudo-solutions *sols*, and *hydrosols* if they were formed in water. The substance which separates from a sol on eliminating the solvent, on heating it or on coagulation by other means, was called a *gel*, or a *hydrogel* if the solvent had been water. The phenomenon of the separation of the gel is called *gelatinisation* or *gelification.*

In the case of a very fine suspension of a solid in a liquid, the sol is called a *suspensoid*, whilst in the case of a very fine suspension of a liquid it is called an *emulsoid.* These latter are generally found already formed in nature (egg albumen, milk fat, &c.). Colloids in general may be considered as heterogeneous systems, the phases or components of which may be separated by physical means.

The dialyser (Fig. 33) which serves to separate colloidal from crystalline substances, is formed of a vessel the base of which is closed by a membrane of natural or artificial parchment. The mixture of the above-mentioned substances is poured into this and the instrument is then partially immersed, in the case of hydrosols, into a vessel containing water, which is gradually renewed. After a certain time the crystalloid substance will have passed almost completely into the external water, and the aqueous colloidal solution will remain inside.

Hydrosols have all the external appearance of true solutions because they appear to be perfectly homogeneous, may be filtered without leaving any solid residue on the filter, and do not even show any discontinuity of the mass under the microscope. All the same they must be considered as heterogeneous systems for the following reasons : On allowing a colloidal solution to stand for a long time in a tall vessel the solution becomes more concentrated below, sometimes even forming a sediment, and becomes more dilute above ; that is to say, through the influence of gravitation, one portion

[1] This phenomenon of diffusion through a semi-permeable membrane cannot be considered as an exclusively mechanical function in which the membrane merely acts as a sieve and allows the smaller molecules to pass through its pores and not the larger ones. We are obliged to admit, on the contrary, a species of free selection by the membrane of the various substances which it allows to pass, by first dissolving them independently of their molecular size. Graham already showed this in the case of gases. Thus, if a mixture of hydrogen and carbon dioxide is enclosed in a soap-bubble, the latter diffuses through the wall of the bubble because it is soluble in soap, whilst hydrogen does not diffuse although its molecules are much smaller, because it is only very slightly soluble

of the colloid is carried to the bottom, which would not be the case for a true solution. Metals have been pulverised under water by electrical means and hydrosols resulted. In this case, the idea that the metals are dissolved is excluded *a priori*. Finally, colloidal solutions offer a great resistance to the passage of the electric current, and the small conductivity which they show is not due to a dissociation into ions, but entirely to the migration of a part of the colloid towards one of the electrodes. If they were true solutions, the boiling- and freezing-points would be different from that of the solvent, which is not the case.

On adding an electrolyte, for example an acid, to a hydrosol, a hydrogel is easily formed, that is, the sol is gelatinised, and this occurs with more or less ease in strict relationship with the dissociation constant of the electrolyte. Thus the action of salts on hydrosols is analogous to that which they produce in fine mechanical suspensions, as is known in the case of kaolin and ultramarine suspended in water. A colloidal solution of silicic acid is immediately coagulated by the addition of minimal traces of soda or by a few bubbles of carbon dioxide.

But the material demonstration that hydrosols are mechanical homogeneous suspensions can be effected by optical examination of these pseudo-solutions as the Tyndall phenomenon[1] can be produced; and by means of the ultra-microscope[2] we are able to see particles of a diameter of 5 $\mu\mu$ (that is, five-millionths of a millimetre). Molecules of medium size have a diameter of about 0·6 millionths of a millimetre, and are, therefore, not visible under the ultra-microscope.

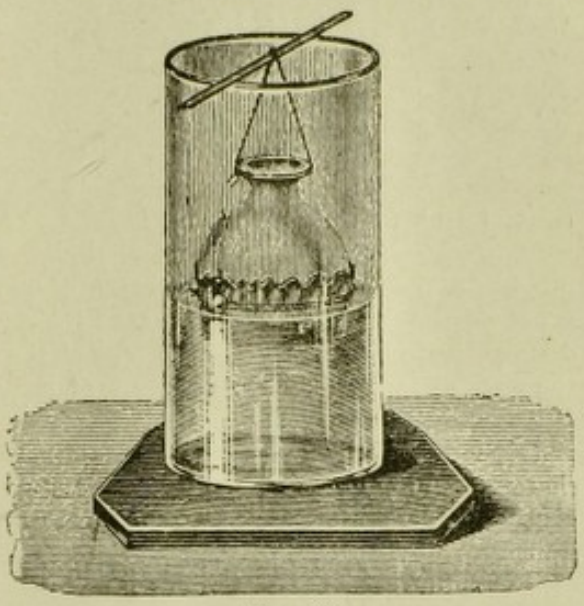


FIG. 33.

A colloidal solution containing 5 mgrm. of gold per c.c. contains about one thousand million particles of suspended gold per cu. mm., that is, one trillion particles per c.c. The total surface of these particles is 625 sq. ms. per c.c., which explains the *catalytic action* of colloidal solutions.

The small suspended particles of hydrosols can be clearly seen with the ultra-microscope. They are endowed with a rapid zigzag movement similar to the *Brownian movement*. There are, however, other hydrosols, the suspended particles of which are still smaller than the limiting size which can be detected by the ultra-microscope, namely, less than 5 $\mu\mu$, so-called *amicroscopic particles*. Lobry de Bruyns and van Calcar subjected colloidal solutions to centrifugation at the highest speeds, and found that the suspended particles

[1] If a luminous ray is concentrated with a lens into a true solution, or also into air freed from atmospheric dust by Spring's process, then on observing the liquid in a direction perpendicular to the direction of the ray, this latter will be invisible. But if, on the contrary, there are particles in the liquid which are suspended and not dissolved, even though they may be extremely small, these are illuminated by the luminous ray and disperse the light in every direction. In this case the observer of the liquid will perceive light reflected from these luminous points, and this light will also be polarised. This is the Tyndall phenomenon. The suspended particles of colloidal solutions are not visible in this manner to the naked eye, but in 1903 Siedentopf and Zsigmondy reproduced the Tyndall phenomenon under the microscope, and the colloidal particles then rendered visible are called ultra-microscopic particles, and this study is now called ultra-microscopy.

[2] The ultra-microscope of Siedentopf and Zsigmondy is an ordinary microscope under which an ordinary transparent object is observed, which, however, is illuminated laterally by powerful light rays. If the object is a true solution, and therefore perfectly clear, none of the rays will penetrate into the objective, and therefore the field appears perfectly dark to the eye, as the illumination is entirely lateral. But if there are still solid particles in the solution, these give rise to groups of luminous rays and show refraction phenomena, and thus certain luminous rays from the particles pass through the objective and arrive at the eye. The appearance is thus produced of a dark field sprinkled with luminous points, much like a starry sky, which denote the existence of these particles which could not be distinguished by any other means. In fact, an analogous phenomenon is produced to that which is observed when a ray of sunlight enters a dark or only slightly illuminated room. The whole of the luminous ray appears to be filled by myriads of mobile corpuscles. These are due to the dust of the atmosphere, which renders a partially luminous ray visible to our eyes by reflection, whilst in ordinary cases, when regarded by transmitted light from a window, we do not see them. The size of these particles varies from $\frac{1}{100000}$ to $\frac{1}{1000000}$, or even to $\frac{5}{10000000}$ of a mm. These particles possess Brownian movements, the cause of which is not known but which appear to some to present a case of perpetual motion, and thus of an exception to the principle of the conservation of energy

accumulated at the circumference and not in the centre, which is a further confirmation of the heterogeneous nature of sols.

Since Rayleigh has found that the light reflected from very small material particles is composed of light of very short wave-lengths, Weimarn (1907) believes that still smaller particles, less than $5\mu\mu$ in size, could be detected by the ultra-microscope by illuminating the field by light rich in ultra-violet rays (by means of fluorescent screens, mercury vapour lamps, or cadmium lamps).

Bredig and Billitzer found that the particles of hydrosols also carry an electric charge, though this is much smaller than that of ions. On passing an electric current through a hydrosol the particles will be carried towards the anode or the cathode, according to their charge, in spite of the great resistance afforded by the solution. The difference of electric potential between the suspended particles and the liquid medium in which they are present is in strict accordance with the surface tension of the liquid or medium which holds them in suspension. This potential difference can be greatly influenced by the addition of certain ions or electrolytes, as was experimentally shown by Hardy and Billitzer among others. Thus, if an electrolyte is added to a hydrosol a hydrogel is precipitated, and this absorbs a definite portion of the ions of the electrolyte, namely, a portion of opposite charge to the particles of the hydrosol itself, forming a neutral gel.[1]

Lottermoser found that a given hydrosol is only stable on condition that a certain number of ions are present by means of which equilibrium is maintained. Therefore it is not possible to completely separate the crystalloid from a colloidal solution by means of dialysis, because a portion of the ions of the former serves to maintain the colloid itself in the state of hydrosol. The presence of this part of the ions in the formation of a hydrosol also explains the electric conductivity of the latter, however small it may be. Colloidal metals are generally carried to the positive pole, therefore they carry a negative electric charge. Aluminium and iron hydroxides, on the other hand, are carried to the negative pole, and therefore carry a positive charge. It has been found possible in practice to even transform a hydrogel into a hydrosol by means of a solution of ions of definite concentration, corresponding to that necessary for the formation of the hydrosol. Thus Graham already succeeded in transforming (*peptonising*) 200 grms. of a gel of silicic acid into a hydrosol by means of a solution of one part of NaOH in 10,000 parts of water by heating for sixty minutes at 100°. In the same way ferric hydroxide or gelatinised aluminium hydroxide may be peptonised with small traces of hydrochloric acid.

If two hydrosols carrying equal electrical charges of opposite sign are mixed, they are mutually precipitated. This also explains the great gelatinising power of certain salts with polyvalent cations, even when present in small quantity, on negatively charged hydrosols. Salts with monovalent cations need to be added in much larger quantities, on the other hand, in order to produce the same gelatinisation. Certain polyvalent cations have a precipitating power (separation of gel) a thousand times greater than that of monovalent cations. If hydrosols of equal electrical charge of the same sign are mixed no gelatinisation takes place, but the mixture has properties different from those of the individual components, as may be shown by their different behaviour with regard to electrolytes. In fact, the properties of that component which is more stable with respect to electrolytes predominates in the mixture, and thus, whilst the red gold hydrosol becomes blue on adding an electrolyte, when mixed with the hydrosol of stannic acid the addition of an electrolyte still causes the separation of the gel, but the properties of the stannic acid are changed and not that of the gold, which retains its red colour in the gel. We may thus say that the stannic acid hydrosol has a protective action on that of gold, and similarly certain organic hydrosols (false hydrosols) which are not gelatinised by electrolytes, when mixed with true hydrosols, which are gelatinisable, exercise a protective action to such an extent that the gelatinisation of the two by the addition of electrolytes is prevented.

[1] Billitzer believes that each suspended particle of a hydrosol is accompanied by a definite quantity of water in a state of latent dissociation (hydrolysis), and according to whether this discharges $H^{\cdot}$ or OH' ions into the solution we have particles of positive or negative character. The actual precipitation of hydrosols in the form of gels by the action of electrolytes appears to be due to the union of cations or anions of the electrolyte with the anions OH' and cations $H^{\cdot}$ accompanying the particles of the hydrosol to form neutral molecules. But free ions of $H^{\cdot}$ or OH' remain, which do not combine, and thus the solution acquires an acid or basic character. If we have, for example, a hydrosol with negative particles, its (OH') anions will unite with the cations of the electrolyte which is added (for example, a salt) and the neutral gel will separate; but free $H^{\cdot}$ cations of the hydrosol will remain after hydrolysis has occurred, and the liquid will acquire an acid reaction. This fact has been actually confirmed in practice in the case of various reactions of colloidal solutions.

These substances are called *protective colloids*,[1] and are capable of transforming irreversible inorganic colloids, that is, those of which the gels are not retransformable into sols, into reversible colloids, and use is made of this fact in medicine in order to retain in solution certain colloids which greatly affect the human organism (collargol, &c.).

The general conditions which are favourable to the formation of hydrosols may be summarised as follows. In solutions in which hydrosols are to be formed, polyvalent ions of contrary charge should be absent, and the concentration of the monovalent ions should not exceed the limiting value above which they cause the formation of a gel, that is to say, in general very dilute solutions are required. Other hydrosols may be obtained by acting on colloids with solutions of electrolytes which give a reversible precipitate, that is, one capable of being reconverted into a hydrosol by the simple action of water. The use of protective colloids facilitates formation of hydrosols, even if the concentration limit of the electrolytes which are present is exceeded.

Bredig, and later Billitzer, have obtained hydrosols of the noble metals by dispersing them by means of the electric spark, under water, and the sols of the other metals by employing indifferent organic solvents (organosols). In these latter cases it is not possible to obtain hydrosols because these metals decompose water when so finely subdivided.

In order to prepare a hydrosol of gold, Bredig's arrangement may be used (Fig. 34). In a vessel, *S*, of about 100 c.c. capacity, cooled externally with ice, purest distilled water is placed, to which a trace of sodium hydroxide (0·01 grm. of normal NaOH) has been added ; 2 cms. below the surface of the water are two electrodes of gold wire, *G*, of about 1 mm. diameter ; the points of these are brought together, a current of 8 to 10 ampères at 100 volts is passed, and they are then separated from one another by 1 to 2 mm., moving them in such a manner that small voltaic arcs are formed which give a special sound. It is more especially the cathode which is then dispersed, forming extremely fine particles which pass through filters and give a bright red solution which remains unchanged on standing even for two years.

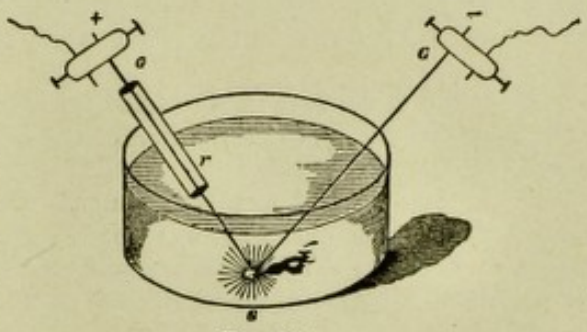


FIG. 34.

A colloidal solution of gold is more easily obtained by dissolving, for example, 15 mgrms. of crystalline gold chloride and 0·6 grm. of potassium bicarbonate in 125 c.c. of pure water distilled through a silver coil. On boiling this liquid and then adding 0·01 c.c of commercial formaldehyde, an intensely red solution of colloidal gold is obtained, which is very sensitive to electrolytes. Colloidal solutions of ferric hydroxide are obtained by dissolving the hydroxide in ferric chloride and then eliminating the latter by dialysis. A colloidal solution of silicic acid may also be obtained by treating a concentrated solution of sodium silicate with hydrochloric acid and then eliminating the sodium chloride and excess of hydrochloric acid with water in a dialyser.

Ethereal solutions of the alkali and alkali earth metals are variously coloured (blue, violet, green, &c.) according to the size of the particles.

The theoretical and practical applications which have arisen from the study of colloidal solutions are much more numerous and important than might appear.

The far-famed production of ruby glass is a phenomenon of this kind. If to a glass paste which is not very hot, but which is molten or half molten, and which may be considered as a solvent with almost infinite viscosity, a gold salt (chloride) is added, it is decomposed, and very fine (amicroscopic) particles of gold remain in the glass. If this is cooled rapidly

[1] The casein in milk is present as an irreversible hydrosol, and its coagulation by means of an acid or of heat may be altered or avoided, and it may be produced in more or less fine and subdivided flocks, by the presence of reversible or protective colloids, such as gelatine, gum, albumen, &c. In cow's milk the ratio of the irreversible casein to the reversible albumen is as 3·02 : 0·53. The larger quantity of reversible albumen in human milk (0·75 : 1·00) renders its coagulation eight times more difficult than that of cow's milk, and the finer coagulum which is obtained explains its greater digestibility and assimilation in the stomach of a child, and also explains why cow's milk cannot be substituted for human milk with impunity for the artificial feeding of infants without suitable treatment of the former.

Zsigmondy has called the number of milligrammes of a protective colloid which are necessary to prevent or hinder the precipitation of 10 c.c. of the red gold hydrosol by the addition of 1 c.c. of a 10 per cent. solution of sodium chloride, the *gold number*.

a transparent, colourless glass is obtained. If the glass is now heated to a given temperature in such a manner that it becomes more fluid, then these gold particles, having less friction to overcome, are enabled to move and to reunite to larger particles, thus imparting to the glass a whole series of successive colorations from violet, through purple to ruby, red, pink, &c., and this has been used in practice to obtain the various coloured glasses, even with as little as 0·05 per cent. of gold.

If the glass paste is heated to even higher temperatures, through a mistake of the operator in not hitting the exact point, then the particles unite to form larger and easily visible aggregates which give to the glass the true reflex of metallic gold. In the case of glasses rendered milky by calcium fluoride and of enamels coloured by means of metals, similar phenomena occur.

The ripening of the silver bromide-gelatine plate in photography is also due to a slow regrouping of the particles of bromide which is indispensable in order to obtain the maximum sensitiveness to light. In ceramics the ripening of the paste of kaolin or clay, which renders it more plastic and sometimes takes three months, is due to the action of alkaline hydroxyl ions which peptonise the small quantity of colloidal organic substances derived from the raw materials and from the water with which the paste is prepared.

In connection with the important question of the purification of effluent waters, it is known to-day that these generally contain extremely fine suspensions of electro-negative character and are therefore easily precipitated by the addition of polyvalent cations, for example, of ferric salts. (In certain towns this system has been applied, *see* Water.)

The action of bacteria in the biological process of sewage purification (*see this*) appears to be partially due to the formation of colloids of opposite electric charge to that of the organic suspensions in the water, so that they are reciprocally precipitated.

In the formation of metallic filaments for the manufacture of incandescent electric lamps it has been found that tungsten, for example, which melts at 2800°, is insufficiently ductile to render it possible to prepare sufficiently fine and regular filaments. By employing, on the contrary, tungsten separated from a colloidal solution regular filaments of a diameter of 0·03 mm. are easily obtained.

The setting and hardening of cement is to-day explained by the formation of gelatinised silica and alumina which surround the crystals of calcium hydroxide and aluminate, thus forming a compact mass which protects these from the action of water and of ordinary reagents.

In agricultural soil many phenomena of colloidal character also occur.

Many phenomena connected with the tanning of hides, the dyeing of textile fibres, &c., also belong to the class of colloidal activities. The life of vegetables and animals is also largely based on reactions between colloids and crystalloids in the cell. Amongst catalytic actions of colloids, we may mention that of a colloidal solution of platinum which causes the combination of H and O, even in the cold. The catalases of the blood, which are colloidal enzymes, cause the passage of the oxygen from the oxyhæmoglobin into the tissues, where it causes the decomposition of hydrogen peroxide liberating oxygen, and by means of this latter reaction we may determine the richness of the blood in catalases and decide if the organism is in a normal condition or not. The same fermentation effects (catalysis) have been obtained by Bredig with colloidal solutions of platinum, to such a degree that he called colloidal metallic solutions inorganic ferments, and they produce numerous and important catalytic phenomena. He also found that the same substances which have a poisonous action on the animal organism, such as hydrocyanic acid, hydrogen sulphide, corrosive sublimate, arsenic, &c., also behave as poisons on colloidal solutions, completely paralysing their action.

MATTER IN THE SOLID STATE

It is supposed that the molecules of solids are placed very closely to one another compared with those of liquids, and that their distance and relative position always remain the same without any movement of the one over the other, though they perhaps remain endowed with oscillatory movement. The sum total of the kinetic energy of these molecular movements is less than that in the same substances in the liquid state; therefore on lowering

the temperature of liquids, and so abstracting energy, they have a tendency to solidify.

Simple or compound solid substances are often characterised when pure by their melting-point, which is determined in various ways which are described in treatises on practical physics, and will be explained in the second volume for organic substances.

SPECIFIC GRAVITY OF SOLIDS

The specific gravity of solids is the relation between the weight of a given volume of the solid substance and the weight of an equal volume of water at 4°.

There are many ways of determining the specific gravity: by measuring the volume of water which a given weight of a solid displaces when immersed in the liquid contained in a graduated vessel, or by determining the weight of water or other liquid of known specific gravity which is displaced, for example, in a filled pyknometer, by a given weight of the solid substance under examination. This method cannot be used when the solid substance is soluble or if it sucks up the liquid into its pores when immersed (water, oil, alcohol, &c.).

In such cases so-called volumeters are employed, which are based on the dilatation of air contained in a given volume before and after the introduction of the body under examination.

A fourth method consists in the immersion of the solid substance in any liquid to which soluble substances of greater density are added until a solution is obtained in which the body under examination just floats. In order to then know the specific gravity of the solid substance, all that is necessary is to determine that of the solution (*see* p. 72), which will be indentical with the former. This method is exact, and is not only employed in laboratories, but also commercially, in order to know, for example, whether eggs are fresh, if potatoes are ripe, and in order to know their exact contents of starch, &c., because in such cases these bodies have a characteristic and sufficiently constant density.

SPECIFIC HEAT OF SOLID SUBSTANCES

In order to heat the same weight of different substances to the same temperature, different quantities of heat are required. On heating 1 kilo of lead and 1 kilo of zinc to 150° and then immersing them separately in equal volumes of water, for example, one litre, the water in which the zinc is immersed becomes much hotter. The physical unit for heat measurements is the calorie (*see* Thermochemistry).

The *specific heat* of a substance is defined as the quantity of heat required to raise the temperature of 1 kilo of the substance from 0° to 1°.[1] It is determined by means of very exact forms of apparatus called calorimeters, in the following manner:

The weighed substance is heated to a definite temperature and allowed to fall into the calorimeter (*see* chapter on Carbon and Combustibles), which contains a measured quantity of water of which the initial temperature is noted. The water is stirred, and when its temperature no longer rises, the rise of temperature which has occurred is read on the thermometer, and by then correcting results for the constant quantity of heat absorbed by the calorimeter, all the data for calculation of the specific heat are obtained.

In 1818 Dulong and Petit found, by a long series of determinations, that the specific heat is smaller the larger the atomic weight of elementary substances, and discovered the following law which bears their names: *the specific heats of solid elements are inversely proportional to their atomic weights;* that is to say, the atoms of the solid elements have the same thermal capacity; and thus, on multiplying the specific heat C by the atomic weight A,

See Table on following page.

we always obtain a constant equal for all the elements. The following table completely explains and confirms this law :

		Iron	Copper	Silver	Iodine	Gold	Bismuth
Specific heat (C)	=	0·114	0·095	0·057	0·054	0·032	0·030
Atomic weight (A)	=	55·9	63·6	108	127	197·2	208·5
Atomic heat ($C \times A$)	=	6·40	6·00	6·15	6·80	6·31	6·20

As we see here, the specific heat of elements diminishes as their atomic weight increases, and the product of the atomic weight (A) and specific heat (C) is almost constant. This constant, which is called the *atomic heat*, has been found by means of many direct determinations to have a value approximating to 6·4.

This law is demonstrated sufficiently well by the very simple experiment illustrated in Fig. 35. Two rings of equal weight of zinc, *a*, and of lead, *a*, weighing, for example, 1 kilo, are heated to the same temperature in an oven and then immersed in two beakers containing equal quantities of water ; this will then be heated to different temperatures. This difference of temperature is easily made evident by immersing in each of the beakers of water a thermometer, formed of a test-tube containing a little coloured liquid at the bottom into which a long glass tube, secured by a stopper, dips. The hotter water causes the air contained in the chamber of the one improvised thermometer to expand more than that in the other, and the coloured liquid will therefore rise to a greater height in the tube. In this case the thermometer will naturally give a larger indication in the case of the zinc, because the atomic weight of this is less, and the specific heat is, therefore, greater. If, on the other hand, quantities of zinc and of lead proportional to their respective atomic weights are taken, the water in the two vessels will be heated to an equal extent.

If the atomic heat is constant for all the elements, then we have a new method for determining the atomic weights of the solid elements by

SPECIFIC HEAT OF VARIOUS SOLIDS (WATER = 1).

Substance	Temperature of experiment	Specific heat	Substance	Temperature of experiment	Specific heat
Aluminium	from 15°–185°	0·2189	Selenium, amorphous	21°–57°	0·1125
Antimony	,, 0°–100°	0·0486	Silver	0°–100°	0·0559
Lead	,, 20°–100°	0·0304	,,	at 700°	0·0590
,, liquid	at 360°	0·4096	Zinc	20°–100°	0·0931
Calcium	0°–100°	0·1804	,,	300°	0·1040
Chromium	0°	0·1039	Tin	20°–100°	0·0551
,,	100°	0·1121	Various bronzes	—	0·1043 / 0·0874
Iron	23°–100°	0·1162			
Cast iron	0°	0·1050	Brass	—	0·0743 / 0·0873
,, ,,	75°	0·1136			
Gold	0°–100°	0·0316	White metal	—	0·0946
Potassium	− 78 to + 23°	0·1662	Alumina, Al_2O_3	0°–100°	0·1879
Cobalt	10°–100°	0·1067	Lead oxide	20°–50°	0·0553
,,	at 800°	0·1845	Iron oxide, Fe_3O_4	24°–100°	0·1678
Coal	24°–68°	0·2040	Sodium hydroxide	0°–98°	0·780
Wood charcoal	0°–100°	0·1935	Quartz	12°–100°	0·1881
Graphite	10°	0·1604	Rock salt	0°	0·2146
,,	200°	0·2966	Iron sulphide, FeS_2	0°–100°	0·1459
,,	977°	0·4670	Gypsum, crystallised	0°	0·254
Diamond	10°	0·1128	Sodium sulphate	17°–98°	0·2312
,,	200°	0·2730	Potassium nitrate	14°–45°	0·232
,,	985°	0·4589	Marble	22°–100°	0·212
Copper	20°–100°	0·0936	Mica	20°–100°	0·2070
Magnesium	18°–99°	0·2460	Ice	− 78 to 0°	0·4627
Nickel	20°–100°	0·1084	Mirror glass	10°–50°	0·1860
,,	500°	0·1233	Portland cement (clinker)	28°–40°	0·186
Platinum	18°–100°	0·0324	,, ,, (set)	28°–30°	0·271
,,	100°	0·0409	Cellulose	—	0·366
Mercury	20°–50°	0·0331	Paraffin	0°–20°	0·694
,,	250°	0·0321	,,	52°–55°	0·700
Sulphur, rhombic	17°–45°	0·1630	Wool, dried	—	0·393
,, liquid	119°–147°	0·2346	,, + 11 per cent. water	—	0·459
Selenium, crystallised	22°–62°	0·0840			

simply determining their specific heat, because $A = \frac{6{\cdot}4}{C}$, and knowing the atomic weight of an element, we are also in a position to know its specific heat, because $C = \frac{6{\cdot}4}{A}$.

Regnault confirmed the law of Dulong and Petit in most cases by a long series of experiments from 1840 to 1855. He observed that silicon, boron, and carbon do not actually follow this law and give very low atomic heats. This abnormality could not be explained for some years and these elements were considered as true exceptions, but in 1875 H. F. Weber, of Zürich, found an explanation for this exceptional behaviour. He found that the specific heat of these three elements varies greatly with the temperature at which the determination is carried out and that the atomic heat increases on elevating the temperature. Thus whilst at 10° carbon showed a specific heat corresponding to an atomic heat of 1·35, at 1000° the atomic heat is 5·6 and is thus very near to the thermal constant, 6·4. The same fact was demonstrated for boron and silicon at 1200°.

It has now been clearly shown that the specific heat of solid and liquid substances diminishes greatly with diminution of the temperature and tends to a value approximating to zero at the absolute zero of temperature.

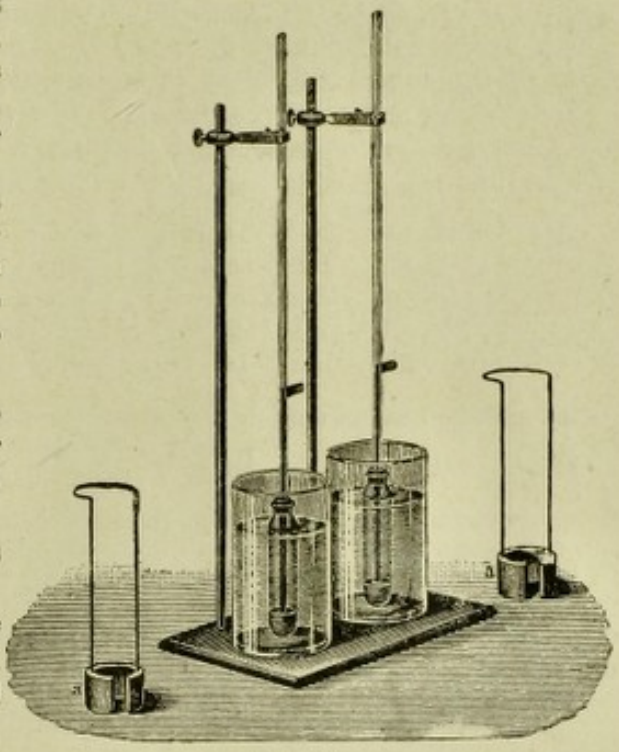


Fig. 35.

In 1831 Neumann found that stoichiometric or equimolecular quantities of compounds which have analogous chemical composition have equal thermal capacities (molecular heats), thus, for example, the metallic perchlorates ClO_4Me and the permanganates MnO_4Me, the metallic nitrates NO_3Me, and the metaphosphates PO_3Me, &c., where Me indicates the atom of a metal.

Joule in 1844 and Woestyn in 1848 showed that the thermal capacity of chemical compounds (molecular heat) is equal to the sum of the thermal capacities of their components (or atomic heats), and this was confirmed by Regnault and Kopp. This law obviously includes that of Neumann.

Thus the molecular heat ($C \times M$) of a compound is equal to the calorific constant multiplied by the number of atoms which the compound contains : $C \times M = 6{\cdot}4 \times N$, where N is the number of atoms and M the molecular weight. This is fully confirmed by experience, as is seen in the following examples :

I. Specific heat of PbI_2 (lead iodide) = 0·0427 ; molecular weight (M) = 459·4 ; number of atoms = 3

II. „ „ $PbBr_2$ (lead bromide) = 0·0533 ; „ „ „ = 365·9 ; „ „ = 3

III. „ „ $PbCl_2$ (lead chloride) = 0·0664 ; „ „ „ = 277·1 ; „ „ = 3

The specific heat being inversely proportional to the molecular weight, $C \times M$ = constant (molecular heat).

In the three examples cited above, we in fact find almost equal molecular heats, namely, I = 20·1 ; II = 19·9 ; III = 18·4.

Knowing the molecular constant or molecular heat, we may deduce the atomic heat

by dividing it by the number of atoms, and in our case, by dividing by 3, we obtain, I = 6·70 ; II = 6·67 ; III = 6·13. But we may also calculate the atomic heats of these elements indirectly without direct experimental determination by using the molecular heats and the known atomic heats of one of these elements.

Thus, if from these molecular heats we substract the atomic heat of lead which is known to be 6·5, there remains in the case of I, 13·6 ; II, 13·40 ; III, 11·90, which are the atomic heats of two atoms of I, Br, and Cl.

On now dividing these by 2, we obtain, I = 6·8 I ; II = 6·7 Br ; III = 5·95 Cl.

From direct control determinations, the values iodine = 6·86 and bromine = 6·74 are obtained ; these values are in sufficiently close accordance with those indirectly deduced from the molecular heats.

In 1864 Kopp found that the atomic heat of the free elements is not always equal to that of the same element contained in various chemical compounds. Thus, in the solid compounds the atomic heat of carbon is always about 1·8, that of hydrogen 2·3, that of boron 2·7, of berillion 3·7, of silicon 3·8, of oxygen 4, of sulphur 5·4, phosphorus 5·4, &c. Taking these values into account, we can equally well determine the atomic weights of the elements if we know the specific heat of a chemical combination.

A practical example will suffice to illustrate the method of determining the atomic weight of an element, for example, of calcium, by the method of specific heats. Analysis shows that 1 kilo of calcium carbonate, which has a thermal capacity of 0·202, is composed of 0·400 kilo of calcium + 0·120 kilo of carbon + 0·480 kilo of oxygen. The atomic heat of carbon in combination is 1·8, and dividing this value by the atomic weight we obtain as the specific heat of carbon $\frac{1·8}{12} = 0·15$, and therefore the thermal capacity of 0·120 kilo of carbon will be $0·120 \times 0·15 = 0·018$. For oxygen, with an atomic heat of 4 and an atomic weight of 16, we arrive at the specific heat $\frac{4}{16} = 0·25$, and the thermal capacity of 0·480 kilo of oxygen will be $0·480 \times 0·25 = 0·120$, and now deducting the thermal capacities of carbon and of oxygen (0·018 + 0·120 = 0·138) from the thermal capacity of 1 kilo of calcium carbonate = 0·203, we have the thermal capacity of 0·400 kilo of calcium = 0·203 − 0·138 = 0·065, and thus the specific heat of calcium will be $\frac{0·065}{0·400} = 0·162$. Having thus indirectly found the specific heat of calcium in combination, and knowing that calcium being a metal will certainly have a normal atomic heat of about 6·4, we may deduce the atomic weight of calcium by dividing the atomic heat by the specific heat, that is, $\frac{6·4}{0·16} = 40$.

By the analysis of many calcium compounds, its equivalent has always been found to be 20·05, and since we know that the atomic weights are equals or multiples of the equivalents, therefore the atomic weight of calcium will be 40, that is, double the equivalent.

The method of determination of atomic weights by means of specific heats is now very little used, because there are so many other methods which are more exact and convenient, but this method may always be employed as a check and also for substances which cannot be evaporated or dissolved. The law of Dulong and Petit is fairly exact for atoms which have an atomic weight greater than 35.

MATTER IN THE CRYSTALLINE STATE[1]

ISOMORPHISM. Before 1800 the law of Hauy was generally believed, which said that a given substance corresponded to a given crystalline form, and that different substances had different crystalline forms, but in 1798 Klaproth showed that arragonite, which

[1] Nicola Steno in 1669 was the first to note the regularity and constancy of the angles between the faces of a crystal, and was followed later by Romé de l'Isle in 1783, who was the first to adopt exact instruments for measuring

is rhombic, and calcite, which is hexagonal, have different crystalline forms, although they have the same chemical composition, $CaCO_3$. Hauy endeavoured to explain this fact by attributing it to impurities in these substances, but in 1807, Thénard and Biot showed that there is absolutely no chemical difference between arragonite and calcite (calc-spar). Numerous substances of different chemical composition and the same crystalline form were found later, and in 1815 Fuchs advanced the idea that in the same crystalline form certain elements can be replaced by others. It was only through the work of Mitscherlich (1820–1823) that light was thrown on this question, and his numerous and exact experiments showed with certainty that compounds of analogous chemical composition have the same crystalline form, that is to say, are *isomorphous*. But a given chemical substance may also crystallise in more than one system (according to the conditions of temperature, concentration, &c.), and such substances are spoken of as *polymorphous*—thus calcium carbonate is *dimorphous*.

Through the phenomenon of isomorphism the possibility thus arises of controlling the molecular weight or chemical formula of a given compound when the formula of an isomorphous compound is known. Generally speaking, isomorphous compounds contain the same number of atoms or groups of atoms which are equivalent to these.

By means of the conception of isomorphism, we may consider as the atomic weight of an element that quantity which is equivalent to or may substitute the atom of another element in their respective isomorphous compounds. In the case of calcium, for instance, which does not yield volatile products, we may deduce its atomic weight by means of the isomorphism of many of its compounds with analogous compounds of magnesium, and those atomic weights of calcium, barium, and strontium have been accepted which express the quantities of these metals which are able to replace 24·4 parts of magnesium, that is, an atom of magnesium, Mg.

Isomorphous substances may be superposed in layers in the formation of a single individual crystal, and thus, if a white octahedral crystal of potash alum is placed in a solution of chrome alum with suitable precautions of temperature, concentration, &c., it continues to enlarge homogeneously, and we thus obtain a new, coloured, reddish layer formed by the enlargement of the same octahedron. We may invert the operation, superposing the white layer of potash alum and may so superpose other strata of various other isomorphous alums.

We here give the formulæ of a series of isomorphous alums which have the same crystalline form :

Potassium aluminium sulphate	$= AlK(SO_4)_2 + 12\ H_2O$
Sodium ,, ,,	$= AlNa(SO_4)_2 + 12\ H_2O$
Ammonium ,, ,,	$= Al(NH_4)(SO_4)_2 + 12\ H_2O$
Potassium ferric sulphate	$= FeK(SO_4) + 12\ H_2O$
Potassium manganese sulphate	$= MnK(SO_4)_2 + 12\ H_2O$
Potassium chromium sulphate	$= CrK(SO_4)_2 + 12\ H_2O$

By analysing these alums we may deduce the atomic weight of the element which replaces another element in an alum by relying on the analogy of the formulæ of the various alums.

It is not very easy to decide by their external appearance whether two substances or two crystals are isomorphous. A safer opinion may be arrived at by mixing the two substances together and then crystallising them. We should then be able to separate so-called *mixed crystals*, that is, crystals of a definite shape, but which combine the two substances simultaneously in varied proportions, the particles of which are not separable by any mechanical means and are not individually perceptible, even when finely crushed. Also on melting solid isomorphous substances together mixed

angles. Hauy, from 1781 to 1801, studied the relations between the angles of a crystal and those of the faces with regard to its axes, and he established the law that each substance has a definite crystalline form and that substances of different composition have different crystalline forms.

The path of modern crystallography was first pointed out by Weiss in 1809, who established rational conceptions regarding the axes and referred the various crystalline forms to these. Various mathematicians, and more especially F. Neumann, perfected and developed these conceptions, and arrived at six fundamental crystalline systems to which all the innumerable crystalline forms which are known to-day are referred, and these studies compose the science of crystallography (*see* succeeding Note).

crystals separate. Van't Hoff called the substances of which these mixed crystals are composed *solid solutions*, on account of the analogy which exists between them and ordinary liquid solutions, although the cryoscopic laws cannot be applied to them because the pure solvent does not separate as ice, as is the case in ordinary dilute solutions.

Potassium perchlorate, the formula of which is well known to be $KClO_4$, is isomorphous with potassium permanganate, and if we wish to determine the atomic weight of manganese we commence by determining the equivalent of manganese in various substances. This is found to be 55 ; and in all analyses potassium permanganate is found to contain 39 parts of potassium (one atom) corresponding to 64 parts of oxygen (four atoms). Knowing that it is isomorphous with potassium chlorate, the formula of the permanganate must be $KMnO_4$, that is, the equivalent 55 corresponds to a single atom of manganese, and thus the atomic weight of the latter will be 55, and not a multiple of this number.

From the study of isomorphism, Roscoe was enabled to find the atomic weight of vanadium ; and it was possible to deduce with certainty the formula Fe_2O_3 for iron oxide on account of its analogy with chromium oxide, which certainly has the formula Cr_2O_3.

There are certain substances which have perfectly analogous chemica composition, but which do not crystallise in the same system when they are pure. Thus, for example, magnesium sulphate when pure always crystallises in rhombic prisms of $MgSO_4.7H_2O$, whilst pure ferrous sulphate always crystallises in monoclinic prisms, $FeSO_4.7H_2O$.

These substances, however, when mixed in solution have the property of forming mixed crystals containing the two substances. If magnesium sulphate preponderates in the solution these are exclusively rhombic prisms, but when the ferrous sulphate predominates, the crystals are exclusively monoclinic prisms. This important phenomenon is called *Isodimorphism*, and such substances are called *Isodimorphous*.

Isodimorphism has to-day lost its former importance for the determination of atomic and molecular weights, because other much more convenient, exact, and certain methods have been discovered. The isodimorphism of certain compounds has even led previous workers astray. Thus calcium carbonate, $CaCO_3$, which, as we have seen, is dimorphous, presents the same crystalline form when in the state of calcite as sodium nitrate, $NaNO_3$, and when present as arragonite has the same form as potassium nitrate, KNO_3.

LIQUID CRYSTALS. At first sight the existence of liquid crystals may seem strange if we refer the expression to the common definition of crystals and of liquids. But if we consider crystals from a more general and rigorous point of view we may easily understand how there may even be liquid crystals.

In 1888 Reinitzer observed that certain pure and unaltered substances melt forming a turbid liquid, and at a higher temperature, which is well defined, they again become clear. On recooling these liquids, the first turbid liquid is reproduced and is then followed by solidification. Gattermann observed the same behaviour in certain substances, for example, para-azoxyanisol, which melts at 116° giving a yellowish turbid liquid which immediately becomes clear at a temperature of 135·2°. O. Lehmann, and R. Schenck somewhat later, found that these turbid liquids light up the dark field which is obtained between crossed Nichol prisms, precisely in the same way as crystals, a property not shared by true homogeneous liquids.

Tamman, and to a certain extent Nernst, pointed out that this apparently strange phenomenon could be explained by the theory of emulsions or of partial polymerisation, or even by the formation of isomers of the substance observed. Weimarn in 1909 stated that under the ultramicroscope these special

liquids showed the presence of small crystals which were already formed. In any case this matter has not yet been definitely cleared up, and it may be considered still premature to suggest that the origin of life was initially due to the formation of liquid crystals![1]

EQUILIBRIUM OF HETEROGENEOUS SYSTEMS AND THE PHASE RULE

The phase rule was deduced and developed by the American, Willard Gibbs (1878–1889–1904), from thermodynamical considerations, and it explains the state of equilibrium in many physical and chemical phenomena very well. It was then generalised in its application by Ostwald. It may be considered, thanks to the work of Roozeboom, van't Hoff, and Bancroft, as one of those modern laws which have contributed most to co-ordinate and explain very many chemical and physical phenomena which may be observed in nature.

Those components of a physical system which can be mechanically separated from one another are called *phases* of that system. In homogeneous systems we have only one phase, in heterogeneous systems there are two or more phases. The phase of a substance, then, is any physical state, so long as it is homogeneous and well defined, in which that substance is present. We know that the condition of a gas is determined by three variable magnitudes, temperature, pressure, and volume. For a given weight of gas we can always give two of these variables any value whatever, and the value of the third variable is known without further determination and is dependent on that of the two given values.

When for a given weight of a gas we fix any values whatever for the temperature and pressure, we then know, or are able to calculate by the general gas formula, $pv = RT$, the volume which corresponds to these values of the two variables, which is well defined. In the same way, if the values for the temperature and the volume are determined, we may calculate the value of the pressure &c.

The density of gases diminishes as the temperature is increased, and as

[1] It has often been affirmed that the characteristic properties of the crystalline state of a substance are anisotropy and perfect homogeneity at all points in the mass. Substances are called anisotropic which do not possess the same vectorial properties in every direction. Thus, the double refraction of crystalline substances is due to vectorially discontinuous properties. Amorphous substances have vectorially continuous properties and they are not doubly refractive. Crystalline matter, in distinction to amorphous matter, has generally regular planes of cleavage, which are those which also establish the constancy between the angles of crystalline faces when the mass is limited by faces and assumes regular geometrical forms.

It cannot be denied, however, that sometimes even amorphous substances are anisotropic, that is, doubly refractive; for example, a sheet of gelatine, a starch granule, a piece of tempered or compressed glass, animal hide, &c., although as a whole they are isotropic and may be considered as consisting of small anisotropic particles only. Thus a piece of tempered glass which is not homogeneous may always be imagined to consist of small isolated particles in which it is no longer possible to distinguish two points arranged differently in respect to the optical ellipsoid; however, in this case we must admit that the more intimate arrangements of the particles of these substances may be a network such as is present in crystalline substances. In amorphous substances, however, the phenomena of cleavage planes meeting one another at definite angles do not exist.

Crystalline masses have also vectorially continuous properties. Thus, they have, for example, optical properties for which the mass of the substance is isotropic, but similar optical properties are common to many amorphous substances.

Lehmann first discovered plastic or flowing crystals, which have all the properties of vectorial discontinuity and of homogeneity in the same way as ordinary crystals. He then discovered the so-called liquid crystals, which have no vectorially discontinuous properties and do not present the same homogeneity in their vectorial properties, although they are anisotropic; and perhaps liquid crystals should more precisely be called *anisotropic liquids* or *drops* which are able transitorily to assume certain geometrical forms by means of the surface tension (homeotropy). They are able to split and to grow like crystals, and sometimes their segmentation and budding is somewhat similar to that of living cells of microscopic plants and bacteria. For this reason they have been rashly denominated living crystals, and the as yet unjustified attempt has been made to attribute to liquid crystals the first origins of life.

The study of liquid crystals can be very well made with silver iodide, ammonium oleate, ethyl-para-azoxybenzoic ester, and para-azoxycinnamic ester.

Anisotropic drops or liquid crystals can be well observed in the case of para-azoxyphenetol and ethyl-para-azoxycinnamic ester and in monobromonaphthalene.

the pressure is diminished. These two variables are called *free variables* or *degrees of freedom*.

In a gas system with a single phase, we have always two degrees of freedom, that is, the system is *divariant*.

If we now consider water in a closed evacuated vessel, we have this substance in two different forms, namely, liquid water and water vapour, which is present above the liquid at a definite pressure and temperature. In this system the vapour and the liquid water are called two phases of the system. We may, however, imagine a coexistent third phase, ice, which may be formed by cooling the preceding system. The *component* of this system is always the same, namely, water in its various states of aggregation. If to the above-mentioned vessel we add an excess of salt in such quantity that a part of it remains undissolved in the water as a solid on the bottom, we then have a system with two components, salt and water, and with three phases, namely, undissolved salt (solid phase), aqueous solution of salt (liquid phase), and water vapour (gaseous phase). If to this system an excess of another salt is then added, for example, sodium sulphate, in such quantity that a portion of this also remains undissolved, we will have a system containing three components, sodium chloride, sodium sulphate, and water; and four mechanically separable phases, namely, two solid phases (solid sodium chloride and solid sodium sulphate), one liquid phase (an aqueous solution of sodium chloride and sodium sulphate), and a gaseous phase formed by the water vapour.

We now see that in any heterogeneous system in equilibrium, whatever may be the number of the components of the solid and liquid phases of the system, there is always only one gaseous phase. Furthermore, the equilibrium between two or more phases is independent of the quantities of the individual phases which are present. In fact, the quantity of salt dissolved in a saturated solution (liquid phase) is independent of the quantity of undissolved salt (solid phase). In a system of more than one phase, when equilibrium is established, it exists both between two phases which lie side by side and between those which are separated, so that one can always eliminate any one phase without the others ceasing to be in equilibrium. A system which contains no gaseous phase, so that a liquid and a solid phase remain, is called a *condensed* system and the equilibrium of the whole is then independent of the pressure, because this has a minimal influence on the volume of solids and liquids.

The conditions of existence of a system, namely, the temperature, pressure, and concentration of the phases, are called the *variables* of the system. It is found, practically and theoretically, that the greater the number of phases resulting from a definite number of substances, the less necessary is it to know the variables in order to define the condition of a system.

In the case of a system containing a single component and three simultaneous phases, as in the case of water, noted above, with the three phases, solid (ice), liquid (water), and gas (water vapour), we know already that such a system can only exist at one definite temperature and at a definite pressure, namely, that temperature at which ice and liquid water have the same vapour tension. We actually know that this temperature is 0·0075° and that the vapour tension is 4·57 mm. of mercury, and that then we possess sufficient data to also calculate the concentration of the phases, that is, the other variable.

In any system with a single component, for instance, water, or in general with n components, *we thus have complete equilibrium when* $n + 2$ *phases are present* (that is, three phases if there is only one component). We have also seen that in this case all the variables remain fixed *a priori*, that is,

there are no free variables to which we may give arbitrary values, but the equilibrium is complete and determined. If in this system we have only two phases, that is, $n + 1$, there will be incomplete but determined equilibrium, because we have one free variable to which we may give any value at pleasure, but having given it this value, the value of the other variables will be consequently fixed and the state of the system will still remain sufficiently defined. For water ($n = 1$) a system with $n + 1$ phases, that is, two phases, can exist with liquid water and water vapour, or water and ice, or even ice and vapour, but in any such case we have a single free variable, and this being given the other two are fixed in consequence. It is sufficient, in fact, to fix the value of any single variable, for instance, the temperature, because we can then deduce the other two, and all the conditions of equilibrium are thus determined. In the case of water and water vapour, for example, if we know the temperature t, we can find the pressure of equilibrium p, by means of a table of vapour tensions, and knowing t and p, we may easily find the concentration of the gaseous phase, that is, the number of c.c. occupied by 1 mol. of water vapour, from suitable tables. If, on the other hand, we only know the concentration C of the gaseous phase, we can deduce p and t from the known equation (p. 63) $C = \frac{n}{v} = \frac{p}{RT}$. With all these data we can then always determine the concentration of the liquid phase if we are dealing with a substance the properties of which are well known. If, however, the temperature or the pressure in one of these systems in equilibrium is altered, equilibrium ceases, and one of the phases must disappear. In the case of liquid water and its vapour, on increasing the pressure or diminishing the temperature, the gaseous phase disappears, because the water vapour condenses. If the temperature is increased or the pressure diminished, the equilibrium is also disturbed, because the water vaporises and the liquid thus disappears. If the temperature is lowered down to 0°, or below, then, on the other hand, the liquid phase is replaced by the solid phase (ice) and the gaseous phase corresponds to the vapour tension of ice. This also will establish a definite equilibrium, because at every temperature it will have a definite vapour tension. In the case of the ice phase, we may simultaneously obtain the liquid phase by strongly increasing the pressure, because the freezing-point is lowered, and for any given pressure we will have a definite temperature at which ice and liquid water can coexist. Thus the motive power of glaciers is well explained, for when the pressure under the glacier reaches a certain magnitude, at the point of contact with the rigid surface on which the glacier rests, a portion of the ice is liquefied and the glacier moves.

In general the number of free variables or degrees of freedom can be deduced from the equation $F + L = S + 2$, where F indicates the number of phases, L the number of free variables, and S the number of substances composing the system, so that $L = S + 2 - F$.

The system of n components with n phases is only determined when two variables are fixed, and a single free variable then remains. We can, for example, have water vapour alone (one component and one phase) in various conditions of concentration, of temperature, and of pressure, but we can at any instant determine the state of the system if we know two variables, because the third may be easily deduced from these. In this case we have incomplete equilibrium, and the system is divariant, as we have noted above.

We may easily represent in a diagram the equilibrium of water by taking as the two axes of co-ordinates the temperature and the pressure (Fig. 36). We have already seen that the three phases of water coexist at the temperature of 0·0075°, and the pressure of 4·57 mm., and in the diagram this point O, called the *triple point*, is fixed by the intersection of the three curves separating the three phases. We may in general call the ***multiple***

point that at which all the phases can coexist, and this may occur for a given number of components of the system under examination.

Starting from the point *O*, if the temperature rises the ice melts and the water remains in two phases, liquid and gaseous, which are only in equilibrium when at each given temperature we have a pressure equal to the vapour tension. If, on the contrary, the system is exposed to a lesser pressure all the liquid will evaporate, and if the pressure is greater all the vapour will disappear and a single phase only will remain. Along the curve *O A*, we have points corresponding to temperatures and vapour tensions of the liquid water representing the conditions of coexistence of these two phases. Naturally the curve cannot be continued beyond the limit *A*, if at this point we have the critical temperature of water, because at this critical temperature the liquid phase disappears whatever may be the pressure (*see* p. 28). This is to say, in a system of two phases the variability is not limitless.

Starting again from the point *O*, if we diminish the temperature the liquid phase disappears, and ice, the solid phase, is formed, although equilibrium may be maintained between the solid and the gaseous phase along the curve *O B*, which represents the vapour tension of ice at various temperatures below zero, which is probably maintained down to absolute zero.

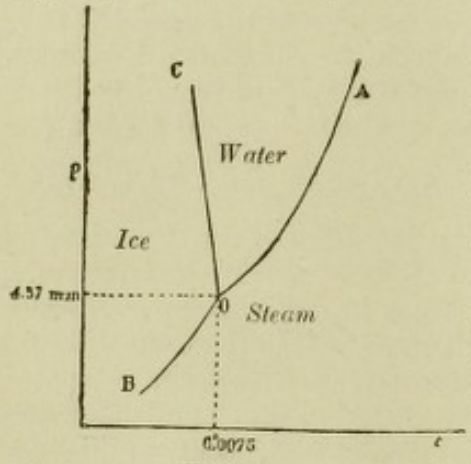


FIG. 36.

Returning again to the point *O*, if the pressure is increased the gaseous phase disappears because the vapour is condensed and ice and liquid water remain. These two phases can exist simultaneously, that is, can be in equilibrium only at temperatures and pressures indicated by the line *O C*. From the direction of this line we see that the freezing-point of water is lowered with increase of pressure, and this is why ice liquefies with increase of pressure unless the temperature is lowered. This is a special characteristic of water, which has a greater volume in the solid than in the liquid state. For all other substances, however, the line *O C* will be directed towards the right, that is to say, for them, in the solid state, no liquefaction can occur with increase of pressure; the gaseous phase is maintained in equilibrium with the solid phase if the increase of pressure corresponds to an increase of temperature, and if this latter is increased it is impossible for the gaseous phase to disappear.

In the special part of this book we will return to this question in connection with the study of the various states of aggregation of sulphur.

We will now study a system containing two components ($n = 2$). In the case of a saturated solution of a salt contained in a vessel together with an excess of undissolved salt, we have a system of three phases which may be even separated mechanically, namely, the solid salt at the bottom of the vessel, the solution, and the vapour of the solvent which occupies the space above the solution at a given vapour tension. The independent components are two in number: the salt and the solvent (this latter being liquid and in the state of vapour), and we have incomplete but determined equilibrium because $n + 1$ phases, that is, three phases, are present; in fact, at a certain temperature the saturated solution has a definite tension. If under these conditions the pressure is diminished a certain quantity of the solvent is transformed into vapour, and the proportion by weight between the phases is altered, because, as the solution is saturated, a certain quantity of solid salt separates from the solution as a part of the solvent evaporates. But the equilibrium between the three phases remains unaltered, because if the temperature remains constant the concentration of the solution, that is the quantity of salt per unit volume of solvent, is unchanged, and thus the vapour has the same tension as before, because the concentration of the solution is unaltered, and there is always the same quantity of vapour in

unit of volume. Equilibrium, therefore, still exists in the complete system independently of the absolute quantity of the components. When equilibrium exists, a definite temperature corresponds to each definite vapour tension, and if at *constant* temperature the pressure continues to diminish or increase, the vapour tension is forced to acquire a pressure corresponding to the fixed temperature, so that the solvent will continue to evaporate if the pressure continues to diminish until only the solid substance and the vapour remain, or vapour will continue to condense until only solution and solid salt remain in the case when the pressure is continually increased.

The same phenomenon is observed if the pressure remains constant and the temperature is continuously changed.

Thus, if we have a system of $n + 1$ phases in equilibrium, we may vary the temperature or the pressure, but in the first case the pressure will remain fixed, and in the second the temperature will remain fixed, and the system is then called *monovariant*, and the equilibrium is incomplete but determined. If in a system of two components we have two phases, then we may simultaneously alter the temperature and the concentration of one phase, by which means the third factor of the equilibrium is fixed in each case. As we have already seen, we have in this case a *divariant system* and an *incomplete and indeterminate* equilibrium. This is the case, for instance, for an unsaturated solution of a salt in which there are two components, salt and water, and two phases, solution and vapour. If we now diminish the pressure, a part of the solvent is evaporated and the concentration of the solution increases, producing at the same time a lesser vapour tension ; a change in the system thus occurs without disappearance of either of the phases ; if we continue to diminish the pressure until the concentration of saturation is reached we continue to change the condition of the phases ; only after this saturation point has been passed there is separation of salt, and we then have three phases, that is, we pass from an incomplete indeterminate equilibrium to an incomplete, determinate equilibrium, which has already been studied above.

In a system with two components ($n = 2$) we may finally study *complete equilibrium* in the case in which we have $n + 2$ phases. This is the case where a salt is dissolved in water to saturation without formation of a chemical compound and is present in excess and thus partially undissolved at the freezing-point of the solution. The two components are water and the salt; the phases are four, that is, $n + 2$, namely, the vapour above the solution, the saturated solution, the excess of undissolved salt, and the ice separated from the solution. In this case the ice is not formed of the solvent (water) only, as is the case for dilute solutions, but is a mixture of ice and salt, that is, it forms a so-called *cryohydric mixture*. The temperature at which such a concentrated saline solution commences to freeze is called the *cryohydric point*, and is the point at which there is complete equilibrium or coexistence of the four phases.

We may render this case clearer by studying it with the help of a diagram (Fig. 37) where we have reproduced by means of dotted lines the three phases of water which we have first studied with the relative triple point O and curves $O\,B$, $O\,C$, $O\,a$. The freezing-point of the saturated solution of the salt (cryohydric or triple point) must necessarily be at a temperature lower than the freezing-point of water, because we know from cryoscopic considerations (p. 86) that dissolved substances lower the freezing-point of the solvent, and thus also the vapour tension, and in the diagram we find this point at O' corresponding to the temperature, t', and the pressure or vapour tension, p', which is common to the ice and to the solution. The point O' is placed at the intersection of the curve $O\,B$ (the vapour tension of the separated cryohydric mixture) and $O'\,A'$ (vapour tension of the saturated solution). On raising the temperature the ice melts, and the curve $O'\,A'$

indicates the various temperatures, concentrations, and vapour tensions corresponding to saturated solutions, that is, to a triphase system.

If we now increase the pressure considerably, at the same time slightly diminishing the temperature, the gaseous phase disappears and along the line $O'\,C'$ are found the values of temperature and pressure corresponding to the equilibrium of the triphase system—salt, saturated solution, and ice. If we alter the temperature or the pressure in such a way that the lines $O'\,C'$, $O'\,A'$, or $O'\,B'$ run to the right or to the left of the lines indicated in the figure, then we obtain a diphase system, because, if we take any point whatever on the line $O''\,A''$, corresponding to a triphase system, salt, saturated solution, and vapour (that is, in which the ice of the cryohydric mixture is absent and therefore the point C'' is at a temperature higher than O'), and decrease the temperature slightly and gradually, leaving the pressure unaltered, we will have a displacement to the left of the curve $O''\,A''$ until the gaseous phase is condensed, that is, until it disappears, and we will obtain a corresponding dilution of the solution which, in order to again become saturated, dissolves more salt ; but in any case only the liquid phase and the solid phase (undissolved salt) will remain, and this modification will be comprised in the area $C''\,O''\,A''$. We may reason similarly for the displacement of other variables.

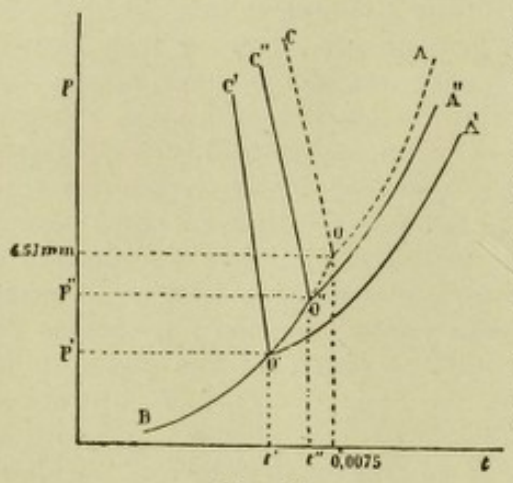


Fig. 37.

The phase rule is not only of considerable theoretical interest, but the result of its applications in other directions has become of the greatest importance. Thus, for example, the metallic alloys are entirely composed of mixtures of compounds which are formed according to the phase rule.

For this reason a certain number of determined experimental data being once known, it became possible to prepare alloys which possessed one or another desired property.

The micrographic study of metals, by means of which it became possible to analyse the state of their component phases, although it is not many years old, has led to great progress in metallurgical processes.

In another direction also all the igneous rocks, such as granites and gneiss, which are formed by the decomposition into phases of a fused mixture, have been studied from new scientific standpoints.

From every side, and especially in cases of complex mixtures which had not been studied until lately, except by certain empirical means and processes, the phase rule offers data of singular clearness, and explains in a marvellous manner facts which could not have been interpreted before and seemed to be due to capricious and fantastic phenomena.

In the special portion of this book we will repeatedly have occasion to apply these conceptions on phases and equilibrium generally.

RADIUM, RADIO-ACTIVITY, AND UNITY OF MATTER

We have studied numerous laws which physical and chemical transformations of matter obey. We have seen that the most varied chemical phenomena occur without loss of weight. By the study of thermochemistry we have shown that in all transformations which occur in nature, the energy is maintained at a constant value with regard to quantity, only varying in quality (*see* p. 58).

Whilst the various forms of energy are capable of reciprocal transformations into one another, in the case of matter we have found that it was impossible to transform one element into another, for example, iron into gold, &c.

If it is easy to-day to show that energy, even in its most varied transformations, can always be referred to a single form ; such a demonstration in the case of matter, on the other hand, has not yet been obtained in spite of many experiments, attempts, and most brilliant philosophic speculations. Until the discovery of radium nothing, or practically nothing, was known on the intimate nature of matter, and compared with the atomic hypothesis

of the ancient Greeks practically no progress had been made in this direction. When our mind searches the horizon on the intimate nature of matter with the insufficient knowledge of natural laws discovered up to our time, it finds at a certain point that it is impossible to rationally solve the problem of the first cause without admitting that matter itself is nothing else than a form of energy.

But if we are to solve this profound secret of nature without falling into the errors of metaphysics and empiricism, we must rely strictly on the positive laws which we know, seeking to discover new laws by the aid of experiment, and also, transitorily, with the aid of rational hypotheses which have already contributed so much to the progress of science.

We have already accepted the hypothesis of discontinuous matter, divided into many small ponderable and invisible particles called atoms, and by means of this hypothesis we have explained all the chemical phenomena (*see* p. 21), but it is not possible to explain by means of this hypothesis certain important physical phenomena, especially those of light, for the explanation of which we must turn to another hypothesis, namely, that of the cosmic ether (*see* p. 5).

An atomic hypothesis of the nature of matter had already been propounded by William Thomson (Lord Kelvin) and by Tait, and had then been developed by Helmholtz by means of his so-called atomic vortices. According to Thomson, matter is nothing but an aggregate of vibrating nuclei formed from something which fills all space (the cosmic ether). These atomic aggregates are nothing else than vortex movements which are different from one another and are stable and indivisible. Such ethereal aggregates with different and perpetual movements would constitute the atoms of the different chemical elements which are not transformable into one another. Tait added that these rotary movements of the various atomic vortices must be the cause of everything which affects our senses and which we call matter.

After these considerations, we will consider somewhat further the experimental data in order to form an idea whether we can arrive at any conception of the unity of matter because, having demonstrated experimentally the unity of energy, it appears strange that the matter present in nature should always be subdivided into seventy-five or eighty different kinds (elements), whilst all the other sciences, including zoology and botany, tend to show the convergence of the most various organisms towards ever simpler organisms, until they arrive at a single primary cell. All this tends towards monism.

After the work of Dalton and his brilliant atomic hypothesis, and after that of Lavoisier, Gay-Lussac, Proust, Berthollet, Richter, &c., at the end of the eighteenth century and the beginning of the nineteenth, after many of the atomic weights had been determined, and after the lightest substance, hydrogen, had been chosen as the element of comparison, W. Prout, a London medical man, started a somewhat hazardous hypothesis in 1815 on the unity of matter. Supposing that the atomic weights of the elements were exact multiples of the atomic weight of hydrogen, he deduced that the atoms of all the chemical elements were nothing else than stable aggregates of various numbers of hydrogen atoms; thus hydrogen would be the single primary material from which all the other elements were derived. Meinecke (in Germany) in 1818 and Thomson (in England) supported this hypothesis strenuously, together with a few other chemists, whilst Berzelius, who was at that time much occupied with the study of atomic and molecular weights, combated it, showing that the integral atomic weights chosen by W. Prout and by Thomson were not deduced from experimental determinations, but had been considerably altered in this direction, which was confirmed by Turner in 1829. On the other hand, the supporters of Prout's hypothesis replied that the small fractions in the values of the atomic weights were the result of inevitable experimental errors. Pointing then to the discovery, just before that time, of the free alkali metals by Davy, who separated them electrically from the alkalis, which had up to that time been held to be simple bodies, many chemists supported Prout's hypothesis as the most plausible and the one which justified the hope of decomposing many other substances which were supposed to be simple. But Prout's hypothesis was rejected by all, under the influence of Berzelius, and was only taken up again with much ardour by the eminent scientists Dumas and Stas, when they found that the atomic weight of carbon was exactly equal to 12, whilst Berzelius had confidently given to it a number which was greater by a fraction of unity.

Dumas and Stas then set themselves to control many atomic weights by means of

an extraordinary wealth of experiments and of scientific apparatus, with a view to confirming Prout's hypothesis. After a prodigious amount of very accurate work lasting several years, during which Dumas was able to rigorously control the atomic weights of more than twenty elements, the two scientists came to diametrically opposite conclusions. In 1858 Dumas declared himself a partisan of Prout's hypothesis, while Stas declared the contrary, thus causing a division of opinion between certain chemists. Marignac in Geneva also contributed to the dispute by means of very valuable work, and in order to support the hypothesis of Prout he supposed that the atomic weight of the atoms was not constant, but oscillated about the nearest whole number. Landolt was, however, able to demonstrate by means of exact determinations that chemical combinations occur in a manner rigorously fixed with regard to weight, and that certain atomic weights are to-day exact with an accuracy which extends to three decimal places.

However, when Ostwald recently succeeded in establishing oxygen with the atomic weight of 16 as the standard for the other elements, with the approval of the majority of chemists, many of the atomic weights of the latter which were found to be represented by fractional numbers when referred to hydrogen, became whole numbers. One part of the difficulties concerning the hypothesis of the unity of matter thus disappeared if the existence of some primary element, two or four times lighter than hydrogen, were admitted. To-day, however, we must talk of a primary and single form of matter which it is necessary to think of in terms of atoms immensely smaller than those of hydrogen, such as we have vaguely noticed in the study of ions and of electrons. In fact the differences of weight found by Landolt and Heydweiller during chemical combination (*see* Note on p. 9) are of an order of magnitude so small that we may perhaps explain them by recent views on the size of electrons, in harmony with important phenomena of radioactive bodies, and we may perhaps confirm the conception of Marignac, whose determinations of atomic weights do not lead to constant weights, but to values oscillating about certain whole numbers.

Many other facts attract our thought towards the seductive hypothesis of the unity of matter, and we must note the periodicity in the chemical and physical properties of the elements which was brilliantly shown by Mendelejew by means of his periodic system of the elements (*see* end of this volume). Certain physical and chemical properties are, in fact, a true function of the atomic weights. The elements of certain groups, taken in the order of their chemical atomic weights, show a regular and gradual modification of physical and chemical properties.

In the allotropic states of certain elements, for example, of oxygen, which also forms ozone, we have two substances with different chemical and physical properties although they are formed of a single elementary material, oxygen, and the difference is explained by the different numbers of equal atoms which enter into their molecules. We have still more important examples in the numerous isomers and stereoisomers of organic compounds which differ from one another physically and chemically, although they are constituted of the same elements (for example, fumaric and maleic acids, $C_4H_4O_4$ and $C_4H_4O_4$) and which are, moreover, transformed into one another with the greatest ease. These facts being known, it does not appear to be heresy to suppose that the atoms of various elements may be composed in their turn of still smaller particles, and that their nature only differs through the number and arrangement of these.

If we also consider the ionic hypothesis of Arrhenius, we see that the molecules and atoms of the free elements have chemical and physical properties very different from those of the corresponding ions. But the relations which were first discovered by Ciamician and later by Grünwald, and especially by Kayser, between the spectroscopic constants of the elements and their atomic weights showed once more how certain physical and chemical properties are functions of the atomic weights.

The important observations of Lockyer on the spectra of heavenly bodies led to the belief in a gradual decomposition of the elements themselves, when these were exposed to very high temperatures. Crookes, in his important work on the rare earths of cerite, enunciated the hypothesis of the evolution of the atoms, referring them all to a primordial material which he called *protyl*.

The current knowledge and hypotheses were in this condition until a few years ago, when a sensational discovery illuminated this field of uncertainty. It was the discovery of radium, which removed the problem from the realm of hypothesis and of hope to that of positive experimental facts, and it was then known that beyond the atom which had, up till then, been known to chemists, a further marvellous world existed which enabled it to be shown by means of rigorous proof that the hope of the alchemists of the transformation of one atom into another was not altogether a dream.

At this point we will deal somewhat shortly with radium and radio-activity.

For many years the phenomenon of fluorescence and phosphorescence have been well known. A fluorescent substance becomes luminous when it is exposed to the action of the ultra-violet rays of the spectrum which are not perceptible by our eyes on account of the greater frequency of their undulations (*see* p. 6). Such substances lower the frequency of the ultra-violet radiations so that they are rendered visible, but the luminosity only lasts whilst the substance is actually exposed to the action of these dark rays. Many phosphorescent substances, on the other hand, become luminous after being subjected to the action of daylight and remain luminous even after the action of the light has ceased, that is, in total darkness. All substances appear to be capable of phosphorescence, but in some cases the phosphorescence only lasts for a single instant, some millionths of a second, whilst in other cases it lasts for longer, for hours or even for weeks. Phosphorescence may also be provoked by percussion, friction, the action of thermal and electrical vibrations, &c.[1] Now to-day very interesting substances have been discovered which are able to emit light and heat continuously, even without the action of any stimulants ; these are the radio-active substances which have been studied during the last few years. In 1896 Becquerel discovered that uraninite or pitch-blende, without having been rendered phosphorescent by exposure to daylight, emitted special radiations capable of influencing a photographic plate, radiations which were propagated in straight lines, but could not be reflected, refracted, or polarised. These rays rendered gases good conductors of electricity and discharged an electroscope even at a distance, that is, converted even so-called insulating substances into conductors of electricity. Becquerel attributed these properties to uranium and uranium compounds, but in 1898 and 1899 Madame Sklodowska Curie and her husband, Professor Curie, showed that these special properties were much more marked in certain pitch-blende residues from which the greater part of the uranium had been extracted. They therefore concluded that the cause of these phenomena must be attributed to another substance, which they called polonium, and which they hoped to be able to isolate from large quantities of these residues.

But they were soon able to separate a substance a million times more active than uranium, to which they gave the name of radium. In 1899 Debierne believed that he had isolated another active substance, to which he gave the name of actinium. To-day we can safely affirm the existence of radium only in the various compounds which have been studied. From the last researches of Curie (1910) the existence of polonium appears to be also confirmed. In 1902 Rutherford, on the other hand, had separated from thorium preparations imponderable quantities of a radio-active substance called thorium X (radio-thorium), and found that this continued to be formed from elementary thorium ; but it developed an emanation and gradually lost its radio-activity. Rutherford concluded from these facts that the material atoms of radio-active substances are in a state of continuous transformation, and this permitted him to form a first theory of radio-active substances. *Radium* is an element which is chemically very similar to barium. From the pure bromide $RaBr_2.2H_2O$ the atomic weight of radium was found to be 225, now corrected to 226·4. Radium compounds have a smell of ozone because they transform the oxygen of the air into ozone. They continuously emit heat and a very small quantity

[1] Many of these phenomena are to-day comprised under the generic term of luminescence. Any body which is at a temperature above −273° emits and exchanges energy with its surroundings. Our eye only perceives true luminous energy due to calorific radiations which bodies emit when they are heated to at least 360° or more. All the other forms of luminosity, even at low temperatures, are comprised in the term *luminescence*, which accompanies many chemical phenomena. Its intensity increases with the thermal tonality and with the velocity of reaction, which, however, has no influence on its colour. The theory of luminescence has not yet been evolved although it is strictly related to the theory of electrons and of dispersion.

of special light. They have an irritating action on the epidermis and, if prolonged, the contact ends in the production of blisters. Radium is found in minimal quantities in nature, but it is, on the other hand, widely diffused. In order to obtain twenty centigrammes of radium bromide, Madame Curie worked up two tons of pitch-blende.[1]

In 1903 Ramsay and Soddy, on studying radium spectroscopically, made the surprising observation that of eight principal lines four or five are common to the helium spectrum, but the spectrum then alters and the radium continues to be transformed into another substance not yet defined, from which, as a final product, helium, which is the most visible in the spectrum, is formed. This interesting phenomenon was later confirmed by Debierne, Giesel, Curie, Dewar, Himstedt, G. Meyer, and others, and the supposition of Lord Kelvin that the helium might have been occluded in the radio-active substance was excluded. Actinium also produces helium, and in general all the radio-active substances produce α-rays, formed of α-particles, the atomic weight of which is identical with that of helium, so that this latter must be formed of α-particles deprived of the electric charge. One gramme of radium produces 144 to 219 cu. mm. of helium per annum and would require tens of thousands of years to be completely transformed into helium. Radium had scarcely been discovered when certain people objected that its inexhaustible activity, which does not diminish, was in contradiction to the fundamental law of the conservation of energy (*see* p. 4). Now, however, it is clear that a diminution of energy, namely, transformation into helium, does take place, but that it is so small that it escapes all ordinary measurements and years of control would be necessary in order to determine it. All the properties of radium remain unaltered even at 180° below zero, although at −150° the radium emanation condenses and then shows no vapour tension. In fact, on passing a current of air at that temperature over radium, the emanation does not pass into the air. Thus, also, the emanation of a radium salt is almost zero in a perfectly evacuated tube. Ramsay and Gray in 1909 liquefied and even solidified the emanation at a very low temperature and in the solid state it became luminous like an arc lamp, first giving a bluish metallic light which then became yellow and orange. The liquid emanation has a specific gravity of 6·8, boils at − 62°, has a critical temperature of 104·5°, a critical pressure of 47·45 mm., and an atomic weight of 176; it melts at − 71°; it rapidly undergoes change to about half of its weight in four days. The whole behaviour of radium was from the beginning a true enigma, for the exact scientific interpretation of which there were not wanting hardened devotees of dogma and metaphysics who attempted to proclaim that science was again bankrupt.

To-day, however, these phenomena have all re-entered the orbit of general and fundamental laws, thus advantageously enlarging our scientific horizon through these new and most important discoveries. We will now interpret these apparently strange phenomena in a simple manner.

If an almost absolute vacuum is maintained in a glass tube containing electrodes united to an induction coil, a vacuum as low as a few millionths of an atmosphere, then when an electric discharge is passed rays are projected from the cathode in a direction normal to its surface independently of the position occupied by the anode. These cathodic rays, also called β-rays, have the power of heating bodies which they irradiate and of rendering them luminous, producing an emanation of X-rays (Röntgen rays or γ-rays). They are able to traverse thin aluminium plates, and cause gases and all bodies through which they are propagated to become good conductors of electricity. It has also been found that these rays are diverted from their rectilinear course under the action of a magnet and behave as though they were constituted of negatively charged material particles. On studying the relation between the electric charge and the mass of these moving particles (Electrons, p. 101), it is found that this ratio is about two thousand times greater than that of the hydrogen ion compared with its charge, 1·008 grm. of hydrogen having a charge of 96,540 coulombs (p. 91). Consequently, if the moving particles of the cathodic rays have a mass equal to that of the ions, they must have a charge two thousand times greater, or if the electric charges are equal to those of the ions, then the mass of these particles must be two thousand times smaller, which is also very probable from

[1] The purest radium preparations which are found in commerce are a mixture of much barium chloride with traces of radium chloride, and cost £1 to £1 4*s*. per gramme; a mixture of barium and radium products containing 10 per cent. of the latter is sold at a price of £40 per gramme, and the radium bromide costs £400 a gramme at that rate. In 1909 the Austrian Government sold the first pure gramme of radium salt prepared at Joachimstal, and there were several bidders at £16,000 per gramme.

considerations of quite another order. We know that the negative rays are constituted of free negative electrons which move with a velocity of 60,000 kilometres per second, and we can thus understand why bodies which receive these particles undergo a kind of bombardment and become heated. The γ-rays are electrically neutral, as they are not diverted by a magnet, but they are endowed with a very great power of penetration of opaque bodies, and according to Tuomikoski (1909) they are able to traverse a block of lead of a thickness of 19 cms. They have vibratory properties similar to those attributed to the cosmic ether. Positive electrons are also known which form the anodic rays or α-rays, Goldstein's rays or canal-rays, which pass from the anode in the evacuated tube mentioned above, and proceed to the cathode by which they are absorbed because they have not the property of passing through metals. But if there is a small hole in the cathode which permits them to pass, they pass through it and then continue their course along a glass tube fixed to the hole behind the anode. On studying these rays it is found that they do not pass through an aluminium plate, and that they are diverted by a magnet in the opposite direction to the cathode rays. They are also repelled by positively charged bodies, so that they are considered to be formed of particles (electrons) positively charged, which have a velocity of about 1000 kilometres per second. The negative electrons, on the other hand, may with certainty be described as units or free atoms of electrical energy (J. J. Thomson). The existence of free positive electrons, on the other hand, has not yet been proved, and as they are always united to particles of matter we have not been able to demonstrate experimentally that these are also formed of an agglomeration of atoms of energy. If this were so, then all matter would have no other form than the various aggregates of positive or negative energy. Ramsay believes that up to this day we are not able to liberate positive electrons, and that these must be considered as *matter* itself or as the essence of matter, whilst energy is represented by negative electrons.

The relation between the electric charge and the mass of the positive electrons is almost equal to that between the electric charge of the ions and their mass. Thus the mass of the positive electrons is about two thousand times greater than that of the negative electrons and corresponds to the mass of the ions. Rutherford showed experimentally that the particles of the α-rays are identical with the atom of helium, as has already been noted above, and this had, moreover, been theoretically predicted by him before Ramsay discovered the formation of helium from radium; the α-particles should have a weight double that of the hydrogen molecule, that is, a weight equal to that of the atom of helium (4).

Now experiments have shown that the electrons of positive sign have different masses and velocities, and for various reasons we may also suppose that the atoms of various substances are nothing else than aggregates of positive electrons of which the electric charge is due to the negative electrons. After these considerations, the nature of radium is rendered less obscure, because it has been shown that this emanates few X-rays and α-rays whilst it continually emanates β-rays formed of negative electrons which have those interesting properties which have already been studied. We also understand, then, why radium does not apparently diminish in weight, because the electrons which are projected consist of such extremely small quantities of matter that we would not be able to appreciate on our most delicate balances the loss which would occur even through a period of many years. But these particles are charged with such large quantities of energy and are endowed with such a velocity that on colliding with surrounding bodies they cause an elevation of temperature. The radiations, and especially the β-rays, produce ozone from the air by slowly decomposing water vapour with formation of hydrogen, hydrogen peroxide, and oxygen (as is also done by the ultra-violet rays; *see* chapter on Argon), whilst the γ-rays do not show any such phenomena.

In harmony with these considerations, we may suppose matter to be probably constituted of particles much smaller than the chemical atom which is found free in ordinary chemical reactions; particles carrying large electric charges and regrouped in varying numbers in more complete and more stable systems, which systems constitute the atoms of the various chemical elements. We thus also understand the slow and gradual transformation of radium into helium, which would be merely an orientation and regrouping of the electrons of radium into a more stable system, that of helium; that is to say, radium is an element in a state of decomposition. The radio-activity would then be due to the continuous liberation of negative electrons from the material nucleus of radium,

in which larger positive electrons would remain in preponderance, round which the negative electrons would rotate. By means of this hypothesis we also have the simplest and most logical interpretation of the unity of matter, as the atoms of the common elements may be considered as being formed by the grouping of various numbers of these electrons, which at the instant of their union lose their powerful electric charges in the form of light and heat. According to Rutherford, these emanations of electrons cause a species of explosion of the complete atoms of radio-active substances, so that a few elementary particles are set free and are projected with an extraordinary velocity (electrons), whilst the remaining particles collect into more and more stable systems until they gradually become atoms of the common elements known to us, for example, helium. Thus radium is first transformed into a gaseous emanation which then becomes solid at the ordinary temperature, forming radium *A*, which gradually gives origin to radium *B*, *C*, and *D*, and finally radium *F*. When this substance is deposited on other bodies, even in minimal traces, these become radio-active. Radium *F* would be the polonium of Madame Curie. Radium is, in turn, the fourth term in the slow transformation of uranium during thousands of years, which has for its first term uranium *X*, then ionium, radium, emanation, radium *A*, &c. Actinium would be derived from the other series, radio-actinium, actinium *X*, emanation, actinium *A*, *B*, and *C*; the third series of radio-active substances would be formed by thorium, meso-thorium 1, mesothorium 2, radio-thorium, emanation, thorium *A*, *B*, and *C*. The γ-rays are specially produced by radium *C*, and can be separated from the α- and β-rays by passing them through lead plates which only allow the γ-rays to pass. All these new radio-active elements are not yet sufficiently studied, and up to the present are distinguished from one another by the various kinds of radiation α, β, γ, by the velocity of these, which is measurable by their power of penetration of an aluminium plate, or by their ionising powers in air. They are also distinguished by the rapidity of transformation of one term of the series into the next, a rapidity which is measured by the diminution of their radio-activity; actinium emanation, for example, is already transformed to half its extent in four seconds, whilst uranium requires six thousand million years.

Ramsay recently suggested, in 1909, that the difference between the various elements depends on the loss or addition of electrons, and that the transmutation of the elements is thus possible; and he declared that he had transformed copper into lithium by the action of radium emanation, a fact which was seriously contested by Madame Curie and by Gleditsch in 1908, and that he had obtained carbon monoxide and dioxide by acting with radium emanation on the following group of elements: silicon, titanium, zirconium, thorium, and lead. In 1909, Rutherford and Royds showed that the α-particles of radio-active substances are nothing else than helium atoms carrying an electric charge, and in the same year Perman showed that copper and gold do not undergo any change through the action of radium bromide. The statements of Ramsay, therefore, need to be confirmed by other experimentalists before they can be accepted as decisive. The formation of radium from uranium appears to have been demonstrated experimentally with certainty by Soddy in 1909; thus a solution of pure uranyl nitrate which did not contain any radium certainly contained radium after three years had elapsed.

The chemical atoms constituting our simple substances would, therefore, be very stable systems, because it has not been found possible by any method to restore to them the energy which they have lost in order to transform them into further electrons. By means of these conceptions we are already better able to explain why our immense source of light and heat, the sun, has not yet been exhausted. The chemical reactions which occur incessantly in the sun and the condensation of matter would not suffice to compensate for the heat lost through continual thermal radiation, and the sun would to-day be cooled in a much more perceptible manner if there were not some continuous and powerful source of potential energy which is incessantly transformed into actual energy (*see* p. 6). The solar mass is perhaps still constituted in part of free electrons, which are gradually being converted into various elements, thus developing heat which compensates that lost by the sun. As a matter of fact helium and uranium abound in the solar photosphere, and this fact increases the possibility of this hypothesis.

In conclusion, although we admit that all these facts tend towards the hypothesis of the unity of matter, or better, of the existence of energy only, up to to-day the experimental results in this field are not yet sufficiently advanced for us to accept this hypo-

thesis as definitely proved. Of all the elements we have seen that radium only is transformed into helium, but not iron into gold, hydrogen into copper, or any better known element into any other. Also the tendency of these transformations is in the sense of a transformation of an element of high atomic weight into an element of lower atomic weight, as was confirmed by Ramsay if he obtained traces of lithium by the action of the radium emanation on copper. He also decomposed hydrochloric acid, ammonia, and carbon dioxide into their elements, and finally regenerated these compounds from their respective elements by means of radium emanation in 1908.

But the close veil which hid these important secrets of nature has been rent. Science and progress will remove it completely in the near future.[1]

We will therefore still continue to refer phenomena to molecules, to atoms, and to the ions of various substances as we have assumed them in the study of the laws which govern matter in its various manifestations; and the basis of these general laws having been explained, we will now undertake the systematic study of the various elements and of their more important combinations.

[1] To the deductions which have just been arrived at we may also add the following new considerations. Since the nature of the electrons is itself independent of the composition of the electrodes, and as any gas which fills the space around us should produce these electrons, and as also the same kind of electron is always produced when any gas is exposed to the action of Röntgen rays or irradiated by a metallic plate with ultra-violet rays, it may be argued that all matter is constituted of a single principle, the electron.

H. A. Lorentz, with his electro-magnetic theory of light, according to which the electro-magnetic undulations which produce luminous impressions on our eye are the product of the movement of particles one thousand times smaller than the atom of hydrogen carrying an electric negative charge, would support this hypothesis. And, furthermore, we may mention the interesting experiments of Zeemann, who succeeded in influencing the spectroscopic character of light emitted from incandescent substances by the action of a magnetic field.

A. Debierne has also recently succeeded in transforming actinium into helium. It has also been shown that the radium which exists represents half the weight of that which was present ten thousand years ago, at which epoch it was probably formed, and probably in a further ten thousand years almost all the radium existing will have been transformed. But during this geological epoch our terra-aqueous globe has not undergone such profound changes as to justify the appearance *ex-novo* of a new element under the earth, and thus the hypothesis becomes plausible that radium itself is formed by the slow and intimate decomposition of another atom of higher atomic weight. We only know two atoms of atomic weight higher than that of radium, namely, thorium and uranium. As a matter of fact, uranium minerals always contain radium, and Soddy succeeded in showing the continuous formation of radium from uranium nitrate even after all traces of radium had been carefully removed. If the disintegration of radium during its transformation into helium lasts ten thousand years, the disintegration of uranium is estimated at ten million years.

Whilst the heat liberated during the formation of a molecule of various substances may rise to a maximum of one hundred thousand calories, that liberated by a corresponding quantity of radio-active matter in its evolution into substances of more stable character is calculated at thousands of millions of calories.

PART II. NON-METALS

CLASSIFICATION OF THE ELEMENTS

THE division of the elements into two classes, non-metals and metals, is somewhat arbitrary. However, we retain this classification, partly because a certain characteristic difference exists between these two groups, partly for didactic convenience, and also because it is usual.

The metals, when polished, have a characteristic lustrous appearance, and are all solid, excepting mercury; the *non-metals* have rarely this appearance, and are never malleable and ductile like the metals; some of them, also, are gaseous.

The metals are good conductors of heat and electricity, and their conductivity decreases as the temperature is raised; the *non-metals*, on the contrary, are less good conductors of heat and electricity, and their conductivity decreases as the temperature is lowered.

The metals rarely combine with hydrogen, and then form solid compounds; on the other hand, *non-metals* usually combine with hydrogen to form gaseous compounds.

The metals unite with oxygen to form compounds which, when dissolved in water, have a more or less basic character, the reaction being generally alkaline or occasionally weakly acid; *non-metals*, on the other hand, combine with oxygen to form compounds which dissolve in water to form liquids of markedly acid character.

On decomposing a substance containing metals and non-metals by the electric current, the latter wander to the positive pole and the metals to the negative pole. In Part III of this treatise the general properties and characteristics of the metals are summarised.

The metals and non-metals are further subdivided into various groups in which those elements are collected which have the same valency and a progressive analogy in their physical and chemical properties, and in the composition and behaviour of the compounds which they form. This more or less complete relation between elements of the same group and their derivatives was made evident by the brilliant classification made by Mendelejew in 1859, in his periodic system of the elements.

Hydrogen cannot be included in any of these groups, and in many of its properties it is related rather to the metals, although a gas. For this reason we will discuss it alone and before the other elements.

HYDROGEN: H, 1.008

This element is a gas which is found free in very small quantities on the earth. Bunsen in 1852 and others later (St. Claire Deville, Leblanc, Fouqué) have found it in volcanic exhalations. It has been found pure in some Stassfurt minerals (Reichardt, 1860), strongly compressed in some meteorites (*e.g.* that of Lenardo and another from South Carolina, 1886), in the inflammable gas which is evolved in certain countries, and in petroleum springs. Free hydrogen is abundantly present in the solar photosphere, in other stars, and in all nebulæ of which the light has been analysed by the spectroscope. It is formed amongst the gases evolved during certain fermentations, especially of cellulose, caused by certain anaerobic micro-organisms, and is thus also found

in coal, in peat, and in the intestines of certain animals, especially cattle, during the fermentation or putrefaction of their food, mixed with other gases.[1]

Excepting oxygen and silicon, combined hydrogen is the most widely diffused element in nature ; it forms 11 per cent. of the weight of water and enters into the composition of all vegetables and animals, many minerals, and industrial products, petroleum, &c.

PHYSICAL PROPERTIES. When pure, hydrogen is a colourless and odourless gas ; it is not respirable when pure, but is harmless when mixed with air.

Its density, compared with air, is 0·06947 (Rayleigh, 1893), and it is thus 14·43 times lighter, so it can be poured from one vessel to another. Small balloons of collodion or soap-bubbles filled with hydrogen rise rapidly in the air. Its density is normal even at a white heat, therefore it does not undergo dissociation, as is the case with chlorine, iodine, &c. After allowing for all corrections, a litre of hydrogen weighs 0·09009 grm. at normal temperature and pressure (Rayleigh, 1895).

Hydrogen has a greater specific heat and is a better conductor of heat than any other gas (about seven times the conductivity of air). It is also a good conductor of electricity, as can be shown by the following experiment :

A platinum wire traverses a glass tube. A current of air is passed through the tube, and an electric current is simultaneously passed through the wire from four Bunsen cells. The wire glows, because the air surrounding it is a poor conductor of electricity. The current of electricity is now stopped and hydrogen passed through the tube for some minutes to drive out all the air, in order to avoid all danger from the explosive mixture. If the current is now again passed through the platinum wire it does not glow any more because the hydrogen which now surrounds it is a good conductor of electricity.

The spectrum of hydrogen gas consists of four luminous lines, of which the two most characteristic are red and greenish blue.

This gas is the most diffusible known, because it is the lightest ; it diffuses through substances which are only slightly porous, such as india-rubber, and at high temperatures even through quartz vessels. It is absorbed in large quantities by porous bodies, in increasing amount as the temperature is lowered and the pressure raised, forming so-called solid solutions.

It is very little soluble in water (1·93 vols. in 100 vols. of water) ; 100 vols. of alcohol dissolve 7 vols. of hydrogen, and 100 vols. of petroleum dissolve 65 vols.

The occlusion or adsorption of hydrogen by heated metals is especially great in the case of platinum, nickel, and cobalt (at 400°). Palladium, according to Graham, absorbs 376 vols. at the ordinary temperature and almost double that amount at about 100°. On using palladium as the cathode in electrolysis this metal absorbs 935 vols (cathodic, active, or metallic hydrogen). Two-thirds of this hydrogen is found to be combined, forming palladium hydride (Troost and Hautefeuille (1875) and Krakau), and the other third is dissolved in the hydride forming an alloy or solid solution in the proportion Pd_3H_2 (Mond, Ramsay, and Shields, 1901). A colloidal solution of palladium adsorbs 420 vols. of hydrogen, which it renders more active.

Hydrogen in the liquid state was first obtained in large quantity by Dewar in London in 1898 at a pressure of 180 atmospheres in the apparatus shown in Fig. 38 (Cailletet and Pictet claim to have liquefied it in 1877, but the characters attributed to it by them were incorrect) :

The hydrogen, obtained from a cylinder, *A*, at a pressure of 180 atmospheres, is cooled in the first spiral tube, *B*, with solid carbon dioxide ; in the second spiral, *C*, it is then cooled

[1] The gas of the intestines of the ox consists partly of hydrogen, and contains also about 70 per cent. of methane ; these gases are formed by the decomposition of cellulose rendered partly soluble by certain enzymes secreted by the special micro-organisms of the intestine (*see* vol. ii., Organic Chemistry).

with liquid air to about − 190°, and, finally, in the third spiral, D, by making use of the great refrigeration produced by the rapid expansion of the same hydrogen, compressed to 180 atmospheres, when the valve, *F*, is opened, the temperature is lowered to −232°, and a jet of liquid hydrogen issues from the aperture, *E*.

Liquid hydrogen is limpid, colourless, and very refractive and dispersive. It shows no absorption spectrum. It boils at −252·6° at the ordinary pressure (that is, at 20·4° on the absolute scale). At this temperature all known gases and liquids become solid except helium, which does not liquefy even at −260°.

The density or specific gravity of liquid hydrogen is 0·070, and it is the lightest liquid known, being fourteen times lighter than water.

On rapidly reducing the pressure above liquid hydrogen its temperature is finally lowered to −258·9°, and the hydrogen solidifies. The lowest temperature obtained by evaporating solid hydrogen was −260° (that is, 13° absolute) and the specific gravity of solid hydrogen is 0·0763 (Dewar, 1904).

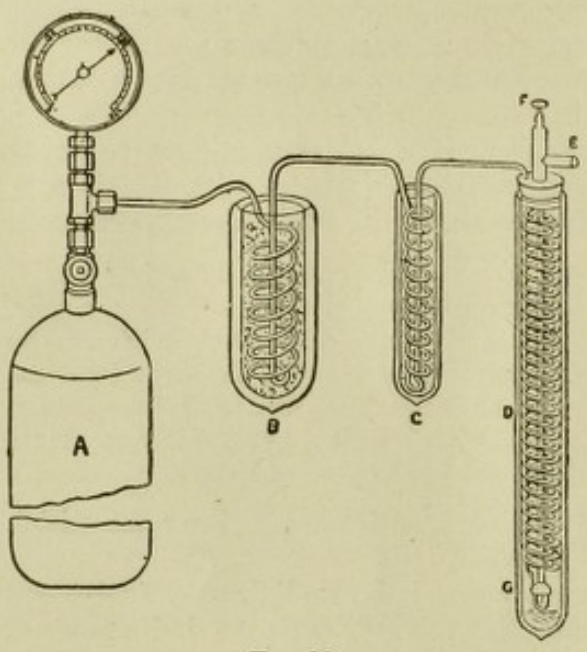


Fig. 38.

CHEMICAL PROPERTIES. Free hydrogen combines directly with fluorine even at − 23°, whilst with chlorine it only unites under the action of light or heat; with bromine both light and heat are required, whilst with iodine it combines very slowly under the influence of light and heat, but if condensed in platinum sponge it combines immediately, acting as nascent hydrogen. The affinity of hydrogen for the other elements diminishes with increasing atomic weight of the latter, for example, it unites with oxygen with explosion; with sulphur the reaction is incomplete and occurs in presence of pumice stone, with tellurium cathodic hydrogen is required (electrolytically nascent), &c.

Two grammes of hydrogen combining with 16 grms. of oxygen to form liquid water develop 68,400 cals. (286 Kj.). The flame of hydrogen burning in pure oxygen reaches a temperature of over 2800° (that of carbon monoxide in oxygen gives 2600° and of acetylene in oxygen 3000°).

Hydrogen is a combustible gas, but does not support combustion. For example, it burns well in air with a colourless flame, but if a burning substance is immersed in it this ceases to burn. But, under certain circumstances it even supports combustion, *e.g.* it maintains the combustion of a chlorine flame.

On introducing a small hydrogen flame into glass tubes of varying lengths and widths very varying notes are produced, forming the so-called *chemical harmonica;* this is due to numerous small explosions which succeed one another regularly and rapidly in the tubes through the combination of hydrogen with the oxygen of the air.

Hydrogen is an energetic reducing agent, because it replaces oxygen or eliminates it in the form of water from many compounds. Thus, for example, on passing hydrogen over red-hot copper oxide, pure copper and water are formed: $CuO + H_2 = Cu + H_2O$.

By *reduction* the elimination of oxygen from a compound, with or without substitution by hydrogen, is ordinarily understood. Ipatjew (1909) has shown that hydrogen separates metals from solutions of their salts at high

temperatures and pressures, for example, it separates metallic copper from the acetate in solution at 120° and 600 atmospheres pressure.

By mixing 2 vols. of hydrogen with 1 vol. of oxygen one obtains *detonating gas*, so called because with a lighted body it gives a powerful explosion. The product of this reaction is water vapour which condenses very rapidly, through which cause the effect of the explosion is to some extent weakened. On mixing 10 vols. of air with 4 vols. of hydrogen the right proportions for detonating gas are obtained, but even with 10 vols. of air and 3 vols. of hydrogen the mixture still explodes. Mixtures of hydrogen and oxygen are explosive within the following limits : a minimum of 8 per cent. and a maximum of 64 per cent. of hydrogen ; below the minimum or above the maximum the mixture does not explode. The temperature of ignition of detonating gas is about 700°.

Hydrogen produced by the fermentation and putrefaction of organic substances is chemically very active, and so is that produced in the nascent state from sodium amalgam or that occluded in palladium ; this hydrogen is not in the molecular condition, but partly in the atomic state. In this state it is an energetic reducing agent, and when hydrogen is greatly compressed it is also much more active and even reduces mercuric chloride : $HgCl_2 + H_2 + 1000$ atm. pressure $= Hg + 2HCl$. This phenomenon is quite common, as has been shown by Ipatjew (*vide supra*).

INDUSTRIAL USES OF HYDROGEN. This gas is valuable on account of the high temperature produced when it is burnt in the presence of oxygen (up to 2800°), and this is made use of in the oxy-hydrogen blowpipe (*see* Oxygen) for the fusion and welding of platinum, iron, lead, copper, &c. Hydrogen and oxygen obtained from two cylinders of the strongly compressed gases are brought together in a single tube and when lighted form the oxy-hydrogen flame.

The *oxy-hydrogen flame* has an oxidising action if oxygen is present in excess and a reducing action when an excess of hydrogen is present (5 vols. hydrogen and 1 vol. oxygen) ; it is neutral if exactly 1 vol. of oxygen is present to each 2 vols. of hydrogen. Ordinarily, for welding metals, a flame is used containing 3 to 4 vols. of hydrogen to 1 vol. of oxygen, and for welding lead (for example, in lead chambers for the manufacture of sulphuric acid), the hydrogen flame is fed with air. For some years the oxy-hydrogen flame has been advantageously replaced by the oxy-acetylene flame (*see* Oxygen).

Hydrogen is used in steel-works for the autogenous welding of iron to iron and for homogeneously filling up, with a perfect joint, the blow-holes which are often found in molten steel castings. The welding is much more perfect than that obtained with the electric arc, which is also rather inconvenient because its very intense light is very trying to the sight of the workmen, and produces bad headaches.

In boiler factories the superposed iron plates were formerly riveted and then caulked ; recently autogenous welding has been applied with great economy of time and money.

Hydrogen and also water gas (*see below*) is used for heating the baking and annealing kilns for ceramic materials.

Many chemical operations can be carried out by means of the oxy-hydrogen flame instead of the electric furnace ; for instance, the conversion of barium carbonate into barium oxide appears to be sufficiently well effected.

In glass-works the heating of furnaces and crucibles is greatly accelerated by the oxy-hydrogen flame.

Limelight is produced by impinging an oxy-hydrogen flame on to a block of quicklime. In this way a very vivid light is obtained which is often used both for lighthouses and for projection lanterns instead of the electric

arc. The Döbereiner lamp is of historical interest only, and consisted of a bottle in which hydrogen was evolved and was passed over platinum sponge, causing this to glow and thus igniting the gas.

During the last few years hydrogen has acquired new and great importance in aeronautics (now that the problem of dirigible balloons has been definitely and successfully solved) for filling balloons, because, compared with coal-gas, hydrogen is much lighter, and when compressed in steel bottles to 200 or even 300 atmospheres' pressure, it occupies little space and is convenient for transport ; also it can be prepared on the spot, as will be shown below, by one of two methods of manufacture. The ascensional force of hydrogen is given theoretically by the difference in weight of a cubic metre of air and a cubic metre of hydrogen (1·293 – 0·090 kilo), and is thus 1·203 kilo, but allowance must be made for the lesser weight of the air at high altitudes (at the Observatory Margherita, on Monte Rosa, the atmospheric pressure is about 440 mm.) and for the greater weight of hydrogen as prepared, in the wet state (about 0·120 grm. per cubic metre). In practice one takes one kilo as the raising capacity of one cubic metre of hydrogen, and it is then easy to calculate the quantity required to raise a given weight (balloon, car, crew, &c.). When coal-gas is used, the theoretical ascensional power is only 700 grms. per cubic metre. For aeronautics it is important that the arsenic hydride present as an impurity should be eliminated, as in some cases it may produce poisoning of the crew, followed by death (at Chalais, on April 3, 1900, two people were killed and three others were seriously poisoned) ; for this reason one should stipulate that the sulphuric acid used for producing the hydrogen should not contain more than 10 centigrms. of arsenic and 1 grm. of antimony per litre.

Hydrogen is indirectly used for illumination, with the Auer mantle, and as a motive force, being an important component of water-gas, together with CO_2 and CO, and of lighting gas.

Much hydraulic power which is still lost in waterfalls, especially at night, can be profitably employed for the electrolytic decomposition of water ; the two separate gases are collected in gasometers, may be kept till the daytime, and then serve as a source of heat and thus also of mechanical power.

Oxy-hydrogen gas is perhaps destined to replace coal in great part for many industrial purposes, as coal-gas is inferior as a source of heat and in some cases is 20 per cent. dearer.

In 1905 the engineer Sanne proposed the use of compressed and heated hydrogen for gas motors, by utilising its greater force of expansion, compared with other gases, under the same conditions. He deduced this from the fact that Boyle's law and the efficiency of Carnot's cycle, in the case of compressed and reheated gases, are not equal for all gases, and that the specific constants of the individual gases, deduced from the thermodynamic equations connecting the specific heats at constant pressure and constant volumes indicate that the thermodynamic value of the hydrogen is greater than that of all other gases.

Electrolytic hydrogen is placed on the market in steel cylinders of 35 litres capacity at 200 atmospheres pressure, and is sold at about 10*d*. per cubic metre of gas, measured at the ordinary pressure.

In Italy 42,000 cu. metres of compressed hydrogen were produced in 1905 and more than 43,000 cu. metres in 1907 of the value of £1720 ; the increase in production is very small because the hydrogen blowpipe is being replaced by the oxy-acetylene blowpipe for welding during recent years.

PREPARATION IN THE LABORATORY. In the sixteenth century Paracelsus already knew that some metals, in contact with certain dilute acids, developed an inflammable gas (*inflammable air*). In 1766 Cavendish succeeded in distinguishing and separating hydrogen from other inflammable gases, and in 1781, together with Watts, showed that the sole product of the combustion of hydrogen was water.

In 1781 and 1783 Lavoisier prepared hydrogen by decomposing water with red-hot iron, by which means he was able to fully confirm the chemical composition of water, both from the synthesis of Cavendish and from his own analysis.

Hydrogen is commonly obtained in the laboratory by the action of dilute hydrochloric or sulphuric acid (one part of concentrated hydrochloric acid and two of water, or one of sulphuric acid and four of water) on small pieces of zinc (or also of iron):

$$Zn + H_2SO_4 = H_2 + ZnSO_4 \; ; \quad 2HCl + Zn = ZnCl_2 + H_2.$$

For this operation a Kipp generator is usually used, as illustrated in Fig. 39; the two lower glass bulbs, *b* and *d*, are in one piece and in communication; the upper bulb, *c*, which terminates below in a long glass tube, communicates directly with the lowest bulb, closing hermetically on to the neck, *c*. Into the middle bulb, *b*, granulated zinc (obtained by pouring molten zinc into water) is introduced through the aperture, *e*, and the dilute acid is poured into the upper bulb so that it also fills the lowest bulb and is driven into the central one, where, in contact with the zinc, it produces hydrogen. The gas escapes from the aperture, *e*, provided with a cock, is washed by bubbling through a solution of caustic soda in the bottle, *S*, and is collected over water in the cylinder, *C*. When the evolution of gas is to be stopped the cock, *e*, is at once closed and the gas which continues to be developed in *b* exerts pressure on the acid and drives it into the lowest bulb, *d*, and partly into the upper bulb. When there is no more acid in the middle bulb the gas evolution stops, and when gas is again required the cock is opened and the acid again comes into contact with the zinc. By using this ingenious apparatus any quantity of gas can be produced at any time by reaction between a liquid and a solid substance (*e.g.* hydrogen sulphide, carbon dioxide, acetylene, &c.), without any loss of time or waste of reagents.

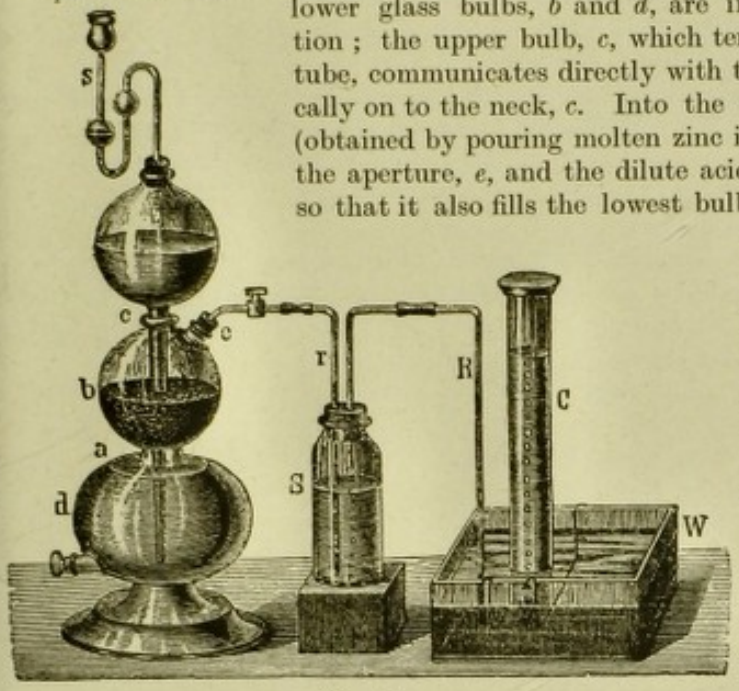


Fig. 39.

Another apparatus, more simple and equally convenient and in general use, is shown in Fig. 40, and consists simply of two tubulated bottles, *S* and *Z*, communicating below by a long rubber tube, *r*. One of these contains the zinc and the other the acid; when the latter is raised, acid passes into the former and the gas is developed; when it is lowered, the acid runs back and the evolution of gas ceases.

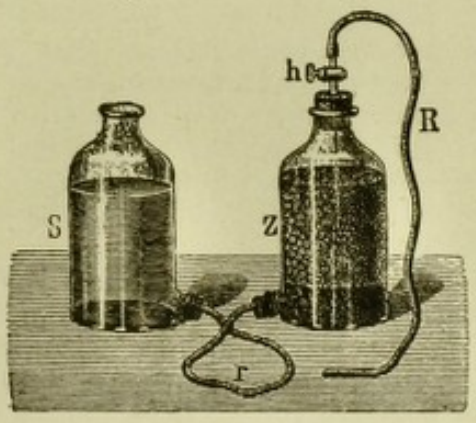


Fig. 40.

During the electrolytic decomposition of water (acidified with sulphuric acid, 1 : 10) the hydrogen collects at the negative pole, and the oxygen at the positive pole. Bunsen proposed an apparatus for collecting purest electrolytic hydrogen (Fig. 41) from acidified water by separating the oxygen at the positive pole with a plate of amalgamated zinc and collecting the hydrogen from the negative pole which is led off through a superposed tube at the top of the apparatus, surrounded by water or mercury to prevent escape of the gas.

Hydrogen is purified by washing with a solution of potassium permanganate, and is dried with fused potassium hydroxide or by being bubbled through concentrated sulphuric acid.

Hydrogen is also obtained by the electrolysis of a dilute aqueous solution of sodium hydroxide, but in this case it is always contaminated with small traces of acetylene

derived from the small quantities of carbides contained in the caustic soda ; this applies in a still greater degree to potassium hydroxide. Hydrogen so obtained contains only 0·001 to 0·005 per cent. of nitrogen.

Hydrogen is formed by the action of various metals on water ; potassium acts even in the cold, with incandescence and catches fire ; sodium acts less violently, and in the form of amalgam gives a steady current of gas : $H_2O + Na = NaOH + H$ (sodium amalgam is an alloy of sodium and mercury).

The alkaline earth metals also develop hydrogen with water. In all these cases the hydroxides of the metals and free hydrogen are formed. Magnesium powder commences to react with water, evolving hydrogen at 70°, and more actively still in presence of a little magnesium chloride which dissolves the magnesium oxide which is formed at the same time.

Iron decomposes steam at high temperatures with formation of hydrogen, commencing at 300°, and attaining a maximum at 800° ; this method finds industrial application :

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2.$$

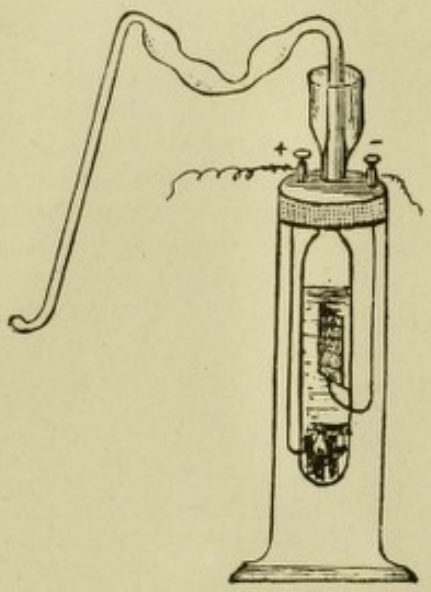


Fig. 41.

The hydrogen which is formed is collected by displacement of water in glass cylinders inverted over a vessel of water. It is recognised by burning with a pale flame, forming water when lighted.

Hydrogen is obtained fairly pure and in great abundance by the action of aluminium powder on boiling water, with the help of the catalytic action of a little dilute solution of potassium permanganate. After the action has been started it continues without further heating. Permanganate in excess is harmful and cannot be replaced by a solution of other oxidising substances such as chlorates, perchlorates, or potassium nitrate.

Pure hydrogen is also obtained by decomposing potassium formate with potassium hydroxide on heating :

$$\underset{\text{Potassium formate.}}{CO_2KH} + KOH = \underset{\text{Potassium carbonate.}}{CO_3K_2} + H_2.$$

Also zinc and magnesium evolve hydrogen from ammonium salts, excepting ammonium nitrate.

One can also obtain hydrogen by heating to redness a mixture of finely divided zinc or iron with quicklime and slaked lime : $Fe + Ca(OH)_2 = FeO + CaO + H_2$.

Very pure hydrogen can be obtained from pure zinc and pure sulphuric acid, but as chemically pure zinc alone does not react with the pure acid a small trace of platinum chloride must be added ; this produces a minute deposit of platinum on the zinc, forming a voltaic couple, which immediately causes the gradual solution of the zinc and regular evolution of pure hydrogen (which can only contain the traces of other gases which may be occluded in the zinc).

PURIFICATION OF HYDROGEN. Hydrogen prepared from ordinary reagents always contains impurities, such as the nitrogen oxides N_2O and NO (produced from the nitrous products contained in the sulphuric acid), hydrogen sulphide (H_2S), sulphurous acid (SO_2), hydrogen phosphide (PH_3), arsenic hydride (AsH_3), carbon monoxide (CO), and dioxide (CO_2). It is purified by washing with a 5 per cent. solution of silver nitrate, then by sodium hydroxide solution, and is finally dried by passing over phosphoric anhydride. If copper sulphate is added to the zinc, H_2S does not occur as an impurity. CO_2, H_2S, and SO_2 may also be absorbed by ammonia ; AsH_3 and PH_3 are removed by fuming nitric acid or by bromine, and the nitrogen oxides by ferrous sulphate.

A satisfactorily complete purification for industrial purposes is obtained with an alkaline solution of potassium permanganate (5 grms. of permanganate in 100 grms. of potassium hydroxide of 10 per cent.). Hydrogen is sometimes purified by passing it through vessels containing quicklime, iron oxide, and sawdust (Laming's material, as used for purifying coal-gas). In a prize competition at Frankfort in 1906 the method of Wentzki was recognised as the most reliable for eliminating arsenic hydride ; by this method the gas is passed into a cylinder of one-third of the volume of the generator, containing a mixture

of two parts of dry calcium hypochlorite with one part of moist sand or other finely divided material.

Hydrogen may be considered to be well purified when it gives no precipitate or coloration on passing through a solution of silver nitrate. When dry hydrogen is required it must be finally passed over quicklime, concentrated sulphuric acid or granulated fused calcium chloride.

INDUSTRIAL PREPARATION OF HYDROGEN. Of the many various processes[1] which have been proposed for the preparation of hydrogen on the large scale, we will only record those which have been successfully applied.

In some chemical industries, and for filling balloons in stationary military camps, hydrogen is prepared by the action of dilute sulphuric acid on iron turnings. For this purpose strongly bound and perfectly gas-tight vats are used: $Fe + H_2SO_4 = FeSO_4 + H_2$.

The inconvenience of this process arises from the fact that the iron finally becomes covered with ferrous sulphate which protects it from the further action of the acid. Among the many ingenious mechanical devices for eliminating this difficulty the column devised by Renard has met with success; this removes the ferrous sulphate gradually as it is formed by means of a continuous circulation; sulphuric acid of 12° Bé. enters at the base of a lead cylinder containing iron turnings, and the ferrous sulphate solution, which no longer contains sulphuric acid, is continuously raised to the top; the gas is washed with water, then passes over Laming's mixture (*see* Coal-gas, vol. ii., "Organic Chemistry") to remove sulphur compounds, and is freed from other acids by passing over granulated sodium hydroxide. For the preparation of 600 cu. metres of hydrogen, 1800 kilos of iron, 3000 kilos of sulphuric acid of 66° Bé., and 100 cu. metres of water are required. If zinc is used instead of iron 2100 kilos of this will be required, with 3600 kilos of sulphuric acid. The sulphuric acid should not contain more than 10 centigrms. of arsenic and 1 grm. of antimony per litre, and to avoid arsenic in the metal steel turnings are used.

In the Russo-Japanese War (1904–1905) the Russians found it convenient, in order to avoid the transport to and fro of heavy steel cylinders of compressed hydrogen for their balloons on the field of battle, to produce hydrogen as required on the spot (in Manchuria) by the action of 30 per cent. caustic soda solution on aluminium scrap. The former was contained in cylinders of sheet iron 2 metres long and 0·5 metres wide, in which a metallic box containing the aluminium in the form of sheets of 1·5 to 2 mm. thickness, was immersed: $Al + 3NaOH = Al(ONa)_3 + 3H$. As the gas so obtained was very warm it was cooled

[1] The preparation of hydrogen on a large scale was already tried without success by Fontana in 1782, by the action of steam on red-hot iron: $3\,Fe + 4H_2O = Fe_3O_4 + 4H_2$. This process was taken up again by Giffard in 1878, but was very soon abandoned. Oettel, according to his Eng. Pat. 16,759 of 1885, prepared hydrogen by passing steam over iron scrap and filings enclosed in heated iron tubes which had been evacuated. In 1887 Belou (Ger. Pat. 43,989), in Paris, prepared pure hydrogen by passing steam over red-hot iron tubes or bars enclosed in a retort. The oxide of iron which was formed was afterwards reduced to metallic iron by sprinkling it with powdered coal and re-heating. A mixture of CO and CO_2 was thus formed which was used for heating the same retort.

Howard-Lane, and also Elworthy and H. Williamson (1902), attempted to make this process industrial by patenting a special form of furnace in which the iron was disposed in thin layers in channels of refractory material, so that the surface of the iron was traversed by the steam (Ger. Pat. 164,721). In a French patent of 1909 (No. 405,200) the use of iron obtained by the reduction of the oxide (burnt pyrites) is proposed; this material, being finely divided, gives a much better yield. The resulting iron oxide is reduced each time to metallic iron by means of water-gas (H and CO) of which the carbon monoxide is absorbed at 180° by a mixture of lime and potassium hydroxide ($KOH + CO = HCO_2K$), and the resulting potassium formate yields hydrogen on heating to 300° ($HCO_2K + KOH = K_2CO_3 + H_2$). This process is used for military balloons at Berlin, and the working costs are less than 1·8*d*. per litre of hydrogen; the cost of prime materials does not raise the total cost much.

W. Majert and G. Richter, in 1888, prepared hydrogen by a process based on the principle of that of Tissié, du Motay, and Maréchal from lime and coal: $C + 2Ca(OH)_2 = 2CaO + CO_2 + 2H_2$; in order to accelerate the reaction they improved it by employing a mixture of zinc powder mixed with calcium or magnesium hydroxide or similar substances: $Zn + Ca(OH)_2 = ZnO + CaO + H_2$. In this way no carbon dioxide was formed but only hydrogen. The lime and zinc were enclosed in small boxes which on heating quickly evolved hydrogen and were used for military purposes and for rapidly filling balloons in time of war. This process, which attracted much interest, cannot be thought of in practice when one thinks of its enormous cost; 1 cu. metre of hydrogen introduced into the balloon costs 4*s*. 2*d*. In 1888 Jacoby proposed the replacement of the zinc by iron, in which way one-third more hydrogen is obtained of purer quality, and free from arsenic, at less cost.

It has been recently shown (Fr. Pat. No. 406,930 of 1909) that a good yield of hydrogen is obtained by heating a dilute (8 per cent.) solution of sodium hydroxide with 14 per cent. of calcium hydroxide and 7 per cent. of elementary silicon; a solution of sodium silicate (Na_2SiO_3), which is a by-product of a certain value, remains. It appears that the Zeppelin balloons in Germany are filled with hydrogen obtained by the explosive decomposition of compressed acetylene, with formation of carbon (carbon black) and hydrogen.

and washed by passing through cylinders of water. The process is, therefore, only of service where there is an abundant supply of water. With twenty-four generators and six coolers a balloon of 400 cu. metres capacity can be filled in half an hour. The generators and washers can be carried on the backs of fifteen horses, and a further thirty to thirty-five horses are required to transport the balloon and accessories, including the chemicals (NaOH and Al). In the Boer War the British employed hydrogen compressed to 200 atmospheres in steel cylinders, and required fifty horses for the transport of all materials for a balloon of 400 cu. metres, apart from the disadvantages already referred to above, of the transport of the cylinders to and from England.

Recently A. Frank has proposed (1907) the preparation of hydrogen from water-gas, which contains as much as 50 per cent. (*see* chapter on Carbon Monoxide), by passing it over red-hot calcium carbide, which absorbs all the other gases, or by first removing carbon dioxide with lime, liquefying the carbon monoxide in a Linde freezing machine (*see* Liquid Air) and finally removing nitrogen and oxygen with red-hot calcium carbide (*see* Calcium Cyanamide); the carbon monoxide can be utilised in a gas motor. G. Claude liquefies all the other constituents of coal-gas, which contains up to 50 per cent. of hydrogen, in a Linde machine at − 193°, leaving hydrogen only; others prefer to pass coal-gas over incandescent coke which decomposes the hydrocarbons, leaving hydrogen mixed with a little carbon monoxide only.

INDUSTRIAL ELECTROLYTIC METHODS. For the production of large quantities of hydrogen electrolytic methods have to-day proved themselves better than purely chemical processes, as they are cheaper. The Englishmen, Carlisle and Nicholson, in 1800, were the first to decompose water electrolytically, using a Volta pile. The method has only acquired practical importance during the last few years.

In electrolysis two gases are separately formed: oxygen at the positive and hydrogen at the negative pole; but if the electrodes are in close proximity the gases are able to mix to some extent, and it is necessary to separate the two electrodes by means of a diaphragm. This latter, however, causes various difficulties (such as high resistance, short life, liability to obstruction, &c.) and the choice of suitable material is not easy. Porous porcelain, asbestos fabrics, parchment paper, glass, india-rubber, &c., have all been tried, but after many attempts the practical solution was found by the brothers Garuti, who employed metallic diaphragms. The objection was at first raised that if the metallic diaphragm became polarised and took part in the electrolysis, then the face opposite the anode (which develops oxygen) would evolve hydrogen, whilst the other face would develop oxygen, and the mixtures of the two gases thus formed would constitute a serious danger through the formation of detonating gas. This difficulty is practically avoided by consideration of the following facts: the electromotive force (E.M.F.) necessary to decompose water is about 1·5 volts, and when the diaphragm is polarised the whole system represents two cells in series; therefore if the two walls of the diaphragm are to play any part in the electrolysis the double electromotive force of 3 volts is required (*i.e.* 1½ volts for each side). If, therefore, the terminals of the cell are maintained at an E.M.F. of less than 3 volts electrolysis can only take place at the electrodes and the diaphragm remains neutral.

This difficulty having been quite overcome by the Garuti system, it was tried for the first time in 1890 in the Brera Palace, in Milan, and was then at once applied on a vast scale in the gun factory at Terni, in the Milanese steel foundry, in the military aeronautical camp at Rome, and later in other Italian and foreign establishments (especially by Garuti and Pompili at Tivoli).

The Garuti batteries were at first made entirely of lead, and the electrolyte consisted of water acidified with sulphuric acid. They consist of a rectangular iron box, *N* (Fig. 42), divided by iron sheets about 1 mm. thick, the diaphragms, coated on both faces

with a metallic net, to facilitate the separation of the small bubbles of gas produced by the current from the ions. We have thus several cells, closed at the top and at the sides (*see* Figure *below*), communicating, on the other hand, below through small holes in the diaphragms, which permit circulation of the electrolyte. In these cells positive and negative electrodes are introduced alternately, consisting of iron plates about 1 mm. thick (the anodes last two to three years, the cathodes much longer) of rectangular shape with a small extension alternately in the one direction or the other (*B* and *C*) in such a manner as to enable all the positive poles on one side of the box (voltameter) and all the negative poles at the other side to be connected.

The walls of each cell are about 20 mm. apart, and between each diaphragm (wall) and the interposed electrode the distance is about 10 mm., so that the resistance is sufficiently small ; in order to prevent the thin electrodes from bending and coming into contact with the diaphragms they are wrapped round at intervals with an asbestos cord, *t*, which keeps them in position.

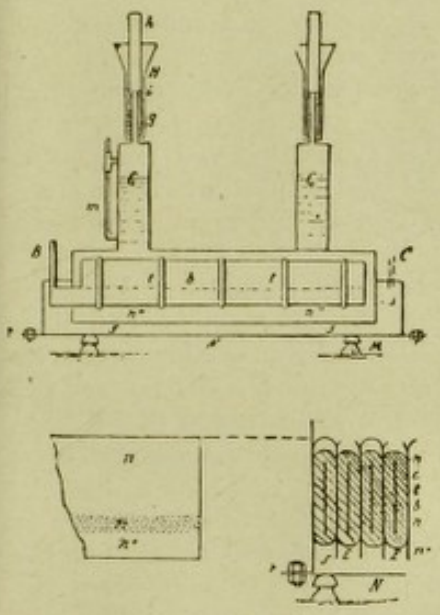


Fig. 42.

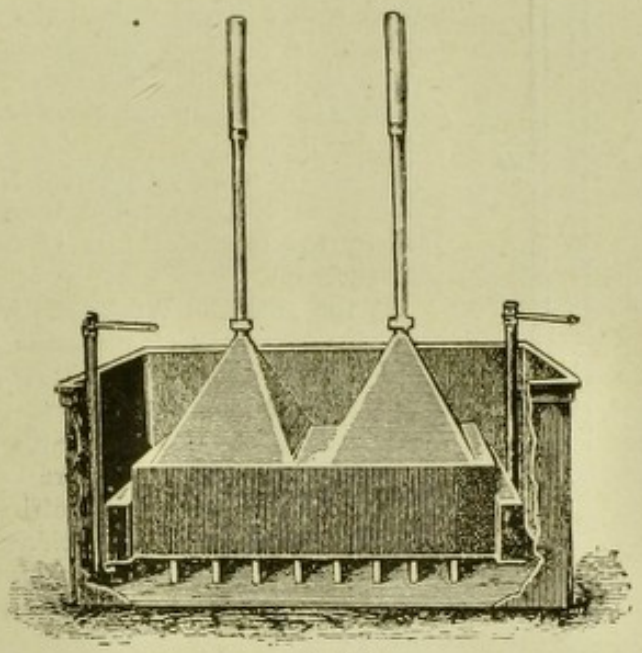


Fig. 43.

The cells containing the cathodes (*b*) develop hydrogen, which passes off through an opening at the top ; the neighbouring cells, containing the anode, *a*, develop oxygen, which also passes off at a hole in the top. A pyramidal chamber, placed above the battery, collects all the oxygen, and another similar chamber all the hydrogen. By means of two tubes made of insulating material, such as glass, porcelain, or rubber, these two chambers communicate with gasometers. Each of these chambers contains a fair quantity of mother liquor.

The electrolyte consists of a 26 per cent. aqueous solution of sodium hydroxide, which remains practically unaltered indefinitely if the water is replaced gradually as the electrolysis proceeds.

The caustic soda must be very pure, as otherwise the electrodes are corroded because of the presence of chlorides and sulphates, which form Cl and SO_4 ions and attack the metal. These iron batteries are welded autogenously throughout with the oxy-hydrogen blowpipe ; they are stronger than the original batteries made of lead, and certain solders are avoided which at one time acted as voltaic couples and produced detonating gas. The lead batteries also polarise more easily. The caustic soda solution has now been replaced by a solution of caustic potash of 31° Bé., because this offers less resistance to the current and thus saves electrical energy.

In an apparatus thus constructed an E.M.F. of 2 volts is sufficient for a current of 2 amps. per sq. decimetre of electrode at a temperature of 30°.[1]

[1] The iron batteries are constructed with capacities of 200, 400, and 3200 amperes, and always for an E.M.F. of 2 to 2·8 volts. With cheap hydraulic power of 1000 h.p. 5000 cu. metres of gas ($O + H_2$) are obtained per day, at an inclusive cost of 0·5*d*. per cubic metre. In small plants 1 kw.-hour produces about 160 litres of hydrogen and 80 litres of oxygen.

An apparatus analogous to that of Garuti was also produced in France by Colonel Renard for military purposes,

In 1901 Schoop introduced a cheap and carefully considered apparatus for the electrolytic production of hydrogen on a large scale. The electrodes are of lead, in the form of tubes, and there are no diaphragms. The baths consist of water acidified with sulphuric acid. The apparatus is also constructed in iron with 15 per cent. caustic soda as an electrolyte. The Schoop electrodes are very simple (Fig. 44). There are two long concentric lead cylinders of which the outer serves as a collecting tube, and more or less as a diaphragm, whilst the inner tube is the true electrode, and is supported by means of an insulating disc, *M*, in the wider neck of the outer tube, which forms a hydraulic seal with water. The inner tube is perforated at the base and near the top (*L L*), so that the gas which is formed may enter the inside of this tube and thus be conducted to the gasometer.

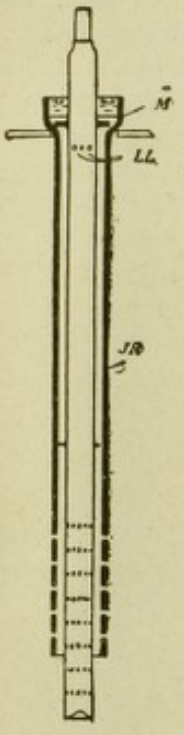


FIG. 44

The cylindrical electrodes are introduced in large number into a tall vessel containing the electrolyte, which is pure sulphuric acid of sp. gr. 1·23. All the negative electrodes, forming hydrogen, are connected with a single collecting tube, and all the oxygen anodes with another. A plant on Schoop's system is worked at the accumulator factory of G. Hagen, at Kalk near Cologne, with a current of 200 amps. and at 65 volts. Schoop calculates that the gas produced costs about 3·7*d*. per cubic metre.

A method not very different from that of Garuti, but with non-porous diaphragms of ebonite, has been proposed and applied at Hanau since 1897 by the electrical firm of Schuckert & Co., and appears to meet with success.[1]

At the Elektron Works at Griesheim-on-Rhine hydrogen is prepared by the electrolysis of potassium chloride: $2KCl = K_2 + Cl_2$ and then $K_2 + 2H_2O = 2KOH + H_2$. By this reaction three important products, chlorine, hydrogen, and caustic potash, are obtained. The Società del Caffaro at Brescia now makes use of the hydrogen evolved at the cathode in the electrolytic manufacture of caustic soda, a practice also followed by many works in other countries.

For some years the Maschinenfabrik Oerlikon (Switzerland) has constructed an electrolytic apparatus devised by Schmidt (1902) for the manufacture of hydrogen and oxygen; in principle it is analogous to the apparatus of Garuti, but occupies less space, being composed of many electrolytic cells combined and connected together as in a filter-press. Ingenious arrangements are attached for the almost automatic control of the purity of the gas. By this process twelve kilowatt-hours are required for the production of 1 cu. metre of oxygen and 2 cu. metres of hydrogen.

ANALYSIS OF HYDROGEN. The qualitative detection of impurities is carried

with iron electrodes, a bath of caustic soda, and diaphragms of asbestos. It was, however, less perfect than the Garuti battery and required double the amount of energy per volume of gas produced. The Société ossidrique française was first formed in Belgium and in 1901 in France, with a capital of £40,000, for the production of oxygen and hydrogen by the Garuti system.

[1] For a small installation and daily production of 100 cu. metres of oxygen and 200 cu. metres of hydrogen the cost of plant and working expenses would be as follows:

	£
40 voltameters for 600 amps.	500
Pipe system, alkaline bath, installation, &c.	200
Roofed building of 70 sq. metres area	200
Total cost of plant	£900

The daily costs of working—using a waterfall which supplies a kilowatt-year at a cost of £7 10*s*. (using steam power the kilowatt-year would cost about £20)—are as follow:

	£	*s*.	*d*.
Daily cost per 60 kilowatts	1	12	9
Consumption of electrodes and electrolyte		3	7
Various repairs to machinery and buildings		4	3
Wages of two workmen		8	0
15 per cent. amortisation on £900		9	7
Sundry expenses		2	10
Total daily expenses	£3	1	0

Thus each cubic metre of gas (H and O) costs 2·5*d*. If this gas is to be sold, 2·5*d*. must be added for the cost of compression in steel cylinders.

It will be clear that where energy is much cheaper than is assumed above, the cost of producing the gas will also be much less.

(*Translator's note.*—In England a kilowatt-year, produced by steam, costs much less than £20.)

out by the ordinary methods ; arsenic hydride is detected with the Marsh apparatus (which also permits of its quantitative determination ; *see* Arsenic Hydride), and hydrogen sulphide is detected by immersing paper impregnated with lead acetate for some time in the hydrogen to be analysed. The quantitative analysis also follows the ordinary methods of gas analysis in an Orsat apparatus (*see* Carbon and Analysis of Furnace Gas) ; by determination of the successively absorbed volumes the percentages of CO_2, O, and CO are found ; that which remains is hydrogen, which may contain admixed nitrogen. This is passed through a hot capillary tube containing a thread of palladinised asbestos which absorbs all the hydrogen leaving the nitrogen. Temperature and pressure must be allowed for in measuring the gases (*see* p. 26).

(A) NON-METALS ; HALOGEN GROUP

This is the first group of non-metals and consists of four monovalent elements, fluorine, chlorine, bromine, and iodine :

$$F = 19 ; Cl = 35{\cdot}46 ; Br = 79{\cdot}92 ; I = 126{\cdot}92.$$

They are called *halogens*, from a Greek word meaning salt-formers, and, in fact, they combine easily and directly with almost all metals and with bases to form salts.

In their physical properties they show graduated differences with increasing atomic weight, with which the density also increases, and they pass from the gaseous to the solid state :

	F	Cl	Br	I
Atomic weight	19	35·46	79·92	126·92
Melting-point	−252°	−101·7°	−7·2°	+ 114°
Boiling-point	−187°	−33·7°	+ 60°	+ 184°
Specific gravity in the liquid state	1·108	1·47	3·18	(as solid) 4·9
Colour	pale yellowish	yellowish green	brown	blackish violet

The affinity of these elements for metals and hydrogen is large in the case of F and Cl, and decreases in the direction of iodine, that is, with increase of atomic weight. Where the affinity decreases in this direction it is possible in many compounds to substitute or displace iodine by bromine, bromine by chorine, and chlorine by fluorine. In the combinations with oxygen the affinities increase in the reverse direction, that is, the oxygen compounds of iodine are more stable than those of chlorine, and fluorine does not combine with oxygen at all.

Minimal traces of the halogens facilitate and often cause chemical reactions which do not take place under ordinary conditions (Schnyten, 1907–1909).

FLUORINE : F, 19

This element has only been known in the free state since 1886. Before that time it was only known in the combined state and therefore its properties were only indirectly utilised by means of its more important compounds (fluorspar or fluorite, CaF_2, cryolite, AlF.3NaF, &c.). The addition of fluorspar to minerals to facilitate their fusion was already known to Basil Valentine in the fifteenth and to Agricola in the sixteenth century as being practised in those times. The luminosity of fluorspar when heated is recorded in various writings in 1667. Moissan stated that he had recognised free fluorine in the gaseous occlusions in a fluorspar from Quincié.

It is also found in small quantity combined as calcium fluoride in the bones of man and other mammals, and in the enamel of the teeth ; therefore

fluorine must pass into the blood in some form, and is provided by certain human foods (milk and vegetables).

PROPERTIES. It is a slightly greenish yellow gas, with an odour similar to that of hypochlorous acid. It has no absorption spectrum and is completely non-magnetic. The red part of its luminous spectrum (emission spectrum) is composed of thirteen characteristic lines.

Fluorine is ordinarily considered to be monovalent, but Blomstrand (1869) on account of the existence of acid fluorides, and Thomsen for the same reason, and from the heat developed on saturating silicic acid with hydrofluoric acid, consider fluorine to be divalent and hydrofluoric acid to have the constitution H – F – F – H. Further work is required to clear up this question, but we now know fluorides of silver and of calcium, Ag_2F and CaF.

Fluorine combines even in the dark with H, I, S, Si, Se, B, As, Sb, Fe, Mn, with all organic compounds, &c. The metals are strongly attacked with the exception of gold and platinum. It attacks water, forming HF and ozonised oxygen (O_3). It replaces Cl, Br, and I from their metallic compounds. It only combines with carbon at a red heat; it does not combine with diamond even at a red heat. Sugar is immediately carbonised. This great reactivity is the cause of the great difficulty encountered in liberating the free element, and it gives ground for hope that important applications await this interesting element in the future.

In 1897 Moissan and J. Dewar succeeded in liquefying fluorine at −187° (with boiling liquid oxygen), but at −210° it was not yet solid. At this temperature it almost completely loses its extraordinary chemical affinity for many substances, and no longer reacts with water, mercury, &c., but still reacts with hydrogen, and ignites benzene and turpentine. When perfectly dry it does not attack well-dried polished glass. The liquid is of yellow colour and has a specific gravity of 1·108 at −187°, that is, at the boiling-point (Ramsay, 1900). In 1903 it was solidified by Moissan and J. Dewar by means of liquid hydrogen at −252°, and then formed a white mass, exploding violently in contact with liquid hydrogen; it boils at −223°.

PREPARATION. It was already known in 1670 that when fluorspar was mixed with oil of vitriol (H_2SO_4) it attacked glass, and in 1781 Scheele obtained free hydrofluoric acid by preparing it in vessels of lead or fluorite, as he knew that it attacked glass and almost all metallic vessels. In 1810 Ampère showed that this acid was a hydrogen compound.

The attempts to obtain free fluorine were very numerous and were prosecuted by many able chemists of the century which has just passed. The more difficulties were encountered the greater grew the determination to solve the problem. From Davy (1818) to the brothers Knox (1841), Louyet (1847), Kammerer (1865), Finkener (1867), Fremy, &c., there was a continuous series of abortive experiments. When they thought they had obtained fluorine the gas was quickly shown to be either hydrofluoric acid or oxygen instead. The action was tried, without success, of chlorine and iodine on the fluorides of silver and of mercury, at high temperatures (Davy) in tubes of glass and of platinum and in vessels made of fluorspar. The same negative result was obtained by the electrolysis of dry hydrofluoric acid with a positive electrode of carbon.

All this proved useless; and even if free fluorine could be traced from various reactions a minimal trace of moisture sufficed to cause it to enter into combination, even with the substances composing the vessels in which it was prepared.

Moissan only succeeded in 1886 in finally obtaining free fluorine with certainty, by employing many precautions to prevent it from combining with other substances. He started from absolutely anhydrous hydrofluoric acid, obtained by heating potassium hydrogen fluoride, HF.KF, and collecting this in a platinum U-tube connected with a delivery tube of platinum and closed by cocks of fluorspar.

The negative electrode, at which liberation of the hydrogen was expected, was made of platinum, and the positive electrode, where the fluorine was to be liberated, was made of an alloy of 90 per cent. platinum and 10 per cent. iridium. The apparatus was cooled to −23° and connected with a battery of twenty Bunsen cells, producing a current of 20 amps., which did not pass through the hydrofluoric acid in the apparatus. The addition of a minimal trace of moisture, however, quickly allowed the current to pass, but free fluorine was not then obtained. Thus this attempt to prepare fluorine electrolytically failed, equally with those of other chemists. Moissan finally succeeded in rendering dry hydrofluoric acid electrically conductive by the addition of a small quantity of dry potassium hydrogen fluoride. At the positive pole a gas was then obtained which proved to be real fluorine.

Moissan then also prepared it by direct electrolysis of fused dry potassium hydrogen fluoride, replacing the platinum by copper vessels.

In 1900 Poulenc and Meslan prepared considerable quantities of fluorine electrolytically in a copper apparatus, which very soon became covered with copper fluoride and then became unattackable ; the anodes and cathodes were of copper and were insulated with india-rubber. The whole apparatus was cooled during the electrolytic decomposition.

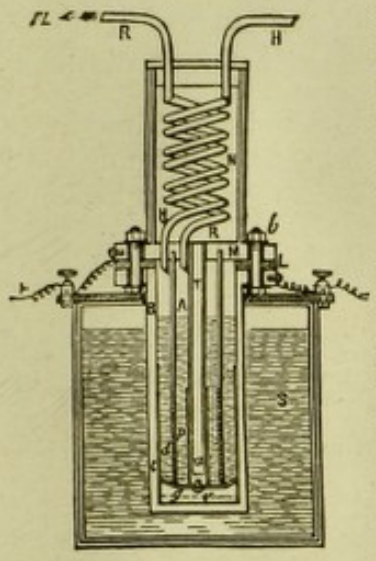


Fig. 45.

A small apparatus for laboratory use is shown in Fig. 45. A small copper box, *B*, supported by the lid, *M*, carries on its inner walls sheets of copper, *G*, which serve as cathodes. The copper tube, *A*, which is perforated near the base, *d*, forms the chamber which contains the platinum anode, *p*, which is cooled by the liquid which circulates in the tube *T*. Fluorine escapes by the tube *R*, and hydrogen by the tube *H*. In the box, *S*, a freezing mixture is contained.

The electrolyte consists of a very cold solution of potassium fluoride in anhydrous hydrofluoric acid. G. Gallo (1910) did not obtain good results with the apparatus of Poulenc and Meslan and replaced it with advantage by a smaller and simpler apparatus of platinum ; this consisted of an ordinary platinum crucible which was attached to a metallic ring serving to connect it with the negative pole of the electric battery. The crucible was closed with a gas-tight lid of sulphur, which is a very excellent material for such work on account of its easy fusibility, and adheres solidly to many metals. Through the centre of the sulphur plug was fixed a small cylinder of platinum which ended inside the crucible but without touching it, and which acted as a diaphragm. The small cylinder is easily made by rolling a sheet of platinum foil on to itself and pressing in the ends on to a rod. It is closed below by a platinum disc and is pierced with lateral holes at the base. Inside it is fixed a fairly thick platinum wire which serves as the positive pole and which terminates outside the sulphur plug. The fluorine which is evolved inside the crucible does not come in contact with the sulphur, as this is first protected by a disc of potassium fluoride.

The inside of the crucible communicates with the outside by means of two spiral copper tubes passing through the sulphur plug, of which one enters the anodic and the other the cathodic space. These serve as delivery tubes for the fluorine and hydrogen respectively. The two spirals are continued through a copper sleeve which is filled with a freezing mixture. The anhydrous hydrofluoric acid and potassium hydrogen fluoride are introduced through a hole in the sulphur lid, which is then closed with a plug of sulphur which may be fixed by fusion.

During electrolysis the crucible is immersed in methyl chloride which boils at − 23°, and under these circumstances free fluorine is obtained by employing a current of 2 to 3 amps. at 50 volts.

CHLORINE : Cl, 35.46

Chlorine is a gas which was discovered by Scheele in 1774, but is never found free in nature on account of its great chemical activity. But it is very abundantly found in the form of chlorides such as rock salt and sea salt (NaCl), sylvite (KCl), carnallite ($KCl.MgCl_2 + 6$ aq.), &c. It is found in combination in small quantities in all vegetables, in blood, animal secretions, &c.

PHYSICAL PROPERTIES. Chlorine is a yellowish green gas of suffocating odour, with a density of 2·45 compared to that of air.

One litre of chlorine weighs 3·167 grms.; it is liquefied at 15° under a pressure of 57 atmospheres or at $-40°$ at atmospheric pressure, forming a dark yellow liquid (sp. gr. 1·557), which boils at $-33·6°$ and forms a yellow crystalline solid at $-202°$. The vapour density at 1200° was found by V. Meyer to be less than that corresponding to the molecular weight, and he assumed that some of the Cl_2 molecules had undergone dissociation; it seems, however, from later experiments that it is a case rather of exceptional behaviour of this gas with respect to the laws of Boyle and Gay-Lussac, and that its density increases by more than the amount calculated from these two laws when the pressure is increased or the temperature diminished; in this way it has been recently shown that even at 1137° there is no appreciable dissociation.

Wood charcoal absorbs as much as 200 vols. of chlorine with evolution of 6780 calories for each 35·5 grms. of chlorine absorbed.

At 90° water absorbs extremely little chlorine; at 20° 1 vol. of water absorbs 2 vols., and at 10° $2\frac{1}{2}$ vols.; chlorine water is thus obtained, the properties of which are almost the same as those of chlorine, though it seems that in solution a state of equilibrium is produced according to the following equation :

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

and as hydrochloric acid is dissociated there will be in the solution altogether a mixture of water, chlorine, hydrochloric and hypochlorous acids, and the corresponding ions. Under the action of light all the chlorine is transformed into HCl (in four days in direct and in thirty-six days in diffused light), passing through the stages of hypochlorous and chloric acids : $Cl_2 + H_2O = 2HCl + O$ (Ferentzy, 1908), from which we are also able to explain the oxidising power of chlorine water. At temperatures below 0° chlorine water deposits crystals of chlorine hydrate ($Cl.8H_2O$).

CHEMICAL PROPERTIES. In certain compounds chlorine is no longer monovalent, but polyvalent, *e.g.* in ClO_2, &c. Chlorine combines directly with all the elements except nitrogen, oxygen, and the new gases argon, helium, &c. The chlorine ions, Cl′, of soluble chlorides combine readily with the silver ions of silver nitrate, forming a characteristic gelatinous white precipitate of silver chloride, soluble in ammonia.

The great reactive power of chlorine may be shown by various simple experiments. A piece of phosphorus immersed in a flask of chlorine first melts and then catches fire spontaneously, giving out a bright light and producing white fumes which deposit as a white powder of phosphorus pentachloride, PCl_5.

Antimony powder when thrown into a jar of chlorine immediately catches fire, and thin foil composed of other metals, such as pinchbeck, tin, &c., behaves in chlorine in a similar manner. But these materials do not react with liquid chlorine at $-90°$.

Hydrogen and chlorine combine with detonation when a flame is brought in contact with the mixture; but bright daylight is also able to bring about

the explosion, especially if the mixture is moist and freshly prepared electrolytically from HCl. The combination proceeds more slowly in diffused light and still more slowly in the dark. The heat of combination of H and Cl is about 92 Kj. (22,000 cals.). A *dry* mixture of H and Cl does not react in the dark, even in fifteen months; at −25° the mixture does not explode even under the action of intense light.

Chlorine combines even with the hydrogen contained in other compounds, for example, with the hydrogen of many organic compounds, and also with the hydrogen in water, yielding oxygen. Thus, a piece of paper soaked in turpentine, which is an organic compound containing carbon and hydrogen, burns rapidly with formation of carbon when introduced into a cylinder of chlorine.

Chlorine has a decolorising action on many coloured organic substances, both natural and artificial; it easily bleaches solutions of soluble indigo, logwood, and litmus, fresh flowers, many artificial flowers, &c. Fabrics dyed with various aniline dyestuffs are not bleached by chlorine when dry, but are rapidly bleached in presence of moisture.

Chlorine does not burn in the air, but it burns in an atmosphere of hydrogen, in which it is a combustible substance. But the property of a substance of being combustible or a supporter of combustion is relative to the conditions under which the reaction takes place; thus, for example, chlorine is also a supporter of combustion, for a flame of hydrogen or coal-gas, or a burning candle continues to burn in a cylinder filled with chlorine, the hydrogen burning with a pale blue flame and the coal-gas and the candle with a sooty flame, as chlorine removes hydrogen from organic compounds with separation of carbon. In all these cases hydrochloric acid is formed and can be recognised by its action on litmus paper.

Chlorine displaces iodine from iodides and bromine from bromides because the heat of formation of chlorides is greater than that of the corresponding bromides and iodides (third law of thermochemistry):

$$KI + Cl = KCl + I + 25{,}500 \text{ cals.}$$

Chlorine also reacts incompletely with steam in presence of heated carbon to form hydrochloric acid: $2Cl + 2H_2O + C = 4HCl + CO_2$ (Lorenz, 1895 and 1897).

In spite of being a supporter of combustion and an oxidising agent chlorine is irrespirable and is quite unable to replace oxygen in our organism.

When inhaled, even in small quantity, it attacks the lungs, causing coughing and spitting of blood. It does not act as a poison on the heart, but paralyses the respiratory centres. Its action on animals is already perceptible when mixed with air in the proportion of 1 c.c. per cubic metre. Air containing one-millionth part of chlorine is already harmful to man. The smoking of tobacco, inhalation of steam, or the vapours of alcohol or aniline, and also of air containing a little hydrogen sulphide are all found to be of benefit in counteracting the effects of chlorine on the system.

It is an energetic disinfectant and is used in cases of epidemics in the form of a solution of chloride of lime for purifying floors, walls of living-rooms, stables, cesspools, &c.

APPLICATIONS OF CHLORINE, PRICES, AND STATISTICS. In order to be able to make use of chlorine it is necessary to obtain it in a convenient form for handling, either as compressed or liquefied gas in cylinders, or as a solid in the form of *chloride of lime*. The preparation of the latter is described in Part III (Hypochlorites).

Chlorine is used industrially for bleaching vegetable textiles, cotton, paper, &c., and for preparing wool for printing, because when it is gently oxidised the dyestuffs are more firmly fixed. It is also used for the preparation of hypochlorites, of chlorinated organic compounds, such as chloroform,

chloral, &c., and also for the preparation of carbon tetrachloride, which has now acquired great industrial importance (*see also* Uses of Chloride of Lime).

Liquid chlorine is used in large quantity at Stassfurt for the preparation of 500,000 kilos of bromine annually, and the Badische Anilin und Soda Fabrik at Ludwigshafen in 1900 used more than a million kilos for the production of chloracetic acid, which is used in the synthetic preparation of *artificial indigo*. In Italy 75,000 kilos of liquid chlorine were produced in 1907 and almost 200,000 kilos in 1909, sold in steel bombs holding 60 kilos at £2 12*s*. per 100 kilos.

The problem of the utilisation of chlorine has become very urgent because the electrolytic soda-works produce it in quantities very much larger than the demand, and whereas in the past hydrochloric acid has been used as a source of chlorine, convenient methods of conversion of chlorine into hydrochloric acid are now being sought for (*see* Hydrochloric Acid).

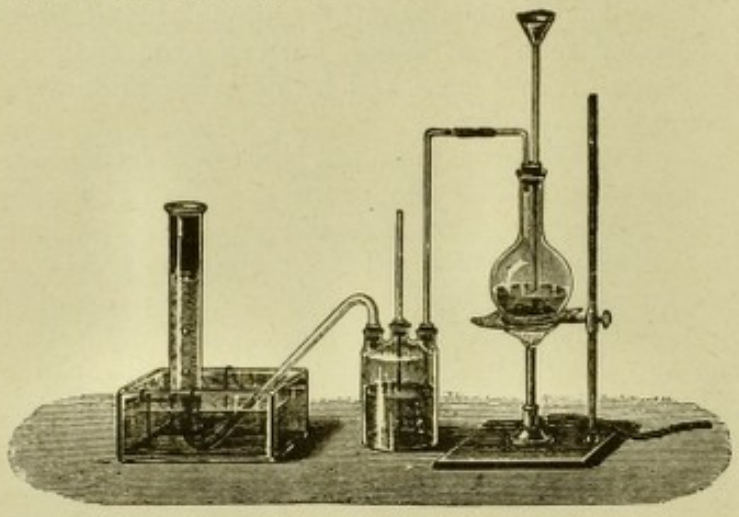


Fig. 46.

The commercial price of compressed chlorine in steel bombs, holding from 5 to 50 kilos, is 1*s*. 2*d*. to 2*s*. per kilo; the empty bomb costs £1 8*s*. for a capacity of 5 kilos of chlorine, and £2 16*s*. for a capacity of 50 kilos; but the bomb is sent out and lent on hire by the manufacturers. Liquid chlorine in bombs costs 6*d*. per kilo. Saturated chlorine water is sold at 12*s*. per 100 kilos, including carboys.

LABORATORY PREPARATION OF CHLORINE. Chlorine was first prepared by Scheele in 1774, by acting on manganese dioxide with hydrochloric acid, but nothing was known as to its nature, so that in 1775 Berthollet declared it to be oxidised hydrochloric acid. In 1810 Davy first demonstrated that chlorine was a simple substance on the ground of its behaviour with red-hot carbon (in contact with which it remained unaltered) and also by showing that when certain metallic oxides are heated in a current of chlorine. oxygen only is evolved in quantity corresponding to the amount of chlorine fixed by the metal and without formation of other products; thus chlorine was shown to contain neither oxygen nor hydrogen. But for a long time, until 1820, Berzelius and Schönbein still regarded chlorine as an oxidised compound of hydrochloric acid.

It is now prepared by the action of hydrochloric acid on substances which readily give up oxygen, which combines with the hydrogen of the hydrochloric acid, liberating the chlorine. As oxidising compounds one may use the oxides of manganese, chromic acid, nitric acid, sodium chlorate, &c.

It is ordinarily prepared in the laboratory by heating manganese dioxide with hydrochloric acid: $MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$. Chlorine is not developed in the cold, as a soluble tetrachloride of manganese is formed: $MnO_2 + 4HCl = MnCl_4 + 2H_2O$. On heating the reaction $MnCl_4 = MnCl_2 + Cl_2$ takes place.

In the laboratory a mixture proposed by Klason is often preferred, as a more regular evolution of chlorine is so obtained on heating on the water-bath; it consists of 5 parts of MnO_2 (of 90 per cent. strength), 11 parts of NaCl, 14 parts by weight of strong sulphuric acid, and 7·5 parts by weight of water (equal in volume to the sulphuric acid):

$$4NaCl + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + Na_2SO_4 + MnCl_2 + 2H_2O + Cl_2.$$

In this manner 95 per cent. of the quantity of chlorine indicated by the equation is obtained in practice. The laboratory apparatus is illustrated in Fig. 46, and the chlorine is washed in hot water in a Woulff's bottle, and then collected in a cylinder inverted over a pan of hot water, as chlorine is somewhat soluble in cold water.

In 1901 Graebe obtained chlorine by heating a solution of sodium chlorate with hydrochloric acid, but a little chlorine oxide, ClO_2, is also formed. This may, however, be decomposed by passing through a red-hot tube; in 1903 he made it advantageously by the action of cold hydrochloric acid (density 1·16) on solid potassium permanganate, and so obtained pure chlorine free from oxides.

Relatively pure chlorine is obtained by heating potassium dichromate (100 grms.) with hydrochloric acid in a flask of about 300 c.c. capacity and collecting over hot water without washing:

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 3Cl_2 + 7H_2O.$$

Another rapid laboratory method, suggested by Winkler, consists in acting in the cold in a Kipp apparatus with hydrochloric acid on small cubes made from four parts of chloride of lime ($CaOCl_2$) mixed to a paste with one part of plaster of Paris:

$$CaOCl_2 + 2HCl = CaCl_2 + Cl_2 + H_2O.$$

Small traces of oxygen are formed by this method.

By decomposing dilute hydrochloric acid with the electric current chlorine is obtained at the anode and hydrogen at the cathode, and in the same way concentrated solutions of sodium chloride give chlorine at the anode and caustic soda and hydrogen at the cathode, as secondary products formed by the action of water on the sodium which is separated as the primary product: $Na + H_2O = NaOH + H$.

According to Ferentzy (1908) it is impossible to obtain absolutely pure chlorine by any of the above-mentioned methods, as it always contains chlorine oxides the presence of which was proved by diffusion through tubes of porous porcelain heated to 1200°, when the oxygen from the chlorine oxides passes through their walls. Chemically pure chlorine can only be obtained by decomposing potassium chloroplatinate at a red heat: $K_2PtCl_6 = 2KCl + Pt + Cl_4$.

INDUSTRIAL METHODS OF PREPARING CHLORINE. Until a few years ago the industrial preparation of chlorine was almost entirely confined to purely chemical processes; to-day, on the contrary, almost the whole supply is produced as an abundant (too abundant) by-product of the electrolytic production of caustic soda and potash. For this reason we will only briefly discuss at this point the chemical methods still in use, and in Part III, in describing the electrolytic soda industry, we will also discuss the preparation of chlorine and chloride of lime.

I. In small industrial installations chlorine is readily obtained by the action of hydrochloric acid on natural manganese dioxide (pyrolusite, polianite, manganite, &c.), which is found in deposits in Germany, Spain, and South America. The value of this mineral is proportional to the quantity of manganese dioxide, MnO_2, which it contains, as the other oxides, MnO, Mn_3O_4, and Mn_2O_3, are less valuable and yield less chlorine and more manganous chloride, thus using more hydrochloric acid:[1]

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2$$
$$Mn_3O_4 + 8HCl = 4H_2O + 3MnCl_2 + Cl_2.$$

[1] *Analysis of pyrolusite.*—Apart from the determination of moisture and of carbonates the percentage of MnO_2 is determined as follows: 1·0875 grm. of dry powdered pyrolusite are placed in a stoppered flask fitted with a Bunsen valve and 75 c.c. of a ferrous sulphate solution are added (prepared by dissolving 100 grms. of pure ferrous sulphate and 100 c.c. of sulphuric acid in water to 1 litre) which has been previously titrated with a $\frac{1}{2}$-*N* solution of potassium permanganate. The contents of the flask are then boiled for some time, the valve permitting the steam to escape whilst preventing the entry of air. The whole is then cooled and the contents of the flask titrated

In order to obtain the same quantity of chlorine from Mn_3O_4 double the quantity of hydrochloric acid is required. A mineral containing less than 57 per cent. of MnO_2 is unsuitable for the purpose, as is also the case if it contains more than 1 per cent. of CO_2 as carbonate. The higher oxides are commercially valued according to the amount of MnO_2 which they are capable of yielding :

$$Mn_2O_3 = MnO + MnO_2 \qquad \text{or} \qquad Mn_3O_4 = 2\,MnO + MnO_2.$$

The industrial preparation of chlorine is carried out in vessels of cast-iron or earthenware containing HCl and MnO_2. These are heated with hot water or steam, and when the reaction has finished the mother liquors, which contain $MnCl_2$, are removed by syphons and used for the regeneration of chlorine and manganese dioxide. The delivery tubes for the chlorine are constructed of lead or earthenware. The heating operation lasts twenty-four hours altogether. Lunge advises the apparatus illustrated in Fig. 47. A stoneware cylinder, *a*, with a perforated double bottom, *b*, contains the manganese dioxide and hydrochloric acid. This cylinder is closed by a bell, *d*, immersed in a larger cylinder, *h*, containing

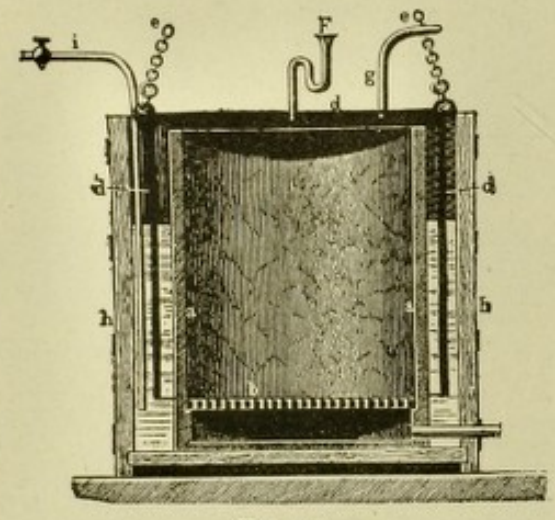


Fig. 47.

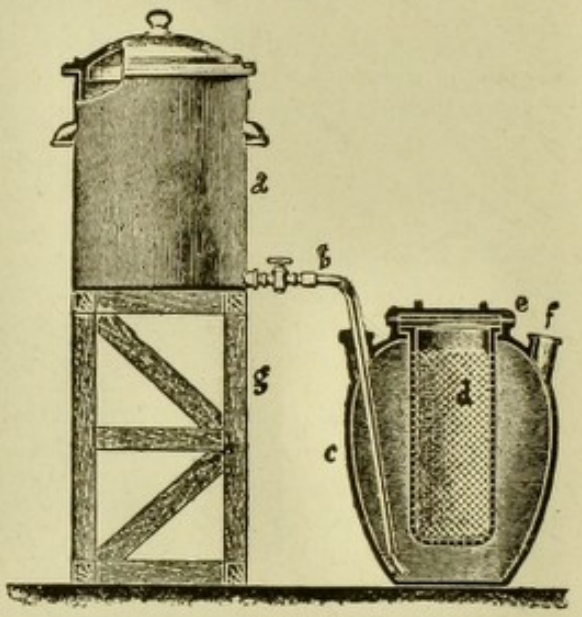


Fig. 48.

water heated by the steam-pipe *i*. The regular stream of chlorine thus produced escapes by the tube *g*. The mother liquor containing manganous chloride is discharged by the tube *c*, and the manganese is then recovered by one means or another.[1]

The apparatus constructed entirely in stoneware and shown in Fig. 48 is simpler and is more commonly used. The vessel *c* contains manganese dioxide in the internal perforated cylinder *d*, which reacts with the hydro-

with ½-N permanganate; if the amount of permanganate required for this purpose is subtracted from the amount corresponding to 75 c.c. of the ferrous sulphate solution, the amount corresponding to the MnO_2 in the sample is found; and on multiplying this number of c.c. by two, the percentage of MnO_2 is found (1 c.c. of ½-N permanganate = 0·02175 grms. MnO_2).

[1] *Treatment of the mother liquor.*—This contains $MnCl_2$ and excess of HCl; it is treated in various ways to recover manganese dioxide.

(A) *Dunlop's method.*—The liquor is heated at four atmospheres pressure with calcium carbonate: $MnCl_2 + CaCO_3 = MnCO_3 + CaCl_2$. The manganese carbonate which is thus formed is then heated in furnaces at 300° in presence of air and forms manganese dioxide: $MnCO_3 + O = CO_2 + MnO_2$. This method is only employed in Tennant's works.

(B) *Weldon's methods.*—(*a*) *With lime.* In 1837 Gossage already proposed to treat the mother liquor ($MnCl_2$ and HCl) with lime and then to oxidise the mass with air: $2MnCl_2 + 3CaO + O_2 = 2CaCl_2 + CaO, 2MnO_2$.

In 1860 Binks and Macqueen patented this process. But the credit of having successfully applied the process in practice and shown the importance of an excess of lime is due to Weldon. Calcium chloride is soluble and the mud separates out; it is then returned to the chlorine generators.

(*b*) *With magnesia.*—The mother liquor ($MnCl_2$ and HCl) is saturated with magnesium carbonate, and then forms a mixture of $MgCl_2$ and $MnCl_2$. The whole is then evaporated and dried in furnaces until HCl commences to be evolved. It is then placed in retorts and regularly heated in a current of air; chlorine is thus developed and can be utilised: $MnCl_2 + O = MnO + Cl_2$, and also $MgCl_2 + O = MgO + Cl_2$. The mixture of the two oxides is again employed in the chlorine generators. On account of many technical difficulties the magnesia method has never found technical application in spite of various improvements.

chloric acid which enters from the reservoir *a*, through the tube *b*. The chlorine gas escapes through *f*, and is developed regularly and completely if the vessel *c* is immersed in a vat (not shown in the figure) containing water which is heated by a steam-jet. The apparatus is completely closed by the heavy cover *e*.

II. CHLORINE FROM AIR AND HYDROCHLORIC ACID. *Deacon-Hurter method*, 1870. This is based on the action of air (oxygen) on hydrochloric acid when heated in presence of an active substance which acts by contact alone (catalytically) or forms an intermediate product which is easily decomposed, continuously producing chlorine. As active material small clay balls impregnated with copper chloride or sulphate have been found to work well. But it has been shown that other substances, even inert materials, such as moist pumice stone, are able to produce the same catalytic effect.

On heating copper chloride, $CuCl_2$, under these conditions, it undergoes the decomposition : $2CuCl_2 = Cl_2 + Cu_2Cl_2$ (cuprous chloride), which latter is reconverted into cupric chloride by hydrochloric acid and the oxygen of the air : $Cu_2Cl_2 + 2HCl + O = H_2O + 2CuCl_2$.

Thus $CuCl_2$ plays a part in the reaction, but is continually regenerated, so that the complete process may be represented by the equation :

$$2HCl + O = H_2O + Cl_2 .$$

In practice many difficulties are met with : the $CuCl_2$ is not completely regenerated, the HCl is not completely decomposed, and the catalytic action of the copper salt becomes exhausted after a short time, on account of impurities which accumulate in the same. The best results are obtained by observing the following precautions :

The temperature should not exceed 470°, otherwise cuprous chloride is volatilised and lost.

The yield of chlorine depends greatly on the proportions in which HCl and air are present, and on the velocity of the current of these gases. The best results are obtained when the reacting gaseous mixture contains 5 to 20 per cent. of HCl, and the emerging stream of gas after the reaction contains 5 to 7 per cent. of chlorine, the rest being air. On using a mixture of 40 per cent. HCl and 60 per cent. air, 70 per cent. of the HCl is converted into chlorine. The presence of sulphuric acid, or SO_2, proceeding from the furnaces which produce the HCl, reduces the yield of chlorine, owing to the following reaction :

$$SO_2 + 2H_2O + Cl_2 = H_2SO_4 + 2HCl$$

(*see below*, Hydrochloric Acid).

The process was improved by Lunge and by Solvay about 1890 ; they endeavoured to eliminate all the above difficulties, and were able to introduce their improvements into many large plants. Still until 1902 a notable loss of $CuCl_2$ was observed (about 50 per cent. in ten days) and Dieffenbach therefore arranged the plant in such a manner as to regenerate all the copper salt by forcing the gas to issue at one point of the catalytic mass where the reaction was less energetic and the temperature lower, thus avoiding volatilisation of the copper salt, and finally (1908) he diminished the volatility of the cuprous chloride by mixing it with sodium chloride.

The Deacon process is now advantageously employed wherever chlorine of a low degree of concentration is needed.

The disposition of the plant is shown in longitudinal section in Fig. 49. To the left is seen the muffle-furnace for producing hydrochloric acid, which gas, mixed with air, is cooled and freed from the greater part of the accompanying moisture by passing through the long pipe *a*. The gaseous mixture is well dried in the coke-tower *b*, and then passes through a series of twenty-four pipes contained in a furnace *c*, at a temperature of 450° to 470° ; it then enters the reaction chamber *d*, consisting of a large cast-iron cylinder maintained at 450° by hot fumes from the furnace *c*, and divided into six compartments filled with fragments of porous brick impregnated with copper chloride or sulphate. After the reaction is completed the gases, consisting of chlorine, excess of hydrochloric acid, oxygen and nitrogen from the air, and steam, are cooled in several long tubes which condense the steam and hydrochloric acid. The last traces of HCl are separated in a coke-tower, from the top of which a fine shower of water descends, and the remaining gases are dried in a second coke-tower with a spray of strong sulphuric acid. Finally only dry chlorine mixed with air remains, the mixture containing 5 to 7 per cent. of chlorine.

III. CHLORINE FROM CHLORIDES. *Weldon-Pechiney Process* (1888–1890).

This process can only be advantageously used where cheap magnesium chloride can be obtained, as at Neu Stassfurt ($MgCl_2 + O = MgO + Cl_2$).

The $MgCl_2$ solution is evaporated and made into a paste with dry magnesia. The hardened mass is broken up and the pieces thrown into a flue heated to 250° to 300° in which a current of hot air circulates. It then evolves almost all the water which it contains (65 per cent.), but only loses 5 to 8 per cent. of chlorine (as HCl). The perfectly dry magnesium chloride, mixed with MgO, is then introduced into a reverberatory furnace, consisting of high, narrow chambers, and heated to 1000°. The heating is continued for six hours, during which a regulated current of air is passed over the mass, causing the formation of chlorine, mixed with very little HCl. The latter is condensed in a suitable column, after which the gases contain about 8 per cent. of chlorine, but after five hours this percentage sinks to 1 per cent.

This process is in use, with trifling modifications, in many large works, and competes with the Deacon and electrolytic processes.

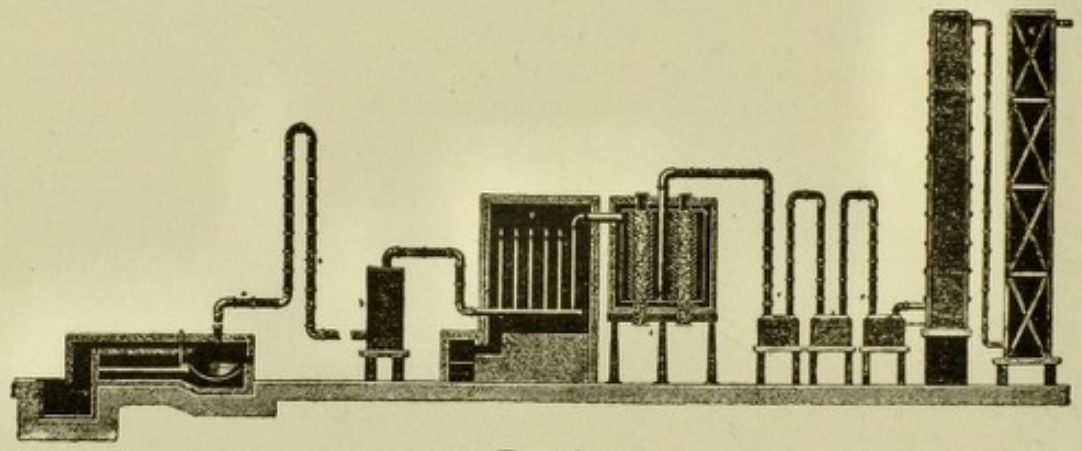


FIG. 49.

In order to utilise the calcium chloride obtained as a by-product in the manufacture of sodium carbonate Solvay proposed to heat it with silica to a high temperature in a current of air :

$$CaCl_2 + SiO_2 + O = CaSiO_3 + Cl_2.$$

This process has not yet succeeded in competing with the electrolytic process. Neither has the process of Dunlop, modified by Goldschmidt, Davis, and Taylor, any technical interest, unless one is able to utilise the NOCl for the bleaching of flour. It is based on the reaction :

$$3HCl + HNO_3 = 2H_2O + Cl_2 + NOCl$$

and a yield of 82 per cent. of the chlorine is obtained. The same may be said of Schlösing's process (1862) :

$$2HCl + 2HNO_3 + MnO_2 = Mn(NO_3)_2 + 2H_2O + Cl_2.$$

IV. ELECTROLYTIC METHODS OF CHLORINE MANUFACTURE. These are associated with the electrolytic manufacture of soda, and the various processes will, therefore, be discussed in detail in Part III, in the chapter on Electrolytic Soda.

However simple the electrolytic preparation of chlorine by decomposition of NaCl may appear, so many difficulties were encountered in practice that they were very hard to overcome and retarded the industrial application of the process.

The chlorine which is formed strongly attacks the metals of the plant and the carbon of the anode, and the caustic alkali also energetically destroys many parts of the machinery. Parchment diaphragms were rapidly destroyed, and equally serious difficulties attended the use of every kind of diaphragm which was tried. Since 1890 there has been a bewildering succession of patents to embody the best arrangement of electrodes and diaphragms, or to eliminate the diaphragms altogether ; to-day the problem may be said to be practically solved.

The patents of Löwe and of Marx (Andreoli employed mercury as cathode, which was also adopted by Castner), of Hermite and Dubose, Kellner and Solvay, Hunt and Watson (1895), the Hargreaves-Bird process (1899), and that of Acker (1900) all indicated the progress of these determined attempts. In spite of the fact that its initiation required such great and very costly efforts the electrolytic process has to-day almost replaced all other processes of making chlorine.[1]

LIQUID CHLORINE. Liquid chlorine was first prepared in the laboratory by Faraday in 1823 and is to-day produced in large quantity for various industrial purposes, especially for the manufacture of bromine and iodine in the Stassfurt salt works.

Hannay prepared it industrially in 1890 by heating chlorine hydrate in a closed vessel of iron, lined with lead, separating the water which floats on the top, and conveying it into a suitable steel cylinder previously dried with strong sulphuric acid.

The Badische Anilin und Soda Fabrik, Ludwigshafen, compress electrolytic chlorine conveyed by the pipe *h* (Fig. 50) over strong sulphuric acid in the iron receiver *m*, and protect the piston *a* of the pump by separating it from the acid with a layer of pure petroleum *c*. The chlorine gas, strongly compressed in this manner, and at a temperature of 50° to 80°, passes into a strongly cooled spiral condenser *K*, where it is liquefied and collects in the steel cylinder *L*. The valves *i* and *k* control the entry of the chlorine in accordance with the movements of the piston. *g* contains water which is kept at 50° to 80°.

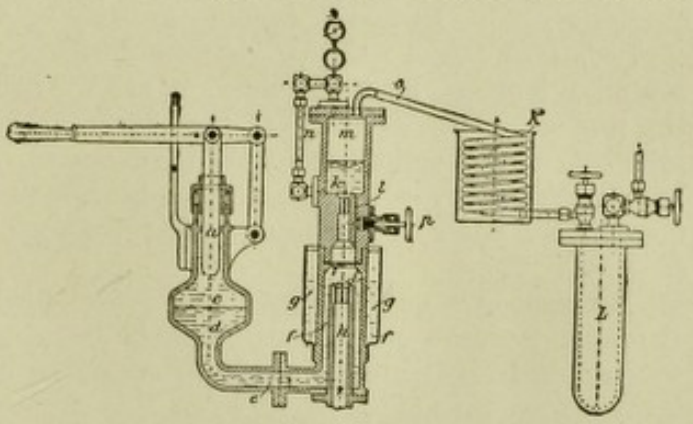


Fig. 50.

Chlorine is now liquefied without the use of a compression pump, as it is found preferable to liquefy it by strong refrigeration without compression.

When chlorine is mixed with other gases, as in the Deacon process, it is necessary to separate it before it can be liquefied, and therefore Th. Goldschmidt proposed in 1907 to absorb it with a liquid chloride free from water, *e.g.* by anhydrous tin tetrachloride, at a pressure near its point of liquefaction. The dissolved chlorine is liberated on diminishing the pressure, finally heating when necessary.

Vessels to be used for the transport of liquid chlorine must be of iron or steel, and resist an internal pressure of 100 atmospheres. In Germany the control of the strength of these cylinders is obligatory once a year. The pressure exerted by the liquid chlorine in the cylinder is about 55 to 60 atmospheres.

When perfectly dry, chlorine does not attack cast or wrought iron, steel, phosphor bronze, brass, copper, zinc, or lead.

The specific gravity of liquid chlorine is 1·6725 at −78·6°, 1·468 at 0°, and 1·113 at 100°. Its molecule consists of Cl_2. Organic substances are not ionised when dissolved in liquid chlorine, even when they form labile combinations with it, but even a trace of hydrochloric acid suffices to render the solution a conductor of the current.

ANALYSIS OF CHLORINE. It is necessary to determine the amounts of Cl, CO_2, and air. Two 100 c.c. burettes are each filled with the gas ; in one the chlorine is absorbed by a solution of potassium iodide, and on titrating the liberated iodine with $\frac{N}{10}$ sodium thiosulphate solution (1 c.c. = 0·003546 grms. Cl = 1·1228 c.c. of Cl) its amount is found ; the diminution of volume alone also shows the approximate volume of the chlorine. In the other burette chlorine and CO_2 are absorbed together with caustic soda solution; the difference between this and the former diminution of volume (with KI) gives the volume

[1] A disadvantage of electrolytic chlorine consists in its excessive chemical activity, which causes loss in the manufacture of chloride of lime, a part of the chlorine being converted into $CaCl_2$, which is valueless, according to the following equation :

$$Ca(OH)_2 + Cl_2 = CaCl_2 + H_2O + O.$$

In order to avoid this loss, Sinding-Larsen has suggested heating the chlorine to 700°–800° before the reaction takes place.

of CO_2 ; the remaining gas is air, which can be analysed if required in the Orsat apparatus (*which see*). The temperature and pressure of the gas have much influence on the result, and must, therefore, be taken into account (*see* p. 26).

BROMINE : Br, 79.92

Bromine is a liquid which does not occur in nature in the free state, but is combined as bromides in many mineral deposits and also in sea water, especially in the Dead Sea, which contains 0·44 per cent. of bromine as sodium bromide, NaBr, and magnesium bromide, $MgBr_2$. The Atlantic Ocean only contains 0·0064 per cent.

It was first discovered by Balard in 1826, in the mother liquors from the production of sea salt. In consequence of its presence in sea water it is found, together with iodine, in the ashes of certain marine plants (*kelp*, *varec*), from which it is obtained. It is now obtained in large quantity from the Stassfurt salts, and in the United States from the mother liquors from the purification of rock salt.

PROPERTIES. Bromine is a dark red-brown liquid, which gives off brownish-red vapours of disagreeable, penetrating odour similar to that of chlorous acid. It has a specific gravity of 3·18, boils at 63°, solidifies at $-7·3°$, and at $-20°$ is transformed into a lead-grey crystalline mass with metallic lustre. Bromine vapour has a normal density corresponding to the molecule Br_2, but at very high temperatures dissociation of the molecule into free atoms commences. With water at 0° bromine forms a red crystalline hydrate, $Br_2 + 10H_2O$, which decomposes at 15° ; 100 parts of water dissolve 3·1 parts of bromine at 30° ; 3·23 per cent. at 15° ; and 3·6 per cent. at 5°.

Bromine water decomposes in the light, forming hydrobromic acid. Bromine is more soluble in alcohol, ether, and carbon disulphide than in water ; it is still more soluble in solutions of HBr, KBr, and HCl (in HCl up to 13 per cent.).

Sulphuric acid of sp. gr. 1·795 dissolves Br in traces only. Bromine decomposes many organic substances with removal of hydrogen. It does not combine with free hydrogen under the influence of light alone, heat being also necessary. It does not combine directly with oxygen or carbon. The vapours of bromine react energetically with P, As, Sb, and Sn, even with production of flame. It has less affinity for the metals than chlorine. The bromine ions of bromides give a slightly yellowish precipitate with silver nitrate solution, less soluble in ammonia than silver chloride. Bromine has a strong corrosive action on the animal organism, and causes great irritation of the eyes. The bromides, on the contrary, are well tolerated by our organism, having a soothing action on the nerves and brain, and predisposing to sleep.

USES OF BROMINE. Bromine is employed as an oxidiser in many chemical reactions instead of chlorine, *e.g.* for transforming manganous oxide into the peroxide, potassium manganate into the permanganate :

$$2K_2MnO_4 + Br_2 = 2KMnO_4 + 2KBr$$

and yellow potassium ferrocyanide into the ferricyanide :

$$K_4Fe(CN)_6 + Br = K_3Fe(CN)_6 + KBr.$$

Bromine is used for dissolving gold and separating it from platinum and silver. It is used as a disinfectant (4 grms. per cubic metre of space), and for this purpose Frank absorbs it in infusorial earth, forming small solid cylinders which are sold as *solid bromine*. Bromine is also employed for the preparation of bromine salts, for pharmaceutical and photographic purposes, and in the manufacture of aniline colours (eosine). It is also used as a depolariser in galvanic batteries.

STATISTICS AND PRICES. At first, in 1865, Stassfurt only produced 300 kilos per year, but the production soon increased enormously. In 1900 it rose to 500,000 kilos, was more than 717,400 kilos in 1905, and in 1906 amounted to 907,000 kilos, of which 171,000 kilos were exported, together with 644,000 kilos of bromides; in 1908 the United States imported 187,000 kilos of bromides. In 1905 Germany exported 634,000 kilos of bromine salts. The production in the United States was 182,000 kilos in 1880, and rose to 225,000 kilos in 1895 and 600,000 kilos in 1907, but the production had to be decreased to 500,000 kilos in 1908. The price, which was at first £4 16*s.* per kilo, rapidly dropped to £2 8*s.*, then 12*s.*, and later 4*s.* per kilo. Then the desperate competition between Germany and the United States, which started in 1904, caused the price to drop rapidly to 1*s.* 7*d.* in 1907 and to 1*s.* in 1908; a partial understanding was arrived at in 1909 and the price of bromides was approximately doubled.

Italy imported 11,800 kilos in 1907, and 13,400 kilos in 1908, of the value of £1072.

LABORATORY PREPARATION. Bromine is prepared by heating in a flask on the water-bath a mixture of sodium bromide, sulphuric acid, and manganese dioxide, or some other oxidising agent, such as potassium dichromate:

$$2NaBr + MnO_2 + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + 2H_2O + Br_2.$$

The oxygen of the oxidising agent combines with hydrogen, which would otherwise form hydrobromic acid instead of bromine.

The red-brown vapours of bromine which are formed are condensed by passing into a long condenser.

In general one can always displace the bromine from a solution of a bromide by chlorine (*see* Chlorine), NaBr + Cl = NaCl + Br.

INDUSTRIAL PREPARATION. This industry has increased remarkably in recent years. In 1865 the remarkable extraction of bromine from the Stassfurt salt works was started, and especially from the Magdeburg deposits, and later on from those of North America.[1]

The final mother liquors from the treatment of carnallite ($MgCl_2.KCl.6H_2O$) (*see* Stassfurt Salts) contain on an average in each cubic metre 3·5 kilos of bromine, as $MgBr_2$, and about 300 kilos of $MgCl_2$.

At Neu Stassfurt the bromine is obtained by Pfeiffer's process; the hot mother liquor falls as a fine spray from the top of a tower filled with fragments of stone or small silica balls, from the base of which a current of steam and chlorine ascends (Fig. 51). The chlorine is supplied by cylinders of the liquefied gas, and the rate of supply can be readily regulated.

The liquid rich in bromine which collects at the bottom of the tower descends into a stone boiler and is heated directly by superheated steam, which drives off the bromine together with a little dissolved chlorine. These vapours ascend the tower and descend the upper delivery pipe into the spiral condenser, where they are condensed; the bromine collects together with water (bromine water) in a large glass bottle. The bromine vapours and chlorine which escape condensation are absorbed in a small tower at the side filled with moist iron filings or turnings, where they form iron bromide and chloride. At the side

[1] Already in 1846 the preparation of bromine was started in Pennsylvania and at Freeport, but to-day this manufacture exists more especially in Michigan, East Virginia, Ohio and Pennsylvania, where the mother liquors from rock salt are treated with dilute sulphuric acid and then concentrated, the hydrochloric acid which is evolved being condensed; on adding manganese dioxide and sulphuric acid to the concentrated liquid, bromine distils over, together with water and a little chlorine, bromine, and bromoform; the whole is first condensed in an empty receiver, the vapours which escape condensation being absorbed in a second receiver with caustic soda solution. According to a patent of the Dow Chemical Co., the saline mother liquors are partially electrolysed and the chlorine liberated in this way sets free the bromine, which is recovered by means of a current of hot air.

In Ohio the saline mother liquors, of 35°–40° Bé., contain a preponderance of $MgCl_2$, together with 0·5 to 1 per cent. of $MgBr_2$; instead of being treated with manganese dioxide, in this case potassium chlorate is used with the sulphuric acid in exactly the quantity theoretically required to decompose all the bromide

$$3MgBr_2 + 3H_2SO_4 + KClO_3 = 6Br + KCl + 3MgSO_4 + 3H_2O.$$

of the drawing, towards the top, the tubes which are fixed in discs at the top of the main tower to convert the mother liquor into the form of fine spray, are shown on a larger scale. These tubes are cut away at the point and have a slit at the top to allow the liquid to enter.

H. Dow (1891) employs a current of air instead of steam, which is passed through the solution saturated with bromine and carries this away as vapour. But this method does not appear to have been adopted industrially.[1]

To free bromine from the small amount of chlorine which it contains it is agitated with iron bromide (obtained from the small tower) or with sodium bromide, or it is distilled. In the latter case all the chlorine passes over first, together with little bromine, and this portion is collected separately from the rest of the distillate, which contains bromine only. Or iron filings may be added to the retort before distillation in quantity just sufficient to combine with all the chlorine present.

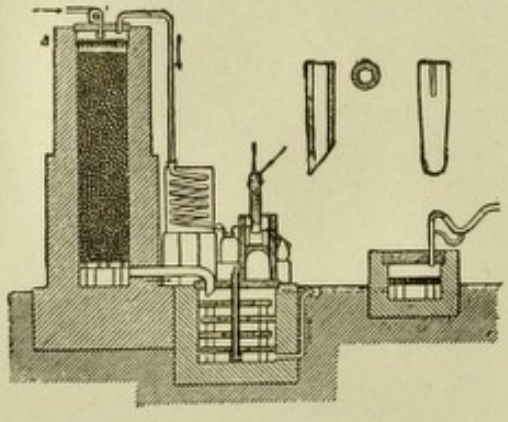


Fig. 51.

In 1890 G. Nahnsen took out a patent for the electrolytic production of bromine, and the process appears to have been worked industrially by Wünsche since 1895. It is based on the fact that when mother liquors are electrolysed, even though they may contain chlorides in large quantity (*e.g.* those from carnallite), these are not decomposed until all the bromine has been liberated. If the current is stopped at this point and the whole distilled, all the bromine will be obtained in the distillate. It is possible to work without diaphragms, but better yields are obtained with diaphragms and with the solution at a temperature of 80°. The current can be utilised with an efficiency of 70 per cent. ; from forty-four baths in twenty-four hours 300 kilos of crude bromine are obtained. These baths are worked with a current of 150 amps. at 3·4 volts. This process is acquiring a certain amount of practical importance.

IODINE : I, 126.92

This element was discovered by Courtois in 1812 in the soda obtained from the ash of certain marine plants. It was named iodine by Gay-Lussac in 1813, and he studied its principal properties. Later on it was also studied by Davy.

Iodine is not found in the free state in nature, but always in combination ; it accompanies chlorine compounds, and sometimes those of bromine. It is found together with other minerals in the form of HgI_2, AgI, PbI_2, and sodium iodate in Mexico and Chili ; it is often found in association with phosphorite and also with coal ; it is also found in sea water and in mineral springs (*e.g.* at Salsomaggiore, at Hall in Austria, &c.). In springs it is found as MgI_2 and NaI ; rarely as KI or CaI_2. As salts of iodine are amongst the most soluble, they are dissolved by rain water, and this explains its frequent presence in mineral springs. Iodine is also found in certain vegetables (*Fucus*, *laminaria*, *ulva*, &c.) and in some animals. It is found in notable quantity in Chili saltpetre.

CHEMICAL AND PHYSICAL PROPERTIES. Iodine is a crystalline solid, forming large rhombic plates, violet-black in colour, with metallic

[1] Betts, in America, proposed in 1901 to remove the bromine from the mother liquors, more especially when these are dilute, by means of pure carbolic acid ; this at once precipitates crystalline tribromophenol : $C_6H_5OH + 6Br = 3HBr + C_6H_2Br_3OH$. Free bromine can be obtained from this compound by the action of chlorine or of sulphuric acid and iron, the phenol being regenerated in the latter case :

$$2C_6H_2Br_3OH + 3H_2SO_4 + 6Fe = 3FeBr_2 + 3FeSO_4 + 2C_6H_5OH.$$

One kilo of phenol (carbolic acid) precipitates 2·5 kilos of bromine. Practically this would result in a mixed process ; a portion of the bromine would first be separated by the phenol, and the rest would be liberated by chlorine. One might also employ acetylene instead of phenol. These processes have not yet found practical application.

reflex. It has a similar odour to chlorine and bromine, colours the skin yellow, and acts as a corrosive, but less so than bromine. Its specific gravity is 4·95; it melts at 114°, forming a dark brown liquid which boils at 184°, producing violet vapours, which recondense without passing through the liquid state, but sublime in black, shining crystals. Its vapour density at 600° corresponds to the molecule I_2, but above 1500° complete dissociation into simple atoms take place.

Iodine is very slightly soluble in water (1 : 3600); it is readily soluble in alcohol (*tincture of iodine*) and also in an aqueous solution of KI. It is soluble in ether with brown colour, and in chloroform and carbon disulphide with violet colour (carbon disulphide dissolves 18 per cent.).[1]

The chemical behaviour of iodine is analogous to that of chlorine and bromine, but its affinity for other elements is much weaker, and indeed iodine can be displaced from its compounds by both chlorine and bromine. It only combines with metals and with hydrogen on heating. It abstracts hydrogen from organic compounds (hydrocarbons) with difficulty. It gives a characteristic blue coloration with starch paste. If, for example, to a very dilute solution of KI starch paste and a few drops of chlorine water are added, a blue coloration is immediately obtained in the cold, due to the liberation of iodine. On heating, the starch paste is decolorised.

Traces of iodides are detected by pouring the solution into a cylinder with 500 c.c. of water and adding two or three drops of fuming nitric acid and fifteen to twenty drops of carbon disulphide; on shaking the whole and allowing the carbon disulphide to settle to the bottom this will be coloured violet, as it dissolves the liberated iodine.

In the secretion of the gland of the thyroid (cartilage of the Adam's apple) Baumann discovered and separated (1895) a product containing 9·3 per cent. of iodine, called iodothyrin, which has proved to be most efficacious in cases of goitre. It appears, in fact, that in districts where goitre is prevalent – *e.g.* in Freiburg, in Baden, and in the Bergamasco valley—the thyroid glands are rather deficient in iodine. Iodine is, therefore, found in nature in true stable, organic combination. In Italy during the years of conscription, from 1896 to 1903, those exempted from military service on account of goitrous deformity numbered 27,554, that is, about 3500 per year, of which two-fifths were in Lombardy, one-quarter in Piedmont, and one-ninth in Venetia. It appears also, according to Carletti and Perusini (1908), that endemic cretinism is caused by goitrous condition of the mother, a fact which allows one to hope that it may be cured by the use of thyroiodine during pregnancy.

With silver nitrate the ions of soluble iodides form silver iodide, a yellow substance, insoluble in ammonia, in which silver chloride is soluble and silver bromide somewhat soluble.

The physiological effect of iodides is to accelerate the metabolism of the organism. In very large doses they produce catarrhal inflammation of the mucous membranes; on prolonged use they may produce nervous disturbances. Iodine salts remove inflammation and swelling of the glands, but with corresponding enfeeblement of the system.

USES OF IODINE. Iodine is used in large quantities for photographic preparations (AgI and KI) and in the manufacture of various dyestuffs (tetraiodofluorescein, iodine green, iodine violet, cyanine, &c.). It is used medicinally as tincture of iodine and as potassium iodide; in the chemical laboratory it is used for various preparations, such as iodoform, iodole, methyl and ethyl iodide, hydriodic acid, &c.

STATISTICS AND PRICES. The European production of iodine is now 180 tons per year. In 1876 only sixty tons in England and forty tons in France were obtained

[1] Hildebrand and Glascock (1909) have shown by cryoscopic experiments that the violet solutions of iodine are true solutions of iodine, whilst the brown solutions are solutions of a labile combination of iodine with the solvent.

from kelp. Germany imported 377 tons in 1905 ; 297 tons in 1906 ; 194·2 tons in 1908 ; and 369·3 tons in 1909. On the other hand, it exported 26·9 tons in 1905 ; 46 tons in 1906 ; 50·7 tons in 1908 ; and 59·2 tons in 1909.

In South America the Chilian nitrate works produced :

In 1879 :	77 tons	of iodine	of the value	of £220,000.
1891 :	425	,,	,,	,, £840,000 (about £20 per ton).
1900 :	590	,,	,,	,, £800,000 (about £13 12*s.* per ton).
1904 :	460 tons.			

Japan exported 1·8 tons in 1902, 15 tons in 1903, 30 tons in 1904, and about 50 tons in 1905 ; the greater portion is sent to the English market.

To prevent a fall in prices an international syndicate has been formed which regulates the production by allowing it to be sold to those customers only who resell at a high price, and thus the price has been forced up to £1 13*s.* 7*d.* per kilo. But Japanese iodine is now appearing on the market at competitive prices. Italy imported 32·4 tons of bromine and iodine together in 1904, 38·1 tons of iodine in 1906, 21 tons in 1907, and 17·8 tons in 1908 of the value of £15,664.

INDUSTRIAL PREPARATION. Iodine is scarcely ever prepared in the laboratory nowadays, as the industrially prepared product, previously purified by repeated sublimation (*vide infra*), is employed. Certain marine organisms accumulate iodine compounds, especially certain algæ which are thrown up by the waves on to the shore. In Japan these are worked up, especially the laminaria, containing 0·144 per cent. of iodine ; *ecklonia cava*, containing 0·140 per cent. ; *ecklonia bicyclis* and *Sargassum homeri* and *patens*, all of which contain less than 0·005 per cent.

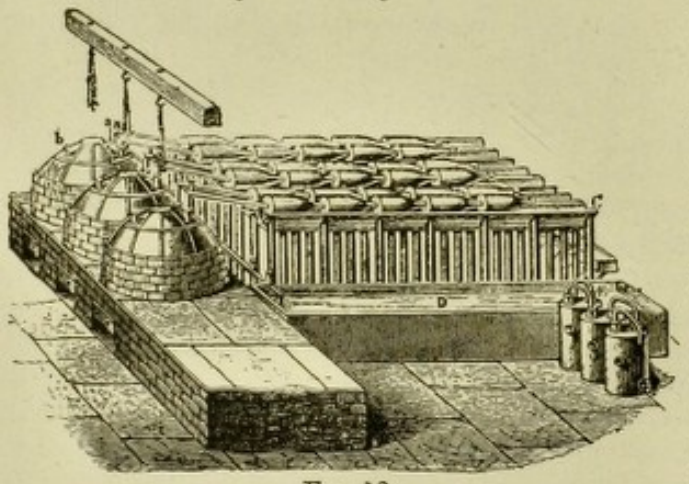


Fig. 52.

In Scotland the ashes of such algæ are called *kelp*, in Normandy *varec*, and they contain K_2CO_3, Na_2CO_3, K_2SO_4, KCl, NaCl, sulphites, thiosulphates, and NaI. One thousand kilos of *varec* give as much as 10·2 kilos of iodine, but during incineration (even when incomplete) of the algæ, iodine is often lost. The ashes are extracted with water and the solution concentrated ; NaCl and KCl separate first, and the sulphides and sulphites are then decomposed with sulphuric acid, with separation of sulphur. In one of Patterson's works the recovered sulphur amounted to as much as 100 tons per annum. The mother liquors, containing much iodine, are distilled together with MnO_2 and H_2SO_4 by one of the following methods :

Two different forms of plant are in use on the large scale. The first consists of a series of cast-iron pans of 1·5 metres diameter (Fig. 52), with lead covers, in which the mother liquors and sulphuric acid are heated. The distillate is collected and condensed in a series of five earthenware receivers (75 × 30 cms.) which are bottle-shaped and fit into one another. The manganese dioxide is added a little at a time, and the operation is finished when no further violet-red vapours are evolved on adding a little more of this substance. About 70 kilos of iodine collect in each receiver in the form of crusts which can be detached and removed through the wider aperture.

In many processes and in many chemical industries iodides of Na, K, and Mg are obtained as by-products. In order to utilise these compounds they are treated in aqueous solution with a quantity of chlorine exactly corresponding to the amount of iodine present (Barruel's method) : $KI + Cl = KCl + I$, and the free iodine which is formed is collected in the solid form at the surface or at the bottom of the vessel. If too little chlorine is used a small

quantity of iodide remains which holds a portion of the iodine in solution, and escapes recovery. With excess of chlorine, iodine chloride is formed, together with iodates, which are very soluble.

Both in the distillation process, which does not yield all the iodine, and in the chlorine process improvements have been introduced.

In 1880 Müller and Böckel proposed an apparatus analogous to that employed in the manufacture of bromine. In a tower filled with coke and stones (Fig. 53) the iodide solution falls from above, meeting a current of chlorine and superheated steam from below. The iodine distils and is condensed in spiral condensers at the side.

In 1860 R. Wagner proposed to acidify with sulphuric acid and then distil in presence of ferric chloride :

$$NaI + FeCl_3 = NaCl + FeCl_2 + I.$$

In this case the formation of ClI, which is a source of loss, would be avoided.

Another very interesting method, which would eliminate all loss, would be the following : The iodide solution is evaporated to dryness and then treated with twice its weight of water ; sulphuric acid and powdered potassium dichromate are then added and the whole well stirred. All the iodine separates in crystals, which are separated from the liquid and sublimed. The general reaction is as follows :

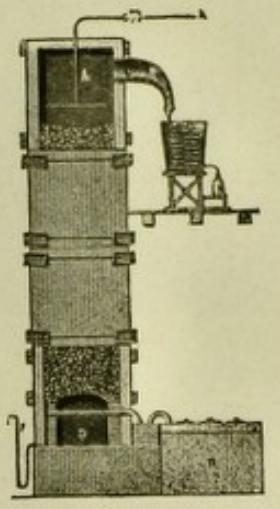


Fig. 53.

$$6NaI + \underset{\text{Potassium dichromate}}{K_2Cr_2O_7} + 10H_2SO_4 =$$

$$\underset{\text{Potassium chromium sulphate}}{K_2Cr_2(SO_4)_4} + \underset{\text{Acid sodium sulphate}}{6NaHSO_4} + 7H_2O + 3I_2.$$

In 1886 Vitali advised the employment of an analogous reaction for treating the ashes of algæ (varec) in some direct manner ; he advised that the algæ should be soaked in potash solution before incineration, in order to lessen the loss of iodine during that process. The ashes were then mixed with dichromate and heated to redness, when the iodine distilled over :

$$6KI + K_2Cr_2O_7 = Cr_2O_3 + 4K_2O + 3I_2.$$

It appears that the yield of iodine from kelp is being much improved in some way, with simpler manipulation.

I. Boirault (Fr. Pat. 393,668 of 1907) treats aqueous solutions obtained from kelp with a solution of copper and ferrous sulphates : $2KI + 2CuSO_4 + 2FeSO_4 = K_2SO_4 + Fe_2(SO_4)_3 + Cu_2I_2$. The precipitated cuprous iodide is dried and decomposed by distillation with sulphuric acid and iron oxide : $Fe_2O_3 + CuI + 3H_2SO_4 = CuSO_4 + 2FeSO_4 + 3H_2O + I$.

A still more rational method consists in the distillation of the dry algæ direct from a retort, avoiding incineration. This method was proposed by Standfort in 1864, and it was applied in a large Glasgow works. From 100 tons of dry algæ 1·3 tons of iodine, more than 28,300 cu. metres of illuminating gas (100,000 cu. ft.), and 1025 litres of paraffin oil were obtained.

As a further improvement the direct treatment of the moist algæ has been proposed, as if it rains during the drying on the shore a portion of the iodides are dissolved and lost.

In South America (Chili and Peru) iodine is obtained from crude sodium nitrate, which sometimes contains 0·2 per cent. in the form of sodium iodate, $NaIO_3$, and a little NaI and MgI_2. The mother liquors obtained during the refinement of the nitrate contain as much as 0·5 per cent. of iodine. The solutions of nitre are treated with disulphite or with sulphurous acid solution (Fauré, 1855) :

$$2NaIO_3 + 5H_2SO_4 = 3H_2SO_4 + 2NaHSO_4 + H_2O + I_2.$$

The iodine separates as a solid black mass ; a little chlorine water is then added to decompose any iodides and the impure iodine is collected on filters ; it contains 80 to 85 per cent. of iodine. The filtrates are then used to again extract the remaining nitrate.

Instead of sulphurous acid the use of nitrous oxide, N_2O_3, has been proposed, obtained by burning a mixture of five parts of nitrate with one part of carbon, but very serious difficulties were encountered in practice.

The nitrate mother liquors are also treated on a large scale by separating the iodine in the form of cuprous iodide, Cu_2I_2. The liquors are mixed with sodium disulphite (or ferrous sulphate or calcium sulphide) and copper sulphate ; the iodine separates in the form of insoluble cuprous iodide which is marketed directly as such and valued according to its contents of iodine and of copper. In 1873 a single works in Tarapaca produced 15 tons of copper iodide and 50 tons in 1874. This method is suited to the separation of iodine from very dilute solutions of iodides. The iodine may also be separated as lead iodide.[1]

The *sublimation of crude iodine* is used for its purification, and is carried out in a terra-cotta retort immersed in a sand-bath (Fig. 54). It is heated moderately in order to obtain large crystals and ensure complete condensation of the vapours. These are condensed in large earthenware receivers D, provided with a perforated false bottom to remove the water which accompanies the distillate. Iodine sublimed in this way is pure and only contains traces of water, Cl and Br. By subliming it a second time it is obtained in a very pure condition (resublimed iodine).

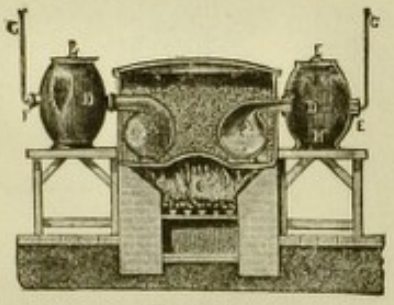


FIG. 54.

ANALYSIS OF IODINE. Pure resublimed iodine should be completely soluble in alcohol and in potassium iodide solution, and should leave no residue on sublimation. It is best analysed by dissolving 10 grms. in water and potassium iodide, making up to one litre and titrating 50 c.c. with a titrated solution of sodium thiosulphate, using starch paste as an indicator towards the end of the reaction (*see* Analysis of Chlorine).

HYDROGEN COMPOUNDS OF THE HALOGENS (HYDRACIDS)

The hydrogen compounds of the halogens are all acids and are called hydracids, to distinguish them from another category of acids which contain both hydrogen and oxygen, and are called oxy-acids.

Each atom of the four elements : F, Cl, Br, I, combines with a single atom of H, forming the following four very powerful acids :

HF	HCl	HBr	HI
Hydrofluoric acid	Hydrochloric acid	Hydrobromic acid	Hydriodic acid

Their reactivity diminishes with increase of the molecular weight. They are all gaseous, but are readily liquefied by refrigeration or pressure. In concentrated aqueous solution they fume in the air, because the small quantity of acid which evaporates dissolves in the water vapour in the atmosphere to form a solution which is more dilute and has a lesser vapour tension than the more concentrated acid from which it is formed ; it is therefore obliged to condense in small globules which form a cloud. Dilute solutions of these acids do not fume in the air, because the acid which evaporates spontaneously forms solutions with the moisture of the atmosphere which are more concentrated than the solutions from which they are derived, have a higher

[1] Many methods have also been tried to recover the small amount of iodine contained in the phosphorite which is treated by superphosphate works ; the phosphorite is heated in closed chambers, and the vapours removed by a current of air and passed through a tower containing coke and iron in presence of steam. In this way iron iodide should be formed, which is soluble in water. Up till now, however, the yield of iodine is very small and the greater part of it remains in the phosphorite.

vapour tension, and therefore do not condense in globules. In dry air even the concentrated solutions do not fume. The vapour density of these acids compared with hydrogen corresponds to their normal molecular weight. The affinity of hydrogen for the halogens diminishes with increasing atomic weight of the latter. HF is very stable, HCl decomposes at 1500°, HBr already at 800°, and HI at a little more than 400°. The metallic derivatives (salts) of the halogens behave in an analogous manner, in respect to their solubility and stability.

These gaseous acids are extremely soluble in water and they do not apparently follow Henry's law, that is, the greater portion of the acid dissolves almost independently of the pressure. More precisely one portion of the acid dissolved in the water is dissociated into its component ions, and this portion does not follow Henry's law as it is no longer a gas and has no longer the same composition as the original acid ; the other portion is dissolved without dissociation, and this portion does obey the above-mentioned law. In the typical case of hydrochloric acid we observe that whilst the pure anhydrous acid boils at −83°, and water at 100°, when the acid and water are mixed in various proportions a liquid does not always result which boils at an intermediate temperature (between −83° and 100°), but that the boiling-point of dilute solutions containing less than 30 per cent. of HCl is higher than 100°, and that a 20 per cent. solution has the maximum boiling-point of 110°. If, then, a concentrated solution of hydrochloric acid is distilled, all the acid which boils at lower temperatures than 110° is gradually boiled off and the temperature steadily rises until the acid which remains contains only 20 per cent. of HCl (with the maximum boiling-point) and the acid which now distils is of constant composition. Also if, on the contrary, an acid containing less than 20 per cent. of HCl is distilled at first the distillate consists of acid boiling at a lower temperature and the boiling-point rises in this case also until it reaches 110°, when an acid containing 20 per cent. of HCl remains and distils unaltered. It might be supposed that this acid, boiling at a constant temperature, was a true chemical compound of water and acid, to which the formula $HCl.8H_2O$ could be assigned, but this is not the case, because the composition of the acid of constant boiling-point varies with the pressure at which the distillation is conducted. In fact we may state generally that any solution of a gas which has a boiling-point higher than those of slightly more and slightly less concentrated solutions will distil without changing its composition.

HYDROFLUORIC ACID : HF

PROPERTIES. Hydrofluoric acid is a colourless gas of pungent odour, fuming in the air. On the skin it produces blisters and ulcerous wounds, difficult to cure ; these should be at once washed with a very dilute aqueous solution of ammonia. It is strongly poisonous, and when inhaled in some quantity is sometimes fatal. The symptoms of poisoning with this acid are nausea, vomiting, and strong salivation.

In the cold it condenses to a colourless liquid boiling at 19·5° ; it solidifies at −102° and melts at −92·5°. On heating a concentrated aqueous solution of this acid it first evolves pure HF, and a liquid remains which distils unchanged at 120°, containing 38 per cent. of HF (corresponding to the formula $HF + 2H_2O$, *see above*). It carbonises sugar, paper, and wood, attacks glass strongly and rapidly, but does not attack paraffin wax, resin, platinum, or gold, and lead only slightly. It is very soluble in water, and the solution, which also attacks glass strongly, is kept in vessels of platinum, gold, lead, or guttapercha (or hard rubber), or also in glass vessels lined with paraffin.

Its action on glass is shown by the following experiment. Powdered calcium fluoride is treated with an excess of strong sulphuric acid in a platinum or lead capsule, which is covered with a sheet of glass covered with wax in which words or figures have been incised. The reaction takes place in half an hour even in the cold. The gaseous HF leaves an opaque mark where it has attacked the glass ; in aqueous solution, on the other hand, the attacked portions are transparent.

Hydrofluoric acid is a bad conductor of electricity. At − 25° it does not

attack metals or non-metals (except the alkali metals). It combines energetically with anhydrides (sulphuric and phosphoric anhydrides, &c.), and displaces all the other halogens from their salts. It reacts energetically with silicates (glass) and on silica, dissolving it in the form of silicon fluoride, SIF_4 :

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

From the electric conductivity of sodium fluoride the dibasicity of the acid has been deduced (1907) and it should now be written H_2F_2 (*vide supra*). Its power of inversion of sugar is large.

Whilst the other halogen salts of silver are insoluble in water, silver fluoride is soluble. On the contrary, whilst the chloride, bromide, and iodide of calcium are easily soluble in water, calcium fluoride is insoluble. The heat of formation of gaseous HF is 161·7 Kj. (38,600 cals.), and its heat of solution is 49·4 Kj. (11,907 cals.).

USES OF HYDROFLUORIC ACID. This acid is used in glassworks to mark graduated apparatus, such as thermometers, cylinders, flasks, &c. In analytical chemistry it is used for decomposing silicates and rendering them soluble. An opaque etching on glass is also obtained by mixtures of certain soluble fluorides with other white, insoluble substances.

In 1899 Malinsky proposed the use of hydrofluoric acid for the inversion of starch, in order to transform it into sugar (glucose) (*see* vol. ii., " Organic Chemistry ").

Hydrofluoric acid is employed in large quantity in the manufacture of spirit from cereals by Effront's process (*see* vol. ii.). It is very destructive to vegetation, and is a potent antiseptic.

PRICES OF HYDROFLUORIC ACID AND CONTAINING VESSELS FOR THE SAME. Commercial fuming hydrochloric acid ordinarily contains 60 to 65 per cent. of HF (30° to 33° Bé.) and is sold at 8½*d.* to 9*d.* per kilo or in large quantities at £2 4*s.* to £2 8*s.* per 100 kilos. The commercial quality, free from arsenic, containing 40 per cent. of HF (20° Bé.), costs 10*d.* per kilo and £2 12*s.* per 100 kilos. The purer quality for medical use costs about double. Chemically pure fuming HF, distilled in platinum, costs up to 5*s.* per kilo ; the common fuming acid for writing on glass costs 1*s.* 3*d.* per kilo.

Guttapercha bottles for holding HF of 100 c.c. capacity cost 1*s.* 3*d.*, of 1000 c.c. capacity 5*s.* 10*d.*, of 10 kilos capacity £2 8*s.*, and of 40 kilos capacity up to £6.

Ordinarily the greater portion of the HF sold is kept and sent out in receivers of lead or of lead-lined iron. Lead vessels of 5 kilos capacity cost 12*s.*, of 40 kilos capacity £1 6*s.* The proposal has recently been made (1907) to store and send out hydrofluoric solutions in beer barrels internally lined with pure resin.

A single factory in Vienna produces five tons of hydrofluoric acid per day. The official statistics for Italy show a production of seventy tons in 1906 and fifty in 1907. Perhaps these figures are exaggerated ; however, a considerable portion is produced by the firm of Carlo Erba in Milan.

PREPARATION. Hydrofluoric acid was first prepared in the pure state as a liquid by Scopoli in 1784 ; he preserved it in internally gilded silver receivers, but did not know its chemical composition. In 1670 Schwankhald already used fluorspar with sulphuric acid for polishing glass.

Hydrogen combines with fluorine even in the dark, and this reaction takes place much more readily than that between hydrogen and chlorine.

In 1856 Fremy prepared anhydrous hydrofluoric acid by first drying potassium hydrogen fluoride KF.HF at 100° and then finally for fifteen days in a desiccator containing strong sulphuric acid and fused caustic soda, *in vacuo*. The dry substance was then distilled from a platinum retort at a gentle heat and the product collected in platinum receivers cooled with snow and salt.

Louyet prepared anhydrous HF by heating silver fluoride (AgF) in a current of hydrogen : $AgF + H = Ag + HF$.

Pure HF is obtained on passing a current of hydrogen sulphide gas over lead fluoride : $PbF + H_2S = 2HF + PbS$.

In the laboratory it is commonly prepared by distilling powdered calcium fluoride with excess of strong sulphuric acid (*see below*) from a small retort of lead or platinum, and cooling the receiver strongly in which it is collected.

INDUSTRIAL MANUFACTURE. Fluorspar is decomposed by strong sulphuric acid according to the following equation :

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

or cryolite by sulphuric acid :

$$2AlF_3.3NaF + 6H_2SO_4 = 2Na_2SO_4 + 2AlNa(SO_4)_2 + 12HF.$$

HF is ordinarily prepared industrially in horizontal cast-iron cylinders holding a charge of as much as one ton of powdered calcium fluoride and one ton of strong sulphuric acid of 66° Bé. The acid, which is evolved on heating gradually, is condensed in large spiral condensers of lead and collected in lead receivers, and has a concentration of 40° Bé. (70 per cent. HF). At first silicon fluoride, SiF_4, also distils and separates gelatinous silica by reacting with water in the first receiver ; this is therefore changed shortly after the commencement of the distillation.

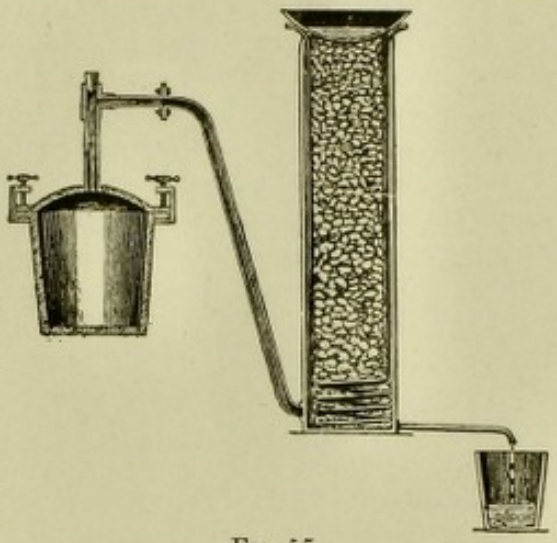


Fig. 55.

Hampel adopted the following apparatus (Fig. 55) : A cast-iron retort holding the charge ($CaF_2 + H_2SO_4$) communicates by means of an iron tube with a tower filled with wood-charcoal ; this is surmounted by a large pan with a perforated bottom, which is filled with water, causing a fine spray to fall on to the carbon below. The lowest portion of the tower is cooled by a lead spiral through which cold water flows ; this causes the hydrofluoric acid to condense and dissolve readily and the liquid is collected in a separate lead receiver. Städeler recommended bottles of guttapercha as being economical for the collection and preservation of hydrofluoric acid, but it has been found that in time they contaminate the acid. Ebonite bottles are better. Vessels of metal and glass, internally coated with paraffin, also serve fairly well.

It is not to be denied that even with well-closed vessels a little HF often escapes, which attacks external objects.

If the hydrofluoric acid contains H_2S, formed by sulphides in the fluorspar, it becomes turbid after a short time through separation of sulphur.

To obtain it pure for laboratory use, starting from the commercial product, the lead is first removed with H_2S, and fluosilic acid then removed with K_2CO_3 ; it is then filtered and the H_2S removed with silver carbonate. By then distilling in a platinum apparatus pure HF is obtained.

Thorpe and Hambly distil the commercial acid with potassium permanganate, and then transform the HF into hydrogen potassium fluoride, KHF_2, with K_2CO_3 or KOH ; they dry the HF.KF and distil it, collecting the hydrofluoric acid in distilled water.

ANALYSIS OF HYDROFLUORIC ACID. A given quantity is removed with a pipette internally coated with wax, the capacity of which has been previously measured, and is treated in a platinum capsule with excess of normal caustic soda solution free from carbonate ; the excess of sodium hydroxide is then titrated back with normal sulphuric acid, using phenolphthalein as indicator (*not* litmus or methyl orange). 1 c.c. N.NaOH = 0·020 grms. HF.

Silicon fluoride is often present as an impurity, and is found by adding potassium

acetate to a given quantity of the hydrofluoric acid and evaporating it to dryness on the water-bath. That part of the residue which is insoluble in water consists of potassium fluosilicate.

HYDROCHLORIC ACID : HCl

The Arab alchemists employed this acid mixed with nitric acid, as *aqua regia*, but did not know it in the pure condition.

The aqua regia was obtained by distilling saltpetre, ammonium chloride, and iron sulphate.

In the fifteenth century Basil Valentine described hydrochloric acid for the first time, calling it spirits of salt. He obtained it in aqueous solution by distilling iron sulphate and NaCl.

In the seventeenth century Glauber obtained it by distilling NaCl with sulphuric acid. Stephen Hales obtained it by the action of H_2SO_4 on ammonium chloride.

Hydrochloric acid was prepared pure by Priestley, who considered it to be an oxidised acid of *murum*, as chlorine was then called, and therefore named it muriatic acid. It was not until 1810 that Davy showed that hydrochloric acid was a hydrogen derivative of chlorine.

This acid is found in nature in volcanic exhalations, for example, in those of Vesuvius. It is found in the water of the Vinagro River which issues from the volcano Purace, in the Andes, and contains 0·111 per cent. of HCl, from which it is estimated that thirty tons of this acid are removed by the river each day. It has also been found in an acid spring near the volcano Paramo de Ruiz, in New Granada, the water of which contains 0·88 per cent.

Hydrochloric acid is a normal constituent of the gastric juices of all mammals and serves an important function in digestion. The gastric juice of the dog contains 3 per cent. ; that of man from 0·05 to 0·32 per cent.

PHYSICAL PROPERTIES. Hydrochloric acid is a colourless gas of acrid, pungent odour, which fumes in the air. Its critical temperature is 52·3°, and its critical pressure 86 atmospheres. When liquefied it has a specific gravity of 0·83 at 15° ; it is solid at − 115°, and boils at − 83°. In 1846 Faraday liquefied it for the first time, under pressure, with a mixture of solid carbon dioxide and ether.

The density of the vapours or gas of hydrochloric acid, compared with air, is 1·26 at 0° and 760 mm. pressure, and a litre of the gas weighs 1·6288 grms. It colours blue litmus paper red. It readily dissolves in water in the proportion of 450 vols. in 1 vol. of water.

Aqueous hydrochloric acid saturated at 15° contains 43 per cent. of HCl, and its specific gravity is 1·212. On distilling the concentrated aqueous solution much HCl is first evolved, and then at 110° an acid of constant composition (about 20 per cent. HCl, *see* p. 155) distils, which corresponds to the composition $HCl + 8H_2O$. The ordinary commercial hydrochloric acid contains 35 per cent. of HCl.

In the gaseous state it is absorbed by wood charcoal with development of heat ; 1 vol. of charcoal absorbs 165 vols.

One volume of alcohol of sp. gr. 0·836 dissolves 327 vols., and the volume of the alcohol is increased to 1·324 vols.

Hydrochloric acid also dissolves in methyl alcohol, ether, ethane, benzene, xylene, &c. An alcoholic solution of HCl has only one-sixteenth of the electric conductivity of the aqueous solution, because in the former solution the acid is much less dissociated into its ions.

CHEMICAL PROPERTIES. Electrolysis shows that HCl is composed of 1 vol. of chlorine and 1 vol. of hydrogen.

It is not combustible, and is not a supporter of combustion, excepting with sodium and some other metals, when they are once burning. When concentrated hydrochloric acid is saturated with gaseous HCl at − 22°, crystals of a hydrate, $HCl.2H_2O$, separate, which melt at 18°, with evolution

of HCl. On mixing two parts of snow with one part of concentrated commercial HCl, the temperature is lowered by 15°. *Aqua regia* is formed by mixing 3 vols. of HCl with 1 vol. of concentrated HNO_3, and dissolves all the metals, including gold and platinum.

When dissolved in water hydrochloric acid is a strong monobasic acid which readily dissolves the alkali and alkali earth metals and also Mg, Zn, Cd, and Fe at the ordinary temperature, with evolution of hydrogen. When heated it dissolves Pb, Cu, and Hg, with evolution of pure hydrogen. In all these cases the corresponding chlorides are formed, which may also be obtained by the action of HCl on the metallic oxides and carbonates. The metallic chlorides are almost all soluble in water, with the exception of AgCl, Hg_2Cl_2, and Cu_2Cl_2, and also $PbCl_2$, which is only slightly soluble. At a red heat almost all the metallic chlorides are volatile, excepting those of Au, Pt, and Ir, which are decomposed.

Anhydrous liquid hydrochloric acid is a transparent, colourless, rather mobile liquid which has no action on metals, even on Zn, Mg, and Fe, although they are easily attacked by its aqueous solution. With aluminium powder, however, hydrogen is evolved; if pure it does not react with calcium oxide, with sulphides, or with metallic carbonates, nor does it even redden dry litmus paper.

HCl acts as a poison on plants; and air containing only 3·5 parts per thousand is fatal to many animals. Human beings cannot for long tolerate the respiration of air containing 1·5 parts per thousand of HCl.

USES OF HYDROCHLORIC ACID. Hydrochloric acid is often used for the preparation of chlorine, ammonium chloride, and many other chlorides, for the purification of animal charcoal from carbonates, for the manufacture of glue, and for etching. It is also used for the preparation of carbon dioxide, the extraction of cupriferous minerals, and for other metallurgical purposes. Large quantities are used by manufacturers of dyestuffs and pigments, and also for the manufacture of many chlorinated organic chemicals.

STATISTICS AND PRICES. In 1895 the European production of hydrochloric acid was about two million tons, of which half was produced in England, which in 1908 contained sixty-five works. In 1882 Germany produced and consumed 148,450 tons, in 1901 about 300,000 tons, and in 1906 350,000 tons of the value of £800,000. In 1909 Germany imported 4923 tons of hydrochloric acid and exported 15,992 tons. In 1908 Russia produced 50,000 tons. In Italy the production of hydrochloric acid amounted to 4600 tons in 1893; 8680 tons in 1903; 11,170 tons in 1905; 12,021 tons in 1906; and attained 14,160 tons in 1907, of the value of £32,000. Italy imported 96 tons in 1906 and 218 tons in 1908. It is a notable fact that the price of hydrochloric acid has occasionally exceeded that of sulphuric acid. In small quantities the price of crude hydrochloric acid of 20° Bé. (32 per cent. HCl) is 3*s.* 9*d.* to 4*s.* 2*d.* per cwt., and in large quantities as little as £1 12*s.* per ton; acid free from arsenic and sulphuric acid costs £4 16*s.*, chemically pure acid of sp. gr. 1·19 (23° Bé.) as much as £14, and the same of 19° Bé. about £10 per ton.[1]

PREPARATION IN THE LABORATORY. Equal volumes of chlorine and hydrogen combine at 150°; they also combine at the ordinary temperature under the influence of the electric discharge, or in contact with spongy platinum, or under the influence of chemically active light rays, for instance, sunlight or the light obtained by burning a mixture of nitric oxide and carbon disulphide vapour, or by burning magnesium. The combination occurs with development of heat and light. Hydrogen burns in an atmosphere of chlorine yielding HCl. Various chlorides of the non-metals decompose with water at the ordinary temperature giving HCl, *e.g.* the chlorides of S, N, P, Sb, Bi, and Si. Thus

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

[1] The condensing plant for hydrochloric acid from a works treating 400 kilos of salt in twenty-four hours, divided into two parts—one for the acid from the muffle-furnace, the other for that from the pans—with condensing and refrigerating towers and 108 receivers of 300 litres capacity (54 for each battery), &c., costs in all, in stoneware, about £480.

HCl is also formed when certain organic compounds containing chlorine are burnt; thus on soaking a little cotton wool in a mixture of alcohol and chloroform and setting fire to it the vapours which are formed contain hydrochloric acid, recognisable by its action on litmus paper, which is formed from the hydrogen and chlorine of the organic substances.

When metallic chlorides are heated with strong acids HCl is formed.

The ordinary method of preparation is based on the action of sulphuric acid on NaCl. At comparatively low temperatures the first phase of the reaction takes place :

$$NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

On then heating up to redness there is the further reaction :

$$NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

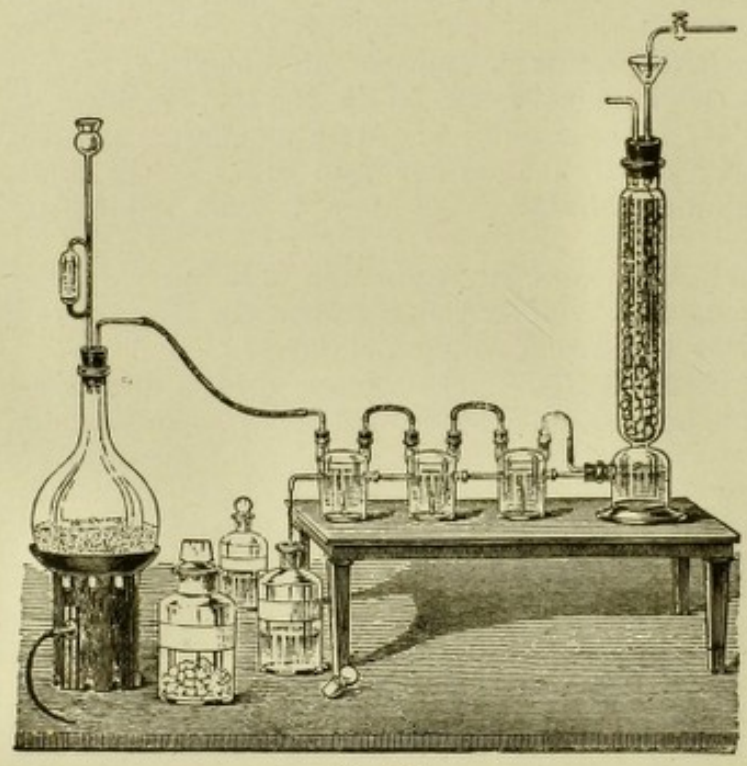


Fig. 56.

In the laboratory HCl is prepared as follows, using the first phase of the reaction :

The sulphuric acid and salt are placed in a flask heated on a sand-bath (Fig. 56), and the escaping HCl gas is passed over the surface of water in the three Woulff's bottles united by tubing above and also by side tubes below, through which a current of water flows in a contrary direction to the gas. A concentrated HCl solution is thus obtained and the escaping gas is condensed in a tower filled with porous material down which water is passed. The dilute solution so obtained is continuously concentrated by passing through the three Woulff's bottles, in the first of which, containing the largest quantity of gas, concentrated aqueous HCl is formed.

INDUSTRIAL MANUFACTURE OF HYDROCHLORIC ACID. Until the commencement of the nineteenth century this substance was prepared by distilling sulphuric acid with sodium chloride in cylindrical cast-iron retorts and absorbing the hydrochloric acid gas which was evolved in a battery of receivers with two necks, half full of water. In certain localities this method is still used for small scale production, but the greater part of the hydrochloric acid is now obtained as a secondary product in the manufacture of sodium sulphate, which is itself used in the manufacture of sodium carbonate by the Leblanc process.

The reaction of the H_2SO_4 on NaCl takes place in two phases in the so-called salt-cake furnaces. The first phase takes place at a moderate, relatively low temperature in a compartment of the furnace of which the bottom is formed by a pan of lead or cast-iron which is heated moderately by the hot gases from the hearth (Fig. 57). Into this pan are introduced the salt and the corresponding quantity of sulphuric acid of 52° Bé. or even 62° Bé. On heating, the mass liquefies and simultaneously develops the first part of the HCl, becoming denser, until sodium disulphate remains : $NaCl + H_2SO_4 = NaHSO_4 + HCl$. The gas is passed through long earthenware pipes which communicate with a battery of double-necked earthenware receivers (*bonbonnes, tourilles*), illustrated in Figs. 60 and 61.

When the central pan no longer develops HCl, which is shown by the lower temperature of the delivery pipes, the pasty mass is passed into two lateral compartments of the furnace, where it is heated to redness by the direct action of the flame and furnace gases. The disulphate (sodium hydrogen sulphate) formed in the pan reacts at this temperature with the remaining portion of the NaCl, and the second phase of the reaction occurs with formation of hydrochloric acid and neutral sodium sulphate: $NaHSO_4 + NaCl = Na_2SO_4 + HCl$. In this portion of the furnace it is necessary to stir the mass by means of suitable iron tools, which are introduced through the openings shown in Fig. 57; the gas is thus completely evolved. The hydrochloric acid developed during this second phase is much less pure, being mixed with the furnace gases, and is, therefore, condensed in a separate battery of receivers (*see* Figs. 59 and 60). These furnaces with direct flame are called *reverberatory furnaces.*

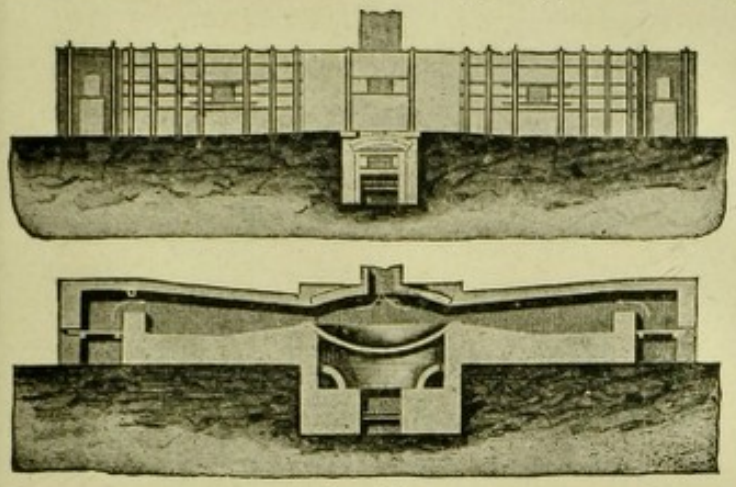


Fig. 57.

In modern furnaces the compartment where the second phase takes place is arranged as a *muffle furnace* (Fig. 58) with a reverberatory arch, *B*. These muffles do not communicate directly with the hearth, but are indirectly heated from outside, as the furnace gases turn and pass between the double walls of brickwork, *f*. By means of muffle furnaces the advantage is gained that the HCl is obtained in a stronger and purer condition, and is, therefore, absorbed more easily, whilst in the old furnaces with direct flame it was obtained mixed with all the products of combustion and with air, which rendered it difficult to absorb it completely. The hot gases from the hearth, *a*, after heating the muffle, pass under it and through the flue, *g*, and then heat the pan, in which the first phase of the reaction takes place, before passing away to the chimney through *q*.[1]

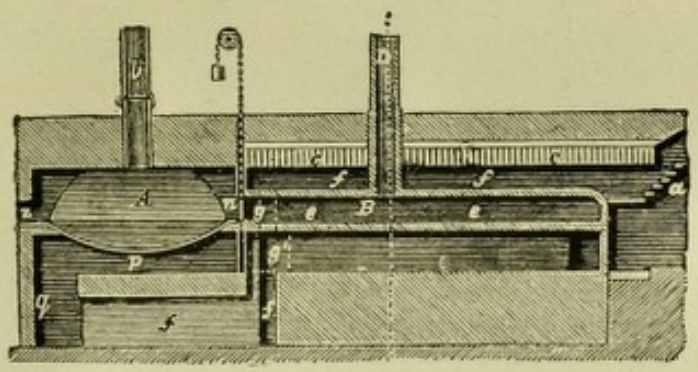


Fig. 58

The acid is absorbed in a battery of receivers communicating with one another as is seen in Fig. 59, which illustrates a complete hydrochloric acid plant, and in which we see the long delivery pipe from the pan, the other delivery pipe from the muffle, the first condensing and purifying tower, *A*, where the sulphuric acid carried over by the gases is caught, and the gases which issue from the furnace at a temperature of 200° to 250° are cooled; then follow the receivers, which are fed with a continuous stream of water from the final condensing towers, which absorb the last traces of HCl by means of a water-spray before the gases pass away into the atmosphere.[2] Even when muffle furnaces are used

[1] A rational method of uniformly distributing the hot furnace gases under the pan was proposed in 1898 by Th. Meyer, based on the same principle as his tangential lead chambers (*see below*, Sulphuric Acid Manufacture).

[2] *Legislation regarding hydrochloric acid works.* During the first period of the manufacture of sodium sulphate for use in the manufacture of carbonate the HCl was not utilised and was allowed to pass away into the atmosphere. The complaints which arose in the neighbourhood of these works induced the manufacturers, especially in England, to erect very high chimneys, in the hope that the HCl when carried to a great height would mix with very much air and cause no more trouble (at St. Rollox a chimney 150 metres high was constructed). But these hopes were not realised, because the HCl, being heavier than air, redescended to earth, extending over the adjacent country as a thick mist and causing serious damage, especially to vegetation. The manufacturers were obliged to condense the HCl in order to remove the nuisance, and as at that time they had no use for the product, they passed the fumes through long channels in which they were washed with water. But a large portion of the gas still escaped into the atmosphere, and the dissolved portion was also largely given off again as fumes. In 1836 Gossage first proposed the absorption of the HCl in a rational manner in condensing towers filled with coke moistened

the acid is absorbed in two batteries of receivers as the HCl from the pan is purer than that from the muffles. The most concentrated acid, which collects in the first receivers, attains a density of 20° to 22° Bé. and is thus placed on the market. The acid which collects at the base of the towers has a density of 7° to 8° Bé., and is passed into the receivers, where it travels in the reverse direction to the gases coming from the furnaces. Figs. 60 and 61 illustrate a couple of receivers as commonly employed. They are made of acid-resisting stoneware, and the tubes uniting them with one another are entirely of the same material and composed of several superposed pieces with rims which hold sufficient water to form a hydraulic seal. For the absorption stone towers with tarred walls may also be employed, and filled with coke, layers of perforated earthenware discs, or earthenware balls. A spray of water falls from the top of the tower, dissolves the acid which ascends from the base, and collects at the base after absorption, being led from there into the receivers. The form

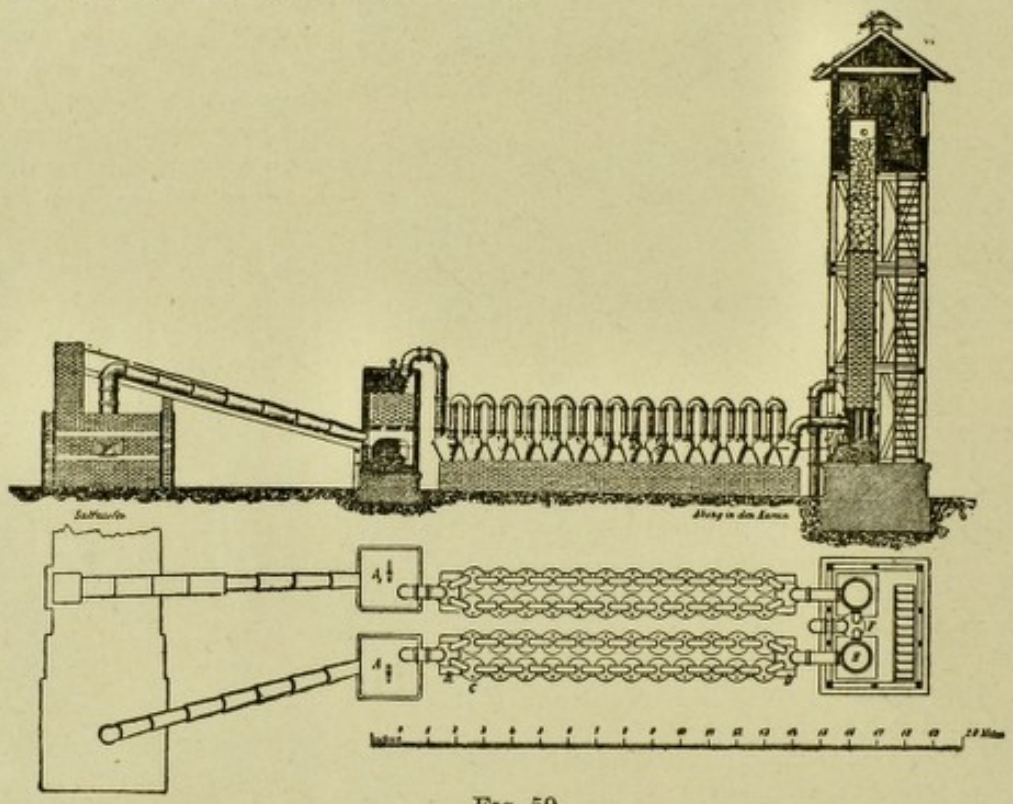


FIG. 59.

of the receivers has also been much modified of recent years, the form which has given the best results having been proposed by Cellarius and perfected by Th. Meyer in 1901 (Fig. 62), and constructed entirely in stoneware ; this form gives the maximum cooling and absorbing effect with the minimum quantity of water, because its arched shape allows of the largest

from above with a spray of water. The condensation was much better effected, but was still incomplete, owing to irregular supervision ; on the other hand, the production of sodium sulphate increased to such an extent that the absolute quantity of hydrochloric in the atmosphere remained unaltered in spite of the fact that it was largely condensed. The continuance of these nuisances led to complaints which necessitated restrictive legislation. In 1855 a law was passed in Belgium which made the employment of muffle furnaces instead of those with direct flame compulsory, as in the latter the escape of HCl was greater. It was actually found that, whilst in 1854 only 75–85 kilos of hydrochloric acid were obtained from 100 kilos of salt in 1870, the same works obtained on the average 120–160 kilos.

In England a law was passed in 1863 which forbade the escape from the condensing towers of more than 5 per cent. of the hydrochloric acid produced, as shown by analysis of the gases entering and issuing from the tower. In a few years results were obtained which were unexpected by the legislators, for it was found that in very few works more than 1 per cent. of the HCl produced was allowed to escape, whilst beforehand they had lost 15 to 36 per cent. But the losses of HCl from the furnaces and receivers were not included, only those from the chimneys and towers. The law was then revised in 1874, and it was laid down that the fumes from the chimneys of works, by which the gases from the condensing towers were carried away, might not contain more than 0·5 grm. of HCl per cubic metre of gas. It has been shown that in the English works to-day the escaping gases do not contain more than at most 0·2 grm. of HCl per cubic metre. In England, in 1893, 1173 chemical works were being controlled.

In Germany, on the contrary, no law regulating this industry exists, as the manufacturers built their plants more rationally and were entirely interested in utilising the HCl as far as possible. In actual fact the HCl represents a value which alone permits many Leblanc soda works to exist in face of the competition of the Solvay establishments.

water surface. It is 80 cms. long, 50 cms. broad, and 30 cms. high, and contains 25 litres of liquid and 45 litres of gas. Under the internal arch there is a stoneware ridge or crest a few centimetres high and extending along about two-thirds of the length of the receiver, shown in black in the longitudinal section (Fig. 63); this forces the water which enters at *a* to traverse the full length of the receiver and back again to the outlet, *b*, along the other side, passing over the point where the crest is lacking. The HCl gas enters and issues by the openings *c* and *d*, thus passing over the surface of the water. These vessels, which have a surface of 1 sq. metre, are united with one another by curved tubes as shown in Fig. 64, and are kept cool by being immersed two by two in vessels in which water circulates, and in this manner each jar has the same efficiency as two or even three of the old type of receiver. In order to cool the gas which issues from the furnace, before it enters the absorption battery it is passed through a battery of empty coolers, shaped, according to Uebel, like inverted Cellarius receivers, as seen in Fig. 65. Between the cooling and absorbing batteries a tower of finely divided material may be advantageously inserted, in order to filter the gases and free them in great part from the impurities, sulphuric acid, arsenic, iron, and selenium. If little space is available these batteries are formed of superposed jars.

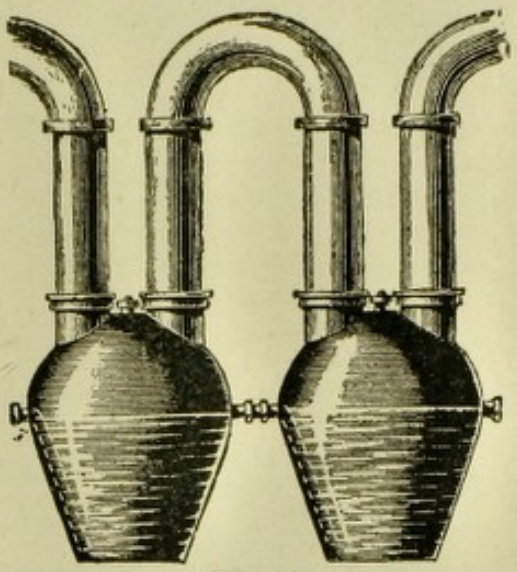


FIG. 60.

FIG. 61.

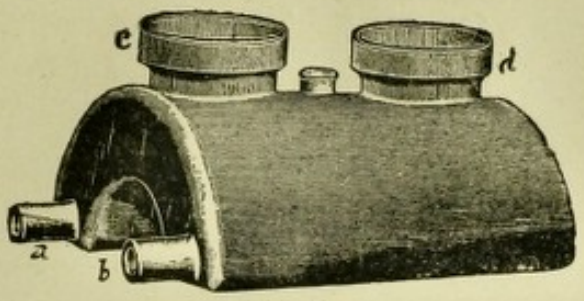


FIG. 62.

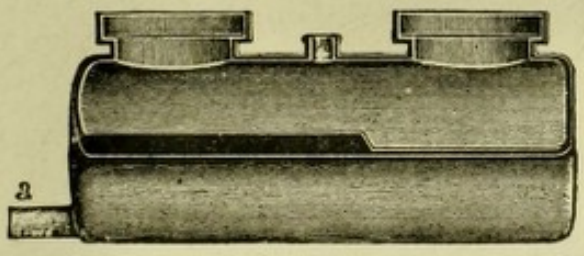


FIG. 63.

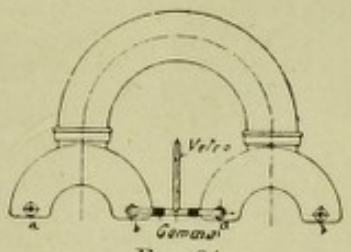


FIG. 64.

In the furnaces with direct flame 35 to 40 kilos of coal were used per 100 kilos of Na_2SO_4, whilst in the muffle furnaces only 30 to 35 kilos are used, because the heat is better utilised, and the product is also superior. In certain modern mechanical furnaces the consumption of fuel is lowered to one half (*see* Soda, Part III).

The *Hargreaves process* for the manufacture of HCl was proposed in 1850, was improved by Robinson, and since 1870 has found industrial application. It is based on the direct action of sulphur dioxide (SO_2) on sodium chloride in presence of steam and of atmospheric oxygen : $2NaCl + SO_2 + H_2O + O = = Na_2SO_4 + 2HCl$.

This method is advantageous when applied to continuous working on

a very large scale. The salt is introduced, moistened and compressed into cakes, into a battery of eight to twelve cast-iron cylinders, 5 metres in diameter and 4 metres high. Below the perforated false bottom of these cylinders sulphur dioxide from pyrites burners enters, mixed with air and steam in the proportion of 2 vols. SO_2, 2 vols. H_2O, and 1 vol. O, and is completely absorbed by passing through all the cylinders in succession. During this reaction heat is developed, but on starting fuel must be used to raise the temperature to 500°, after which the temperature is maintained constant and the operation is then continuous. A notable amount of fuel is thus saved, and sodium sulphate is manufactured without the need for sulphuric acid, and therefore without lead chambers.[1] It is necessary to work with large quantities of salt; every charge requires up to forty tons of NaCl. In order to prevent salt from remaining unattacked in the interior of the cakes it is mixed with coal or sawdust, which then burns and leaves a more porous mass.

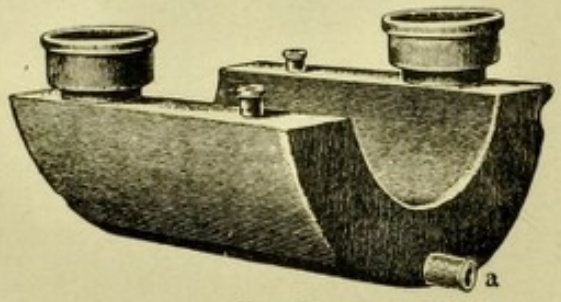


FIG. 65.

This process was tried in Sardinia, but without success, whilst it is much used in England and France, and has been used in Germany in two establishments of the Rhenania Company.

In the Solvay process of manufacturing soda from NaCl, carbon dioxide and ammonia, all the chlorine of the NaCl is converted into ammonium chloride (NH_4Cl). This is then decomposed with lime, which liberates ammonia and forms calcium chloride ($CaCl_2$) in large quantity. In 1878 and 1885 Solvay tried to prepare HCl by treating $CaCl_2$ with silica (SiO_2, kieselguhr, clay rich in silica, &c.), and superheated steam:

$$SiO_2 + CaCl_2 + H_2O = CaSiO_3 \text{ (calcium silicate)} + 2\,HCl.$$

According to Lunge up to 65 per cent. of the theoretical quantity of HCl may be obtained in this way, but this process has not yet had any important application. All the same,

[1] **Thermochemistry of the formation of HCl and Na_2SO_4 by the Hargreaves process**: To produce SO_2, firstly we have $2FeS_2 + 11\,O = Fe_2O_3 + 4SO_2 + 419{\cdot}8$ cals., and in detail the dissociation of 2FeS requires 57·6 cals., the formation of Fe_2O_3 evolves 191 cals., and that of $4SO_2$ gives $71{\cdot}6 \times 4 = 286{\cdot}4$ cals. (thus $191 + 286{\cdot}4 - 57{\cdot}6 = 419{\cdot}8$); the quantity of heat corresponding to one molecule of SO_2 is thus $\frac{419{\cdot}8}{4} = 104{\cdot}95$ cals.

In the production of sodium sulphate we have, on the one hand, the heat absorbed by dissociation, from which must be subtracted the heat produced as shown by the right side of the equation:

$$2NaCl + H_2O + O + SO_2 = Na_2SO_4 + 2HCl$$

$$\underbrace{2 \times 97{\cdot}3}\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\underbrace{2 \times 22}$$

Cals. 194·6 59 71·6 326·4 44

Thus the heat evolved by this reaction is

$$(326{\cdot}4 + 44) - (194{\cdot}6 + 59 + 71{\cdot}6) = 45{\cdot}20 \text{ cals.},$$

which when added to the preceding 104·95 gives a total of 150·15 cals. We must now consider the heat which is lost by the hot gases remaining after this reaction, which include nitrogen from the air and water vapour; we find, on calculating the amounts, but with reference to 1000 grms. of sodium sulphate produced and taking the specific heats of the gases into account, that per degree loss of temperature the following amounts of heat are lost:

513·38 grms.	HCl	× 0·1845 (sp. ht.)	=	94·7 cals.
80·64 ,,	O	× 0·2175 (,,)	=	17·5 ,,
1681·54 ,,	N	× 0·2317 (,,)	=	389·6 ,,
73·24 ,,	vap. H_2O	× 0·4805 (,,)	=	35·2 ,,
		Total .		537·0 cals.

As these gases emerge at a temperature of about 500°, we must multiply this value by 500 = 268,500 small calories carried away by them, per 1000 grms., of Na_2SO_4, or 38,127 per grm. molecule (142 grms.), corresponding to 38·1 Cals. (large Calories). Furthermore, the heat which is lost on removing the sodium sulphate of specific heat 0·254 from the chambers at 650° will be, for each grm. molecule, $142 \times 0{\cdot}254 \times 650 = 23{,}440$ cals., that is, 23·44 Cals. Therefore the complete loss in the products of reaction will be 38·1 + 23·44 = 61·54 Cals. Therefore the heat available in the complete reaction of the Hargreaves process will be 150·15 − 61·54 = 88·61 Cals.

It will thus be seen that, if the apparatus is well insulated, once the process is started it will not be necessary to supply heat, and in certain cases it will even be necessary to cool the mass to prevent fusion of the salt (at 772°) and of the sulphate (at 860°).

it is probable that in the near future the $CaCl_2$ from the soda works will all be utilised for the production of HCl, either by means of silica or of magnesia.[1] Attempts have already been made to prepare HCl from the enormous quantities of magnesium chloride ($MgCl_2$) at Stassfurt, by heating it to an elevated temperature with more or less steam, thus obtaining a mixture of HCl + Cl + MgO. The HCl so obtained is condensed in towers and is very pure as it does not contain either sulphuric acid or arsenic. The method appears to have been introduced at Neu Stassfurt with satisfactory results.

In Solvay's works ammonium chloride vapours were passed over red-hot MgO, $MgCl_2$ and NH_3 being obtained. On then heating $MgCl_2$ in a current of steam HCl was formed and the original magnesium oxide recovered: $MgCl_2 + H_2O = MgO + 2HCl$. J. Th. Schlösing (Fr. Pats. 360,356 of 1905 and 394,037 of 1908) heated a concentrated solution of $MgCl_2$ until this showed a boiling-point of 132°, then added a quantity of magnesia corresponding to one-third of the magnesium present as chloride, stirred the viscous mass and dried it at 200°, and then decomposed it in a pan over which hot furnace gases were passed, condensing the hydrochloric acid in the usual manner.

PURIFICATION OF THE CRUDE COMMERCIAL ACID. The commercial acid contains various impurities, especially arsenic chloride, ferric chloride, $FeCl_3$, Cl, SO_2, H_2SO_4, derived from the ordinary impurities of the H_2SO_4 employed, and also NaCl. The ferric chloride turns the acid yellowish, as do also traces of selenium, tellurium, and organic substances.

The purification of the crude acid is complicated and difficult:

To remove ferric chloride the acid is diluted till its specific gravity is 1·145, and then distilled. Fuming hydrochloric acid of 36 to 38 per cent. HCl is first obtained, and then a weaker acid. The ferric chloride only distils with the last portions which are collected separately; or the ferric chloride may be fixed by adding phosphoric acid or calcium phosphate before distillation.

The elimination of arsenic is most difficult; it is first treated with MnO_2 to oxidise the SO_2, then diluted with water and left in contact with bright copper sheets for some days, after which it is distilled in presence of copper, but this acid often still contains traces of arsenic.

If it is distilled in presence of ferrous chloride, $FeCl_2$, the arsenic passes over with the first portions and fairly pure HCl can be obtained. It is often purified by first separating the arsenic with hydrogen sulphide or barium sulphide (which separates both As_2S_3 and H_2SO_4) and then distilling from glass retorts.

Better results are obtained by treatment with stannous chloride in scrubbing towers, but the best results appear to be obtained by the recent process (1905) of Messrs. Meister, Lucius, and Bruning in Höchst, who employ vanadious salts which can be obtained cheaply and can be regenerated electrolytically.

[1] The method proposed by Lorenz in 1894 and 1897 attracted for some time a certain amount of interest, but has not yet been practically adopted; he proposed to utilise and transform into HCl the extraordinary and excessive quantities of chlorine from the electrolytic alkali works, as the quantity of HCl from Leblanc soda works is diminishing strongly on account of the rise of the Solvay process.

Lorenz states that by passing a current of steam and chlorine over barely red-hot carbon the chlorine is quantitatively converted into HCl, a mixture of CO_2 and CO being formed at the same time (the CO being more or less abundant according to the thickness of the layer of carbon traversed by the gases); this mixture can be used as a source of energy for heating the apparatus, and the process then continues without requiring further fuel, as the reaction develops heat: $2Cl + 2H_2O + C = 4HCl + CO_2$; one portion of the CO_2 is reduced by carbon, but is again burnt and so made use of: $CO_2 + C = 2CO$ and $CO + O = CO_2$. Experiments carried out by A. Naumann in 1897 showed that the reaction was not quantitative, and up to the present it has not acquired practical importance.

Again, with the intention of utilising chlorine, endeavours have been made to prepare HCl and sulphuric acid simultaneously by passing a current of SO_2 and Cl up a tower filled with stones down which a spray of water passes (or of concentrated HCl in order not to raise the temperature); heat was disengaged and a yield of 65 to 80 per cent. was obtained (Ger. Pat. 157,044 of 1903)

$$2Cl + SO_2 + 2H_2O = H_2SO_4 + 2HCl.$$

This process had already been patented by W. Haner in 1854, was modified by Macfarlane in 1864, and patented, with various improvements, by Deacon in 1868; the last patent but one was that of W. Masson in France in 1892.

In 1909 Coppadoro studied the conditions necessary for a maximum yield and for facilitating the separation of the sulphuric and hydrochloric acids, but the process does not appear to have yet been sufficiently developed for practical purposes.

The preparation of HCl has also recently been proposed by distilling wood at 300° in presence of chlorine, with a yield of 70 per cent. together with the usual products of wood distillation (Ger. Pat. 158,086). Finally, the industrial manufacture of hydrochloric acid has been attempted by burning the hydrogen and chlorine obtained in the electrolytic manufacture of caustic soda in a kind of blowpipe (J. L. Roberts, Ger. Pat. 194,947 of 1905).

According to a recent patent (179,514 of 1907) the arsenic can be separated by bubbling the gas as it comes from the furnaces through oil ; the arsenic is then removed from the oil by washing with water, then with lime, and finally with hydrochloric acid.

The only way of obtaining the purest HCl in the laboratory consists in starting from pure NaCl and pure sulphuric acid and distilling with due precautions.

SPECIFIC GRAVITY OF SOLUTIONS OF HYDROCHLORIC ACID AT THE TEMPERATURE OF 15°.

Specific gravity at $\frac{15^\circ}{4^\circ}$ (vacuum)	Degree Baumé	100 parts by weight of pure aqueous solution of the acid contain:		One litre contains grms. of HCl.
		HCl per cent.	Per cent. by weight of acid of 20° Bé.	
1·000	0·0	0·16	0·49	16
1·005	0·7	1·15	3·58	12
1·010	1·4	2·14	6·66	22
1·015	2·1	3·12	9·71	32
1·020	2·7	4·13	12·86	42
1·025	3·4	5·15	16·04	53
1·030	4·1	6·15	19·16	64
1·035	4·7	7·15	22·27	74
1·040	5·4	8·16	25·42	85
1·045	6·0	9·16	28·53	96
1·050	6·7	10·17	31·68	107
1·055	7·4	11·18	34·82	118
1·060	8·0	12·19	37·97	129
1·065	8·7	13·19	41·09	141
1·070	9·4	14·17	44·14	152
1·075	10·0	15·16	47·22	163
1·080	10·6	16·15	50·31	174
1·085	11·2	17·13	53·36	186
1·090	11·9	18·11	56·41	197
1·095	12·4	19·06	59·37	209
1·100	13·0	20·01	62·33	220
1·105	13·6	20·97	65·32	232
1·110	14·2	21·92	68·28	243
1·115	14·9	22·86	71·21	255
1·120	15·4	23·82	74·20	267
1·125	16·0	24·78	77·19	278
1·130	16·5	25·75	80·21	291
1·135	17·1	26·70	83·18	303
1·140	17·7	27·66	86·17	315
1·1425	18·0	28·14	87·66	322
1·145	18·3	28·61	89·13	328
1·150	18·8	29·57	92·11	340
1·152	19·0	29·95	93·30	345
1·155	19·3	30·55	95·17	353
1·160	19·8	31·52	98·19	366
1·163	20·0	32·10	100·00	373
1·165	20·3	32·49	101·21	379
1·170	20·9	33·46	104·24	392
1·171	21·0	33·65	104·82	394
1·175	21·4	34·42	107·22	404
1·180	22·0	35·39	110·24	418
1·185	22·5	36·31	113·11	430
1·190	23·0	37·23	115·98	443
1·195	23·5	38·16	118·87	456
1·200	24·0	39·11	121·84	469

ANALYSIS OF HYDROCHLORIC ACID. The specific gravity does not always indicate the contents of HCl exactly, and, therefore, 10 c.c. of the acid (of known specific gravity) are taken, diluted with water to 200 c.c., 10 c.c. of this neutralised with a solution of soda, and the chlorine then titrated with $\frac{N}{10}$ silver nitrate solution, using potassium chromate as an indicator. The HCl may also be directly titrated with a normal solution of sodium hydroxide.

The amount of sulphuric acid present as an impurity is determined in 100 c.c. of the solution prepared as above ; this is neutralised with soda and precipitated whilst hot with $BaCl_2$. From the weight of barium sulphate that of the H_2SO_4 is deduced. Iron is determined by reducing with zinc, and, after adding manganese sulphate, titrating with potassium permanganate solution of known strength. Arsenic is detected qualitatively with Marsh's apparatus (*which see*). Dissolved salts may be determined by evaporation to dryness in a platinum capsule of a definite quantity of acid.

HYDROBROMIC ACID : HBr

PROPERTIES. This acid was discovered by Balard in 1830. Hydrobromic acid is a gas resembling hydrochloric acid ; it fumes in moist air, is 2·8 times heavier than air, can be liquefied at −73° and solidified at −120°. It is very soluble in water and the saturated solution at 0° contains 82 per cent. of HBr, and has a specific gravity of 1·78 ; a solution saturated at 15° contains 50 per cent. of HBr, and its specific gravity is 1·51.

On heating this solution up to 125° a product of almost constant composition distils, of sp. gr. 1·49, containing one molecule of HBr to 5 mols. of water. On saturating an HBr solution at −20° with HBr gas crystals of $HBr.2H_2O$ separate which melt at −11°.

Chlorine displaces bromine from bromides and hydrobromic acid. Hydrobromic acid is less stable than hydrochloric acid and decomposes or dissociates at 800°. The soluble bromides give with silver nitrate a whitish precipitate, feebly yellowish, not very soluble in ammonia. At a red heat the bromides are more volatile than the chlorides, but less so than the iodides. Hydrobromic acid in aqueous solution is a very energetic acid, and dissolves all those metals which are dissolved by hydrochloric acid ; it dissolves Ag, Cu, Pb, and Hg more readily. A rather concentrated solution dissolves some sulphides ; when still more concentrated it dissolves lead sulphate ($PbSO_4$) very readily, and in presence of amalgamated copper it also dissolves sulphur. A mixture of HBr and HNO_3 behaves like *aqua regia*.

The heat of formation of HBr is 35·2 Kj. (8400 cals.) and on dissolving in 400 parts of water it evolves a further 83·3 Kj. (19,909 cals.). Wood charcoal absorbs much hydrobromic acid evolving up to 64·8 Kj. (15,487 cals.).

USES AND PRICES. Hydrobromic acid is used in the analysis of natural sulphides and in various reactions in organic chemistry. It comes into commerce in 48 per cent. solution (sp. gr. 1·49) at a price of about 7*s.* 4*d.* per kilo ; in 40 per cent. solution (sp. gr. 1·38) it costs 4*s.*, and in 25 per cent. solution (sp. gr. 1·208) 3*s.* 5*d.* per kilo.

PREPARATION. Bromine does not combine with hydrogen in the cold, even in the light, but slowly combines under the action of heat or of the electric discharge, and more rapidly under the catalytic influence of spongy platinum at high temperatures. Hydrogen gas saturated with bromine vapour burns in the air, giving a cloud of HBr.

Bromine decomposes water in sunlight and also in the presence of oxidisable substances such as P, S, Se, and As, producing oxygen and hydrobromic acid. Various hydrogen compounds, such as H_2S, HI, and NH_3, give HBr with Br.

The method analogous to that used for the preparation of HCl, namely, the action of strong sulphuric acid on bromides, is not of much use for preparing HBr, as the sulphuric acid is partially reduced by the hydrobromic acid with production of bromine and sulphur dioxide :

$$2HBr + H_2SO_4 = H_2SO_3 + H_2O + Br_2.$$

But in presence of water Br is an oxidising agent which is able to convert sulphites into sulphates with formation of HBr :

$$Na_2SO_3 + Br_2 + H_2O = Na_2SO_4 + 2HBr.$$

HBr is more readily formed by the action of dilute sulphuric acid on a bromide in presence of phosphorus.

Hydrobromic acid is easily prepared by dropping bromine into a paste of one part of red phosphorus with two parts of water ; in this way phosphorus tribromide is formed which reacts with water, producing non-volatile phosphorous acid and volatile HBr :

$$3H_2O + PBr_3 = H_3PO_3 + 3HBr.$$

To free the gas which is evolved from bromine vapours which it carries over it is passed through a tube filled with glass fragments mixed with moistened red phosphorus. A very regular current of HBr is also obtained by dropping bromine into benzene or crude anthracene : $\underset{\text{benzene}}{C_6H_6} + Br_2 = \underset{\text{bromobenzene}}{C_6H_5Br} + HBr$, and purifying the gas by passing it through a cylinder containing anthracene or paraffin.

Hydrobromic acid may also be prepared by the method of Lorenz which we have already discussed in the case of chlorine (*see* p. 165) : $C + 2Br_2 + 2H_2O = CO_2 + 4HBr$.

On passing a current of hydrogen sulphide (H_2S) into a flask containing bromine and water HBr is formed with separation of sulphur : $H_2S + Br_2 = 2HBr + S$. To free this from traces of sulphuric acid, which are also formed, it is distilled in presence of barium bromide and an aqueous solution of pure HBr is thus obtained.

If a current of hydrogen is passed through a flask containing bromine and the gas is then ignited a considerable quantity of HBr is formed which fumes in the air and shows acid reaction.

HYDRIODIC ACID : HI

PROPERTIES. Hydriodic acid is a colourless gas which was discovered by Clément and Désormes in 1813 ; it fumes strongly in moist air, has a specific gravity of 4·4 (air = 1), becomes liquid at − 34° and solid at − 51°. A litre of water at 10° dissolves 450 volumes of HI gas. Light and air decompose the aqueous solution of HI, liberating iodine. The saturated aqueous solution at 0° has a specific gravity of 1·99, and at 126° aqueous HI distils with constant composition ($HI.5H_2O$) of sp. gr. 1·70 and containing 57 per cent. of HI. Oxgyen decomposes hydriodic acid at high temperatures : $2HI + O = H_2O + I_2$. On bringing a flame or a red-hot glass rod to the mouth of a cylinder full of HI gas, the cylinder suddenly becomes filled with violet iodine vapours. The same result is obtained on introducing an oxidising agent such as a little hot fuming nitric acid into the cylinder. Thus HI acts as a strong reducing agent, as it easily removes oxygen from oxidised bodies, and it is therefore often employed as a reducing agent in organic chemistry. This acid reacts with silver and mercury even at moderate temperatures with formation of hydrogen :

$$2HI + Ag_2 = 2AgI + H_2.$$

Chlorine and bromine readily decompose HI :

$$HI + Cl = HCl + I.$$

In 1900 Volhard showed that traces of hydriodic acid are able to act catalytically as an oxidising agent, and then to convert considerable quantities of sulphur dioxide into sulphuric acid in presence of water, possibly because free iodine is formed amongst the intermediate products and then reacts with the oxidising agent regenerating hydriodic acid :

$$4HI + 3SO_2 + 2H_2O = S + 2H_2SO_4 + 4HI.$$

The I′ ions of iodides give a yellowish precipitate of AgI, insoluble in ammonia, with silver nitrate :

$$AgNO_3 + KI = KNO_3 + AgI.$$

Wood charcoal absorbs much HI gas, developing 92 Kj.

USES AND PRICES. Solutions of HI of 49° Bé. (sp. gr. 1·5) cost 17*s.* 6*d.* to 19*s.* 2*d.* per kilo, and if of 60° Bé. (sp. gr. 1·7) from £1 5*s.* 7*d.* to £1 8*s.* per kilo; they are more especially used in organic chemistry as a reducing agent and to introduce iodine into organic compounds.

PREPARATION. Iodine does not combine with hydrogen at the ordinary temperature, not even under the influence of light which is chemically very active. At high temperatures it only combines partially, as even at 440° hydriodic acid commences to dissociate into its components. On the other hand, the action is complete if a mixture of hydrogen with iodine vapours is passed over warm platinum sponge, which acts as a catalyser. In this manner pure HI is obtained.

HI cannot be prepared by the action of sulphuric acid on an iodide, as HI, like HBr, readily gives the reverse reaction :

$$2HI + H_2SO_4 = H_2SO_3 + H_2O + I_2.$$

But it is readily obtained in abundance by the action of phosphorus tri-iodide on water, in the same way as was mentioned in the case of HBr :

$$PI_3 + 3H_2O = H_3PO_3 + 3HI.$$

In practice 1 part of red phosphorus is mixed in a flask with 15 parts of water, and 20 parts of powdered iodine are gradually added with constant cooling ; the whole is then heated gradually and HI is evolved, which is absorbed by water ; but the product is impure. A better result is obtained by starting with a mixture of 1 part of yellow phosphorus in small pieces with 10 parts of iodine and gradually adding a little water. The HI gas which is evolved is freed from the iodine which it carries over by passing it through a tube containing red phosphorus. If the gas is required it is collected by downward displacement of the air in a dry bottle or cylinder as it is very heavy and very soluble in water and attacks mercury. By heating the concentrated aqueous solution a regular current of the gas is obtained which can be dried with phosphorus pentoxide.

According to Auger (1909) HI is easily obtained by gently heating to 250° 2 mols. of crystallised phosphoric acid with 1 mol. of KI, and in order to obtain a 56 per cent. solution 2 mols. of phosphoric acid in a 60° Bé. solution are heated with 1 mol. of KI.

A pure aqueous solution of HI is obtained by passing hydrogen sulphide through water containing iodine in suspension until this is decolorised, then heating to drive off the excess of H_2S, filtering from sulphur and finally distilling the HI : $H_2S + I_2 = S + 2HI$.

COMPOUNDS OF THE HALOGENS WITH ONE ANOTHER

These compounds have not much stability, in common with all compounds of elements which resemble one another closely chemically.

IODINE MONOCHLORIDE : ICl. This is a red crystalline mass which is obtained by the action of excess of dry iodine on chlorine. It is easily decomposed by water : $5ICl + 3H_2O = HIO_3 + 4I + 5HCl$.

IODINE TRICHLORIDE : ICl_3. This compound is formed in presence of excess of chlorine (or from iodic anhydride and phosphorus pentachloride, PCl_5). It forms yellow crystals which yield Cl_2 and ICl at 25°. It dissolves unchanged in a little water.

IODINE BROMIDE : IBr. This is obtained from I + Br. It forms crystals similar to iodine which melt at 36°.

IODINE PENTAFLUORIDE : IF_5. In this compound the iodine is seen to be either tri- or pentavalent. It is formed by the action of iodine on silver fluoride, and is a colourless liquid which fumes in the air.

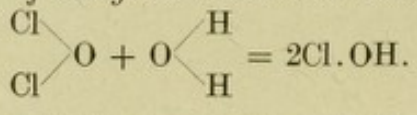
OXYGEN COMPOUNDS OF THE HALOGENS

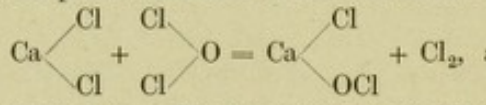
These compounds form with water the corresponding acids, from which the oxides are re-formed when the water is abstracted. They are therefore called *anhydrides* of the respective acids.

Whilst the affinity of the halogens for hydrogen decreases from fluorine towards iodine, their affinity for oxygen decreases from iodine towards fluorine, and whilst iodine and oxygen unite directly, bromine and chlorine only combine with oxygen by means of intermediate products or indirectly. No oxygen compounds of fluorine are known. The more highly oxidised compounds are more stable than those containing less oxygen.

OXYGEN COMPOUNDS OF CHLORINE. The principal oxygen compounds of chlorine are the following :

$HOCl$, hypochlorous acid, corresponding to hydrochlorous anhydride, Cl_2O.
$(HClO_2)$, chlorous acid, not known free, but only as salts.
$HClO_3$, chloric acid, derived from the mixed chlorous-chloric anhydride, Cl_2O_4.
$HClO_4$, perchloric acid, of which the anhydride, Cl_2O_7, is not known.

In general from one molecule of anhydride and one molecule of water two molecules of acid are obtained, e.g.  $= 2Cl.OH$.

HYPOCHLOROUS ANHYDRIDE (chlorine monoxide $= Cl_2O$). This compound is obtained by the action of chlorine on precipitated yellow mercuric oxide, *dried* and cooled: $2HgO + 2Cl_2 = HgO.HgCl_2 + Cl_2O$. It is evolved as a yellow-brown gas which is condensed in the cold to a red-brown liquid, which boils at $+ 5°$. It is also obtained by dehydrating hypochlorous acid. This compound is very unstable and explosive. It is a powerful oxidising and bleaching agent. When mixed with water it forms hypochlorous acid : $Cl_2O + H_2O = 2HOCl$; with porous calcium chloride it forms chlorine and calcium hypochlorite (chloride of lime) :  and, therefore, it is able to render active the ordinarily inactive chlorine of calcium chloride.

HYPOCHLOROUS ACID : HOCl. This compound is known in aqueous solution only. It is found in chlorine water : $Cl_2 + H_2O \rightleftharpoons HCl + HOCl$.

The concentrated solutions of this acid (5 per cent.) are of a yellowish colour and decompose partially on distillation, forming chlorine and chloric acid. Dilute solutions are more resistant to light and are less decomposed on distillation. These solutions have a powerful oxidising and bleaching action on vegetable fibres due to the nascent oxygen which they form. From a given quantity of hypochlorous acid double the amount of oxygen can be obtained than from the corresponding quantity of chlorine : $Cl_2 + H_2O = 2HCl + O$, whilst, on the other hand, $2HOCl = 2HCl + O_2$; but one must bear in mind that to form 1 mol. of $HOCl$ two atoms of chlorine and 1 mol. of $NaOH$ are required (*see below*).

With HCl the aqueous solutions yield chlorine and water : $HCl + HOCl = H_2O + Cl_2$, and double the amount of chlorine contained in the hypochlorous acid is evolved. When shaken with mercury aqueous solutions of hypochlorous acid form a yellow-brown precipitate of mercury oxychloride, $HgO.HgCl_2$ (the hypochlorites form HgO). This reaction serves to distinguish hypochlorous acid from chlorine (aqueous) as this latter under the same conditions gives with excess of mercury mercurous chloride, $HgCl$ (calomel), a white substance insoluble in HCl (Wolters' reaction).

Hypochlorous acid is a weak acid which is displaced from its salts even by carbonic acid.

Pure hypochlorous acid is obtained by the action of chlorine in the dark on freshly precipitated HgO covered with water, with strong agitation (Balard) :

$$2HgO + 2Cl_2 + H_2O = HgO.HgCl_2 + 2HOCl.$$

The whole is then filtered and the liquid distilled; the excess of chlorine is removed by a current of air, when a pure aqueous solution of HOCl remains.

Hypochlorous acid is also obtained by passing chlorine into water in presence of powdered marble or of an alkaline carbonate:

$$CaCO_3 + 2Cl_2 + H_2O = CaCl_2 + CO_2 + 2HOCl \text{ (Williamson)}$$

$$\text{or: } K_2CO_3 + Cl_2 + H_2O = KCl + ClOH + \underset{\text{Potassium bicarbonate.}}{KHCO_3}.$$

It is also obtained pure by distilling its salts (hypochlorites) with another weak acid (boric acid), or by acting on a solution of sodium hydroxide with excess of chlorine: $NaOH + Cl_2 = NaCl + HOCl$. In presence of too little chlorine sodium hypochlorite is formed.

HYPOCHLORITES AND BLEACHING COMPOUNDS (*see* Part III, Sodium Hypochlorite).

CHLORINE DIOXIDE or TETROXIDE: ClO_2 or Cl_2O_4. This was formerly called *hypochloric acid.*

Effront prepared Cl_2O_4 by dropping portions of 5 grms. each of potassium chlorate into a litre of sulphuric acid of 62° Bé. and then carrying over the gas in a current of air into a carboy of water, where it was absorbed.

It is formed on treating potassium chlorate with concentrated sulphuric acid in the cold; chloric acid is first formed: $2KClO_3 + H_2SO_4 = K_2SO_4 + 2HClO_3$, which decomposes instantaneously into chlorine tetroxide, water, and perchloric acid (stable): $3HClO_3 = Cl_2O_4 + HClO_4 + H_2O$.

It is more easily prepared, and with less danger, by treating a mixture of one part of potassium chlorate and 4·5 parts of oxalic acid with sulphuric acid diluted with two volumes of water. On heating the mixture gently a greenish-yellow gas is formed which liquefies in a freezing mixture.

It is a greenish-yellow gas which forms a red-brown liquid in the cold, boiling at 10°, and which is solid at −79°. If it is pure and free from organic substances it may be distilled on the water-bath at 30°. When exposed to high temperatures it easily explodes. It is therefore always dangerous to treat potassium chlorate with sulphuric acid without taking precautions. To illustrate this violent reaction 3 or 4 grms. of potassium chlorate crystals and a few pieces of white phosphorus are placed in a test glass full of water; a few drops of strong sulphuric acid are then introduced below the water with a pipette. Green vapours of chlorine tetroxide are at once evolved which set fire to the phosphorus under the water.

The tetroxide dissolves in water with lemon-yellow colour, but is decolorised by potassium hydroxide solution, giving salts of chloric and chlorous acids:

$$\begin{matrix} Cl\text{——}O \\ \\ Cl\text{-}O\text{-}O \end{matrix}\!\!>\!O + 2KOH = ClOOK + ClO_3K + H_2O,$$

behaving as a mixed anhydride of chloric and chlorous acids.

In sunlight the aqueous solution of chlorine tetroxide is decomposed thus:

$$3Cl_2O_4 + 2H_2O = 4HClO_3 + O_2 + Cl_2.$$

Its vapour density corresponds to the formula ClO_2; in this case the chlorine is either divalent, $Cl\begin{matrix}\diagup O \\ | \\ \diagdown O\end{matrix}$, or tetravalent, $Cl\begin{matrix}\diagup\!\!\diagup O \\ \diagdown\!\!\diagdown O\end{matrix}$; but in solution or in the liquid state the formula is probably Cl_2O_4, that of a mixed anhydride.

USES. Effront advised the use of aqueous solutions of chlorine tetroxide in the manufacture of spirit from cereals, because ordinarily 20 per cent. of the maize which is treated does not germinate and, according to Effront, by washing these grains with the dilute solution one is able to increase the germination of the grain by 10 per cent. Experiments made in the distillery Sessa in Milan gave negative results, but in other distilleries it has been used with advantage, especially for damaged maize.

CHLORIC ACID: $HClO_3$. This acid is obtained by decomposing an aqueous solution of barium chlorate with sulphuric acid:

$$Ba(ClO_3)_2 + H_2SO_4 = BaSO_4 + 2HClO_3.$$

After filtration the liquid can be concentrated *in vacuo* and a 40 per cent. solution of $HClO_3$ obtained (sp. gr. 1·28).

This solution is oily and decomposes at 40° into Cl, O, and perchloric acid, $HClO_4$; it is thus an energetic oxidising agent and in this concentrated solution sulphur, alcohol, and paper catch fire.

Chloric acid and the chlorates give free chlorine with concentrated HCl :

$$HClO_3 + 5HCl = 3H_2O + 3Cl_2,$$

or : $$KClO_3 + 6HCl = 3H_2O + 3Cl_2 + KCl.$$

INDUSTRIAL PREPARATION OF SALTS (CHLORATES) (*see* Part III).

PERCHLORIC ACID : ClO_4H. This is the most stable of the oxygenated chlorine compounds. It is formed by the decomposition of chloric acid, and potassium perchlorate is obtained by the decomposition on heating (fusion) of the chlorate :

$$2KClO_3 = KClO_4 + KCl + O_2.$$

Since the perchlorate is but little soluble in water whilst potassium chlorate is very soluble, their separation is easy.

By distilling potassium perchlorate with strong sulphuric acid (96 per cent.) under reduced pressure in an oil-bath at 140° to 190°, perchloric acid is obtained, which can be rectified by distillation at 50° to 65° at reduced pressure.

When anhydrous it is a colourless liquid of sp. gr. 1·76 (at 22°) which does not solidify even with solid carbon dioxide and ether. It is a strongly corrosive liquid and produces painful wounds on the skin. It reacts violently, with explosion and flame, when mixed with phosphorus, carbon, &c. When kept in the dark and also in the open, it decomposes slowly, and if kept in closed vessels it finally bursts them open. It readily absorbs water.

Two hydrates of this acid are known : the monohydrate, $HClO_4 + H_2O$, which at 110° is decomposed forming $HClO_4$, and the dihydrate, $HClO_4 + 2H_2O$, which is a stable oily liquid, of sp. gr. 1·82, which distils unaltered at 203°.

PREPARATION OF PERCHLORATES (*see* Part III).

BROMINE and **IODINE** form oxygenated compounds analogous to those of chlorine ; there are thus bromates and perbromates, iodates and periodates, &c.

OXYGEN GROUP

This group comprises **Oxygen, Sulphur, Selenium,** and **Tellurium.**

This group consists of divalent elements, that is to say, they combine with two atoms of hydrogen, but only the three last have much chemical and physical analogy with one another. These are solids, whilst oxygen is a gas which forms compounds analogous in their chemical formulæ only, but not in their properties, as can be seen at once from the following compendium :

	O	S	Se	Te
Atomic weight .	16	32	79·2	127·5
Specific gravity .	1·18 (at − 182·5°)	2	4·5	6·4
Melting-point .	− 227°	114·5°	217°	452°
Boiling-point .	− 182·5°	440°	600°	1390°

With increase of the atomic weight, matter becomes denser ; as the density rises the appearance becomes more metallic, but the non-metallic chemical character is preserved. The same fact has already been encountered in the case of the halogens.

At high temperatures these elements all unite with hydrogen giving compounds of the formula $X''H_2$, but as the temperature rises still further these compounds are dissociated into their components. Oxygen may really be considered as an element apart, as it has very few of the properties common to this group ; for instance, oxygen is a gas which, with hydrogen, forms the liquid water, non-poisonous, and solid already at 0° ; the other elements,

on the contrary, are all solid and combine with hydrogen to form gaseous compounds, which are poisonous and difficult to liquefy.

Even from a thermochemical standpoint water differs considerably from the other hydrides, being strongly exothermic, with a heat of formation of 186 Kj., whilst hydrogen sulphide, during its formation from H and S, absorbs 1·67 Kj. Selenium and tellurium also form endothermic compounds with hydrogen.

The aqueous solutions of the hydrogen compounds of S, Se, and Te are decomposed by the oxygen of the air, like the hydrogen compounds of the halogens ; water, on the contrary, is quite unaltered.

OXYGEN : O, 16

Oxygen exists in three allotropic modifications : (1) active oxygen, composed of free atoms not combined to molecules, chemically very active, and capable of transforming CO into CO_2 in the cold ; (2) common oxygen, formed of molecules containing two atoms of oxygen (O_2), as it is found in the air ; (3) ozone, O_3, in which the oxygen has almost the same properties as active oxygen (but is not able to convert CO into CO_2 in the cold).

Common oxygen was discovered and studied by Scheele in 1771 ; he prepared it by heating manganese dioxide with sulphuric acid, arsenic acid, or nitric acid, from mercuric oxide, &c. It had already been prepared by Hales in 1727, by heating minim, but without having been characterised. At about the same time as Scheele Priestley independently obtained the gas from saltpetre, but only succeeded in isolating and characterising it in 1774 (in August) when he prepared it by heating mercuric oxide. Bayen also prepared it in 1774 from mercuric oxide.

Condorcet called this gas vital air ; the name of oxygen was given to it by Lavoisier, on account of its property of forming acids.

According to Duckworth, the Chinese already knew oxygen and also the composition of water in the seventeenth century, and, therefore, a long time before Europeans.

Lavoisier predicted the use of oxygen instead of air in order to obtain more rapid and complete combustion in furnaces and for heat production generally in many various industries, in order to avoid heat losses through the chimneys, through the useless heating of inert gases (nitrogen) in the air

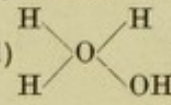
Oxygen is the most abundant and important component of terrestrial matter, being found free in the air (21 per cent. by volume and about 23 per cent. by weight), combined in water (about 89 per cent. by weight), in minerals, in acids, in organic compounds, and in the constituents of animals and plants. In the vital processes of plant assimilation oxygen is also set free under the action of sunlight and especially of the rays constituting the spectrum from B to C (red-orange) ; the minimum development of oxygen is caused by the rays E to *b* (green). Some vegetable cells produce oxygen without the action of light, for instance, the photometric bacterium and other purple bacteria. The oxygen emanating from plants does not contain ozone, as was believed at one time.

PHYSICAL PROPERTIES OF OXYGEN. Oxygen is a colourless, inodorous gas. Its specific gravity, compared with air, is 1·1056 ; one litre of oxygen weighs 1·4303 grm. Natterer was not able to liquefy it by pressure even at 1354 atmospheres. In 1877 it was liquefied almost at the same time by Cailletet and by Pictet (*see* p. 29).

The critical temperature of oxygen is − 118° and its critical pressure is 50 atmospheres. When liquid, it boils at − 182·5°, at which temperature its specific gravity is 1·118, and it is slightly bluish in colour. It solidifies at − 227° on throwing a jet of liquid hydrogen on to liquid oxygen. It then forms a bluish mass, which has a specific gravity of 1·426 at − 252°.

The solubility of oxygen in water is, per 100 vols. of water : 4·1 vols. at 0° and 2·84 vols. at 20°.

Platinum and silver absorb oxygen when melted, giving it off again during solidification. Four grammes of charcoal absorb 105 c.c. of oxygen.

Oxygen is ordinarily divalent, but some recent researches and some organic compounds cause it to be considered as tetravalent in certain cases, as these compounds may be derived from a hypothetical substance, ozonium (dihydrol)  (two molecules of water condensed to one molecule).

CHEMICAL PROPERTIES OF OXYGEN. Oxygen does not itself burn, but supports the combustion of other substances much more energetically than air, as is shown by the following experiments, which also serve to distinguish oxygen from other gases.

(*a*) Combustion in oxygen of a glowing splinter ; this catches fire and burns vividly.

(*b*) Combustion in oxygen of a lighted taper ; this burns with a bright light, forming CO_2, which renders a solution of barium hydroxide milky.

(*c*) Combustion of lighted sulphur in oxygen ; burns with a bright blue flame and forms SO_2, which reddens blue litmus paper.

(*d*) Combustion of lighted carbon disulphide in oxygen ; same as sulphur.

(*e*) Combustion of white phosphorus in oxygen ; this melts, catches fire, and burns with a very intense white flame, producing a white powder of P_2O_5.

(*f*) Combustion in oxygen of an iron spiral to which lighted tinder is attached ; this burns, forming a shower of sparks and producing brown iron oxide.

(*g*) Combustion of magnesium wire in oxygen ; this gives an extraordinarily intense white light.

(*h*) Combustion of an iron wire with a spirit lamp and jet of oxygen ; the iron burns vividly with a shower of luminous sparks.

Oxygen combines directly or indirectly with all the elements except fluorine, helium, and argon.

The combination of oxygen with other substances is generally called *combustion* if accompanied by flame, fire, and light, as shown in the experiments just recorded ; if it takes place without production of fire, it is called *oxidation*, *e.g.* iron oxidises in the air, producing rust, &c.

The temperature of ignition of various substances in oxygen and in air varies greatly ; phosphorus ignites at 60°, hydrogen at 580° in air and in oxygen, the vapours of carbon disulphide at 149° in air, moist carbon monoxide at 650° in air and in oxygen, acetylene at 420° in air or oxygen, hydrogen sulphide at 220° in oxygen and at 360° in air, ammonia at 700°–860° in oxygen, and in general the temperature of ignition depends also on the velocity of the jet of gas and the nature of the vessel. The temperature of the flame varies with the nature of the burning substance (*see* p. 128).

There are substances which catch fire spontaneously in the air when in a state of extremely fine division, and these are called *pyrophoric substances*. Pb, Fe, Cu, Ni, P, &c., are easily obtained in this condition. A simple experiment may be performed with pyrophoric lead, which is obtained by thoroughly igniting lead tartrate in a test-tube, wiping off the water from the sides of the tube, and then closing it with a rubber stopper. After the lead, which remains in a state of very fine subdivision, has cooled, it is thrown suddenly into the air, when it catches fire with production of sparks and flame.[1]

[1] A pyrophoric alloy is manufactured which produces numerous sparks by gentle friction ; a single gramme of this powdered alloy can be used thousands of times for the production of fire, and it has been proposed for many practical applications, such as for fireworks, for kindling gas-jets, firing mines, kindling motor lamps, firing motors, for signalling lamps, &c. This alloy contains rare metals, especially cerium, lanthanum, praseodymium, and neodymium. Ten years ago a single gramme of this alloy cost a considerable sum, but to-day it is sold at £4 16*s.* per kilo, as the price of these rare metals, which are obtained by the electrolysis of their fused chlorides, has diminished. The mixture or alloy with the other metals is prepared by special machinery, but always out of a contact with the air, as it easily oxidises or catches fire. The alloy is known as *Auer* metal and is sold in 10-kilo blocks. Its pyrophoric character is attributed to the formation of suboxides of the rare metals. The best effects are produced with an alloy containing 30 per cent. of iron or 10 per cent. of copper, &c. ; magnesium produces fewer sparks, so that it is necessary to find out the proportions of each metal which are needed to form a pyro-

The ignition of moist hay in ricks and of oily cotton and woollen waste is also due both to the action of special ferments and to the spontaneous oxidation of finely divided oil, with consequent rise of temperature and final ignition. The spontaneous combustion of coal-heaps containing pyrites is also a pyrophoric phenomenon, as the moisture and oxygen of the air sometimes convert the pyrites into $FeSO_4$ and H_2SO_4, and in this way produce so much heat that the coal is ignited. Finely divided platinum is also able to accelerate the oxidation of many substances. Fires in many coal-mines are due to very fine coal-dust suspended in the air, and similarly spontaneous fires in many flour mills may be ascribed to very fine flour dust in suspension ; similar remarks apply to some sulphur refineries. C. Engler (1907) has shown that the danger of explosion in mines or other places where powdered inflammable substances are present is much greater when minimal quantities of inflammable gases, such as firedamp (methane), coal-gas, hydrogen, &c., are also present in the air. When such gases are absent explosion does not easily occur, even with a spark.

Oxidations and all direct combinations of oxygen with other elements only occur in presence of minute quantities of water. If the reagents are absolutely dry no reaction occurs. Dry phosphorus does not burn in dry oxygen, and dry hydrogen appears not to combine with dry oxygen, even with the electric spark. In these cases water may exert a catalytic contact action which initiates the reaction. A mixture of one volume of oxygen with two volumes of hydrogen (detonating gas) produces a strong detonation if fired with a flame, the temperature of ignition being 650°.

By projecting the flame of the oxy-hydrogen blowpipe on to a piece of quicklime, a dazzling light is obtained, known as the Drummond light, which is used in lighthouses, for lanterns, and for other purposes. The oxy-hydrogen flame (from H and O) melts iron, platinum, &c.

Oxygen is respirable even alone, and may also revive vitality ; it is therefore employed in grave cases of illness when the breathing is hindered and the patient would certainly succumb if it were not possible to meet the needs of the organism by breathing more concentrated oxygen than that present in the air, and so facilitating a more rapid oxidation of the blood. By respiration of purer oxygen the blood acquires a brighter red colour. The oxygen of the air which we breathe transforms venous into arterial blood by its absorption, forming CO_2. Plants also breathe air, but they absorb the carbon dioxide more especially and emit oxygen, in which way equilibrium is more or less established in nature between the activities of animals and plants, as the oxygen consumed by animals and by combustion, with production of CO_2, is regenerated by plants which absorb the carbon of the CO_2 and return free oxygen to the air. For the life of fishes a minimal quantity of oxygen is required.

A. Mosso showed that in oxygen at two atmospheres pressure many animals are able to live even in presence of 6 per cent. of carbon monoxide, which is very poisonous, whilst under ordinary conditions they cannot stand even one part per thousand. But if suddenly removed from such an atmosphere into the outer air these animals quickly died. This fact, studied by Mosso, may have useful application in the case of miners who are the victims of firedamp explosions. Many of these unfortunate people die, even after a week, by slow poisoning, whilst if, after being rescued, they were placed under a bell in oxygen compressed to two atmospheres or air at ten atmospheres they might be saved.

Trials made in 1901 and 1902 appear to have given favourable results.

APPLICATIONS OF OXYGEN. It is used with hydrogen for the fusion and welding of platinum, since the method was perfected by Deville and Debray during their important work on this metal (1852–1857). In spite of its very high melting-point (1770°), they succeeded in melting, welding,

phoric alloy with these rare metals. Some authorities attribute the pyrophoric character to traces of oxide which form on the surface of these metals, whilst others maintain that it is due to the fineness of the particles yielded by the more or less coarsely roughened surface.

and shaping it in various ways by means of the oxy-hydrogen blowpipe. In this way they contributed considerably to the progress of certain branches of chemistry and physics, as before that time it was not possible to construct platinum apparatus of complicated form for any purpose; since that time much platinum apparatus has found industrial application. Fig. 66 shows an oxy-hydrogen blowpipe fed by hydrogen and oxygen from two steel cylinders which contain the compressed gases. Oxygen is supplied to the inner and hydrogen to the outer tube of the blowpipe, and the quantity of either can be regulated at pleasure, so that a reducing or oxidising flame can be obtained as required. For autogenous welding of iron a reducing flame is commonly used. For some years the oxy-hydrogen flame has been very advantageously replaced by the oxy-acetylene flame, that is to say, the hydrogen has been replaced by acetylene either from a gasometer or from an acetylene solution. It has the advantage of yielding a higher temperature, and whilst in a reducing flame about 4 cu. metres of hydrogen are required per cubic metre of oxygen, only 700–800 litres of acetylene are required (*i.e.* 2·5 kilos of calcium carbide).

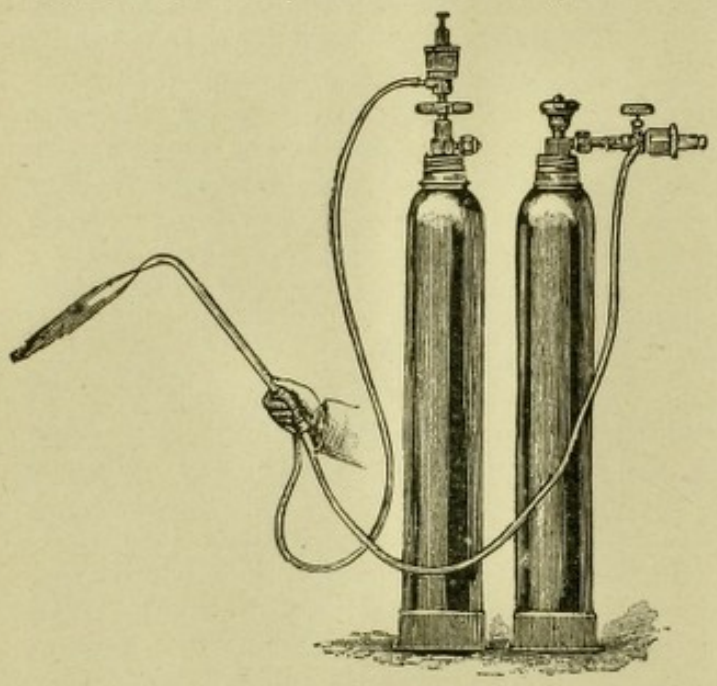


Fig. 66.

With the oxy-acetylene flame large plates of steel can be cut with the greatest facility and precision (armour plates, &c.), and in a few minutes holes of 5 to 10 cms. diameter can be made in blocks of iron half a metre and more in thickness. The autogenous soldering of iron, aluminium, and copper is performed with the greatest ease and perfection.

The employment of oxygen in combustion in general has a secure future, and trials which have been made in large works have shown very promising results. By its employment the useless heating of enormous quantities of nitrogen, which constitutes four-fifths of the air, and enters cold into the furnaces to issue through the chimneys at 250°–350° without having played any part in the combustion, is avoided. In order to use oxygen for this purpose furnaces and hearths of special type, more resistant to high temperatures, are required; also the chimneys will be smaller, as smaller quantities of gas are formed.

Trials made in the glass industry with melting furnaces gave good results; better melts were obtained in less time with a saving of 50 per cent. of fuel (Thomas's patent 1886 and 1891).

Oxygen is used in England to purify coal-gas from hydrogen sulphide; Laming's material is revivified by a current of oxygen, which oxidises the ferrous sulphide and separates the sulphur (44 litres of oxygen oxidise 100 grms. of H_2S).

Oxygen is also used to free spirits from fusel oil, and for oxidising oils used in varnish manufacture, and for bleaching.

Divers are able to use oxygen prepared by the action of sodium peroxide on water, the sodium hydroxide which is also formed serving to absorb the expired CO_2 (*see below*).

Oxygen is also used by aeronauts, who sustain themselves by its use at high altitudes where the air is rarefied and respiration needs to be assisted. The more delicate varieties of fish have now been successfully transported alive for journeys of 100 hours' duration by being kept in vessels in communication with oxygen.

The oxy-hydrogen or oxy-acetylene blowpipe is used to perforate plates or blocks of iron; the jet is impinged on to the object, and when it is hot the hydrogen or acetylene is cut off and the stream of oxygen continued; in a block of iron more than a metre thick a hole as thick as a man's arm can be made in three or four minutes.

The use of pure oxygen is now widely diffused medicinally, as it is advantageously used in cases of asphyxia, asthma, autointoxication, pulmonary diseases, heart diseases, anæmia, and diabetes; it has a cicatrising action in the cure of wounds and purulent inflammations. In 1907 a private hospital was established in London where treatment by means of oxygen alone is practised.

It may be used for the production of ozone, instead of air, in order to avoid the formation of nitrous products.

The various uses of oxygen for high temperature production by burning together with hydrogen have already been discussed under the heading of the latter element (p. 129).

SALE OF OXYGEN. Oxygen is supplied in cast-steel cylinders at 120 to 130 atmospheres pressure; the cylinders are tested every two years to a pressure of 250 atmospheres; obviously each cylinder contains 130 times its capacity of oxygen at the ordinary pressure. These steel cylinders ordinarily contain $1\frac{1}{2}$, $4\frac{1}{2}$, or $6\frac{1}{2}$ kilos of compressed oxygen, that is, 1, 3, or 6 cu. metres, and the weight, including cylinder, is 12 to 13 kilos per cubic metre of oxygen. A knowledge of these data is useful as from them the cost of transport of the bomb backwards and forwards can be calculated.

When oxygen is required in the laboratory at a lower pressure a pressure-regulator of very simple character is used, consisting of a glass cylinder almost full of mercury closed with a glass stopper fitted with two tubes; one of these dips more or less deeply into the mercury and serves as a delivery tube for the oxygen from the cylinder, whilst the other conducts the gas to the apparatus in which it is required.[1] The current of gas can thus be regulated by immersing the tube more or less deeply in the mercury. The pressure regulators used industrially are analogous to those illustrated in the chapter on Liquid Carbon Dioxide.

The price of oxygen in small quantities for the laboratory, for medical use, &c., is about 5*s.* to 6*s.* 8*d.* per 1000 litres, compressed in steel cylinders. The steel cylinder costs £1 12*s.* to £2 8*s.*, according to size, but is lent on hire by the manufacturers. On the large scale 1000 litres of industrial oxygen (containing 8 to 12 per cent. of nitrogen) cost about 2*s.* 6*d.*

According to the official statistics the amount of oxygen produced in Italy was 21,000 cu. metres in 1906 and 29,000 cu. metres in 1907, valued at £6600, and the production should be notably increased, as several new works are being started to produce it from liquid air.

In Germany, in 1908, 8000 cu. metres of oxygen were produced by Brin's process, 342,000 electrolytically, and 2,200,000 cu. metres from liquid air. This latter, when for industrial use (with 10 to 12 per cent. of nitrogen) and when used on the spot without compression, costs about $1\frac{1}{4}d.$ per cubic metre.

LABORATORY PREPARATION. Apart from the electrolytic decomposition of water (*see* Hydrogen, p. 134) oxygen is commonly obtained by heating potassium chlorate in a retort; the reactions are as follows:

$$(a)\ 4KClO_3 = KCl + 3KClO_4; \quad \text{and } (b)\ KClO_4 = KCl + 2O_2.$$

The development of oxygen commences when the chlorate is quite fused,

[1] *Translator's note.*—It is obvious that by this means the pressure could only be lessened to a very limited extent.

that is, above 350° ; on heating still further the mass swells up and the gas evolution becomes copious and almost tumultuous.

By adding a small quantity of the following oxides a regular gas evolution is produced at a lower temperature :

Oxides added	Fe_2O_3	MnO_2	CuO	Platinum black	PbO_2
O developed at	120°	205°	235°	270°	285°

The first three oxides also cause spontaneous decomposition of the mass during the reaction. An addition of NaCl or KCl retards the reaction and renders it more regular (12 parts of $KClO_3$, 6 parts NaCl, 1 part MnO_2).

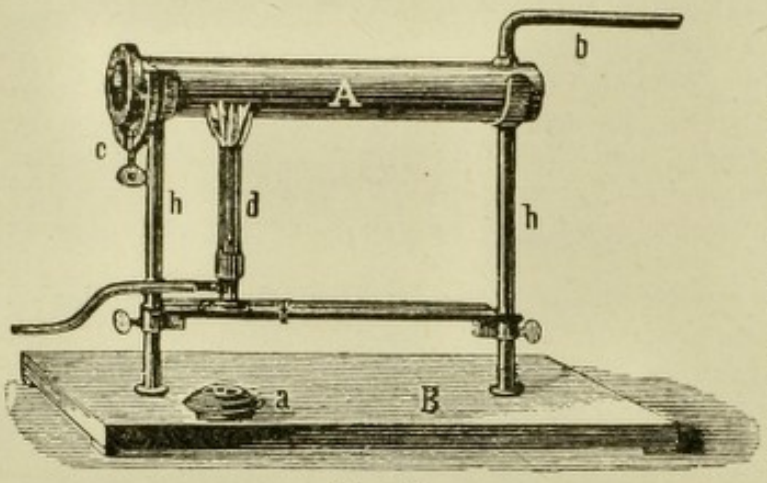


Fig. 67.

When the above-mentioned oxides are employed the oxygen contains small traces of chlorine, and also of CO_2 if the chlorate is impure. The chlorine is eliminated by washing the oxygen with a solution of NaOH, or by suspending a little bag of copper hydroxide in the gasholder.

The preparation of oxygen from $KClO_3$ by inexpert operators has led to terrible explosions and loss of life. Admixture with the chlorate of small pieces of organic rubbish (paper, fibres, wood, &c.) may cause fatal explosions. The same thing may happen if the tube in which the gas is developed is too narrow. In the laboratory a cylindrical iron tube, *A*, is often used for heating the mixture, closed with a screw cover (Fig. 67), and with a wide delivery tube, *b*. The front portion of the tube, near the delivery tube, is first heated and the flame is then gradually moved to the other extremity, *c*. With this apparatus large quantities of oxygen can be prepared without danger.

The oxygen which is evolved is washed in Woulff's bottles with NaOH, and is then collected in a gasholder by displacement of the water by entry through the lower opening *B* by means of the tube *G* (Fig. 68). As the gas enters the same volume of water escapes. When the gasholder is full the opening *B* is closed with a stopper, and when oxygen is required it is withdrawn from the tube *R*, provided with a tap, being replaced in the gasometer by water from the funnel *T* through the tap *H'*, and the long tube reaching to the bottom of the gasometer. Such gasholders of glass or metal are very useful in any case in which a gas is to be collected by displacement of water.

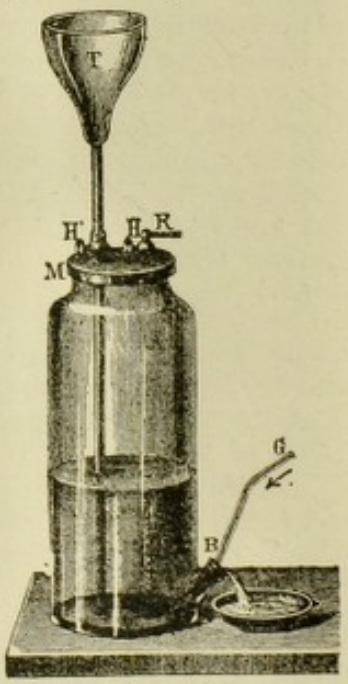


Fig. 68.

Another method of preparing oxygen is by heating certain metallic oxides such as mercuric oxide : $2HgO = 2Hg + O_2$, or the peroxides of manganese, barium, lead, &c.

$$3MnO_2 = Mn_3O_4 + O_2 \text{ (at a red heat).}$$
$$3PbO_2 = Pb_3O_4 + O_2.$$
$$BaO_2 = BaO + O \text{ (industrial method).}$$

Webster's method consists in heating various potassium oxy-salts, for example, potassium nitrate, which yields oxygen and potassium nitrite :

$KNO_3 = KNO_2 + O$. If the temperature is too high nitrogen is also formed : $2KNO_2 = K_2O + N_2 + 3O$; by the addition of a little ZnO the reaction can be made to take place at a lower temperature. The development of oxygen by this reaction can be shown by throwing a small piece of lighted carbon on to the surface of fused potassium nitrate in a capsule ; the carbon immediately burns away rapidly in contact with the nascent oxygen which is evolved.

Pure oxygen is obtained by heating potassium permanganate moderately : $4KMnO_4 = 2K_2MnO_4 + Mn_2O_3 + O_3$.

Oxygen can be prepared, as was already done by Scheele, by heating MnO_2 with sulphuric acid or with sodium disulphate, $NaHSO_4$, as this does not destroy the retort at a dull red heat :

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O.$$

If, however, these reagents contain chlorides the oxygen will be mixed with chlorine. MnO_2 may also be heated with silica, when it forms oxygen and manganese silicate : $MnO_2 + SiO_2 = MnSiO_3 + O$.

A very regular development of pure oxygen is obtained by heating in a retort 3 parts of potassium bichromate and 4 parts of strong sulphuric acid :

$$K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O.$$

Oxygen can be prepared at the ordinary temperature from a mixture of 3 mols. of BaO_2 and 1 mol. of $K_2Cr_2O_7$ with dilute sulphuric acid. Or a mixture of equal parts of barium and lead peroxides (BaO_2 and PbO_2) with dilute nitric acid may be employed. In both these cases hydrogen peroxide (H_2O_2) is first formed and yields oxygen in contact with chromium or lead oxide. Cubes made of a paste of two parts of BaO_2 and one part of gypsum are very useful as they can be employed in a Kipp apparatus with dilute HCl (Neumann, 1887). In this case the oxygen contains chlorine, and explosions often occur.

Instead of BaO_2 Volhard proposes the use of chloride of lime, $CaOCl_2$, with hydrogen peroxide sufficiently acidified with HCl or HNO_3 to neutralise all the lime :

$$CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2.$$

More precisely, he uses 300 grms. of $CaOCl_2$ (showing 35 per cent. Cl on titration), 1 litre of H_2O_2 (of 3 per cent. O) and 73 c.c. HNO_3 of sp. gr. 1·36 or 57 c.c. HCl of sp. gr. 1·17. Oxygen is obtained in the cold from calcium hypochlorite by a mixture of iron sulphate and copper sulphate, which acts as a catalyser (Jaubert, 1905).

Also 100 c.c. of hydrogen peroxide (3 per cent.), made alkaline with ammonia, develops one litre of oxygen in the cold when treated with a dilute (0·3 per cent.) solution of potassium permanganate. Hydrogen peroxide, made alkaline with ammonia, easily develops oxygen with a solution of potassium ferricyanide, which is converted into the ferrocyanide :

$$\underset{58\text{ grms.}}{2Fe(CN)_6K_3} + 2KOH + \underset{100\text{ c.c.}}{H_2O_2} = 2Fe(CN)_6K_4 + 2H_2O + \underset{2\text{ litres}}{O_2}\ \text{(Kassner's method).}$$

Instead of H_2O_2 one may also employ BaO_2 in this process. In both these cases we have an apparently paradoxical result, namely, the reduction of the ferricyanide by an oxidising agent.

Sulphuric acid, in common with some sulphates, such as zinc sulphate, decomposes as follows when thrown on to a red-hot plate : $H_2SO_4 = SO_2 + H_2O + O$; by passing the gases through water and KOH solution the SO_2 is absorbed and free oxygen obtained (Debray and Deville). By the action of chlorine on steam at 120°, we have : $Cl_2 + H_2O = 2HCl + O_2$.

Mallet transforms Cu_2Cl_2 with steam at 100° to 200° into CuOCl, which gives $Cu_2Cl_2 + O$ at 400°. Industrially oxygen is prepared by the electrolysis of water, either acidified or made alkaline as we have seen when considering hydrogen.

We give below a summary of the yields of oxygen prepared by various chemical methods ;

1 kilo $KClO_3$	produces	274	litres O,	and 100 litres	cost	$7\frac{1}{4}d.$
,, $MnO_2 + H_2SO_4 + H_2O_2$	,,	129	,,	,,	,,	4*s.* 5*d.*
,, MnO_2 (at red heat)	,,	86	,,			
,, H_2SO_4	,,	114	,,			
,, $ZnSO_4$	,,	39	,,			
,, $NaNO_3$	,,	329	,,			
,, $CaOCl_2$ (35 %) + H_2O_2	,,	52	,,	,,	,,	4*s.* 10*d.*
,, BaO_2 (theoretically, but practically one-half)	,,	120	,,			

PHYSICAL METHODS OF PREPARING OXYGEN. Mallet based a method on the property of water of dissolving more of the oxygen than of the nitrogen of the atmosphere, so that by liberating the gas and absorbing it anew it is continually enriched in oxygen, and after the operation has been repeated four times contains 75 per cent. Helouis improved this method by employing a 20 per cent. solution of glycerine instead of water.

By repeated passages through a sheet of india-rubber air can be enriched in oxygen up to 90 per cent. (Graham, Margis, &c.).

Montmagnon, de Laire, and E. Schmidt prepared oxygen by making use of the fact that charcoal absorbs more oxygen than nitrogen from the air.

On the large scale oxygen is prepared by liquefying air and then allowing the nitrogen to evaporate (*see below*).

Oxygen is paramagnetic, that is to say, it is attracted by a magnet, whilst nitrogen is magnetically inactive ; this property of the former gas is especially evident in the liquid state, so that the proposal has been made to separate the oxygen from the nitrogen of the air by a centrifugal machine in presence of a magnet ; the oxygen is also the denser of the two liquids, and separates as a distinct layer ; however, the process is not practical.

INDUSTRIAL METHODS OF PREPARING OXYGEN. The largest quantities are produced by the physical methods just discussed.

The chemical method which has been most successful up to the present is that of the brothers Brin (formerly Brin's Oxygen Company, London), which is based on reactions already discovered by Boussingault : On heating barium oxide, BaO, in porcelain tubes to 500° in a current of air, free from CO_2, it forms barium peroxide, BaO_2, and at a temperature of 800° this is again split up into BaO + O. On now lowering the temperature again to 500° the regenerated barium oxide absorbs further oxygen from the air with formation of the peroxide, which again gives up this oxygen at 800° ; 100 grms. of BaO yield in this way 5–6 litres of oxygen. This method is interesting on account of the continuous regeneration of the intermediate product, BaO_2, without any loss of secondary products.

In practice, however, many difficulties were encountered, the most serious being the fact that the barium oxide was found to gradually lose its power of absorbing oxygen and had therefore to be often renewed.

In 1868 Gondolo tried to avoid this inactivity of the BaO by adding CaO, MgO, potassium permanganate, &c., but all proved useless. The true reason why the BaO became inactive was not discovered till much later. In 1881 the brothers Brin discovered that in order to keep the BaO active it was necessary to employ dry air, free from CO_2 and organic substances, and generally from substances capable of yielding CO_2 on combustion, as otherwise barium carbonate, $BaCO_3$, is formed, and with water barium hydroxide, $Ba(OH)_2$, which are inactive products, and only decomposed at much more elevated temperatures.

In 1883 the brothers Brin took out a patent for this method (Ger. Pats. 15,298 and 59,132), and after various improvements they applied it industrially in England and Germany. The air is purified by passing through sodium hydroxide solution or granulated sodium hydroxide, the sodium carbonate which is formed being otherwise utilised ; it is then dried with quicklime, after which it enters cylindrical, vertical, cast-iron retorts, *R*, contained in a furnace, *C* (Fig. 69). The retorts contain hard porous BaO, obtained by heating barium nitrate to 880° : $Ba(NO_3)_2 = BaO + O_2 + N_2O_3$, the yield being 50 per

cent. by weight of the nitrate ; the BaO costs about £80 per ton (*see* other methods of preparation in the chapter on Barium Nitrate, Part III). The temperature of the BaO in the retort is kept at about 550° by means of the producer, *G*, the hot gases from which enter through *B* into the space, *C*, surrounding the retorts. The air is under a pressure of 1½ atmospheres, and in this way the absorption of oxygen is very rapid. The air is then shut off, the temperature raised to 700°, and the retorts evacuated to a pressure of 5 cms. of mercury only. *In vacuo* the oxygen is given off more easily and at a lower temperature (700° instead of 800°). The air which enters through the tubes *J* and *Y* has to pass through the whole length of BaO in the long retorts, and when the temperature has been raised to 700° the evolved oxygen is led to the gasometers by the tube *Z*.

Each operation lasts about fifteen minutes, and the yield is about 10 litres of oxygen per kilo of BaO. At one time as much as 40 litres of oxygen per kilo of BaO were obtained, but the operation lasted two hours ; now the yield is apparently less, but in reality very much more is obtained per unit of time, the cost remaining the same.

The Brin process was improved in 1900 by increasing the useful life of the BaO by depositing it in thin layers on the surface of inert materials in a finely divided state ; it then lasts as long as forty days without diminution of the yield.

Oxygen prepared in this manner contains 90 per cent. of O and 10 per cent. of N, and costs 1·4*d*. to 1·9*d*. per cubic metre altogether, including amortisation, fuel, power, &c.

The manufacture of oxygen by means of *liquid air* has now acquired great importance. This method, which is becoming of more importance than all the others, will be discussed in detail further on in the chapter on Liquid Air.

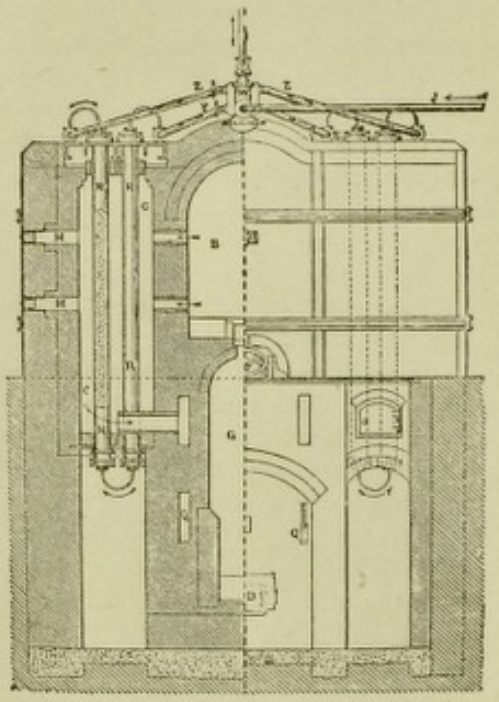


Fig. 69.

To obtain pure oxygen industrially, for the laboratory and for medical use, free from carbon monoxide and dioxide and from hydrocarbons, Dutremblay and Lugan revived in 1897–1899 a method of Tessié du Motay, proposed in 1867 and then forgotten. This consists in the decomposition of sodium permanganate in numerous vertical retorts (14 cms. in diameter and 2·40 metres high) which are heated to 500° in a furnace and evacuated in presence of superheated steam. The first phase of the reaction is :

$$Na_2MnO_4 + H_2O = 2NaOH + MnO_2 + O ;$$

the oxygen is then washed with a cold alkaline solution and collected in gasometers. In the second phase the manganate is regenerated by passing through the retort a current of dry purified air at 300° :

$$MnO_2 + 2NaOH + O = Na_2MnO_4 + H_2O \text{ (the inverse reaction).}$$

With twenty retorts in twenty-four hours 100 cu. metres of pure oxygen are produced.

The production of oxygen by electrolysis of copper sulphate has been proposed, by which means electrolytic copper, sulphur trioxide, and oxygen would be obtained. But there would always be danger of obtaining hydrogen mixed with the oxygen.

Oxygen is also obtained by the action of water on sodium peroxide, slowly in the cold, but rapidly on warming : $Na_2O_2 + H_2O = 2NaOH + O$.

This method is used on the large scale for the bleaching of woollen and silken fabrics ; but it is necessary to bear in mind that the alkaline solution of sodium hydroxide is injurious to wool and silk ; the alkali must therefore be neutralised with an acid as it is formed.

By means of this reaction, then, which takes place in the cold, we are able to produce conditions favourable to the oxygenation of the air and absorption of CO_2 in confined spaces in cases of illness or where large numbers of people are assembled, as the sodium hydrate which is formed absorbs CO_2 ; Na_2O_2 may, therefore, also be used in diving-bells.

Dr. Coehn in 1894 (Ger. Pat. 75,930) proposed to electrolyse water, using a depolariser at the negative pole to avoid the evolution of hydrogen and collecting the oxygen at the positive pole ; in order to utilise the half of the electrical energy which disappears at the negative pole through the action of the polariser, lead-accumulator plates are used for this purpose and become charged with electric energy. This method has not yet been actually used.

Among the various electrolytic methods, the best results have been obtained by the electrolysis of alkaline water by Garuti's system (*see* Hydrogen) or by that of Schuckert & Co. in Hanau, who since 1897 have used alkaline solutions with a non-porous diaphragm of hard rubber (*see* Hydrogen) producing oxygen at 0·48*d*. to 1·9*d*. per cubic metre as against 2*s*. per cubic metre by the chemical methods.

G. Kassner proposed in 1890 and perfected in 1900 his calcium plumbate method, which became of practical importance. Whilst oxygen prepared by other methods only contains 75·8 per cent. of pure oxygen, by his process oxygen of 98 per cent. is obtained. Calcium plumbate, Ca_2PbO_4, is heated in presence of *pure* CO_2 and is then regenerated (Ger. Pat. 52,459).

The electrolysis of dicarbonates may have a certain practical importance for the simultaneous preparation of oxygen, caustic soda, and hydrogen.

$$NaHCO_3 + H_2O = \underbrace{H_2 + NaOH}_{\text{negative pole}} + \underbrace{CO_2 + O}_{\text{positive pole}}.$$

This method has been practically studied since 1901, but is not known to have yet achieved industrial success.

We will record on account of their curiosity the attempts made by Mazza to prepare oxygen by centrifugating air. The experiments were started at Turin in 1901 in a cylindrical sieve with a velocity of 1000 revolutions per minute. The process has now been patented by Claude of Paris. The results were absolutely negative and could not have been otherwise. The method has not taken into account the substantial difference between a liquid (such as milk) and a gas which has a very large molecular velocity (hydrogen about 2000 metres per minute) and which would be influenced with difficulty by the ordinary methods which are at our disposal ; to this must be added that the molecular velocity of oxygen differs slightly from that of nitrogen. In 1906 Mazza believed that he had perfected his method, and took out new patents.

The methods which are now contending for the ascendancy in the production of large quantities of oxygen at a cheap rate on a commercial scale are : Brin's method with barium oxide ; the electrolytic method, by which very pure oxygen can be obtained (in practice as much as 3 per cent. of hydrogen may be present without any danger), the most used process of this character being that of Garuti, which we have described in the chapter on Hydrogen (and in this case oxygen is also obtained, together with double the volume of hydrogen) ; finally the method by means of liquefaction of air, of which we will give further details later (Liquid Air).

ANALYSIS OF OXYGEN. Ordinarily qualitative tests are made for impurities (CO_2, H_2S, Cl, &c.) by passing through suitable reagents. The quantitative examination is usually confined to a determination of the quantity of oxygen absorbed by an alkaline solution of pyrogallic acid in the Orsat apparatus described later in the chapter on Carbon Dioxide.

ACTIVE OXYGEN

For some years this was supposed to be identical with ozone, but Baumann, Hoppe-Seyler, and Traube have all repeatedly shown that active oxygen has certain more energetic oxidising properties than ozone, for instance, it oxidises CO to CO_2, even in the cold.

Active oxygen is formed particularly by contact of air with water under certain conditions ; also by contact of O with hydrogenised palladium and by phosphorus in contact with air and water, in which case hydrogen peroxide and ozone are also formed.

It is supposed that active oxygen is oxygen in the atomic state, and that this accounts

for its great chemical activity. A substance other than hydrogenised palladium, phosphorus, &c., which is capable of activating oxygen is turpentine, which exerts this power strongly in the cold, and still more actively at 100°.

Engler and his pupils have devoted themselves more especially, during the last few years (1898–1901), to the study of active oxygen, and have arrived at the hypothesis that it is not composed of atoms of free oxygen but is formed of active compounds, a species of peroxides of oxygen, which very easily cede one atom of very active oxygen in various chemical reactions.

The question is not yet completely settled.

OZONE : O_3

Van Marum already noticed, in 1785, the special odour which is developed when electric discharges take place in oxygen or air, and how these gases have then the capacity of increasing the luminosity of mercury. It was not until 1840 that Schönbein discovered the cause of these phenomena, and named the substance which was formed and had this odour, and which he succeeded in preparing by various methods, *ozone*. He prepared it, mixed with oxygen, by electrolysis of water, and by the slow combustion of phosphorus.

Ozone and hydrogen peroxide are present in small quantities in atmospheric air. De Thierry determined the ozone at various altitudes ; at 1050 metres he found 3·5 mgrms. per cubic metre of air and at 3020 metres he found 9·4 mgrms. per cubic metre (four times more than in Paris). Ozone is formed in the neighbourhood of waterfalls, and in general is abundant where much water is evaporated spontaneously. During thunderstorms appreciable quantities of ozone are formed.

According to Arnold, fresh unboiled milk turns guaiacum tincture blue and, therefore, contains ozone (?). It is admitted by many that the oxygen expired by plants contains no ozone.

FORMATION OF OZONE. Ozone is formed on heating peroxides, *e.g.* barium peroxide, BaO_2, or potassium permanganate, with strong sulphuric acid, or on heating peroxides in a current of oxygen to the temperature at which they decompose :

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O + O \text{ rich in ozone.}$$

Ozone is formed during the electrolysis of water together with the oxygen at the positive pole. It is formed by slow oxidation in a large bottle containing moistened phosphorus, partly immersed in water, and still more easily if a few drops of bichromate are added. It is also formed on burning hydrocarbons or by passing electric discharges through oxygen or air.

Ozone is also formed when fluorine acts on water at 0° (Moisan, 1899).

Generally speaking, one is unable to transform more than 9 per cent. of the oxygen present into ozone (whether it is pure or present in the diluted form as air).

However, F. Fischer and K. Massenez (1907) obtained oxygen containing 23 to 28 per cent. of ozone by electrolysing sulphuric acid of density between 1·223 and 1·07 by a current of 80 amps. per sq. cm., cooling the platinum electrodes continuously. By working at a tension of 7·8 volts they obtained a yield of 7·2 grms. of ozone per kw.-hour.

Nernst showed in 1903 that free atoms of oxygen condense to ozone only when their concentration is ten to twenty times greater than in ordinary oxygen. The equilibrium conditions for the system ozone-oxygen at high temperatures can be calculated to be 0·3 per cent. of ozone at the absolute temperature of 1569°, 1 per cent. at 2321° absolute, and 10 per cent. of ozone at 4773° absolute ; therefore one can deduce that ordinary oxygen should be transformed spontaneously into ozone when exposed to an elevated temperature and pressure. In order to separate the ozone rapidly in such a manner that it should not decompose, it was passed directly at this elevated temperature into liquid air, and the nitrogen oxides which had formed together with the ozone then separated as a flocculent solid, whilst the ozone remained

in solution, and on filtering the liquid air to remove the nitrogen oxides and then evaporating it, the liquid ozone remained; it was of an intense blue colour and evaporated at $-119°$. Ozone is formed very easily by passing the electric arc through liquid air or, better still, through liquid oxygen, as in this way the formation of nitrogen oxides is avoided.

Ozone is also formed by impinging a jet of air on to a Nernst lamp (1909); also by the action of ultra-violet rays from an electric mercury lamp with a bulb of quartz, which does not absorb the ultra-violet rays as does glass (1909).

PROPERTIES. Ozone is a relatively stable gas which decomposes slowly at the ordinary temperature and rapidly at 400°; therefore on passing ozone through a red-hot tube it is transformed into oxygen, and no longer shows the characteristic reactions of ozone (*see below*); during this transformation its volume is increased, as two molecules of ozone produce three of oxygen.

It is slightly soluble in water; it dissolves and combines with the ethereal oils, especially with turpentine, cinnamon oil, and with aqueous quinine solutions; it is somewhat soluble in paraldehyde.

Ozone is an endothermic substance and requires for its formation 151·5 Kj. (36,208 cals.), hence its lack of stability and greater oxidising power when compared with oxygen.

Being an energetic oxidising agent, it decolorises solutions of litmus and of indigo; it transforms phosphorus, sulphur, and arsenic into the corresponding acid anhydrides, converts sulphides into sulphates, nitrogen into the oxide, N_2O_3, and also into ammonium nitrite and nitrate in presence of water. Even minimal traces of manganese salts in aqueous solution are quantitatively precipitated by ozone as MnO_2. It attacks almost all organic compounds, and rapidly corrodes rubber tubing and stoppers of cork or vulcanised india-rubber; only the albuminoids and the saturated hydrocarbons are attacked very slightly or not at all. With certain organic compounds it produces a species of phosphorescence. Ag and Pb are converted into black peroxides and iodine into I_4O_9.

Silver, however, only forms the peroxide in places where it is already covered with a trace of invisible oxide (*e.g.* by heating the silver to 200°).

Harries found that unsaturated organic compounds with a double bond between carbon and carbon absorb ozone quantitatively, forming characteristic ozonides. In 1906 Molinari showed that unsaturated organic compounds with a triple bond between carbon and carbon do not absorb ozone, and in this way the two classes of unsaturated compounds may be distinguished.

Ozone has a strong bactericidal action (*see* Water).

LIQUID OZONE. Until a few years ago ozone had never been isolated and was only known by its odour and by certain chemical reactions, but always in admixture with much air or oxygen. In 1898 Troost, and afterwards Ladenburg, liquefied the mixture of air and ozone by cooling with liquid air; on then allowing the oxygen to evaporate they obtained an opaque blue liquid consisting of pure liquid ozone, boiling at $-119°$, which easily exploded.

CHARACTERISTIC REACTIONS OF OZONE. Ozone was detected in air by Schönbein by the blue coloration with starch paste and potassium iodide, due to the liberation of iodine which colours the starch. But it must be noted that this reaction is also shown by the higher nitrogen oxides and by hydrogen peroxide, all of which may also occur in the atmosphere. This reaction of ozone does not occur after passing the air through a hot tube (Andrews), but hydrogen peroxide also behaves in the same manner in this respect.

In 1868 Houzeau showed that during the blue reaction of ozone and of hydrogen peroxide with starch and potassium iodide an alkaline reaction was also

produced, whilst this is not the case with the reaction produced by nitrogen oxides: $2KI + O_3 + H_2O = 2I + O_2 + 2KOH$ and also $2KI + H_2O_2 = 2I + 2KOH$. There still remains the doubt whether the Schönbein reaction is due to ozone or to hydrogen peroxide.

Very numerous attempts were made to discover a characteristic reaction of ozone which would distinguish it from the nitrogen oxides, the halogens, and more especially from hydrogen peroxide. Potassium iodide, metallic silver and lead, guaiacol tincture (with a trace of iron sulphate, which becomes blue with ozone), manganese sulphate, lead acetate, thallium hydroxide, &c., were for long all considered in turn to be capable of characterising ozone, but the most recent work of Anord and of Mentzel (1902) decides unfavourably against the use of any of these reagents, and the only one which remains is benzidine (p-p′-diamino-diphenyl), which becomes brown with ozone only, whilst the nitrogen oxides and bromine turn it blue; with chlorine it passes through blue to red-brown and with hydrogen peroxide it gives no reaction. If, however, a drop of a 10 per cent. copper sulphate solution is added to the benzidine solution it gives a blue precipitate with H_2O_2, whilst with ozone it gives a reddish-yellow precipitate.

According to F. Fischer and Marx (1906) it is better to use paper impregnated with a methyl alcoholic solution of tetramethyl-p-p′-diaminodiphenylmethane (called *tetrabase*) to which a drop of acetic acid has been added; when moistened this gives with ozone a pale violet colour, whilst with nitrous oxide the coloration obtained is yellow to dirty brown; with hydrogen peroxide it does not react even in presence of copper sulphate, and chlorine and bromine give a deep blue coloration.

H. Kaiser and Master (1908) distinguish between the components of a mixture of ozone, nitrogen peroxide, and hydrogen peroxide in the following manner: The gas is passed through a dilute permanganate solution, which absorbs the NO_2 and H_2O_2, but not the ozone, which is detected with KI. Nitrogen peroxide and hydrogen peroxide decolorise the dilute permanganate solution. Another portion of the mixture is passed over a layer of manganese dioxide which decomposes both ozone and hydrogen peroxide, whilst nitrogen peroxide remains unaltered and decolorises a dilute permanganate solution, or produces nitrite (detected with aniline sulphonic acid and α-naphthylamine) if passed into a solution of pure sodium hydroxide free from nitrites (even when mixed with ozone and H_2O_2). Finally, hydrogen peroxide is detected in the presence of the other two gases by passing them through a brown solution of potassium ferricyanide and ferric chloride, in which hydrogen peroxide alone produces a characteristic green or blue coloration of Prussian blue.

Metals and organic substances which have been acted on by ozone become radio-active and affect the photographic plate.

CONSTITUTION OF OZONE. Williamson and Baumert, independently of one another, after many experiments, pronounced ozone to be an oxide of hydrogen peroxide, H_2O_3. Marignac, Delarive, and Cahours maintained, without being able to prove it, that ozone must be a more condensed oxygen molecule (allotropic oxygen). This was, however, shown with certainty by Andrews and Tait.

The molecular weight, corresponding to O_3, was determined with the diffusiometer by Soret in 1886 and confirmed by M. Otto in 1897, but doubt was thrown on these determinations by Stadel in 1899. The recent work of Ladenburg in 1901 and 1902 has, however, definitely confirmed the fact that the molecule of ozone consists of an aggregate of three atoms of oxygen. This may also be demonstrated by a very simple experiment; thus Soret passed the silent electric discharge for some time through a given volume of oxygen, and noted the diminution of volume caused by the formation of ozone. He then placed half the remaining volume of ozone and oxygen in contact with turpentine and measured the diminution of volume (due to absorption of ozone); he heated the other half and noted the increase of volume due to conversion of ozone into oxygen; he was thus able to determine the relation between the weight of ozone and that of the same volume of oxygen, and found that the ozone weighed one and a half times as much as oxygen, and that two volumes of ozone gave three volumes of oxygen.

On the other hand, if mercury is placed in contact with a given volume of ozonised oxygen, the mercury is oxidised at the expense of an atom of oxygen from the ozone, and oxygen remains, but without alteration of volume; 2 vols. $O_3 + 2Hg = 2$ vols. $O_2 + 2HgO$. Ozone is thus an allotropic form of oxygen, and from these two examples we may infer that the ultimate particles of matter are not molecules, but atoms or perhaps still smaller units.

In general if an element is known in various forms, with different properties, containing varying amounts of energy, these forms are called *allotropic*. The difference between oxygen and ozone is due to the larger amount of energy contained in the latter.

APPLICATIONS OF OZONE. The most important of all is the sterilisation of water to render it potable. But this most important subject will be discussed in detail later in the chapter on Water.

Ozone is used in medicine by being inhaled, diluted with much air and free from nitrogen oxides, by those suffering from pulmonary infection. In France a therapeutic institute for the use of ozone was started in 1909.

Fröhlich proposes the use of ozone against phylloxera, but it does not appear to be practical. Trillat employed it as an oxidising agent in the perfume industry, and transformed 25 kilos of isoeugenol into vanillin in one operation. The Société Anglo-Française of Courbevoie prepares notable quantities of piperonal (heliotropin) and vanillin in this way. The latter cost £360 per kilo in 1876, £28 per kilo in 1890, and now costs less than £4 per kilo. In 1904 the new Ozone Vanillin Company was formed at Niagara Falls with a capital of £40,000.

The employment of ozone for bleaching textile fibres is perhaps premature as it cannot compete in price with chlorine and is not suitable for bleaching silk or wool, as its bleaching powers are not large.

In the Bouillat sugar refinery at Noyon, France, the sugar syrup is treated with ozone to remove organic impurities; in this way crystallisation is facilitated and less molasses obtained; the action of the ozone is followed by treatment with sulphuric acid, after which this is removed with barium oxide and the liquor passed on to the filter-presses.

Engledew, in England, declared that he had perfectly purified foul beer barrels, which could not be cleaned in any other way, by the use of ozone, and maintained that a large brewery would shortly use plants for the production of ozone.

Ozone has also given good results for aging very alcoholic wines and liqueurs.

It does not appear to have been successful for the bleaching of flour, as this acquires an unpleasant taste and odour.

It has been proposed and tried, with uncertain and often negative results, for the manufacture of vinegar (from eight parts of water and two of alcohol), for the purification of alcohol from fusel oil, for bleaching fats, oils, sugar, syrup (molasses), mineral oils, &c. Many optimistic expectations on the application of ozone have proved delusive, but the experiments should certainly be tried again under other and more rigorous conditions.

By decomposing the ozonides of oleic acid and other oils by the method of Molinari and Soncini (1906) nonylic and azelaic acids can be prepared at a price of about 4*s*. per kilo, whilst under present conditions those two acids cost about £20.

The last word on the application of ozone has not yet been said, and the future will perhaps bring surprises. The actual cost of ozone is not yet of serious moment for industrial processes yielding products of great value, such as vanillin, &c., or for the sterilisation of water, which is attained with a relatively very small quantity of ozone.

INDUSTRIAL PREPARATION OF OZONE. Until a few years ago ozone was not of much practical importance and was prepared in minimal quantities in the laboratory electrically, by means of the silent discharge at high tension, in an atmosphere of oxygen or air.

An apparatus was adopted devised by Siemens as long ago as 1857 and consisting of two concentric glass tubes (Fig. 70), of which the inner was filled with tin in connection with one pole of a Ruhmkorff coil and the outer was covered with tinfoil which was connected with the other pole of the induction coil; a current of air or oxygen was passed between the two tubes, whilst the silent discharge passed across, producing numerous blue sparks.

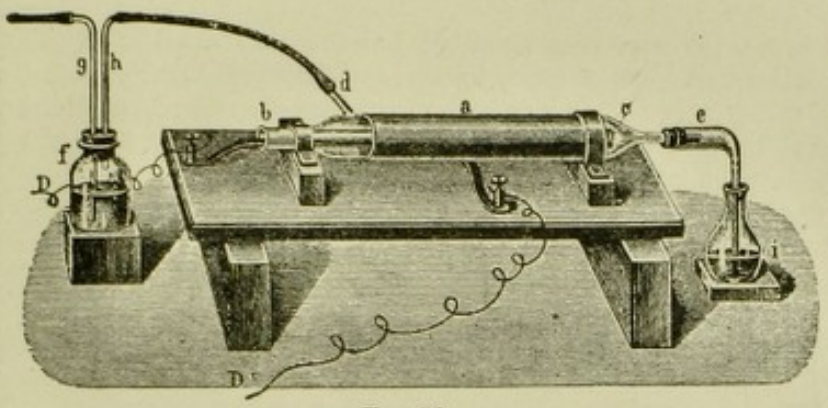


Fig. 70.

The quantities of ozone obtained were very small, and appreciable quantities were only obtained with an improvement devised by Fröhlich in 1891. He constructed ozonisers with an internal tube of aluminium or tin and an external tube of celluloid, mica, or paper covered with tinfoil, the internal tube being cooled by a continuous current of water. In this way he succeeded in preparing 4·5 grms. of ozone, diluted with much air, by means of a battery of ten such ozonisers by the use of one h.p.-hour of energy.

Berthelot advantageously replaced the metallic coverings by dilute solutions of sulphuric acid or simply by water, using the very simple glass apparatus shown in Fig. 71. The tube *g* closes the mouth of a wider tube, which has an inlet tube, *o*, conducting the air or oxygen to the apparatus, and between the walls of the two main tubes, and an outlet tube, *s*, through which the ozonised gas escapes. The tube *g* is full of water into which an aluminium wire dips, forming one of the electrodes of a high-tension current (10,000 to 12,000 volts); the whole apparatus is suspended in a larger vessel, *w*, also filled with water, into which the other aluminium electrode, *d*, dips. In the dark the blue discharge between the two tubes is easily seen. These ozonisers are arranged in batteries of four, six, or ten such tubes, and the ozonised air is collected in a single tube of glass or metal leading to the reaction chamber, care being taken that all the joints are of glass or consist of a mercury seal.

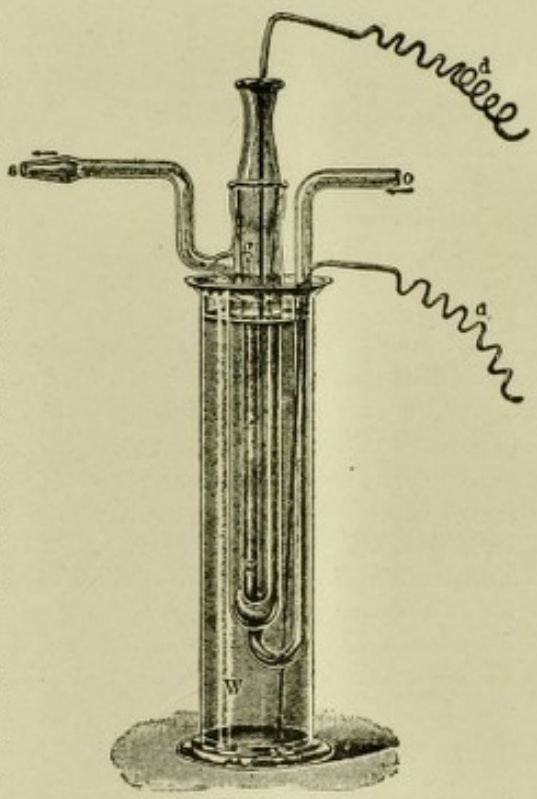


Fig. 71.

For the production of ozone high-tension currents at six to ten thousand volts and certainly not less than four thousand volts are required; some forms of apparatus require fifty thousand volts. Rotary commutators are generally found serviceable. Care must always be taken that very dry air or oxygen is employed, though when working at a low temperature (0°) a little moisture is permissible. The yield of ozone diminishes with rise of temperature and increases when the temperature is lowered. In all cases a part of the oxygen only is converted into ozone and under no circumstances more than 9 per cent. The quantity of ozone formed is always in the same proportion to the oxygen present whether pure oxygen or air is used; in the latter case the ozone is obtained in a more dilute state, but it is more economical as the air costs nothing.

Andreoli, in London, in 1896 (Ger. Pat. 96,058) patented a very ingenious ozoniser which paved the way for the industrial preparation of ozone.

Another more complicated but well-considered apparatus is that of Otto (Ger. Pats. 96,400 and 129,688) in which the danger of short circuits is avoided and a silent discharge of numerous blue sparks is obtained, without any arcing. At first very dilute currents of ozonised air were obtained and these were ultimately applied in various industries and for the production of potable water (at Nice).

Many other forms of apparatus were then patented, but few only found application. Among these we must also mention those of Otto, Verley, and Marmier-Abrahm, and the more important ozonisers, constructed for large output, of the firm of Siemens and Halske, Berlin. These are formed of iron boxes weighing 40 kilos in all, containing eight ozonising tubes, fixed inside the box between two planks and hermetically sealed.

In the middle compartment cold water circulates round the eight tubes ; perfectly dry air is passed into the lower compartment, enters the space between the two tubes of each ozoniser, and when ozonised enters the top compartment.

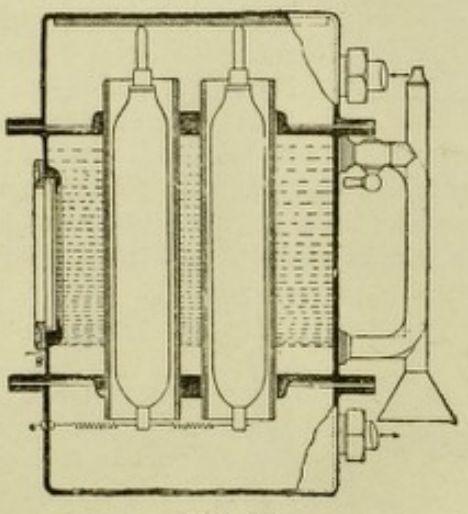


Fig. 72.

The ozonising tubes consist of an external tube of glass or porcelain, cooled by the water, and a concentric internal tube of metal, varnished with a substance resistant to ozone or simply formed of aluminium. The space between the two tubes, through which the air passes, is a few millimetres wide. The internal tubes communicate with one pole of the high-tension current, by means of perfectly insulated wires which are enclosed in the supporting column of the apparatus and thus avoid all danger to those who work or touch the apparatus ; their safety is further provided for by the fact that the other pole is connected to earth by means of the water which continuously circulates through the apparatus. The box containing the eight ozonising tubes has a glass front so that one can at any moment see the blue colour of the sparks of the silent discharge and so assure oneself that the apparatus is in order. There are also devices which ensure automatic interruption of the current in case of breakage.

With the Siemens-Halske ozonisers more than 60 grms. of ozone per h.p.-hour can be obtained. The air to be ozonised is previously dried, either by condensing the moisture by passage through an ice-machine, or better still by passing it over strongly hygroscopic substances, such as lime, sulphuric acid, fused calcium chloride, &c.

ANALYSIS OF OZONE. Now that the industrial importance of ozone has become so great, a knowledge of the amount of ozone contained in a given volume of air or produced by an ozoniser is often required. A given volume of the ozonised air is passed through a neutral solution of potassium iodide ; this is then acidified and the liberated iodine titrated with a solution of sodium thiosulphate of known strength : Ladenburg, Quasig, Treadwell, and Anneler, on the other hand, first weigh a bulb full of oxygen, and then weigh it when full of the ozonised gas. The difference of weight multiplied by 3 gives the weight of ozone.

A convenient and exact method for large quantities has been studied by Fenaroli (Soc. chim. di Milano, 1906) based on the property of the unsaturated fats (oleins) and fat-acids of absorbing ozone quantitatively, as shown by Molinari and Soncini. All that is therefore required is to pass any known quantity of the ozonised air over a weighed quantity of olein and determine the increase of weight of the latter, which gives the amount of ozone. Ruata showed in 1910 that this method is more exact than that with potassium iodide.

ANTIOZONE. Schönbein believed in the existence of electropositive ozone, as well as the electronegative ozone already known, and attempted to show that it had certain characteristic reactions. But several chemists showed that it did not exist, and that hydrogen peroxide vapour had been mistaken for it. To-day the conception of anti-ozone has again been revived and it appears to be nothing else than atomic or ionic oxygen liberated from ozone.

SULPHUR: S, 32.07

Sulphur was already known to the ancients, and was employed as a medicine and for fumigation, as was recorded by Homer, 900 years before Christ. More recently it was used for bleaching textile fibres.

In the Middle Ages it was considered by Gebir, about the year 800, to be one of the two components of metals, sulphur and mercury, and it was then believed to be possible to pass from one metal to another by increasing or diminishing one or other of these components; with more mercury one expected to obtain the more brilliant metals, silver and gold, and with more sulphur the baser metals such as copper, iron, &c.

It was already known to the alchemists that sulphur dissolved in aqueous alkaline solutions, and that from these it was liberated by acids as milk of sulphur. It was also known that it dissolved in aqua regia, but it was not known in what way the sulphur was transformed. It was known that it dissolved in some oils, and balsams with a sulphur base were thus prepared.

Sulphur kilns were first recorded by Basil Valentine (1456). At the period of the phlogiston theory sulphur was considered to be a combination of phlogiston with an acid.

Lavoisier recognised it to be a simple substance; all the same, Davy, in 1809, held it to be a species of resin, but after that time sulphur was considered as an element.

In nature it is found in various forms:

(1) In the native state, that is, ready formed, crystalline, or mixed with gypsum and earthy matter; the most abundant natural source (about 80 per cent. of all native sulphur) is in this last condition.

(2) It is found as metallic sulphides, such as iron and copper pyrites, zinc blende (ZnS), galena (PbS), &c.

(3) As hydrogen sulphide (H_2S) in sulphurous springs, sometimes accompanied by carbon oxy-sulphide.

(4) As sulphur dioxide, SO_2, in volcanic fumes.

(5) As sulphates in various mineral deposits.

(6) In organic substances, especially nitrogenous substances, such as albuminoids, hairs, horn, &c. It is also found free in certain bacteria (Beggiatoa) and in the cells of some algæ (*e.g.* oscillaria and ulothrix).

PHYSICAL PROPERTIES OF SULPHUR. Solid sulphur has a bright yellow colour, which almost disappears at $-50°$, and becomes more intense at 100°. It is insoluble in water, is slightly volatile with steam, and very slightly soluble in alcohol, ether, ethereal oils, and fats. It is very soluble in carbon disulphide (39 per cent. in the cold and 74 to 180 per cent. when heated), in sulphur chloride, and in hot aniline (80 per cent.); it is also soluble in petroleum ether (*see* vol. ii.). Sulphur crystallises from carbon disulphide in large rhombic crystals. Sulphur is easily electrified by friction.

Its specific gravity is 1·92 (amorphous) or 2·06 (rhombic). It melts at 114·5° (rhombic) or 119° (monoclinic), yielding a yellow mobile liquid, which acquires a deep orange colour at 160°; at 220° it becomes viscid, reddish, and adhesive, and between 240° and 260° is still more consistent and viscous, and of a red-brown colour; beyond 340° it again becomes a little more liquid, but remains of a dark colour, and at 445° it commences to boil, giving red-brown vapours.

Sulphur is known in three conditions or allotropic forms:

The most stable condition is rhombic sulphur (sulphur α) octahedra, which are generally obtained when it is crystallised at ordinary temperatures and from various solvents, such as carbon disulphide.

Another form is prismatic sulphur (sulphur β) of the monoclinic system, which is obtained from hot solvents (alcohol and benzene), and is stable above 95°. At ordinary temperatures this form is slowly and spontaneously

converted into the rhombic form, with evolution of heat (72·6 cals. per 32 grms. of sulphur).

A third form of sulphur is amorphous, plastic sulphur (sulphur γ), which is obtained by pouring fused boiling sulphur into water; it is insoluble in carbon disulphide, and is darkened in colour, even to blackness, by minimal traces of organic compounds (fats, paraffin, &c.).

A further variety of amorphous sulphur is that which is obtained from solutions of hyposulphites or polysulphides with acids (precipitated sulphur, magister of sulphur[1]). It has a whitish appearance and is soluble in carbon disulphide.

On heating sulphur with soda, black amorphous sulphur is obtained, which, when thrown into fused borax or calcium chloride, acquires an intensely blue colour. A blue colour is also formed on heating sodium sulphocyanide (NaCNS) to 430° (Paterno and Mazzucchelli, 1907).

Other varieties of sulphur have been prepared; thus, for instance, on passing hydrogen sulphide into a solution of SO_2, sulphur soluble in water (colloidal sulphur or sulphur δ) is prepared and is obtained yet more readily according to Sarazon (1910) by passing SO_2 into a saturated solution of H_2S in glycerine (Ger. Pat. 216,825).

According to the vapour density at low temperatures the molecule of sulphur is S_8; but as the temperature is raised it commences to dissociate, and at 850°–900° only S_2 molecules are left. The molecule S_6 appears not to exist, and the variety of sulphur insoluble in carbon disulphide ($S\gamma$) perhaps corresponds to the molecule S_8.

The colour of sulphur vapour is orange slightly above the boiling-point, redder at 500°, becoming rapidly lighter at higher temperatures. On passing a current of air over sulphur at a temperature slightly below 200° a marked odour of camphor is produced (perhaps inherent to sulphur vapour); above 200° the sulphur oxidises slightly, emitting a phosphorescent light; and at 250° the air current contains ozone, but is not ionised (difference from phosphorus, Bloch, 1909). The valency of sulphur varies in its different compounds; it is divalent in hydrosulphuric acid, SH_2; tetravalent in sulphur dioxide, SO_2; and hexavalent in sulphur trioxide, SO_3.

We have seen that at low temperatures sulphur always exists in the rhombic form, that is, in octahedra, like the natural sulphur which is found in the mines. If such sulphur is heated slowly in a suitable dilatometer its volume is observed to increase uniformly with the rise of temperature until it attains the temperature of 95·4°, when there is an abrupt and notable increase of volume and the sulphur, which had a light yellow colour, acquires a much more intense, almost orange, colour; the sulphur has been transformed at this temperature into monoclinic sulphur. Also the two forms of sulphur have different melting-points; on heating rhombic sulphur rapidly, so that it has not time to be transformed into prismatic sulphur, the melting-point is found to be 114·5°, whilst on heating prismatic sulphur or on heating rhombic sulphur slowly, the melting-point is found to be 119°. Rhombic sulphur has a specific gravity of 2·06, whilst that of prismatic sulphur is 1·92. At temperatures below 95·4° monoclinic sulphur slowly becomes rhombic. The temperature 95·4°, at which the two forms are able to co-exist, is called the *point of transformation.*

[1] Precipitated sulphur (magister of sulphur) is prepared as follows: One part of quicklime is made to a paste with 5 parts of water, and 2 parts of flowers of sulphur are added; a further 24 parts of water are then added and the whole boiled in an iron vessel until all the sulphur is dissolved, replacing the water as it evaporates. The liquid is decanted after settling and the residue boiled for half an hour with a little more water and filtered. The liquids thus obtained, containing calcium polysulphides, are brought to a specific gravity of about 8° Bé., and hydrochloric acid, diluted to 10° Bé. and free from arsenic, iron, and sulphuric acid, is then added little by little, with vigorous stirring, either under a hood or in the open, until only a very slight alkaline reaction remains (due to unaltered calcium sulphide). The very fine precipitated sulphur is quickly collected on a cloth filter and washed until the washings no longer become turbid with silver nitrate solution. It is then dried at 30°. It is well to treat with the acid in a closed apparatus with a delivery tube to carry off the hydrogen sulphide, which is abundantly formed (and is very poisonous), up a chimney. If the operator should inhale the H_2S he loses his senses, and the best method of treatment is to quickly drench him with much cold water, otherwise he remains under the influence of the poison. The calcium polysulphide is formed according to the following reaction: $3CaO + 11S = CaSO_3 + 2CaS_5$. The calcium pentasulphide reacts with the acid as follows: $CaS_5 + 2HCl = CaCl_2 + H_2S + 4S$. Precipitated sulphur is sometimes adulterated with gypsum or other mineral substances, but these can be detected by incineration. Pure sulphur leaves no residue (less than 0·5 per cent.).

The two forms of sulphur, at the point of transformation, have the same vapour tension ; and a substance which can be modified, like sulphur, in two senses at the point of transformation is called *enantiotropic ;* the melting-point of that modification which melts first is always higher than the point of transformation of the two substances, for if it were lower we would have a *monotropic* substance which could only transform in a single sense at the point of transformation. In point of fact, in some cases the less stable modification melts below the transformation point (*e.g.* iodine chloride, ICl, in which the less stable modification melts at 14°, and the more stable at 27°).

If a crucible of molten sulphur is allowed to cool slowly, and then, when it is covered with a crust of solidified sulphur, this is broken and the liquid sulphur poured off, needle-shaped monoclinic crystals are found in the crucible ; if these are allowed to cool they become lighter in colour, and though they preserve their external form they are then found to be formed of a large number of small octahedra ; thus the internal transformation has taken place and the needle-shaped crystals are called *pseudomorphs.*

If we consider the transformations of sulphur in connection with the phase rule we are able to compare its behaviour with that of ice and water. These can co-exist in complete equilibrium only at the temperature of 0·0075°, because at this temperature only can the sole component (H_2O) be present as the three phases, ice, water, and water vapour. The point at which the three phases can co-exist is called the triple point, or in general for more phases than one the multiple point. On pp. 114 to 118 we have demonstrated that for a system of n components equilibrium is only complete when $n + 2$ phases are present ; then for each phase the pressure temperature and composition are fixed.

If in such a system the pressure remains constant and the temperature varies, or *vice versa*, one of the phases disappears and complete equilibrium ceases. If of such a system two phases remain ($n + 1$, *e.g.* liquid water and vapour) the equilibrium is incomplete, but determined, and we speak of a *monovariant* system (*see* p. 117) because equilibrium between the two phases can exist at various temperatures provided that to each of these a determinate pressure corresponds, or *vice versa ;* if, on the other hand, the temperature remains constant whilst the pressure is continuously varied, or *vice versa*, then one of the phases will disappear and this determined equilibrium will also cease, and only vapour or liquid water will remain. By altering the pressure in the complete equilibrium of three phases, water, ice, and vapour, we are able to displace, by a very small amount, the point of transformation (melting-point of ice). This theoretical deduction has been theoretically confirmed, and we know now that for each atmosphere of pressure the point of fusion of ice is altered by 0·0079°, and that 136 atmospheres are required to displace it by one degree.

By means of the phase rule we can explain the transformations of sulphur into its various modifications. Below 95·4° we have two phases, namely, solid rhombic sulphur and sulphur vapour[1] ; above that temperature we have, on the other hand, the phase of monoclinic sulphur and sulphur vapour, the tension of which is variable, up to 119° (melting-point of monoclinic sulphur). At the temperature of 95·4° we have the triple point, at which the three phases of sulphur can co-exist, namely, monoclinic sulphur, rhombic sulphur, and sulphur vapour ; at this point equilibrium is complete as we have three phases and only one component, S.

In this case also, as in that of ice, the point of transformation (triple point) varies with variation of the pressure, and by exactly 0·05° for each atmosphere. At 119° we have another triple point, that is, three phases can coexist in equilibrium : solid monoclinic sulphur, liquid sulphur, and sulphur vapour. Between 95·4° and 119° we have incomplete but determined equilibrium, that is, we have a monovariant system (one component with two phases—solid sulphur and sulphur vapour) and the equilibrium is determined, because for any given temperature between these limits there is also a fixed and definite pressure at which equilibrium is still able to exist, and *vice versa* on fixing the pressure the temperature is similarly determined.

On p. 116 we have studied the bivariant systems which show the behaviour of non-saturated solutions of a salt, where we have two components, salt and water, with two phases, liquid solution and vapour. In this case, the composition of the solution being fixed, it was necessary to fix the temperature and the pressure ; that is, there is only a

[1] We must suppose that solids also have a vapour tension, though this may be very small : in the case of ice it is easily measurable ; for other solid substances it is so small that it is not measurable by ordinary methods.

single concentration of the solution which at a given temperature possesses a definite vapour tension. The equilibrium is in this case of two dimensions.

CHEMICAL PROPERTIES OF SULPHUR. On heating sulphur in the air it burns with a pale bluish flame, giving sulphur dioxide : $S + O_2 = SO_2$. It also burns in pure oxygen, to form the same compound, without alteration of volume. If, however, compounds are present which generate active oxygen, or catalysers, such as platinum sponge, iron oxide, &c., sulphur trioxide (sulphuric anhydride) is formed directly with diminution of volume (*see* Catalytic Sulphuric Acid *below*) : S + 3 vols. O = 2 vols. SO_3. On burning, 1 kilo of sulphur evolves 2165 calories.

Sulphur combines directly with the greater number of metals and non-metals, and in varying quantities with the same element. Thus, *e.g.* it forms trisulphides and pentasulphides of arsenic, antimony, &c.

A hot copper spiral burns directly in sulphur vapour.

Flowers of sulphur commonly show acid reaction, owing to the formation of traces of sulphuric and sulphurous acids. The acid reaction can be removed by repeated washing with water.

Sulphur combines with hydrogen to form H_2S. Oxygen burns in sulphur vapour, and it is thus both combustible and a supporter of combustion.

USES OF SULPHUR. The greater part serves for the preparation of pure H_2SO_4, of SO_2, and of salts related to these (sulphates, sulphites, thio-sulphates). It serves for the preparation of metallic sulphides, gunpowder, and carbon disulphide, for the vulcanisation of india-rubber and guttapercha, for bleaching silk and wool (*see* vol. ii.), and for treating with sulphur dioxide barrels of wine and beer, in order to remove from the wine the odour of hydrogen sulphide :

$$2H_2S + SO_2 = 2H_2O + S_3.$$

It is used in the wine-growing industry against a cryptogram which attacks the young bunches of grapes, and shoots of the vine ; this is a microscopic fungus, oidium (or *uncinula Americana*), the reproductive and vegetative system of which simply adheres to the surface of the part attacked and does not penetrate, as does peronspera, which, on the other hand, develops in the interior of the leaf and sends to the exterior of the lower surface only the conidiophoric branches with the conidi (*see* vol. ii.) forming scabs like mould, which then dry up the leaves, thus causing poverty of sugar in the grapes and unsound wine, which keeps badly. In Europe more than 100,000 tons of sulphur are used yearly to combat oidium, apart from the various polysulphides proposed during recent years. It is supposed that the sulphur acts on the oidium through formation of SO_2, which is in part already present in small quantity in the sulphur itself. Pollaci (1876) attributes the action of the sulphur to the formation of H_2S produced by lower organisms.

Sulphur is employed as a cement, by melting it together with iron filings and ammonium chloride ; on cooling, this mixture expands and hermetically closes fissures and empty cavities when employed for fixing metal to glass, &c.; a good cement which quickly hardens very satisfactorily is also obtained by mixing 100 parts of steel filings and turnings with 3 to 15 parts of sulphur, then adding 3 to 5 parts of ammonium chloride, moistening with water and mixing. When fused alone or with other substances, it is used for taking casts and impressions.

It is used medicinally for skin affections in the form of ointment or in baths, also combined with iodine for other treatment.

It is also used in fire extinguishers, especially when mixed with 2 parts of sodium nitrate and about 4 per cent. of carbon.

COMMERCIAL VARIETIES OF SULPHUR. According to their origin there are various brands of commercial sulphur with varying fracture and colour. Amongst crude sulphurs there are recognised: (1) *Licata;* (2) *common Licata* or *good Licata f. m.* (mixed flowers); (3) *good Licata f. m.* or "*vantaggiata Licata uso*," &c. Flowers of sulphur are sold as: *Solfo extra finissimo A* and *T* (A = Albani in Pesaro; *T* = Trevella in Catania), *solfo acido finissimo puro A, solfo sublimato V* (*V* = Verderame in Licata), *sublimato extra impalpabile T*, (also *acido*), &c. Of winnowed and ground sulphur we have: *impalpable sulphur T, double refined T*, "*doppio ventilato*" *T and V, extra fine impalpable T*, "*molito raffinato*" *T, ventilato vergnasco T*, &c. The term *fuori miscela* (mixed flowers) refers to sulphur in whole loaves or in pieces, free from powder and heterogeneous particles.

The brands called "raffinate" (refined) vary in purity from 99 to 100 per cent.; the impurities are not more than 0·5 per cent., and the hygroscopic moisture is often less than 1 per cent. (sometimes only 0·04 per cent.). Sulphur marked "greggio" (crude) contains 3 to 10 per cent. of impurities.

STATISTICS, PRICES, AND POSITION OF THE SULPHUR INDUSTRY.[1] The production of Sicily and of other countries and the international trade in sulphur is shown in the following table:

Sicily					United States	
Year	Production Tons	Price in Lire per Ton	Export Tons	Stock Tons	Production Tons	Imports Tons
	In all					
Up to 1830	2,000,000					
1830 to 1870	4,250,000					
1870 to 1880	2,250,000					
1880	312,000	100				
1890	328,000	77 (1892-95)				
1895	353,000	65 (1894)	364,417[2]			
1900	501,000	95	570,000	300,000	2,000	134,000
1901	548,000	95		310,000		
1902	496,300	95		340,000	30,000	177,000
1903	527,000	96		361,000	137,292 (1904)	156,000
1905	537,000	95	456,000	462,000	181,677	84,300
1906	471,000	92	387,430	527,000	294,000	72,560
1907	446,000	91	345,000	592,000	295,000	4,073
1908	380,000		384,000	586,150	372,000	12,484
1909	396,000		349,000	623,260		

The Romagna produces from 30,000 to 40,000 tons of sulphur.

Of the Sicilian sulphur from 140,000 to 150,000 tons are refined (partly ground and partly winnowed [*ventilato*]) in Italy, especially in Sicily; in 1908 204,240 tons of crude sulphur were exported from Italy in loaves and lumps to the value of £760,000; 68,300 tons of ground sulphur to the value of £300,000; 55,700 tons of refined sulphur to the value of £220,000; 1770 tons of flowers of sulphur, valued at £8840, and 8500 tons of sulphur mixed with 3 per cent. of copper sulphate.

The *world's production* of sulphur (exclusive of 80,000 tons recovered from Leblanc soda residues) consisted up to 1900 to the extent of 95 per cent. of Sicilian sulphur, but in 1908 45 per cent. of the total production came from the United States. The other nations only produce minimal amounts: In 1900 Germany, Austria, and Russia produced from

[1] It is calculated that the deposits still unexploited in Sicily contain about fifty-five million tons of sulphur; and will be exhausted in about one hundred years.

It is now believed that the formation of the sulphur in the natural deposits in Sicily lasted about ten thousand years.

[2] In 1893 and 1894 there were revolutionary movements in Sicily due to misery and hunger, which should have found their explanation and extenuation in the above figures, but instead they were repressed with bloodshed by the fierce and ignorant authorities.

1000 to 2000 tons each, Spain 6500 tons (in 1905 12,500 tons from Albocete, Murcia, and Almeria), France 11,500, and Japan 14,200 tons, and 24,200 in 1907.

In 1900–1901 84,000 tons of Sicilian sulphur were consumed on the Italian mainland, in 1905 99,000, and in 1908 60,000 tons ; 30,000 tons were consumed in Germany (in 1905), 104,000 tons in France (in 1907 60,000 tons and in 1908 94,500 tons) ; England, Belgium, Greece and Turkey (together), Sweden, Norway, and Denmark (together), Austria, Russia, and Portugal each took from 15,000 to 25,000 tons of sulphur, and in 1909 England imported 21,000 tons.

Crude sulphur is despatched in sailing vessels from Porto Empedocle, Catania, and Licata.

In commerce, for small consumers, the prices for sulphur are :

		£	*s.*	*d.*	
Sulphur, refined, in loaves	about	5	12	0	per ton
,, ,, ,, rolls	,,	6	8	0	,,
,, double refined, ground and winnowed (*ventilato*) 75°–80° Chancel	,,	8	0	0	,,
Flowers of sulphur	,,	6	16	0	,,
Precipitated sulphur for medical purposes, milk of sulphur, or magister of sulphur	,,	£38–£40			,,
Green commercial precipitated sulphur for rubber manufacture	,,	£32			,,

In large quantities the prices are from 10 to 20 per cent. lower f.o.b. Genoa.

The cost of production of sulphur per ton has been estimated as follows (Ann. Agricoltura, 1890, 171) : 6765 kilos of ore at 4*s.* 1*d.* per ton = 27·6*s.* ; labour at the kilns, 3·44*s.*— total, 31·04*s.* ; but 200 kilos are due to the owner of the property, so that for the 31·04*s.* only 800 kilos of sulphur are obtained, and thus 1000 kilos of crude sulphur cost £1 18*s.* 10*d.* at the locality where it is obtained ; to this must be added the cost of transport to the nearest port, 5*s.* A ton of sulphur thus costs £2 3*s.* in all to produce, to which must be added the cost of refining. But to-day these figures must be slightly altered as the price of labour has risen and the extraction processes have meanwhile been improved.

In Sicily in 1897, after the prolonged crisis of the preceding years, which led to the abolition in 1896 of the export duty, which had yielded £120,000 per annum to the Government, the lot of the sulphur industry improved, more especially through the efforts of the Anglo-Sicilian Sulphur Company, which associated a large number of the producers of sulphur and regulated the sale rationally in such a manner that the sale prices rose from £2 8*s.* to £3 16*s.* 9*d.* per ton.

The Anglo-Sicilian Sulphur Company continued to exist until 1906, but meanwhile a new and unforeseen circumstance arose on the horizon, namely, the intense exploitation of the important sulphur deposits of Louisiana by the Frasch process (*see below*). In 1905 the first consignments of American sulphur already arrived at the port of Marseilles at very low prices, so that the Anglo-Sicilian Sulphur Company were obliged to come to an agreement with the Union Sulphur Company of New York, for one year, in order to prevent a fall of prices. Meanwhile the Italian Government sent the engineer, Baldacci, to Louisiana to study the threatening problem of American sulphur. Early in 1906 it was known with certainty that the American Company, though only four of its mines were working, would be able to throw on to the market a further 400,000 tons of sulphur per annum, at the following prices : 14*s.* 9*d.* per ton at the mine ; 19*s.* 3*d.* at New Orleans ; £1 6*s.* 4*d.* in the ports of New York, Boston, &c., and £1 11*s.* 7*d.* in European ports. On the other hand, the United States, which imported 177,000 tons in 1902, commenced appreciably to diminish their imports (*see* Table).

Thus a very grave calamity menaced Sicily, which was to be the economic ruin of many producers and many works.

There were actually in Sicily in 1903 757 active sulphur mines, employing 37,500 operatives, of whom 8700 were hewers in the mines and the rest porters, 57 per cent. of the ore raised being still carried on the backs of these people.[1] The average wages of the

[1] In 1907 L. Borri reported that these operatives formed an organically degenerated body of people, deformed, with swollen thorax, head imbedded in the shoulders and the lower limbs compressed against the abdomen ; the progenitors of these people were a strong and beautiful race ! The first labour law introduced (1902) was concerned with the women and girls—small girls of seven and eight years old, to the misery of their parents—who were by this law prevented from carrying the ore from the galleries at the working face to the surface, up

operatives are 1*s.* 7*d.* per day ; in 1907 the number of operatives had decreased to 27,000, and in 1909 80 small mines were closed and only 500 were still working, of which only six yielded more than 1000 tons of crude sulphur per annum.

In any case the whole Sicilian sulphur industry is still menaced with ruin if a more rational and economical method of sulphur extraction and of its sale is not found, and if the production is not limited. Meanwhile when the Anglo-Sicilian Sulphur Company came to an end, on July 15, 1906, the Government established by law the "Consorzio obbligatorio per l'industria solfifera Siciliana," which is charged with the sale of sulphur of all the Sicilian producers for twelve years.[1] Sulphur for agricultural use in Italy enjoys a rebate of 5 per cent. Various other concessions were made diminishing the taxes with which the Sicilian sulphur industry is burdened. During 1908 and 1909 there was an agreement between the American company and the "Consortio Siciliana" limiting the regions of sale to two localities and thus avoiding a too rapid fall of prices.

EXTRACTION OF SULPHUR

NATIVE SULPHUR. This is found in large quantity in Sicily, principally on the southern watershed, from Etna to Sciacca, and more especially in the provinces of Caltanisetta and Girgenti, where it forms large deposits mixed with limestone or gypsum (up to 80 per cent. of sulphur). It is also found in Romagna (less abundantly), especially in the provinces of Forli, Rimini, and Cesena. Small deposits are also found in the Caucasus, Spain, Greece, and Japan. Important deposits are also worked in Louisiana, U.S.A.

Ores containing less than 15 per cent. of S do not pay for working.

Solfatare are deposits of flowers of sulphur in the ground, formed by the interaction of gases which are still evolved from the craters of spent volcanoes, namely, fumes of sulphur and hydrogen sulphide (H_2S). The former burn to form sulphur dioxide (SO_2), and this reacts with H_2S with separation of all the sulphur, as explained by Dumas in 1830 :

$$2H_2S + SO_2 = 2H_2O + S_3.$$

The layer of sulphur in these solfatare is sometimes so poor that it does not

a steep slippery passage, roughly hewn in the rock ; the ore was carried in loads of 30–50 kilos on the posterior thorax and the neck. These poor ill-nourished *carusi* had to make twenty-five or thirty journeys a day, half-naked, bathed in sweat, covered with dust, with a closed lamp affixed to the top of the head, accompanying their steps with groans forced from them by their heavy labour. This overwork weakens the muscular resistance and that of the bones ; the lungs, heart, and blood-vessels are unable to recover rapidly from its effects, and the flower of youth soon succumbs. The *caruso* of to-day will be the hewer (*picconiero*) of to-morrow ! The sad economic conditions of these people have urged these same operatives to implore the Government to suspend the law preventing the employment of women and girls, as owing to the low wages of these *carusi* this is said to be indispensable if their families are not to die of hunger ! And the proprietors have supported this demand, and the Government . . . piously concedes it !

[1] The principal stipulations of the law of 1906 were as follows : (1) A monopoly of the sale of all Sicilian sulphur is granted to the Consorzio ; (2) the Consorzio is empowered to limit the production of the individual proprietors in order not to be forced to sell sulphur at too low a price ; (3) the Consorzio acquired 360,000 tons of sulphur accumulated by the Anglo-Sicilian Co. at a price of £2 7*s.* 2*d.* per ton, in return for the issue of obligations at 3·65 per cent., guaranteed by the State and amortisable in twelve years ; (4) the Bank of Sicily is empowered to exceed, up to ten million lire, the sum of six millions allowed in Article 30 of the law regulating that institution, for the emission of warrants to the credit of the sulphur deposited in the warehouses of the Consorzio.

The producers receive in advance four-fifths of the value of the deposited sulphur. On the Council of the Consorzio the producers, the Chamber of Commerce, the Bank of Sicily, and the Government are represented. But, as happens so often in Italy through natural economic laws, the law has in this case again been of use to the local *camorra* and to illicit private interests. In fact, the power to regulate and diminish the production in order not to increase the already enormous stock has not been enforced, and further production proceeds merrily, quite independently of the demand, as the producers are assured of four-fifths of the established price in advance, however high this may be. In 1907 the stock rose to 592,000 tons ! Then the Bank of Sicily, in fear of an imm nent financial disaster through the growing American competition, which might lead to a strong fall in prices, reduced the advance to three-fifths, because it was already liable for ten million lire. But they had better have left it alone ! The producers threatened revolution and the end of all things, and not succeeding in exciting the operatives, they suddenly diminished their wages and so forced them to unemployment and disorder. Their object was thus gained, and in October 1907 the Government authorised the Bank of Sicily to advance the four-fifths and raise their liabilities by a further two millions. The appetite grows by eating, and though the production has been slightly reduced, the stock of sulphur rose in 1909 to 623,000 tons (*see* Statistical Table). The heads of the Consorzio freed themselves from all responsibility by resigning, and now the Government has ordered a Royal Commission in Sicily for the reorganisation of the Consorzio.

pay for extraction (at Pozzuoli), even though it is sometimes 6 to 10 metres in depth.

Solfare are layers of sulphur at varying depths below ground, and consist of a thick deposit of sulphur, probably formed by condensation of sulphur vapours coming from internal points in the earth's crust. Almost all the sulphur is to-day obtained from solfare.

Mottura explains the formation of sulphur in solfare by the decomposition of calcium sulphate by means of carbon, hydrocarbons, or organic matter, at high temperatures and pressures; the calcium sulphide (CaS) formed by this reaction, being soluble in water, would be carried to higher strata, and in contact with air and carbon dioxide would deposit the sulphur:

$$CaS + O + CO_2 = CaCO_3 + S.$$

The sulphur mines (solfare) are 50 to 100, and sometimes even 200 metres deep. They are penetrated by inclined galleries with a winding shaft. The ore is mined by *picconieri*, who are the workpeople engaged at the working face, and the *carusi*, who are children, carry the material to the surface on their backs (*see* preceding Note).

Modern shafts have now also been sunk, especially in the deeper solfare, and the ore is then brought to the surface by mechanical means; the galleries are well ventilated and provided with suitable pumps to remove the water which accumulates.

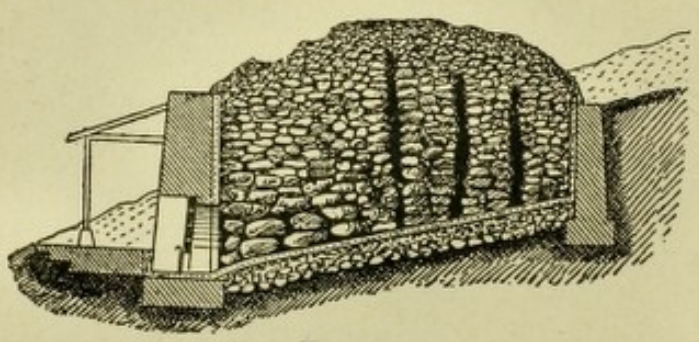


Fig. 73.

The ores from the solfare are divided into three qualities: Rich ores with 30 to 40 per cent. of total S, yielding 20 to 25 per cent.; good ores with 20 to 35 per cent., yielding 15 to 20 per cent.; and ordinary ores containing 20 to 35 per cent. and yielding 10 to 15 per cent. of sulphur; ores with 10 to 12 per cent. of sulphur do not ordinarily pay for working.

Until 1850 the sulphur was extracted by fusion, by burning the ore in small heaps called *calcarelli*, or small calcaroni, of about 2½ metres diameter. By this system only 20 to 30 per cent. of the total sulphur was extracted; the rest was burnt to sulphur dioxide, which polluted the air and caused enormous damage to the health of both populace and vegetation.

The methods of extraction were then much improved, and in 1850 the system was started of collecting the ore into much larger heaps covered outside with earth or ash from the already treated ore (called *ginisi*).

These large heaps are called *calcaroni* (Fig. 73). They hold up to 2000 cu. metres of ore, containing not less than 15 per cent. of sulphur, and the combustion lasts from one to two months. A third of the sulphur is consumed as fuel.

The calcaroni are built up in places sheltered from the wind in a circular excavation in the ground, ten to twenty metres in diameter and two to three metres deep. The floor is well beaten down and is inclined towards one point where the fused sulphur collects.

Large lumps of ore are placed at the bottom and are arranged in diminishing size upwards to the top, which is covered with material which has already been treated. The sulphur is set on fire from the top by introducing lighted wood through channels which are left for this purpose; the heat then spreads, melting all the sulphur, which collects at the base in boxes of moist wood where it solidifies and forms loaves of 50 to 60 kilos weight, forming crude fused sulphur which is very impure and of a dark colour.

The maximum yield obtained in the calcaroni is 60 to 65 per cent. of the total sulphur

(for an ore containing 25 per cent. of sulphur, 70 per cent. of limestone, and 5 per cent. of moisture), whilst theoretically the yield should be about 85 per cent., consuming 11 to 15 per cent. of the sulphur in order to raise the temperature of the ore sufficiently for the fusion of the remainder.

A more rational manner of working, with a better yield, is attained with the regenerative furnaces patented by Robert Gill in 1880, in which the heating is performed in closed chambers of brickwork, holding up to 30 cu. metres of ore. A yield of 70 to 75 per cent. of the total sulphur can thus be obtained without polluting the air and damaging the neighbourhood. In this case also the heating takes place at the expense of the sulphur which burns.

These regenerative furnaces (Fig. 74) are formed of two large brickwork chambers, both communicating with the same chimney in such a manner that combustion can be readily regulated. When combustion is finished in one chamber it is commenced in the other, so that there is continuous working. With the two chambers of such a furnace forty-five to ninety charges can be worked per annum. The charge of ore is arranged as in the calcaroni, with the larger lumps below and finer material at the top, so that the molten sulphur may readily find its way to the bottom, where it collects on a floor which is gently inclined and is sometimes separated from the ore by means of a double floor.

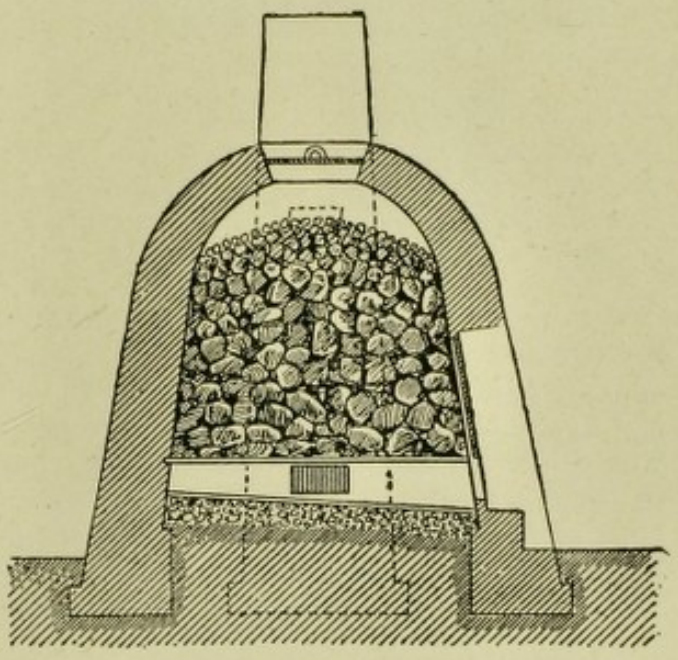


Fig. 74.

These furnaces have been still further improved by replacing them by circular furnaces with six chambers, which permit of the better utilisation of the heat of combustion emitted by them in turn. In this way yields of more than 75 per cent. of the total sulphur have been obtained. Of late years the Sanfilippo furnaces have also come to the front and allow of a still better yield and of the utilisation of poor ores, as the chambers of the furnace are traversed by numerous perforated vertical chambers which allow access of air to all points of the mass to be regulated.

Sulphur is also extracted from its ores by making use of its easy fusibility under the action of superheated steam at three and a half atmospheres pressure.

This principle was proposed by Payen and by Gill at the close of 1867 ; the first apparatus was constructed by Thomas in 1869 and applied by Gill after 1884. A final improvement, indicated in a patent of 1891, rendered the use of this apparatus possible.

The steam extractors of Thomas consist of large horizontal iron cylinders, encased in wood, 6 metres long and 80 to 100 cms. in diameter. Fig. 75 shows a portion of such a cylinder. Small waggons with perforated bottoms are charged with the ore and run on the rails S inside the cylinder ; the door is firmly closed after charging, and superheated steam at 130° is admitted by the cock C, which is closed when steam only escapes. The molten sulphur collects in the receiver g, carried in the small car B, and connected with the main extractor by a steam-tight joint ; this can be removed when the extraction is complete. The steam is discharged under pressure from the valve h into another similar apparatus and a fresh batch of ore is then treated. Eight to twelve batches can be treated daily of four to five tons each.

In order to treat 24 tons of 25 per cent. ore in twenty-four hours 600 kilos of coal (£1) are required, and five tons of sulphur are obtained. If the same quantity of ore is treated in calcaroni a ton of sulphur is lost and costs more than the coal. Extraction with steam gives a yield of 80 to 90 per cent. of the total sulphur, but requires greater expenses for plant and for fuel (which is rather dear in Sicily) so that this method cannot

be extended in the island. On the other hand, it has been introduced advantageously, with suitable improvements, in Romagna (*see below*). When the mineral contains much gypsum the losses on steam extraction are heavy.

Of the sulphur produced in Sicily in 1891 75 per cent. was obtained in calcaroni, 17 per cent. in regenerative furnaces, and 8 per cent. by steam extraction. In 1903 only 32 per cent. was obtained in calcaroni, 55 per cent. in regenerative furnaces, and 13 per cent. of the total production in steam extractors. In 1906 the proportion obtained from regenerative furnaces rose to 66 per cent.

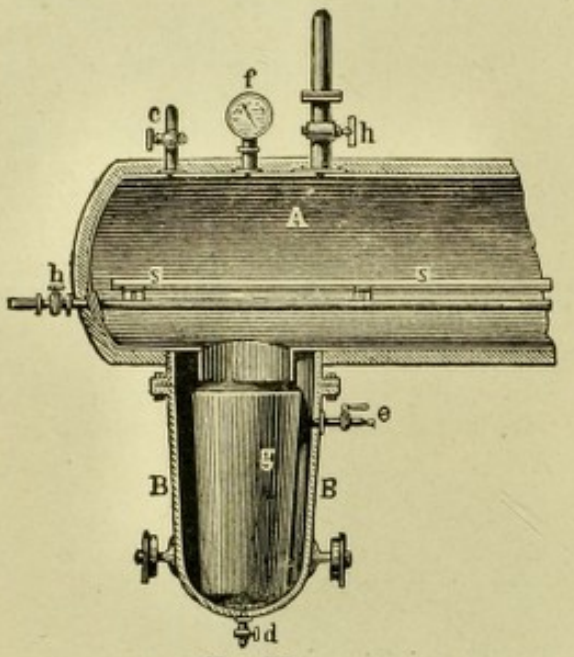


Fig. 75.

In Romagna, the ore is mixed with bituminous substances and is then burnt in calcaroni, giving a dark product. In small quantities it is treated by distillation in numerous "*pignatti d'argilla*" (clay retorts) of 20 litres capacity, heated in a suitable furnace called a "*galera*." The sulphur vapours are condensed outside the furnace in other *pignatti*.

For larger production "*doppioni*" are used (Fig. 76), consisting of eight cast-iron retorts, 1 metre high and 0·5 metre in diameter, obliquely arranged in a furnace. The sulphur vapours pass through the tube *j* into a condenser, *h*, common to two retorts, and the liquid sulphur so obtained collects in receivers, *i*, which are kept hot by the furnace gases passing along the flue *K*. It takes twelve hours to treat a batch of ore in a set of eight retorts. Each retort takes 150 kilos of ore per twelve hours. The "*doppioni*" are not used for production on the large scale, as production is too expensive on account of the small output, high cost of plant, and easy damage to the retorts.

At Latero, near Rome, good results have been obtained from a poor ore (13 per cent. S) by extraction with steam. A special apparatus was used, devised by Gritti, and patented by the Compagnia francese delle cave di Latera. For some years, however, the extraction of sulphur at Latera has ceased.

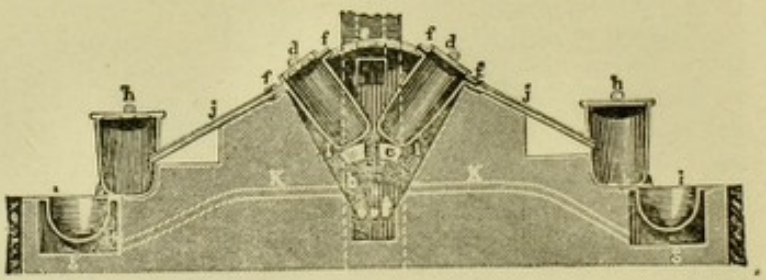


Fig. 76.

The extraction of sulphur with carbon disulphide has been tried at Naples and at Swoszowice with poor ores (15 per cent.), and 99 per cent. of the sulphur was obtained. For special reasons the extraction with carbon disulphide at Naples was not continued.

New deposits of sulphur have recently been found in the Caucasus, and it has been calculated that they are capable of yielding, altogether, nine million tons of sulphur; at present this is burnt on the spot for the direct production of sulphuric acid.

A proposal has been made to extract it by Petcanoff's method, as follows: The ore is thrown into brickwork chambers, which can be hermetically closed, provided with a false bottom, and water is added which fills the interstices in the ore; the whole is then heated with superheated steam, which causes the sulphur to melt and collect in the pure state on the bottoms.

At Charles Lake, Louisiana, America, the sulphur deposits have been known since 1868, and the sulphur has recently been extracted from fairly deep strata by H. Frasch's method without sinking shafts ; by this method it is possible to pass through layers of the hardest rock to a depth of 240 metres, where there are compact deposits of sulphur, 30 to 40 metres thick and fairly pure. Frasch sank a well, 25 cms. in diameter, just as in boring for petroleum, lined with an iron tube, until he arrived at the rock under which lay the sulphur. In this tube three other concentric tubes, lined with aluminium, were suitably fixed, of 15, 7·5, and 2·5 cms. diameter, which were driven into the sulphur layer. The 15 cm. tube was then surrounded with superheated water at six atmospheres pressure (155° temp.) which melted the sulphur and forced it to ascend the middle tubes as a liquid of density 2 ; it was here surrounded by hot air at 130° C. The molten sulphur rose to a certain height in the tube and attempts were made to extract it by a pump with aluminium valves ; the valves resisted the corrosive action of the sulphur, but were unable to support the strokes of the pistons, and the difficulty was ingeniously surmounted by introducing a current of air through the central tube which so strongly emulsified the column of molten sulphur that it was rendered lighter and rose to the surface without a pump. Thus the principles of the Kuhlmann emulsifier and the Mammoth pump, already used for raising acids and other liquids, were here applied together (*see* illustration to the chapter on Sulphuric Acid). At the surface the fused sulphur is collected in large wooden boxes where it solidifies, and the water and hot air are utilised again.

In 1902 the Union Sulphur Company of New York obtained 100 tons of sulphur per day by this process ; by the end of 1903 the production had risen to 550 tons daily ; in 1904 it rose to 800 tons, and in 1905, with four boreholes and plant and 600 workmen, the daily production was about 1500 tons. At first about 1000 kilos of coal were used for boilers, &c., per 300 kilos of sulphur, but to-day this has been advantageously replaced by petroleum.

By simply melting the extracted sulphur with steam in iron boilers a product of 99 to 99·6 per cent. purity is obtained with a loss of only 1·5 per cent. It is easily understood that the Frasch process is only applicable to very pure sulphur deposits.

The sulphur deposits of Louisiana have been estimated to contain forty million tons, and important surface deposits of sulphur of volcanic origin (solfatare) which have not yet been exploited are found at Kadiak and generally in the volcanic islands of Alaska.

A special and rather complicated method has been suggested by Stickney for the recovery of sulphur from iron pyrites ; the ore moves automatically in a cylindrical furnace, and is heated with either water-gas, petroleum, coal, or steam. The sulphur vapours are condensed by a spray of saline solution.

Small quantities of sulphur are also obtained, mixed with Laming's material, in the purification of coal-gas, and may be removed by extraction with carbon disulphide.

The recovery of sulphur from the residues of the Leblanc soda industry is to-day of great importance. If all these residues were worked up by Chance's method, employing chimney gases (CO_2), 180,000 tons of sulphur would be obtained per annum. At present more than 80,000 tons are so obtained (*see* Soda, Part III).

REFINING SULPHUR. The first subliming plant was constructed by Michel at Marseilles in 1805 and improved by Lamy in 1844. 888 kilos of sulphur are heated in the pan *D* (Fig. 77), where it melts and passes through the tube *F* into the iron retort *B*, which is 1·5 metres long and 0·5 metre in diameter, and holds 300 kilos of sulphur. This is heated directly by the hearth *A*, and the fire-gases rise through the flue *C* and heat the pan *D*. When distillation from one retort is finished, the other is charged and heated, the first being meanwhile shut off by closing the damper *I'*. The sulphur vapours condense in the chamber *G*, which has a volume of 80 cu. metres.

The distillation of the contents of each cylinder takes four hours, and from the two cylinders 1·8 tons of sulphur are obtained in twenty-four hours.

If the condensing chamber is kept at a temperature above 114° molten sulphur collects on the floor, flows into the receiver *L*, and is poured into the moulds *M*, where it solidifies. If the temperature in the condensing chamber is below 100°, flowers of sulphur are formed, and in this case only 300 kilos are produced per day.

The method of Dujardin, who replaces the Lamy retorts by shallow retorts, is more rational, and only 2·5 per cent. of the sulphur is then lost. In twenty-four hours 3·6 tons of sulphur are obtained, using 0·5 ton of coal.

Much sulphur is refined at Marseilles and Anvers, but a considerable quantity is also refined in Germany and Italy, especially in Romagna and Catania.

In order to decrease the losses in preparing flowers of sulphur, the use of inert gases such as N, CO_2, &c., instead of air in the condensing chamber, has been proposed.

Ground Sulphur. Formerly in Sicily the flowers of sulphur were simply sieved, but the product was only slightly adhesive to the vine-leaves. To-day

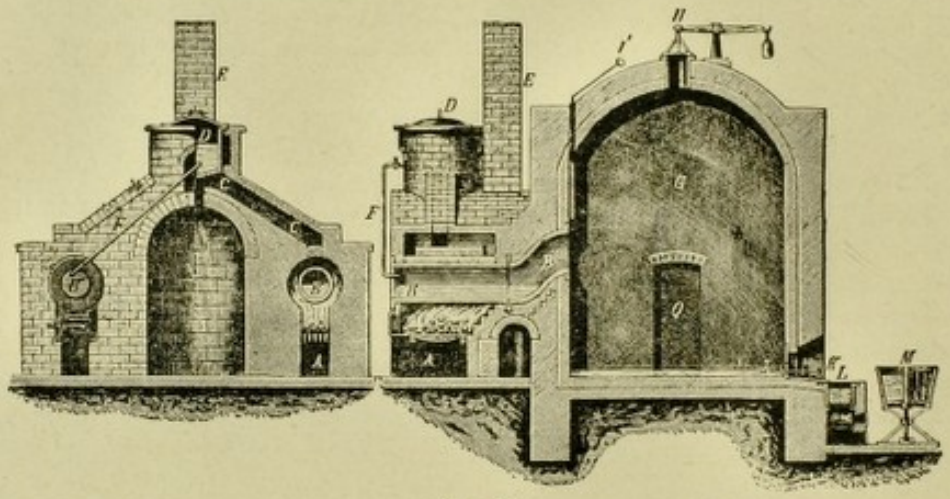


Fig. 77.

the crude sulphur, melted and cast into loaves, is refined in the Sicilian ports by being remelted and transformed into flowers of sulphur, or is ground between millstones and the product passed through silken sieves, of 170 meshes to the inch. Sometimes the sulphur catches fire during grinding, but is easily extinguished with damp sacking. Seventy per cent. of this sulphur adheres to the foliage of the vine.

Winnowed Sulphur (*solfo ventilato*) is much superior for viticultural purposes, as it is more adhesive to the foliage. It was first prepared by Dr. A. Walter, at Bagnoli, near Naples. Lumps of refined sulphur are placed at the bottom of a conical vessel of stone in which a vertical millstone revolves. During the grinding a continuous current of air from powerful fans is introduced at the bottom of the apparatus. The finest sulphur is thus carried to the farthest points of the large closed chamber in which the operation is conducted. In order to allow the air to escape, there are windows covered with large sheets of cloth which retain the sulphur whilst allowing the air to escape. Each mill consumes 2 h.p., and yields 1 to 1·5 tons of winnowed sulphur per twenty-four hours.

Sometimes the very finely divided sulphur explodes with the oxygen of the air; air containing little oxygen has been suggested for this purpose, and is easily obtained by passing ordinary air over a layer of glowing charcoal, or by employing furnace gases directly (Delilla, Ital. Pat. 51,474).

The firm of Walter and Tremwella in Naples and Catania alone produced

5000 tons of winnowed sulphur in 1890. This product is also manufactured in Romagna, Lombardy, and Piedmont. This sulphur has a pale yellow colour, similar to that of precipitated sulphur, and contains less than 0·5 per cent. of ash. The degree of fineness is determined by Chancel's method.[1]

SELENIUM : Se, 79.2

This element is rare, and is mainly found in certain Bohemian and Swiss pyrites. These pyrites are burnt in sulphuric acid works and the selenium is then found in the dust-chambers and in the mud of the lead chambers.

It has also been found in the lava of Vesuvius and of the island of Lipari ; some is also produced in the Argentine and the United States, where it is obtained from the anodic mud of the electrolytic copper refineries.

It was first discovered by Berzelius in 1817 in the mud of the lead chambers of a works at Gripsholm. It is extracted by treating the mud with a concentrated solution of potassium cyanide ; the selenium is precipitated from the filtrate with HCl. It is then collected, oxidised with nitric acid, and evaporated, when selenium dioxide (SeO_2) remains, and is purified by sublimation. This oxide is reduced to metallic selenium by an aqueous solution of SO_2.

A. Koch has recently obtained good results (Ger. Pat. 167,457, Dec. 1903) by treating the lead chamber mud (consisting of lead sulphate and free selenium) at moderate temperatures with moderately concentrated sulphuric acid and potassium permanganate ; sodium chloride is then added and the solution diluted and filtered. The selenium is then precipitated from the filtrate with sulphur dioxide.

PROPERTIES. Selenium melts at 217° (the variety in red crystals at 170°–180°) and boils at 665°, forming dark yellow vapours, the density of which diminishes up to temperatures of 1400°, when it consists entirely of molecules of diatomic Se. It burns in the air with a bluish-red flame to form SeO_2, with an odour of rotten radishes. When heated with carbon, it yields red vapours of disagreeable odour.

It dissolves in strong sulphuric acid with green colour, reacting according to the following equation :

$$Se + 2H_2SO_4 = 2SO_2 + SeO_2 + 2H_2O.$$

Sodium selenite is coming into use for determining whether a given medium is sterile or contains bacteria ; in the latter case a noticeable amount of reduction takes place, and can be confirmed by the use of potassium tellurite (Gosio).

[1] *Analysis of sulphur.* Chancel's sulphurimeter is used for determining the *fineness* ; this consists of a glass cylinder, closed below, 23 cms. long, 12·68 mm. in diameter, and provided with a ground glass stopper. A volume of 25 c.c. is divided into 100 parts, which indicate degrees of fineness, according to Chancel. The apparatus is constructed by J. Greiner, Monaco. The sample to be examined is first passed through a sieve of 1 sq. mm. mesh to break up the lumps, and precisely 5 grms. are then weighed into the apparatus, which is filled up with pure ether, free from alcohol (distilled over metallic sodium), to 1 cm. above the 100 mark, at a temperature of 17·5° C. The whole is then strongly shaken in a vertical direction for thirty seconds and the apparatus suspended in a vessel of water at 17·5° without allowing it to touch the sides or bottom of the vessel, as any impact alters the results. The sulphur settles and the ether clears. When the layer of sulphur does not further decrease in a few minutes a reading of its height is taken. The finer the sulphur the larger will be this reading. The shaking is repeated and the mean of four readings taken ; this series of readings is then repeated with another 5-grm. sample of sulphur, and the mean of the two results is taken (H. Fresenius and P. Beck, 1903). Commercially there is an allowance of 5°. Sulphur of 40°–45° and also of 80°–85° Chancel is sold.

The *mineral impurities* (*ash*) are determined by burning 10 grms. in a tared porcelain capsule and weighing the residue.

Moisture is determined in a 100-grm. sample, after powdering and rapidly weighing, by heating for an hour each time in an oven at 100° ; it is weighed after cooling in a desiccator.

Arsenic is tested for qualitatively by treating 1 grm. of sulphur with 15 drops of ammonia and 2 c.c. of water ; after half an hour the liquid is filtered off and 30 drops of hydrochloric acid and 15 drops of oxalic acid solution added ; a strip of polished brass is then immersed in the liquid, which is heated to 60°–100°. In presence of arsenic the brass quickly acquires a grey or black colour. The quantitative determination of arsenic is carried out by Schoppi's method, which we will not describe here.

The *specific gravity* is determined with Schumann's volumeter.

Selenium is tested for by melting a little of the sulphur with potassium nitrate, then dissolving the mass in hydrochloric acid and treating with sulphurous acid, which precipitates the selenium as a red powder.

In order to distinguish molten sulphur from flowers of sulphur, it is only necessary to remember that the former is completely soluble in carbon disulphide, in which the latter is mainly insoluble.

Selenium can exist, like sulphur, in various allotropic forms: amorphous selenium (by reducing SeO_2 with SO_2) is a red-brown powder of sp. gr. 4·26, soluble in carbon disulphide, from which it separates in small crystals of sp. gr. 4·50. A solution of potassium selenide on standing in the air deposits black scaly crystals of sp. gr. 4·80, isomorphous with sulphur, and insoluble in carbon disulphide. On rapidly cooling molten selenium it is transformed into a vitreous amorphous mass, black in colour, of sp. gr. 4·28, soluble in carbon disulphide; on cooling slowly, on the contrary, a crystalline mass is obtained, insoluble in carbon disulphide, of sp. gr. 4·80. On heating amorphous selenium to about 100°, its temperature suddenly and spontaneously rises to over 200°, and it is transformed into a dark greyish, metallic, crystalline substance of sp. gr. 4·8, insoluble in carbon disulphide and a good conductor of heat and electricity, as is that obtained on slowly cooling molten selenium; on exposure to light the one form is transformed into the other. According to Coste (1910) only three forms of selenium exist at the ordinary temperature, namely: (1) vitreous, red selenium, of sp. gr. 4·30, obtained by precipitation; (2) crystalline red selenium, of sp. gr. 4·45, which melts at 144° and solidifies, changing into (3) metallic selenium, which melts at 219°, has the sp. gr. 4·80, and forms more easily in presence of traces of impurities. The study of the various allotropic forms of selenium has lately been pursued with much activity on account of important applications which are expected.

Amorphous selenium is a bad conductor of heat and electricity, whilst crystalline selenium is a good conductor, and its conductivity increases when it is illuminated, and with the amount of illumination; this sensitiveness to light is very great, but is retained for a short time, a fact which has greatly hindered any large practical application of this most interesting property. Even traces of contamination with certain metals influence this special behaviour of selenium very greatly, and also after sudden illumination the original electric resistance is only slowly regained (after twenty-four hours), which renders any practical application still more difficult. It has recently been found that the sensitiveness and its duration are increased if the selenium is heated to 200° in an atmosphere which is dry and free from oxygen, and is then allowed to cool and crystallise slowly; also the addition of 0·1 to 0·5 per cent. of silver, and of other catalysers, increases the sensitiveness; a method is still needed of protecting active selenium from moisture (R. Marc, 1907).

The activity of selenium is not due to chemical action and has nothing to do with heat effects, as it still exists at the temperature of liquid air (− 190°), but is strictly connected with the action of light, which form of energy causes the transformation of one allotropic form into another, with alteration of density and probable formation of free ions or electrons, which are good conductors of the electric current.

Already in 1886 Graham Bell (the inventor of the telephone) succeeded in producing with the aid of selenium a wireless telephone, for transmitting sounds for a short distance (radiophone); the method was based on the observations of W. Smith in 1873. But in 1904 E. Ruhmer, in Berlin, obtained much more important results by applying selenium to the speaking arc, discovered by Simon in Göttingen in 1898: If in a circuit containing an arc lamp a secondary coil is interposed, then if the primary circuit is connected with a telephone transmitter, the light of the arc will be influenced by sounds which impinge on the transmitter, thus varying the intensity of the light; this is the speaking arc. A telephonic transmitter of which the microphone is connected with selenium reveals these oscillations of light, reproducing the sounds which influence the arc, and in this manner E. Ruhmer was able to speak at a distance of sixteen kilometres with his wireless telephone.

It is clear that the distance could not be very large, as in wireless telegraphy, as the electric arc and the telephone receiver had to be in the same straight line—in fact, had to be within sight of one another.

Photographic transmissions are to-day sent over large distances by using the circuit of Duddel and Poulsen, which produces continuous oscillations of high frequency (500,000 to 600,000 electromagnetic oscillations per second) which can be received at a syntonic

station, that is, one with oscillations of the same period. Commercial selenium powder costs £5 12*s*. per kilo, and is used for producing a red colour on porcelain and glass ; as sublimed powder it costs £8, and in small rods £6 per kilo.

TELLURIUM : Te, 127.5

This element is not abundant in nature ; it is found in the metallic state and mixed with gold and silver, lead, and bismuth, especially in Transylvania and in the Russian gold mines in the Altai Mountains. It is also found in the volcanic formations of the Lipari Islands.

Tellurium is separated by sulphurous acid from solutions of tellurous acid as a black powder, of sp. gr. 5·9. When fused it has a silvery white, metallic appearance and is a good conductor of heat and electricity. It crystallises in rhombohedra of sp. gr. 6·4, melts at 452°, and boils at 1280°, forming simple molecules of Te, even at 1400° to 1700°. The atomic weight was believed to be 128, but according to the periodic system it should be less than that of iodine (126·9), and Brauner actually found it to be 125 ; but the latest and more exact work (Standenmayer, 1895) brings us back to the atomic weight 127·5.

Some gold ores contain tellurium. To obtain this element these ores are heated in cast-iron vessels with strong sulphuric acid ; the gold and silica remain undissolved ; the liquid is concentrated, diluted, and then treated with boiling water and with 10 to 15 per cent. of HCl to precipitate the silver.

It is then filtered into lead-lined vats and treated with gaseous SO_2 from cylinders of the liquefied gas (70 to 100 grms. of SO_2 per litre of the solution of tellurium) ; this precipitates tellurium of 75 to 80 per cent. purity (without selenium) and it can then be purified, yielding a 95 to 97 per cent. product. The remaining mother liquors contain Cu, Pb, Sb, &c.

Outside the laboratory tellurium has not yet received any important application, but experiments are always in progress to find a use for it in medicine, for colouring porcelain, or for electrotechnical purposes. Gosio has employed potassium tellurite in order to discover whether substances are properly sterilised, as it is reduced by the action of bacteria. Tellurium powder costs £18 per kilo, and when cast into sticks it costs £22 per kilo.

HYDROGEN COMPOUNDS OF THE GROUP : O, S, Se, Te

At high temperatures these four elements combine with hydrogen to form compounds of the general formula $X''H_2$. At still higher temperatures these are decomposed into their components. But whilst water (H_2O) is a liquid and non-poisonous, the hydrogen compounds of the other elements are gases and poisonous to the human system. Water is also a strongly exothermic compound, whilst hydrogen sulphide, H_2S, is but weakly exothermic (2600 cals.), and hydrogen selenide and telluride are endothermic. The aqueous solutions of the three last compounds are decomposed by oxygen and still more easily by the halogens, forming oxides.

WATER : H_2O

This compound is found in nature as meteoric, spring, river, lake, and sea water.

Water is found very abundantly in nature and covers three-quarters of the earth's surface ; a very large quantity is also present as vapour in the atmosphere, from which it separates continually in the forms of fog, dew, rain, snow, hail, &c., which are all forms of meteoric water. More meteoric water falls in the tropics and in the neighbourhood of the sea than in more northern countries ; more falls in the mountains than on the plains, and more in summer than in winter.[1]

[1] *Translator's note.*—This last remark only applies to certain portions of the earth's surface.

On investigation of the amount of water which falls in various parts of the earth's surface, measured in height of water by means of suitable rain-gauges, it is found that the average rainfall in St. Petersburg is 45 cms. per year ; in Berlin it is 57, in Rome 78, in Genoa 118, in Milan 60 to 100, at Tolmezza (in the Alps in the Province of Udine) 244, and at Bergen (Norway) 225 cms. per year.

The amount of water which falls annually varies very much : thus the mean annual rainfall in Frankfort during thirty years was 60 cm. ; but it was only 36 cm. in 1864 and 140 cm. in 1867 ; hence the great difficulty of establishing rigorous meteorological laws. About half the rain water evaporates almost immediately into the atmosphere, whilst the other half descends under the action of gravitation into the lower layers of the earth's crust and reappears as springs, rivers, and in the sea.

Large pine forests appear to increase the quantity of rain, and certainly cause it to be better distributed over the ground ; they also act advantageously by hindering avalanches and inundations during storms, as the leaves and the vast network of roots retain the water.[1]

Meteoric water is of the greatest importance in the economy of nature, because it supplies the necessary water to man for domestic purposes, drinking, and hygiene ; it supplies water for agriculture, and is also important as a source of energy, as it supplies a means of utilising indirectly the solar heat which is apparently dispersed over those three-quarters of the globe (seas and lakes) where there is no vegetation and no crops to ripen. This solar heat is not in fact lost, but serves to transform part of the water at the surface of the seas, lakes, and rivers into vapour which is deposited in the form of rain on the plains and mountains and returns to the sea, furnishing motive power for innumerable enterprises during this cycle and producing work and wealth everywhere.

Meteoric water contains in solution the component gases of the air in the ratio of their solubilities. One litre of rain water contains in winter 32 c.c. of gas (air) and in summer 25 c.c., containing 27 per cent. O, 64·2 per cent. N, and 8·8 per cent. CO ; it also contains traces of NH_3, HNO_3, nitrous acid, H_2SO_4, and during storms also a little hydrogen peroxide.

The following is the average composition of rain water, deduced from that of seventy samples collected in England : total solids per litre 39·5 mgrms., ammonia from 2 to 5 mgrms., N_2O_5 from 0·18 to 2·7 mgrms. and even more.

The rise in level of the water of the subsoil which occurs in certain rainy years is often characterised by pollution of the water of the wells and an increase in the number of typhus cases.

Meteoric water dissolves various substances during its infiltration through the ground, including CO_2, which in turn forms bicarbonates by dissolving the salts of Mg, Fe, Mn, Ca, &c.

PHYSICAL PROPERTIES OF WATER. Water solidifies at 0°, or below this temperature if completely undisturbed ; before solidifying at 0° it has a density of 0·99987.

In vacuo, or when covered with a layer of oil, it solidifies at −10°, or even at −20°. Aerated water can be cooled to some degrees below zero without solidifying, and if water free from air is added, this latter alone solidifies. Some dissolved substances retard solidification very much, for instance, ether and various salts (*see below*, Freezing Mixtures).

On cooling, water continues to diminish in volume until 4° is reached,

[1] Ill-considered deforestation in the past has deprived large regions of water reservoirs and has given rise to continuous lack of temperature equilibrium ; rain occurs when it is not required, as well as excessive and prolonged frosts and violent winds which destroy vegetation and cause immense damage. Woods avoid damage from floods because they partly hold back the rain water and restore it slowly to the brooks and to the atmosphere ; they cause less torrential and more frequent rain by maintaining in their neighbourhood a fresher zone which facilitates condensation of the moisture of the atmosphere. (*Translator's note.*—And more especially on account of the enormous quantities of moisture absorbed by the roots and restored to the atmosphere by the leaves in the processes of plant metabolism.)

In the island of Malta, since large deforestation has occurred to make room for cotton cultivation, the rainfall has been insufficient, sometimes for three years on end. In St. Helena, on the contrary, the large afforestations have increased the rainfall to double the amount which fell in the time of Napoleon.

Torrential rains remove the most useful components of the soil very easily, and the mountains and hills are soon denuded until bare rocks remain (in absence of trees). In Italy in 1870 there were 5,200,000 hectares of forest, but in 1905 these had been reduced to 3,500,000 hectares. In 1910 the minister Luzzatti passed a law in favour of re-afforestation and the creation of a State domain of forests. In Germany there are 17,000,000 hectares of forest, of which 4,000,000 belong to the State ; in Sweden, 20,000,000 ; in the United States, 200,000,000 ; and in Canada, 323,000,000 hectares.

when one litre of water weighs 1000 grms., whilst at 0°, before freezing, it weighs only 999·8 grms. ; during transformation into ice great dilatation takes place, and one litre then weighs 916·74 grms. For this reason ice formed in rivers and in the sea floats ; if ice had not this important property all our lakes would consist of nothing but enormous masses of ice, and the earth would perhaps be uninhabitable for man.

If water is cooled in strong vessels, completely full and so closed that it cannot expand, it does not solidify even at very low temperatures (at −24°, Boussingault).

At a pressure of 760 mm. ice always melts at 0° (fundamental temperature in thermometry, triple point, *see* p. 115).

Ice partially evaporates even below 0°. It is a bad conductor of heat and completely adiathermic for dark rays. It is electrified by friction, but does not conduct electricity. One kilo of ice at 0° absorbs 80 Cals. in melting and yields 1 kilo of water at 0°. It crystallises in the hexagonal system, as can easily be seen by examining the crystals forming snowflakes.

Pure water has neither smell nor taste, and is colourless if seen in thin layers ; in layers of more than 2 metres thickness it is slightly bluish in colour, but varies with the dissolved or suspended substances. Its coefficient of compressibility is very small : 0·000,045 per atmosphere. The critical temperature of water is 365°. The velocity of transmission of pressure in water is equal to that of sound in the same medium.

The conductivity for heat is small, but greater than that of all other liquids except mercury.

It has been noted already that water evaporates at all temperatures (vapour tension, *see* p. 81), and the more rapidly the higher the temperature, the drier the air, and the less the pressure. In closed vessels a constant quantity evaporates at each temperature, and the vapour is thus at a definite pressure which increases and diminishes with the temperature. At 100° the vapour pressure of water is 760 mm., that is, it is equal to the normal atmospheric pressure, and therefore water boils at 100° ; even at low temperatures water has a definite vapour pressure.[1] The temperature of ebullition of water alters with the pressure ; in a vacuum of 90 mm. water boils at about 50°. When water evaporates without application of heat it abstracts the necessary heat from its surroundings. To maintain water as such, even above 100°, a pressure is required which alters with the temperature ; the corresponding densities of the steam and its heats of condensation also increase at the same time.[2]

[1] VAPOUR PRESSURE OF WATER, ACCORDING TO REGNAULT, IN MM. OF MERCURY

t	mm.	*t*	mm.	*t*	mm.	*t*	mm.	*t*	atm.	*t*	atm.
−20°	0·916	16	13·536	26	24·988	60	148·791	130	2·6 at.	180	9·9 at.
−5	3·115	17	14·421	27	26·505	70	233·093	135	3·1 „	185	11·1 „
0°	4·525	18	15·357	28	28·101	80	354 643	140	3·6 „	190	12·4 „
+ 5°	6·471	19	16·346	29	29·782	90	525·692	145	4·1 „	195	13·8 „
10	9·165	20	17·391	30	31·548	100	760·(1 at.)	150	4·7 „	200	15·3 „
11	9·792	21	18·495	35	41·827	105	1·19 at.	155	5·4 „	205	17·0 „
12	10·457	22	19·659	40	54·906	110	1·41 „	160	6·1 „	210	18·8 „
13	11·162	23	20·888	45	71·391	115	1·67 „	165	6·9 „	215	21·0 „
14	11·908	24	22·184	50	91·982	120	1·94 „	170	7·8 „	220	22·9 „
15	12·699	25	23·550	55	117·478	125	2·29 „	175	8·8 „	230	27·5 „

These temperatures also show the boiling-point of water at the corresponding pressures.

[2] At 1 atmosphere 1 kilo of steam, in condensing to water at 0°, gives off 636 Cals., and at 16 atmospheres 670 Cals. When the pressure of the steam falls from 12 atmospheres to 0·12 atmosphere the volume increases from 1 to 100, but the steam does not lose much heat. The thermal equivalent of a horse-power is $\frac{3600 \times 75}{426} =$ 600 Cals., and since steam enters a steam-engine with about 660 Cals., the theoretical output of a steam-

On evaporation water acquires a volume 1696 times greater than before. The ebullition of water is more regular the greater the quantity of dissolved air which it contains; it proceeds more regularly in metal vessels; in glass vessels with smooth walls water boils at about 101°, and even greater superheating easily occurs, producing irregular ebullition (bumping). This superheating can be avoided by placing a few fragments of glass or metal in the vessel.

On pouring water into vessels heated to more than 200° a thin layer of steam is formed, which is a bad conductor of heat, and insulates the water from the sides of the vessel, causing it to acquire the so-called *spheroidal state;* on cooling the sides of the vessel below 171° the water comes in contact with them and is suddenly transformed into very large quantities of steam, which may cause the violent bursting of the vessel if this is closed; in this way the bursting of boilers which are badly supervised or are lined with heavy incrustations is explained.

In order to transform 1 grm. of water at 0° into steam at 100° 636 cals. are required; to transform 1 grm. of water at 100° into steam at 100° 536 cals. are required, and this is called the *heat of evaporation.*[1]

engine would be about 1 h.p.-hour per kilo of vapour. In practice there are cases where 6 or even 16 kilos of steam are required per h.p.-hour, so that the output is only 16·7 per cent., or even 6 per cent. of that to be theoretically expected, but it must be remembered that part of these calories are furnished by the condensation of the steam to water, so that, for example, when the 6 kilos of steam at 10 atmospheres escape from the motor at 1 atmosphere they have only given up 35 Cals. and are therefore not able to produce the horse-power which requires 600 Cals., for this would require that part of the 6 kilos of steam should be condensed to water (as they ordinarily are!—*Translator*).

TEMPERATURE, DENSITY, AND HEAT OF CONDENSATION OF STEAM AT VARIOUS PRESSURES

Pressure in atmospheres	Temperature in degrees	Density of steam in kilogrms. per cubic metre	Heat of condensation in Calories, per kilo of steam, to water at same temperature	Pressure in atmospheres	Temperature in degrees	Density of steam in kilogrms. per cubic metre	Heat of condensation in Calories, per kilo of steam, to water at same temperature
1·0	100°	0·606	536·0	3·25	136·6°	1·835	510·3
1·1	102·7°	0·663	534·3	3·50	139·2°	1·968	508·5
1·2	105·2°	0·719	532·5	3·75	141·6°	2·099	506·8
1·25	106·3°	0·747	531·7	4·00	144·0°	2·230	505·0
1·50	111·7°	0·887	527·9	4·25	146·2°	2·361	503·5
1·75	116·4°	1·023	524·6	4·50	148·3°	2·491	502·0
2·00	120·6°	1·163	521·6	4·75	150·3°	2·621	500·6
2·25	124·3°	1·299	519·0	5·00	151·2°	2·750	500·0
2·50	127·8°	1·434	516·5	5·25	154·0°	2·817	498·0
2·75	130·9°	1·569	514·3	5·50	155·8°	3·007	496·7
3·00	133·9°	1·702	512·2	5·75	157·5°	3·135	494·5

[1] The *heat of evaporation* of a liquid comprises the work necessary to overcome the cohesion or mutual attraction of the molecules (internal work) and that necessary to overcome the external pressure (external work). The internal work is always much greater than the external work; thus, for water we have the following values when it is evaporated at various temperatures. We also add the heat of evaporation of some other substances.

——	Heat of evap.	Heat of ext. work	Heat of int. work	——	Heat of evap.	Heat of ext. work	Heat of int. work
	cals.	cals.	cals.		cals.	cals.	cals.
Water at 0° . .	607	31·1	575·9	Carbon tetrachloride at 0°	52	3·4	48·6
,, ,, 50° . .	571·6	35·5	536·1	,, disulphide at 0° .	90	7·2	82·8
,, ,, 100° . .	536·2	40·2	496	Liq. sulphur dioxide .	94·5	—	—
,, ,, 150° . .	500·8	44·1	456·7	,, ammonia . .	315	—	—
Ether at 0° . . .	94	7·5	86·5	,, air . . .	125	—	—
Alcohol at 0° . .	236·5	13·1	223·4	Methyl ether . .	130	—	—
Acetone . . .	140·5	8·7	131·8	Carbon dioxide . .	84	—	—
Chloroform at 0° . .	67	4·5	62·5				

Water dissolves some salts with absorption of heat, but with others (anhydrides), and with some acids, oxides, &c., heat is evolved on solution. The solubility of salts increases in general on heating, and is constant at any given temperature, so that the density of saturated solutions at varying temperatures also varies. The freezing-point of saline solutions is lower than 0°, and the more so the more salt is dissolved. For each molecule of anhydrous salt dissolved in 300 mols. of water, the freezing-point is lowered by 0·685° (Raoult, 1883).

The ice which separates from salt solutions is almost pure and only contains traces of salt which are mechanically enclosed. Therefore on freezing sea water the ice which separates only contains 1·58 grms. of chlorine per kilo, that is, about a twentieth of the original quantity. In this way aqueous saline solutions can be concentrated, by separating the ice as it is formed. In the Middle Ages already the light wines of bad years were concentrated by freezing.

The boiling-points of aqueous saline solutions are higher than 100° and increase with the concentration. The saturated solutions have the highest boiling-points.[1]

A thermometer immersed in the vapours of a boiling saline solution always indicates 100°, although the vapours in the vicinity of the liquid may be hotter, and this occurs because pure water condenses on the bulb of the thermometer and boils at 100°. If the thermometer were previously heated to above 100° it would then indicate the true temperatue of the vapour.[2]

The vapour tension of saline solutions is lower than that of pure water and inversely proportional to the concentration.

The density of aqueous solutions of gases (*e.g.* NH_3 and HCl) may be greater or smaller than that of pure water. On freezing such solutions the gas evaporates completely (when it does not form solid compounds, such as chlorine hydrate).

CHEMICAL PROPERTIES. The chemical composition of water was first discovered by Cavendish in 1781 by burning hydrogen in oxygen. But the certain demonstration of its quantitative composition was first given by Lavoisier in 1783; he succeeded in decomposing water by passing its vapour through a tube containing red-hot iron, which combined with the oxygen of the water, setting free the hydrogen, which was collected in a measured bell-jar. Until 1750 water was held to be a simple substance.

By burning hydrogen under a bell-jar filled with air the formation of water, which condenses on the walls, can be immediately observed, and the water can easily be collected. The heat of formation of liquid water from the elements $H_2 + O$ is 286·2 Kj. (68,400 cals.), or 58,800 cals. for water in the form of vapour.

In order to demonstrate the chemical composition of water it is made feebly acid and decomposed in a voltameter with two limbs; two volumes of hydrogen collect at the negative pole and one volume of oxygen at the positive pole.

It can also be shown that two volumes of hydrogen and one of oxygen combine to form two volumes of steam by introducing the mixture into a eudiometer surrounded by a mantle in which the vapour of a substance which boils above 100° circulates (*e.g.* amyl alcohol, which boils at 132°). On passing an electric spark through the three volumes of gas ($2H_2 + O_2$ = three volumes) two volumes of steam are formed.

[1] By adding the following quantities of salts to 100 parts of water the following boiling-points are obtained:

Boiling-point	101°	102°	103°	104°	105°	106°	110°	115°	120°	130°	160°
Calcium chloride . .	10·0	16·5	21·6	25·8	29·4	32·6	44·0	58·6	73·6	104·6	212
Sodium ,, . .	7·7	13·4	18·3	23·1	27·7	31·8	—	—	—	—	—
,, nitrate . .	9·3	18·7	28·2	37·9	47·7	57·6	98·9	153·7	212·6	—	—

[2] *Translator's note.*—It is generally recognised that the true temperature of the vapour in these cases *is* 100°.

The exact gravimetric control of the chemical composition of water was first undertaken by Berzelius and Dulong in 1820, by passing hydrogen over a given weight of red-hot copper oxide and then weighing both the resulting water and the partially reduced copper oxide ; the results obtained did not agree very well on account of imperfections in the apparatus. In 1843 Dumas, in co-operation with Stas, started a series of very careful experiments, taking all possible precautions to arrive at exact results, employing large quantities of dry hydrogen and weighing much water, in order to reduce the errors to a minimum ; the weights were corrected to vacuum, &c. The quantities of hydrogen forming the water were deduced indirectly by subtracting the weight of oxygen, found from the reduction in weight of the copper oxide, from the weight of water formed. From nineteen analyses Dumas obtained as a mean result the percentage composition 11·23 per cent. of H, and 88·77 per cent. of O, which is very near to the theoretical composition as calculated from the formula.[1]

Many salts contain considerable quantities of water of crystallisation, which is liberated on heating, *e.g.*, the alums with 12 mols. of water and sodium carbonate, which crystallises with 10 mols. of water ($Na_2CO_3 + 10H_2O$), &c.

Dalton in 1840, and Joule and Playfair at a later date, found that when many of these salts are melted they occupy precisely the volume which the water of crystallisation alone would occupy in the form of ice ; this applies to sodium carbonate among other salts ; in the case of other salts, however, the volume which they occupy when melted is equal to the sum of the volumes of the anhydrous salt and of the water which they contain, in the state of ice.

Some salts, *e.g.* crystallised calcium chloride, dissolve in water with absorption of heat ; others, on the contrary, such as the same calcium chloride when fused (and free from water), dissolve in water with heat evolution, as they combine with a certain number of water molecules during solution.

Finally, in discussing the chemical properties of water we must refer to its great importance as a factor in almost all chemical reactions, either as solvent, as a cause of electrolytic dissociation on which the possibility of so many chemical reactions depends, or as a catalytic substance in numerous reactions which do not take place except in presence of traces of moisture as has been shown by Baker (1894–1900) by the most various examples.

SURFACE (DRAINAGE) WATER. This is abundant in some localities. When the water of the subsoil is unable to descend into lower strata it stagnates in the ground and may even rise to the surface or above it. By a suitable system of pipes (drainage) it can be caused to flow into channels with advantage to the ground. This water is ordinarily polluted by all the organic matter and manure which is present on the land. From the analysis of such water the amount of fertilising materials which it is removing may be deduced.

RIVER WATER. Water derived from melting snow and ice contains about 50 mgrms. of dry solids per litre, which ordinarily consist of Na_2CO_3, K_2CO_3, and organic substances which sometimes colour the water in various tints. River water contains less bicarbonate than that of springs because whilst flowing in contact with air it liberates CO_2 from the bicarbonates and deposits carbonates of Ca, Mg, and Fe, whilst spring water holds these salts in solution in the form of bicarbonates. Thus the water of rivers contains less mineral matter in solution in the lower reaches than near the source. It is then also poorer in organic substances as these are oxidised or gradually reduced through the agency of bacteria, except in cases where the original composition of the water is altered by the influx of tributaries or the drainage of towns.

The temperature of river water varies greatly at various seasons and according to the quantity of the water. With increase of temperature and slackening of the current (through the effect of dams) the amount of dissolved organic matter is increased, as the foam and rubbish more easily undergo putrefaction. River water always contains the gases O, N, and CO_2.

LAKE WATER. This is sweet when the lake continuously receives water and there is a continuous outflow ; and salt when an outflow is lacking. Sometimes freshwater lakes have a composition the same as that of the inflowing rivers. Lakes are regular reservoirs which are of the greatest value in dry seasons.

[1] *Translator's note.*—It is generally understood that the ratios of the atomic weights of these two elements are calculated from experimental results on the composition of water, and therefore the latter cannot be checked by the formula.

SALT LAKES are closed basins into which saline springs flow ; or they have a bottom formed of salt or are remnants of seas which have at some time been separated by a rise of the land level, such as the Caspian and Dead Seas, Lake Aral, &c.

The composition of their waters varies greatly ; thus those of the Caspian Sea and of Lake Aral contain considerable quantities of $MgSO_4$ and $CaSO_4$ and only small quantities of $MgCl_2$; on the whole they are not very salt. The two small lakes which communicate with the Caspian Sea, Lakes Trinetzky and Rosso, have a different composition and are much more concentrated, because there are rapid evaporation and a considerable inflow, without any outflow ; therefore they contain scarcely any calcium sulphate because they are rich in other salts which throw the calcium sulphate out of solution, and contain, on the other hand, a much larger amount of $MgCl_2$, which is very soluble.

The lake with the most concentrated water is the Dead Sea (sp. gr. 1·194 to 1·212), the water of which contains neither Sr, Mn, iodides or nitrates, but is a concentrated solution of NaCl, $MgCl_2$, and $CaCl_2$; it contains 22·7 per cent. of salts in all, which in turn are composed of 28 per cent. NaCl, 47 per cent. $MgCl_2$, 15·8 per cent. $CaCl_2$. The Pacific Ocean contains 3·4 per cent. of salt only. In some lakes in Egypt and the Ararat district there is also Na_2CO_3, Na_2SO_4, and K_2CO_3. Some volcanic lakes contain free sulphuric acid, HCl, and boric acid.[1]

SEA WATER. This contains large quantities of NaCl, $MgSO_4$, $MgCl_2$, and $CaSO_4$; it has therefore a salty bitter taste. It contains traces only of potassium salts, $CaCO_3$, $MgCO_3$, phosphates, F, Ba, Sr, Mn, As, Cu, Pb, Ag, Li, S, and also minimal traces of all substances which form the earth's crust. It contains more bromine than iodine (there is 0·01 grm. of NaI per litre). The numbers of bacteria in sea water ordinarily diminish at greater depths, and in certain localities are almost absent at greater depths than 200 metres, whilst in other places they are found even at depths of thousands of metres.

On the average sea water contains 3 to 4 per cent. of salts, or less where there are large affluents as in the Baltic, the water of which contains 0·7 to 2 per cent. of salts only. It is less salt near the shores, and more salty, on the other hand, at great depths.[2]

The water of the Mediterranean is more concentrated than that of the Atlantic Ocean because few rivers flow into it and evaporation by the hot winds which blow across from Africa is very strong. The Red Sea is still more concentrated, owing to the absence of feeders (*see* preceding Note). Sea water has a total hardness of 750° to 1000° (French degrees) and a temporary hardness (French) of 44° to 70° (*see* Hardness *below*) ; we need not discuss the hardness of the Dead Sea, as it is of very little importance.

Sea water has a strong corrosive action on metals, which is best resisted by copper of all the common metals, especially if it contains five parts per thousand of arsenic. The resistance of iron is increased if it contains phosphorus or nickel and still better if it is coated with zinc ("galvanised").

PROVISION OF POTABLE WATER FOR COMMUNITIES

The nations of antiquity had only water from springs or from cisterns in which rain water was collected ; dug-out wells, constructed of masonry, were first devised by the Egyptians and then perfected by the Jews, who exercised much care in their construction. The Greeks, who had only used cisterns and springs, imported the use of wells from the East. The Romans at first used tanks and the bad water of the Tiber ; but as their power progressed the necessity arose of satisfying more efficiently the growing needs of the community, and the supply of water was recognised as a question of State ; covered aqueducts of stone were then constructed which carried the water from distances as far as thirty hours' journey.[3]

[1] According to the recent analyses of Stutzer and Reich (1907) the water of the Dead Sea has the following composition : sp. gr. 1·1546 at 17·5° ; 13·57 grms. per litre of KCl ; 87·88 of NaCl ; 23·84 of $CaCl_2$; 89·91 of $MgCl_2$; 3·68 of $MgBr_2$; 1·41 of $CaSO_4$; and a trace of iron. The total solids amounted to 220·2 grms. per litre.

[2] Recent analyses (1906) showed the following composition per litre : I. is from the Mediterranean near Tunis ; II. from the Atlantic near Dieppe ; and III. from the Red Sea.

		Acids :				Bases :				
	Density	$CaCO_3$	H_2SO_4	Cl	Br	CaO	MgO	Na_2O	K_2O	Total
I.	1·0287	0·126	2·516	21·676	0·072	0·617	2·365	15·584	0·510	38·97
II.	1·0239	0·099	2·120	17·830	0·060	0·519	1·993	13·410	0·413	32·42
III.	1·0270 at 10°	—	2·100	20·900	—	0·680	2·000	16·000	—	36·70

[3] Of the fourteen aqueducts constructed by the Romans the following are the most important :

Appia	(312 B.C.), 66½ kiloms. long, carrying	65,000	cu. metres of	spring	water	daily.
Aniente Vetera	(272 „), 64	„	„	268,000	„	river „
Marcia	(143 „), 91½	„	„	101,000	„	spring „

In other countries, such as Germany, France, and England, the use of spring water, which is abundant in those countries, was simply continued for some time; but other nations followed the example of Rome and constructed conduits of good water, recognising the disadvantages of tanks and wells, which became polluted and foul. But gradually, as the communities collected into large centres and in towns closed in by walls and fortifications, subdivided by narrow streets, wells were excavated for drinking water in the narrow yard of each house, in the vicinity of stables, latrines, and refuse heaps. Things remained in this condition until our times. Now only the utility of pure-water mains and of aqueducts is being realised. In many towns, and especially in the country, sad to say, there is still no potable water, in spite of the fact that it has been shown that many infectious diseases are caused by bad water and claim many victims every year in the towns, and especially in the country. (*Translator's note.*—These remarks must be taken to apply more especially to Italian conditions.)

The Chinese of antiquity already recognised the hygienic importance of pure and abundant water, and at the commencement of their civilisation they already knew how to bore into the ground and obtain good water from the subsoil, and possessed such wells, now called artesian wells in Europe, by thousands. To-day in the province of U-thung-khiao alone, in an area of 1000 sq. kiloms. there are over 10,000 of these wells, and some of them are 900 metres deep with a diameter of 10 to 15 cms. These wells were known to the Egyptians, but at a much later date, and the first artesian wells in Europe were constructed in the county of Artois as late as about 1000 A.D., being named after the locality. In 1600 to 1700 artesian wells were also introduced into Italy, Germany, and England, and since those times their number has continually increased up to the present.

TANKS. These serve to collect rain water in countries where springs are rare, especially in hot countries. They are excavated in the ground or rock, so that the water may remain fresh, and are lined with masonry or cement. But rain water finally undergoes putrefaction, on account of the impurities collected and carried down from the atmosphere, and should be filtered before use. The tanks of Venice have a layer of sand at the bottom, which serves as a filter. There are large and fine tanks at Constantinople, Alessandria, &c. There were 1430 public tanks in Italy in 1903, of which only 398 gave potable water.

WELLS. Ordinary wells are excavated down to the first water-level of the subsoil, the so-called freatic water, and their sides are clad with masonry. These are old-fashioned wells, open above and ready to receive any impurity whatever; the water is almost always polluted and is withdrawn in more or less dirty buckets mounted on a cord passing over a pulley; whenever rain is abundant they become turbid and to them typhoid infection is very largely due. In 1903 7000 of these existed in Italy for public use, distributed in 2700 communes. Instead of excavating wide and deep wells in masonry one may excavate a shallower well and then drive in at the centre an iron tube of a few centimetres diameter in order to arrive at a level where the subsoil water is deeper and purer. The lower end of the tube is perforated and protected by a grating which keeps out sand. A narrower tube dips into the first tube and is connected with a pump by which the water is drawn up. These wells are called American or Norton wells, from the name of the English engineer who first constructed them.

If iron tubes are sunk, by means of drilling, to greater depths, deposits of water are sometimes struck in the subsoil contained between two impermeable strata and coming from higher regions. When the upper impermeable layer is perforated the water often issues under pressure and may rise to the surface in the form of a fountain. If it does not rise to the surface it is pumped into reservoirs, from where it is distributed to the fountains and dwelling-houses. These wells are called artesian wells (*see above*). The artesian well of Grenelle at Paris is 647 metres deep, took seven years to drill (1833–1840), and supplies three million litres of pure water daily at a temperature of 37·7°. On the Place Hébert in Paris there is an artesian well, finished in 1888, 719 metres deep, which supplies water

Giulia, Vergine, Alsietina, carrying together 135,000 cu. metres of spring water daily.
Claudia (A.D. 52), 69 kiloms. long, carrying 101,000 cu. metres of spring water daily.

Of the ancient Roman aqueducts only four remain to-day (Marcia, Vergine, Felice, and Paola), which furnish a good third of the supply of potable water of modern Rome. At the time of Julius Cæsar there were in Rome no fewer than 970 public baths, which consumed 700,000 cu. metres of water daily. The thermal springs of Diocletian and of Caracalla were world-famous, and their vestiges remain to-day. All over Germany, France, and Spain there are ruins of large aqueducts and celebrated thermal wells constructed by the ancient Romans.

at 34·5°, has a mouth one metre wide, required twenty-two years to sink, and cost £100,000. The well at Mondorf, in Luxembourg, is 730 metres deep. At St. Louis, U.S.A., there was a very deep well which yielded rather sulphurous water, and it was decided to deepen it in the hope of obtaining a purer supply; when a depth of 1200 metres was reached the granitic rock of the primitive formation was met with, and it was thus found impossible to obtain water from the deeper well of other character than before. The water of artesian wells is characterised by the absence of nitrates, and by only containing traces of sulphates and of organic matter; on the other hand, it contains much sodium as carbonate and chloride and does not contain oxygen if it has not been in contact with the atmosphere, because this is absorbed by the ferrous and manganous compounds and organic substances of the strata through which it passes.

The deeper the well the hotter the water; below the first 30 metres the temperature increases by about one degree for every 20 to 30 metres of depth. However tanks and ordinary excavated wells only satisfy modern hygienic requirements very exceptionally, whilst artesian wells (drilled) often provide potable water. The firm of Piana of Badia Palesine alone constructed 5233 artesian wells up to 1901.

POTABLE WATER. DRINKING WATER. This is water which passes all requirements necessary for human consumption. These requirements are enumerated below. For twenty-five years medical men have debated the question whether impure water is an important factor in spreading infectious diseases, such as cholera, typhus, dysentery, &c.

The greater part of the German and English doctors reply in the affirmative, and of late years a large part of the doctors of all nations have come to share this opinion.[1]

It is difficult to detect these specific bacteria, as it is not easy to distinguish them from the innumerable perfectly harmless species; it has therefore been found safer to determine the amounts of impurities derived from the decomposition of animal residues by the action of bacteria which are the true carriers of infectious diseases.

Potable water should be colourless, odourless, limpid, not too cold in winter nor too hot in summer, of a temperature of 10° to 14°. It should be carried in iron and not in leaden pipes.

All town and village well-water contains, in larger or smaller quantity, the waste products of the animal organism. During infiltration through the soil these are transformed into numerous compounds which have not yet been well studied, and after a certain time are mainly transformed into nitrates. In the soil in contact with air, these products mainly produce carbon dioxide, ammonia, nitrites, nitrates, and chlorides. The phosphates, potassium salts, organic nitrogen compounds and ammonia are retained by the soil, whilst the chlorides, sulphates, and nitrates find their way into the wells or springs. When, however, the soil is no longer absorbent or is saturated, or only slightly aerated, ammonia and the decomposition products of the nitrogenous organic matter also find their way into the water. Thus not more than a minimal amount of chlorides and nitrates should be present in potable water; there should be no nitrites, much less ammonia, and exceedingly little organic matter (*see below*, Water Analysis).

[1] The mortality through typhus in Milan in 1880 was 10 per 10,000 inhabitants; gradually, as drainage and good water were introduced, the mortality from typhus diminished, and in the quinquennium 1901–1905 the average mortality from this cause was 3 per 10,000, that is, 180 deaths per annum, whilst if the conditions had been as in 1880 the number of deaths would have been 600. At Frankfort the mean annual mortality from typhoid from 1854 to 1875 was 6·2 per 10,000 inhabitants, whilst from 1876 to 1879—that is, after the introduction of a drainage system and drinking-water supply—it decreased to 2 per 10,000. In Hamburg the mean total mortality from 1845 to 1855 was 500 per 10,000 inhabitants, whilst after the drainage works, drinking-water supply, combustion of town rubbish, and sewage works were completed, the total mortality decreased to 220 per 10,000 per annum; that is to say, whilst Hamburg has 13,000 deaths per year, the number would have risen to 30,000 under the hygienic conditions of the past. In the United States there are 400,000 typhus cases per annum with 35,000 deaths, that is, 12 per cent.; whilst in Norway, Sweden, Germany, and Switzerland the percentage of typhus deaths is only 6 to 8 per cent. Very many honest people make a great humanitarian fuss about the horrors of war and do not trouble about the terrible war by which the nations suffer each year through insufficient attention to drinking-water supply and drainage.

The economic requirements of the modern State compel thought for the supply of good and abundant water to the population. At the International Congress of Brussels in 1896 there was indicated as a minimal limit for towns of moderate importance the supply of 150 litres of potable water for each inhabitant per twenty-four hours. In Germany the mean supply is 150 litres, in England 200 litres, in France 250 litres, and in America 500 litres. In Milan the mean consumption per inhabitant has increased rapidly of late years and has now risen to 250 litres.

The water of common wells is not ordinarily potable because it is very easily polluted, and therefore the supply of good water to the people to-day constitutes one of the most important problems of social economy, the solution of which should not be left in the power of private citizens, more or less ignorant, or in that of speculators, more or less dishonest, but should be attended to by the collective social community.

The distribution of water should not take place through leaden pipes for reasons which will be explained below, but through pipes of cement or, better still, of cast or wrought iron.

Abundant water for the people and not only for those in the towns but also for the countryside may be obtained in the following ways :

FROM RIVERS AND LAKES. When these are clean their water may sometimes serve for the supply of towns, but should always be filtered, as it contains many substances in suspension : clay, lime, eggs of insects and of worms, animal and vegetable remains, fibres, hair, &c. (*see below*, Filtration).

It is not desirable to leave this filtration to the consumers, as it will then be less careful and more costly ; the filtration should be carried out at the central distributing station. Bacteria are only partially removed by filtration. The water of rivers is often too cold in winter and too warm in summer. Works for obtaining potable water from rivers are established at Lyons, Zurich, Trieste, &c., where it is purified by filtration.

WATER FROM THE SUBSOIL. Water from the first water horizon, which is often found a few metres below the surface, can sometimes be used if taken from localities far from inhabited places. It does not matter if there are cultivated fields above, as the harmful substances and the greater portion of those which are soluble are retained by the soil, if the water horizon is sufficiently deep.

The water may be pure and its temperature more constant than that from a river. It is collected in channels and then in wells, from which it is raised by pumping to high reservoirs, from which it is distributed to the inhabitants.

The water of the subsoil which flows between two layers of impermeable clay is usually much purer and proceeds from higher levels. This water is raised by artesian wells (*see above*) and costs relatively little : from 0·2*d.* to 0·5*d.* per cubic metre.[1]

[1] In Milan the problem of potable water has been solved since 1889 by taking water from the subsoil at depths of 30 to 80 metres by means of wells excavated by the Canadian method, one at least each year, and there are now about forty wells which supply 25,000,000 cu. metres of water per annum, one-third of which is destined for the public service (street watering, fountains, urinals, public buildings, schools, markets, &c.). Whilst in 1889 only 4300 cu. metres were consumed for domestic purposes, in 1905 this figure had risen to 500,000, in 1900 to more than 3,000,000 cu. metres, whilst to-day the distribution of potable water in Milan is shown by the following figures :

USE		1909	1908	1907
Private	cu. metres	14,771,580	13,023,860	11,070,781
Works	,,	3,747,587	3,261,344	2,633,288
Public roads	,,	6,335,920	5,747,486	5,296,000
Total	,,	24,855,087	22,032,690	19,000,069

In Milan there are four wells in the Arena, which together yield 140 litres per second ; six wells at the Rondo del Sempione, 31 to 62 metres deep, yielding 200 litres per second ; one in the Via Parini, yielding 50 litres ; and six wells in the Loreto suburb, yielding 150 litres per second. In 1904 ten more wells were sunk in the Arena, which together yield 400 litres per second. In 1905–1906 ten more wells were sunk in the Corso Vercelli and Via Cenisio. Thus Milan to-day has a supply of more than 7000 litres per second, that is, 640,000 cu. metres per twenty-four hours. The cast-iron tubes of the wells are of 0·80 metre diameter, and the wells cost about £12 16*s.* per metre. Each well when finished, including all implements, &c., costs from £480 to £600, which is not inclusive of the installation of buildings and machinery (pumps, boilers, motors, &c.) attached to each group of wells (each installation costs from £4400 to £6000). The water is collected in two large reservoirs at the height of the two towers of Castello Sforzesco. The first was of iron, of the Intze type, and was constructed in 1893, with a capacity

AQUEDUCTS. When good water is not to be obtained from rivers or from the subsoil it is necessary to transport it from more or less distant lakes or natural springs, which yield fresh pure water, rich in carbon dioxide ; and before starting works of so costly a character it is necessary to study all the hydrological factors of the locality over a series of years in order to be certain of the yield and continuity of the springs during various seasons. It is not to be denied that when the springs are fed by glaciers or by snow they only flow abundantly in spring and summer. It is also necessary to carefully control the materials of construction and to exercise a vigilant supervision to prevent infiltration.

For potable water in general, but especially for water rich in dissolved CO_2 and air, it is necessary to avoid leaden pipes. The lead is dissolved most readily by aerated water, and in proportion to the amount of oxygen present, whether the water flows rapidly or remains stagnant in the pipes. Free carbon dioxide also facilitates solution of lead, though to a less extent than oxygen, whilst carbonates, on the other hand, are harmless. It is necessary to avoid replacement of the water in the pipes by air. In order to avoid all danger the use of leaden pipes for the transmission of potable water should be prohibited.

For large mains pipes of cement, or better of cast iron, are used, and for small mains wrought-iron tubes. Recent researches (Ruzickas) show that the nitrates in water dissolve notable quantities of lead. Galvanised (zinc-lined) iron tubes contaminate the water with zinc. Water which is not very hard and is rich in CO_2 and bicarbonates and much aerated attacks even iron pipes ; in such cases pipes of tinned iron are used, as is now done in many towns abroad (*i.e.* outside Italy) when iron and leaden pipes are rapidly corroded. In Germany glass tubes are used in certain cases.

The presence of organic matter greatly increases the corrosion of leaden and iron tubes.

Potable water supplied by aqueducts is generally dearer than that from artesian wells. In a project to supply water to the city of Cremona, with a conduit forty kilometres long (twenty-five miles) and at an expense of about £80,000, the water would have cost 1·5*d.* per cu. metre, whilst by obtaining it from the subsoil it will cost less than 0·4*d.*

The APULIAN AQUEDUCT will cost £5,000,000, and will furnish potable water to 228 cities and boroughs, at the rate of 60 to 200 litres per inhabitant per twenty-four hours.[1]

of 1200 cu. metres ; the second, of 1500 cu. metres capacity, was constructed in 1904, in armoured concrete, of cylindrical shape, with a flat base. The potable water-mains of Milan have to-day reached a length of 200 kilometres (125 miles) and supply water to about 7000 houses, which pay from 1·44*d.* to 1·92*d.* per cu. metre (4·2*d.* to 5·4*d.* per 100 cu. ft.).

The mean temperature of the drinking water of Milan is 13° and 15° in the mains ; the composition per litre of the water from various wells in 1905 was as follows :

	Grms.		Grms.
Total residue at 150°	0·145 –0·250	Lime (as CaO)	0·0500–0·0800
Loss on ignition	0·0400–0·0550	Magnesia (as MgO)	0·0130–0·0210
Organic matter (as oxygen)	0·0004–0·0007	Soda (as Na_2O)	0·0070–0·0100
Sulphates (as SO_3)	0·0040–0·0170	Iron	trace–0·0010
Nitrates (as N_2O_5)	0·0009–0·0036	Ammonia	zero
Silicates (as SiO_2)	0·0150–0·0180	Total hardness	9°–17° (French)
Chlorides (as Cl)	0·0054–0·0092	Permanent hardness	3°–5° (,,)

The subsoil water of Milan shows a dry residue of 0·500 grm. per litre at a depth of 4 metres, whilst at a depth of 18 metres there is only 0·220 grm. of dry residue per litre, and the amounts of nitrates and chlorides diminish in the same proportion.

[1] For twenty-five years the southern population of Italy have persistently demanded the construction of the Apulian aqueduct, which would have regenerated the life of that beautiful but neglected region.

Finally, in 1898, the Government approved of a law which arranged for the consideration of a definite project for conducting and distributing water from the Sele in Apulia. The laws of June 26, 1902, and July 8, 1904, declared it to be a work of public utility and claiming the attention of the State. A *consorzio* (partnership) was then established between the State and the provinces of Foggia, Bari, and Lecce, and the respective councils were invited to nominate their representatives on the Board of Administration.

The concessionaire was to complete the construction of the aqueduct by 1910 and was then to work it and maintain it for ninety years, after which it passed freely into the ownership of the consorzio, who were then to be responsible for its working and maintenance. The State contributed £4,000,000 to the cost and the provinces £1,000,000.

In an international competition the most advantageous offer was made by the Societa Ercole Antico e Soci, and the concession was awarded to them after they had deposited the necessary guarantee of £240,000.

The large canal of masonry into which the springs will be diverted, after passing through a first tunnel of about 400 metres, will pierce the Apennines by a tunnel which will be 19 kilom. (12 miles) long and will then discharge into the Ficocchia torrent, an affluent of the Ofanto River. In this way the water of the Sele springs, which actually form part of the drainage system of the Tyrrhenian Sea, will be diverted into one of the affluents of the Adriatic.

The grand canal, of navigable dimensions, will be constructed of masonry, will pass along a portion of the Ofanto Valley, turn to the east at the base of Monte Vulture, with a stretch, generally in galleries, as far as the neigh-

In order to supply the 300,000 inhabitants of Los Angeles, California, with potable water an aqueduct has been constructed of cement, 386 kiloms. long (241 miles), 4·58 metres wide, and 2·75 metres deep, costing £4,000,000, which takes water from the Owens River. The City of New York is constructing an aqueduct which will cost more than £40,000,000, and will deliver two million cubic metres of water daily, and thus the mean supply of water per head of the population will rise from 125 to 500 litres per day (500 litres = 114 gals.).

In 1893 the City of Paris disposed of 710,000 cu. metres of potable water, of which 290,000 cu. metres were obtained from various springs by means of aqueducts, of which the most notable is that from Havre, 102 kiloms. (64 miles) long and of 1·5 metres diameter. In 1906 900,000 cu. metres per day of potable water were available at Paris. The daily stock in the various reservoirs was 500,000 cu. metres in 1900.

WATER ANALYSIS. In order to decide whether a water is potable it is sometimes necessary to make a bacteriological examination, which should be conducted by a specialist, as well as a chemical analysis. The sample of water for this examination should be collected directly in sterilised bottles on the spot; these bottles must be immediately placed in an ice chest and sent to the bacteriologist, in order to avoid multiplication of the bacteria.

The samples for the chemical analysis should be collected in clean glass bottles, if possible with glass stoppers. In the greater number of cases the analysis of the water must show whether it is potable, and also whether it is suitable for various industries (*see below*). In order that a water should be potable the dissolved substances should not exceed the following limits: Per litre of water: Dry residue 0·300 grm.; organic matter (expressed as oxygen) 0·0025 grm., or expressed as permanganate 0·01 grm.; lime and magnesia (CaO + MgO) 0·200 grm.; sulphuric acid as sulphates (expressed as SO_3) 0·100 grm.; nitric acid (as N_2O_5) 0·012 grm.; chlorine (Cl) 0·030 grm.; ammonia, zero or not more than 0·0002 grm. of proteid ammonia; nitrites, zero; total hardness 30 (French). (Prescription of the municipal laboratory of Milan.)[1]

bourhood of Venosa, where the large branch for the province of Foggia will start; it will then proceed past the Palace of San Gervasio and Spinazzola, meeting the mountainous chain of the Murge, which it will follow to its extremity at the boundary of the provinces of Bari and Lecce. This canal will be 236 kiloms. (148 miles) long. To it will be attached the numerous branches which will distribute the water to the three Apulian provinces, which will together be 1600 kiloms. (1000 miles) long, and to which it will be necessary to add 800 kiloms. (500 miles) of pipe-lines for the urban distributing systems. It will also be necessary to construct 146 reservoirs of a joint capacity of about 263,661 cu. metres.

[1] We will here very shortly give the methods of water analysis.

The *dry residue* is determined by evaporating 300–350 c.c. on the water-bath in a tared platinum dish, then drying in an oven at 170° and weighing the residue. By heating to redness and reweighing, the *residue on calcination is obtained*, the organic matter being burnt.

The dry residue of a potable water should show no blackening or volatility on incineration, as this would indicate an excessive amount of organic matter.

The *lime*, *magnesium*, and *iron*, which are present in the water as bicarbonates, and the alumina and silica, are determined in the dry residue from at least 1 litre of water; the residue is dissolved in HCl and the silica separated on a tared filter; in the filtrate the iron and alumina are precipitated with ammonia, filtered, dried, and weighed; in the second filtrate the lime is precipitated with ammonium oxalate and filtered; in the third filtrate the magnesia is precipitated with sodium phosphate. All these substances are expressed in the results as oxides: CaO, MgO, Al_2O_3, Fe_2O_3, SiO_2; or as metallic cations: Ca, Mg, Al, Fe.

The *chlorides* are determined by titrating 100 c.c. of the water with an $\frac{N}{10}$ solution of silver nitrate, employing as indicator one drop of a concentrated solution of potassium chromate, which becomes red when all the chloride has been precipitated as white AgCl. The results are expressed in chlorine (Cl).

Nitrates are detected qualitatively by the blue coloration formed on adding a crystal of diphenylamine and 2 c.c. of strong sulphuric acid to 1 c.c. of the water; they are quantitatively determined by the Schlösing-Schulze-Tiemann method by evaporating 100 c.c. of the water to 10 c.c., decomposing with ferrous chloride and acid in a suitable apparatus, and measuring the nitric oxide evolved. The results are expressed as nitric anhydride (N_2O_5); 1 c.c. of NO at 0° and 760 mm. corresponds to 2·417 mgrms. of N_2O_5.

Nitrites are quickly detected qualitatively by adding to 50 c.c. of water 2 c.c. of starch paste and zinc iodide and 1 c.c. of dilute sulphuric acid (1 : 3), when a blue coloration is shown in a few minutes if they are present; or 1 c.c. of sulphuric acid and 1 c.c. of metaphenylenediamine sulphate solution may be added, which give a red coloration.

Sulphates are precipitated by barium chloride, and the results expressed as SO_3.

Ammonia is tested for qualitatively only, with Nessler's reagent (*see* Mercuric Iodide), after separation of the lime, magnesia, &c., with sodium carbonate. A mere yellow coloration shows the presence of ammonia, whilst a precipitate indicates a large amount.

Carbon dioxide, combined and half combined (CO_2), is precipitated by a measured excess of titrated lime-water, and the excess is then titrated back with a titrated solution of oxalic acid

PURIFICATION OF WATER FOR ALIMENTARY PURPOSES.

The use of chemical reagents is generally inadvisable, and they are only used in exceptional cases to diminish the hardness, as is explained below for industrial purposes, where the methods of diminishing the amounts of organic matter and eliminating iron are also explained.

To obtain potable water from suspicious sources, one has recourse to filtration or sterilisation.

FILTRATION. In order to eliminate suspended matter (and in part also the bacteria) and to decompose to a very small extent any dissolved substances, the following materials have been proposed: wool, sponge, felt, porous soil, blast-furnace slag, asbestos, bone charcoal, briquetted charcoal (consisting of a mixture of wood charcoal, bone charcoal, sawdust, and tar or asphalt, all compressed in a mould and then gently roasted). The organic materials, wood, felt, sponge, &c., are to be condemned as they assist the putrefaction of the water. Excepting the filters with a carbon base they all have a minimal absorbent capacity for the suspended matter, and filters which have little absorptive power end by making the water worse than before. As the filters are but little aerated only a minimal chemical decomposition of the dissolved matter takes place.

The large filters for towns consist exclusively of layers of sand, more or less fine; the more finely divided the suspended matter in the water is, the less water will pass in a given time through the same filtering materials of a given thickness and area. If, for example, 3 to 5 cu. metres of Thames water will pass through 1 sq. metre of a filtering medium in twenty-four hours, only 1·7 cu. metres of Elbe water will pass through in the same time, as the suspended matter in the latter is much finer. Large filters are formed of large tanks of masonry or iron; the water enters below, first passes through layers composed of gravel and clay, then through coarse quartz, and finally through fine sand with grains of 0·5 to 1 mm. diameter. The complete bed may be 60 cms. deep, and each single layer about 15 cms.

The bacteria are not at first retained, but when the pores of the filter bed are partially closed by mud from the water the number of bacteria diminishes noticeably. For example, at Zürich the lake water contains 50 to 2000 bacteria per c.c. before filtration; after filtration it contains only one to thirty bacteria per c.c. The upper layer of fine sand is changed more frequently as it easily becomes clogged.

In America these filters are improved by mixing aluminium sulphate with the sand.

For small domestic use various small and convenient filters are sold in which the water passes through compact but porous stone blocks analogous to the Chamberland filters, with good results. Malfitano has recently proposed filtration through semipermeable colloidal membranes, which would give the very best results from the bacteriological standpoint.

STERILISATION OF WATER. In order to sterilise water, that is, to kill all the pathogenic germs and diminish the organic matter, Schenilowa proposed in 1898 to add a solution of potassium permanganate and then filter through charcoal. This method is not always certain, even if calcium permanganate is used together with the electric current. In the same way the effects of adding small quantities of bromine as proposed by Sckumburg in 1899, or of 15 grms. of chloride of lime per litre proposed by Lode in 1900 (although Mason still insisted on its efficiency in 1909), are not certain, as has been clearly shown by Schüder,

The organic matter is determined with a $\frac{N}{100}$ solution of potassium permanganate which is first titrated with a solution of oxalic acid; the permanganate solution is added to 100 c.c. of the boiling water acidified with sulphuric acid. By multiplying the number of c.c. of permanganate used by 0·00316 the organic matter is expressed in terms of permanganate, whilst by multiplying by 0·0008 it is expressed as oxygen required per litre of water. It is estimated that one part of permanganate oxidises about five parts of organic matter.

The *total hardness* is due to the calcium and magnesium bicarbonates and sulphates, and is determined according to Boutron and Boudet with a titrated alcoholic solution of soap (20 grms. of potassium oleate in 520 c.c. of alcohol of 56 per cent. by volume), by adding this until a persistent froth is obtained on shaking strongly, indicating the complete fixation of the calcium and magnesium as calcium and magnesium soaps. The titre of the soap solution is determined by gradually adding a solution of 0·574 grm. of barium nitrate (dried at 100°) in a litre of water; 40 c.c. of this solution correspond to 22 French degrees of hardness.

The *permanent* hardness is due to the sulphates of calcium and magnesium only, and is determined by boiling the water for half an hour, filtering and making up to the original volume with distilled water; the bicarbonates are thus removed as they remain on the filter as insoluble carbonates.

The *temporary* or *transitory hardness* is deduced from the difference between the total and permanent hardness.

The burette of Boutron and Boudet for measuring soap solution indicates the results directly in grammes of calcium carbonate contained in 100 litres of water, that is, in French degrees. German degrees indicate the grammes of calcium oxide in 100 litres of water. Thus one French degree is equal to 0·56 German and 0·70 English degree.

by Engels (1902), and by Hetsch (1906); the last has found the ferric chloride method of Duyk to be useless (mixture of ferric chloride and sodium or calcium hypochlorite) and that the silver fluoride (tachiolo) of Paterno and Cingolani (1903), and the silver fluosilicate (isotachiolo) of Paterno are not always effective; Foa and Corsini (1904) came to the same conclusion with regard to tachiolo.

G. T. Moore in America (1905) uses 1 grm. of copper sulphate per hectolitre of water, but the soundness of this method is still contested, whilst more satisfactory results, though they are not yet definite, have been obtained with hydrogen peroxide.

Sterilisation by boiling has the disadvantage that all the spores of the pathogenic organisms are not killed, and that the gases and bicarbonate dissolved in the water are lost, thus altering its taste and digestibility. Heating under pressure at 110° (Vaillard's system) is preferable, but is never economical and is not adaptable to large scale production.

Of all methods of sterilisation proposed up to the present the safest and most economical is the treatment of the water with ozone. In 1891 Dr. Ohmüller first investigated the behaviour of the various species of bacteria in presence of slightly ozonised air, and succeeded in showing that none of the pathogenic bacteria, especially when distributed in water, resisted the action of ozone, even when much diluted. The bacterium subtilis (hay microbe) alone resists the action of ozone (and also a temperature of 110°), but it is a perfectly inoffensive organism both for man and for animals.

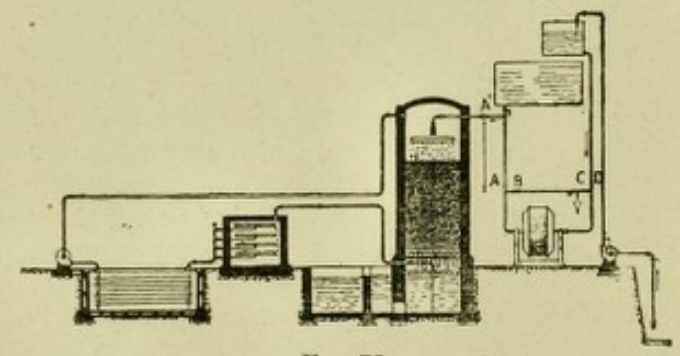


FIG. 78.

From that time the solution of the great problem of the sterilisation of water only awaited the time when it would be possible to obtain ozone cheaply and in large quantity (*see* Ozone, p. 187).

To-day the solution of the problem is an accomplished fact, and there are in Europe many important plants for the ozonisation of water.

In 1900 the firm of Siemens and Halske erected the first plant in their own works at Martinickenfelde, near Berlin, employing water from the Spree contaminated with Berlin sewage. Ten cubic metres were purified per hour with a current at 15,000 volts. The water first passed through the tube *D* into an upper reservoir and then through the tube *C* into a rapid Krönhke filter in order to remove suspended matter (Fig. 78). It was then pumped into another reservoir over a tower lined internally with cement and filled with pebbles below and sand above. A current of ozonised air entered at the base of this tower, whilst the water fell from above as a fine spray, meeting the current of ozone. The ozonised air was produced by the passage of previously dried air through an ozoniser. The water was collected at the base of the tower in reservoirs, and a few minutes afterwards it no longer gave any reaction for ozone and was sterilised. The Spree water contained 200,000 and sometimes 600,000 bacteria per c.c. The ozone first attacked the dissolved organic matter and then the bacteria.

The sterilisation was always satisfactory and the results were checked by Dr. Ohmüller of the Imperial Bureau of Hygiene in Berlin, Prof. Proskauer and Dr. Schüder of the Koch Institute. The quantity of ozone required varies with the nature of the water, being the greater the more organic matter there is present in the water; generally at least 1 cu. metre of ozonised air, containing 8 to 9 grms. of ozone, is required for each cubic metre of water; the water which has just passed through the ozonising tower should always still show a strong reaction for ozone with potassium iodide-starch test papers.

Artificial cultures of the microbes of cholera and typhus were also passed through the plant in order to ascertain whether they could be detected by careful special cultures in the water which had been treated.

In every case the water proved to be absolutely free from pathogenic organisms and only very few common microbes remained, such as are found in the purest spring water. After the action of ozone the water does not ordinarily contain more than five to ten microbes per c.c., and often none at all are shown by the gelatine cultures even on the third day.

After these satisfactory results the firm of Siemens and Halske erected a much larger plant at Wiesbaden in 1902, for a maximum production of 250 cu. metres of potable water per hour.

Shortly afterwards the same firm erected another plant, providing 60 cu. metres of water per hour, for the supply of all the drinking water of the Prussian city of Paderborn, with 50,000 inhabitants. Since that time Paderborn has been free from the typhus epidemics which had previously occurred every year. The cost of sterilised water at Wiesbaden, including all expenses, amortisation, and interest for the complete plant, is less than 0·3*d*. per cu. metre (1*d*. per cu. ft.). In the Russo-Japanese War the Russians used with advantage water-ozonising plants mounted on small carts.

At Nice the ozonisation of the water was commenced with Otto's apparatus in 1906 (120 cu. metres of water per hour). At Philadelphia a large plant for the ozonisation of water has also been erected (1905) and other plants have been recently erected in some French towns. In Italy an experimental plant has been erected at Casalmonferrato. In order to economise ozone De Fries obtains a more intimate contact between the water and the ozonised air by passing the emulsified mixture through a tower divided into many superposed chambers by means of finely perforated celluloid discs ; the contact between the water and the ozone may be prolonged by diminishing the influx, and therefore the rate of outflow, of both.

It was shown by numerous experiments in 1908–1909 that the ultra-violet rays have a bactericidal action, and that water can be sterilised by passing it over a mercury lamp emitting light rich in these rays. Some French chemists maintain that the phenomenon is due to a specific action of the ultra-violet rays, whilst many German chemists maintain that the sterilisation is due to the formation of ozone and hydrogen peroxide, which are produced by the action of the ultra-violet rays on water. Billon-Daguerre (1910) obtained a sterilisation of water twenty-five times more efficient than that obtained with the ultra-violet rays of the mercury lamp by using the rays of the invisible spectrum between 1030 and 1100 units (Angst) ; with a small special lamp five litres of Seine water, containing 29,000 colonies of bacilli coli per c.c., were completely sterilised per minute.

WATER FOR INDUSTRIAL PURPOSES

Every industry has its own special requirements, and sometimes that which is suitable for one is fatal to another. It is, therefore, necessary to always remember the uses to which a given water will be put, and to thus be guided as to its goodness by the results of chemical analysis, and sometimes also by bacteriological examination. We will enumerate briefly the principal requisites of water for certain important industries :

Boiler-feed Water should be as soft as possible and should not contain much nitrate or organic matter, in order not to form incrustations or corrode the boiler-plates (for treatment, *see below*).

Water for Breweries. The influence of the water on successful brewing is often exaggerated. Decomposing organic matter, with ammonia and nitrites and the attendant micro-organisms, is certainly prejudicial in the manufacture of beer. The lime contents should be moderate, because water with little lime (little hardness) w thdraws more extractive matter from the malted barley, and also more salts, including phosphates, but water containing much lime and magnesia (very hard) is harmful, because it renders the albumnoids insoluble.

Water for Spirit Distilleries should be pure and fresh, and should contain few micro-organisms and little NaCl and $MgCl_2$.

Water for Sugar Factories. If water rich in sulphates and alkaline carbonates, and especially in nitrates, is used, the crystallisation of the sugar is rendered more difficult, molasses are more abundantly obtained, and the sugar becomes deliquescent on exposure. Water rich in micro-organisms partially decomposes the sugar.

Water for Paper Mills. The presence of iron is harmful, and an excess of lime and magnesia decomposes the resin soaps.

Water for Starch Factories. This should be free from organic matter or suspended matter. Iron is harmful and so are all kinds of algæ or bacteria.

Water for Tanneries. The bicarbonates and sulphates of lime and magnesia are advantageous because they assist the proper swelling of the hides; but when the water is less hard, thinner, softer, and neater hides are obtained. If the water contains much bicarbonate, it is sufficient to add a little sulphuric acid in order to form a little sulphate. When the water is very hard, it is better to work the hides at a tepid temperature (about 20° C.).

Water for Bakeries should be potable, and is very harmful to panification if it contains decomposing organic matter, because the action of the yeast is then notably modified.

For **Glue Factories** the water should be rather soft, as otherwise the glue is lacking in limpidity and the solutions form deposits.

Water for Laundries, public and domestic, should contain little hardness as otherwise more steam is used and the washing is also bad.

Water for Cooking should not possess much hardness, in order that vegetables may be easily cooked.

In **treating Cocoons and Silk,** a water which is very soft dissolves much gummy matter and renders the silk less brilliant and resistant. On the other hand, the dyer encounters much difficulty in dyeing silk worked with very hard water, and the resulting shades are less brilliant.

Water for Dyeing should be limpid, free from iron, and should possess little hardness, as the colouring matters otherwise form insoluble lakes, producing impure shades, and sometimes also spots. In **Turkey Red Dyeing,** on the contrary, hard water is advantageous.

For **Wool and Cotton Spinning,** where the crude (wool) fibre or worked fibres (threads and tissues of wool or cotton) are washed, notable quantities of soap are wasted if the water is hard, and insoluble calcium and magnesium soaps are formed which adhere tenaciously to the fibre, producing serious inconvenience in dyeing and communicating a rancid odour to the tissues when they are stored for long in hot warehouses.

TREATMENT OF WATER FOR INDUSTRIAL PURPOSES. If water for feeding boilers has more than 15° of total hardness, it is necessary to correct this in order to hinder or prevent the incrustations which are formed on the internal walls of the boiler (boiler scale).[1]

In order to soften hard water, the numerous substances (water softeners) which one is advised to add directly to the water of the boiler are not generally to be recommended, because these are often useless or even harmful. The only one which has given good results is sodium carbonate, which forms powdery $CaCO_3$ and Na_2SO_4 with $CaSO_4$.

Also ammonium chloride appears to directly retain $CaSO_4$ in solution or to dissolve it when already deposited. It acts, however, incompletely and is dangerous for the bronze portions of the valves. Stannous chloride transforms calcium salts into $CaCl_2$, forming

[1] On heating the soluble bicarbonates of the alkaline earths, we already separate the corresponding insoluble carbonates in the form of a white powder. Furthermore, as the water gradually evaporates and new water is introduced into the boiler, to be evaporated in turn, the soluble salts are also concentrated more and more, and then commence to separate. For this reason calcium sulphate is abundantly formed in powder and more or less thick and hard scales. SiO_2, Fe_2O_3, organic matter and fatty acids derived from the lubrication of the feed-pumps, are also deposited.

A thin incrustation already renders the boiler a bad conductor of heat. Thus more fuel and higher temperatures are required to evaporate the same quantity of water. Scales 1 mm. thick cause a 10 per cent. greater consumption of fuel, and when the thickness is as much as 5–6 mm. 40–50 per cent. more fuel is consumed. Sometimes the heat is sufficiently great to render the boiler-plates red hot, and in this way they are easily worn out. If at such moments a part of the incrustation is detached, the water coming into immediate contact with the red-hot plate instantly produces so much steam and pressure that in certain cases explosions are caused. The powdery sediments are carried over by the steam and obstruct the pipes and lodge in working parts of the engine, in contact with which they cause continuous abrasion.

The cleaning of an incrusted boiler is a laborious and long operation. It also causes hindrance and interruption in working and damage to the boiler itself, because the blows of the hammer necessary to loosen the scale damage the plates.

The colour of boiler scale varies from yellowish grey to black, and in composition it consists mainly of calcium sulphate which is separated in the form of gypsum $CaSO_4 . 2H_2O$ if the temperature of the boiler is below 120° pressure less than 2 atmospheres), or $2CaSO_4 + H_2O$ or even $CaSO_4$ (anhydrite), according to the height of the temperature and pressure in the boiler; together with $CaSO_4$, there is always $Mg(OH)_2$, and more or less alumina. Incrustations from sea water contain no $CaCO_3$, but only $CaSO_4$.

stannous oxide, but is very dear. Barium chloride separates sulphates very well from tepid water in the form of powdery $BaSO_4$, which is readily deposited, and after emptying the boiler this can be removed with a jet of water.

But it is more rational and convenient to separate the principal incrusting agents before introducing the water into the boiler.

Kolbe proposed to add the necessary quantity (determined by analysis) of caustic soda dissolved in water, and thus to separate the bicarbonates and sulphates according to the following reactions, which, however, are very slow and occur best on heating.

$$(a) \quad Ca(CO_3H)_2 + 2NaOH = CO_3Na_2 + CaCO_3 + 2H_2O.$$

$$(b) \quad CaSO_4 + CO_3Na_2 = SO_4Na_2 + CaCO_3.$$

For economy, and in order to avoid heating, it is better to add lime-water in order to diminish the temporary hardness, and at the same time to use a solution of sodium carbonate to diminish the permanent hardness. Calculated quantities of clear lime-water are added, remembering that an aqueous solution of lime-water, saturated and clear at ordinary temperatures, contains 1·3 grms. of $Ca(OH)_2$ per litre, and that 0·74 grm. of calcium hydroxide $Ca(OH)_2$, that is, 600 c.c. of the clear solution, are required for each French degree of temporary hardness per 100 litres of water. (One French degree = 0·7 English degree.) In this way the bicarbonates of Ca, Mg, and Fe are precipitated as neutral insoluble carbonates: $Ca(CO_3H)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O$; on separation the carbonates carry down with them the greater part (about two-thirds) of the suspended and dissolved organic matter, and, therefore, a little more than the calculated quantity of lime-water is always added. The water thus treated settles with difficulty, and it is convenient to filter it in order to obtain a perfectly clear liquid, thus also re-absorbing carbon dioxide from the air which had been lost and so imparting a normal taste to the water.

By this method calcium sulphate is naturally not separated and magnesium salts only incompletely (the separation is more complete on heating).

ALUMINIUM SULPHATE, $Al_2(SO_4)_3$, is sometimes employed instead of lime and gives better results than alum, which was once used. It clarifies turbid and coloured waters very well. The bicarbonates form basic sulphate or hydroxide of alumina in the state of a voluminous precipitate which, during deposition, carries down with it suspended and dissolved organic matter in the form of lakes. 12 grms. of anhydrous aluminium sulphate or 2·3 grms. of the crystallised sulphate are used for each degree (French) of temporary hardness per 100 litres of water. The reaction is as follows:

$$Al_2(SO_4)_3 + 3Ca(CO_3H)_2 = 3SO_4Ca + 2Al(OH)_3 + 6CO_2.$$

However, the permanent hardness is increased through the formation of calcium and magnesium sulphate, and this method is therefore suitable for the treatment of water for domestic use but not of boiler-feed water.

In order to diminish the permanent hardness (due especially to calcium and magnesium sulphates) sodium carbonate is advantageously employed in the proportion of 1 grm. of dry (Solvay) soda for each (French) degree of permanent hardness and 100 litres of water. In the case of water the permanent hardness of which is great compared with the temporary hardness, a solution of sodium silicate (soluble glass) is advantageously used, containing 1·5 grms. of combined SiO_2 for each (French) degree of hardness and 100 litres of water. It is advisable to also add an equal quantity of soda so that the bicarbonates may be better separated.[1]

[1] In 1873 De Haen advised the treatment of water by the following method, which has given good results in practice: The water is heated to 40°–50° and treated with the necessary quantity of $BaCl_2$ in order to decompose all the sulphates (2 grms. of anhydrous barium chloride for each (French) degree of permanent hardness and per 100 litres of water); lime-water is then added in such quantity that after ten minutes of strong stirring clearly visible flocks are precipitated. If the amount of bicarbonate is small compared with that of sulphate, the clarification requires much more time because there is a lack of $CaCO_3$, which, during precipitation, also carries down the $BaSO_4$. This difficulty is overcome by adding more $Ca(OH)_2$ and then passing CO_2 (flue gas) through the water.

To avoid the formation of froth in boilers fed with treated waters, containing soda and sodium sulphate, the use of barium carbonate and calcium hydroxide has been proposed. The process would also yield clear water in less time.

Bohlig (1877), F. Fischer (1877), and Gunsberg (1878) treat the water with magnesite which has been heated to dull redness. When thrown into water this is slowly transformed into $Mg(OH)_2$, which reacts on bicarbonates (but only completely on heating) in the same manner as $Ca(OH)_2$. The magnesium carbonate which is so formed reacts by double decomposition with $MgSO_4$. If the sulphate is in excess compared with the carbonate which is so formed, then it is necessary to pass CO_2 (flue-gas) through the water to convert $Mg(OH)_2$ into $MgCO_3$.

The employment of hydrochloric acid to transform the carbonates into soluble chlorides has also been

In no case is it possible to completely eliminate the hardness of water even if an excess of the reagents is added, because the following reaction is partially reversible:

$$CaSO_4 + Na_2CO_3 \rightleftharpoons CaCO_3 + Na_2SO_4.$$

AUTOMATIC PLANT FOR THE PURIFICATION OF BOILER-FEED WATER.

Many forms of plant have been proposed, but they are all based on the idea of simultaneously passing through a pipe a definite quantity of water and a corresponding quantity of solutions of sodium carbonate and lime-water in the proportions required by the permanent and temporary hardness of the water under treatment. The plants of Gaillet, Dervaux, Dehne, &c., are much used. Figs. 79 and 80 illustrate Dervaux's plant. The water passes into the vertical pipe *E* from the pipe *P*, which is united to the main *A*, and is automatically regulated by means of floats. Clear lime-water passes simultaneously through the tube *U*, which is fed by the reservoir *S*. By means of the siphon *Q N*, sodium carbonate solution also passes in from the vessel *B*, which is fed by the reservoir *C*. The mixture is homogeneous and the sulphates and carbonates which are precipitated collect at the bottom of the large reservoir *D*, and may be removed from time to time through the cock *O*. The turbid water is clarified by passing slowly and by a lengthy path along the numerous inclined plates *M*, which are fixed in the large vessel, and the deposit continually falls to the bottom. In order to finally obtain the water in a perfectly clear condition, it passes through the filter *F*, formed of a compact layer of beech-wood shavings, before issuing from the tube *T*. The sodium carbonate solution is maintained at a constant concentration because there is always an excess of solid sodium carbonate in the perforated container *Z*. The lime-water is prepared in the conical tank *S*, at the bottom of which quicklime is introduced through the tube *J*, and the water entering through the tube *V* becomes saturated and clarified as it rises. The final suspension of fine calcium carbonate which is always present, together with the lime, is deposited in the cone *K*, and removed through the tube *G*. The insoluble impurities in the lime are removed through the cock *L*. The course of the water from *H* to the exit *T* takes more than an hour, and thus it is well clarified. Plants are built to produce 50, 100, and even 250 cms. of purified water per day, and the velocity of the water in the plant is regulated in such a manner that it issues in a clear condition.

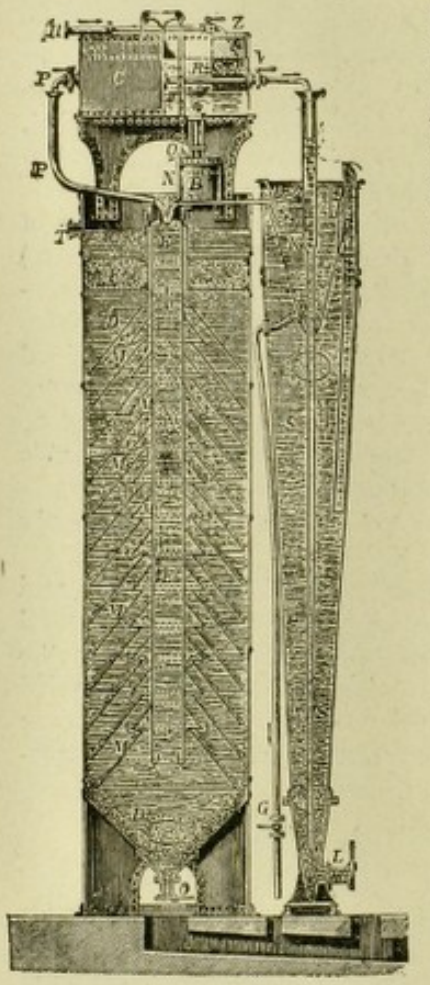


Fig. 79.

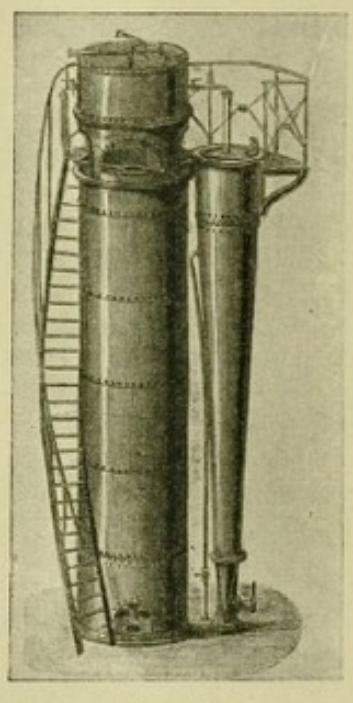


Fig. 80.

Gaillet's plant is very similar to that of Dervaux, but the lateral tank containing lime is dispensed with, and the lime-water is prepared in a small vessel above and close to that in which the soda solution is prepared. In other plants the vessel in which the lime-water is prepared is placed centrally inside the purifying tower. Some plants, finally,

proposed, but the slight excess of HCl damages the boiler. HCl must not be employed if the water contains much magnesium bicarbonate, because the $MgCl_2$ which is then formed damages the boiler at high temperatures by liberating HCl. It is advisable to pass water treated with HCl through tubes containing lumps of limestone before its introduction into the boiler.

are fed with the exact necessary quantity of sodium carbonate by means of a bucket wheel the velocity of which can be modified as desired.

ELIMINATION OF ORGANIC MATTER. If this is suspended, or even in solution, the use of metallic iron is advisable. With water this forms ferric hydrate, which separates almost all the organic matter. In 1892 Piefke proposed to pass the water through a revolving drum containing spongy iron and iron turnings. In Paris 4000 cu. metres of Seine water are treated per twenty-four hours by means of 2000 kilos of iron by Anderson's process. This same Anderson process is also used at Monaco and Nice. The organic matter which gives water a yellowish tint is readily separated by adding a powdered mixture of chalk and a ferric salt and then filtering.

SEPARATION OF IRON FROM FERRUGINOUS WATERS. Many waters obtained from the subsoil contain dissolved iron which is ordinarily in the state of bicarbonate or of organic compounds. Even if the liquid is clear when obtained, it becomes opalescent and then forms a brown deposit after standing for a little time in the air. Water in this condition is unpleasant to drink, because there is always uncertainty as to whether the impurities consist only of iron or also of other substances. The separation of the iron is not very easy and simple aeration is not always sufficient.

During the last few years, various processes have been invented, but the best results have been obtained with those similar to the type which we will describe and which represents the plant erected in 1903 at Frankfurt-on-Oder by the Städtereinigungs Gesellschaft of Wiesbaden for ferruginous water obtained from a peaty subsoil. The water of these

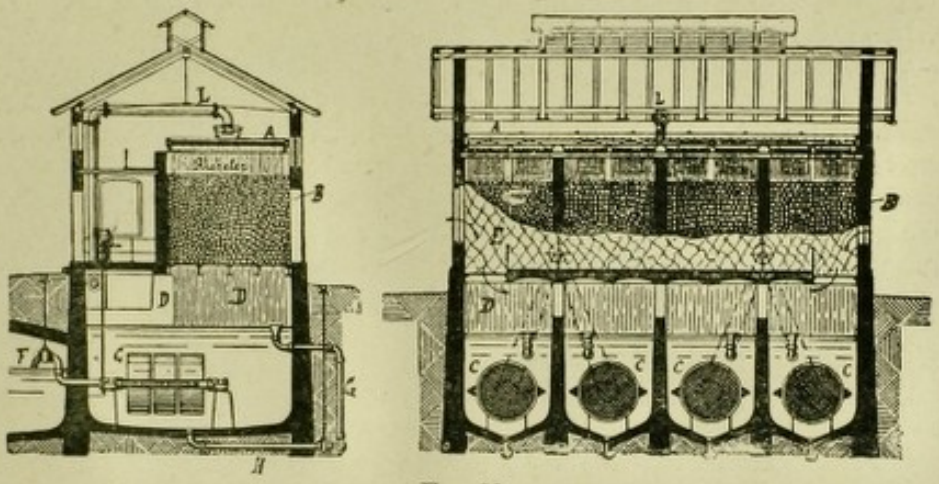


FIG. 81.

soils, which is yellowish and opalescent, is raised by means of a pump to the top of the tube *L* (Fig. 81) and is then distributed by ramified tubes over a perforated plate *A*, which subdivides it into a fine spray, on to a layer of gas coke in large pieces, *B*, contained in a sort of stout galvanised iron wire cage about one metre high in such a way that the air circulates through the coke in every direction, energetically oxidising the iron dissolved in the water and separating it in the form of insoluble oxide.

After passing over this first layer the water is poured in the form of spray over a second layer of coke which is not indicated in the figure, and then, still as a spray, *D*, through which much air passes continuously, it falls into the tank *C*, which is always kept full so that the water may penetrate through the rapid Kröhnke filters full of sand, issuing as a clear liquid from the central tube of the same filter, when it is collected in the tank *F*.

The deposits from the tank *C* are always able to escape by the tube *H*, and the excess of unfiltered water passes away through the tube *G*. When the filters are obstructed, they are washed abundantly with water, whilst being kept in motion by suitable tools in order to stir up the sand of the filter.

In cases in which humic substances are abundant, the separation of iron from the water is more difficult and necessitates repeated treatment. The separation of the iron occurs more easily when the carbon is coated with ferric hydroxide, because it is this substance which acts catalytically, yielding oxygen to oxidise the humic substances and continually being regenerated by means of the atmospheric oxygen (hence the aeration). For this reason

the addition of ferric salts to the filter or contact medium is often advised. We have seen on p. 106 how the study of colloidal solutions may also serve to explain this process of the separation of iron from water.

PURIFICATION OF EFFLUENT WATERS

With the progress of chemical industry and increase of population in large centres, the establishment of hygienic standards became necessary and important for the protection of the public health. The large drainage systems of the cities did not suffice, because the sewage water often defiled the watercourses and even carried infection to great distances. It was thus necessary to have recourse to a system of rational purification of effluent and sewage water. Mere clarification did not suffice, because organic matter remained dissolved and this easily underwent putrefaction and became dangerous to vegetation and fishes. Even chemical precipitation is not always sufficient because lime, aluminium sulphate, and ferric sulphate or calcium hypochlorite only separate the coagulable albuminoids and suspended matter, and the quantities of sludge which are produced are very large and are not willingly employed by agriculturists: at Leipzig 2,000,000 cu. metres of effluent water are purified in this way per annum, consuming 8,000,000 kilos of iron sulphate and producing 100,000 cu. metres of mud. During the last few years good results appear to have been obtained with colloidal ferric hydroxide in the proportion of 1–1000 which is completely precipitated, carrying down a large part of the organic matter. True purification is only obtained when all the organic matter is decomposed and transformed into nitrates, N, CO_2, H, hydrocarbons, &c.

Certain micro-organisms are alone able to produce this kind of transformation and it is actually to these that the decomposition of stable manure distributed on the fields and of the corpses in the cemeteries is due, and the same is the case with the natural purification of the waters of rivers into which the sewage of the cities is poured.

Ternary compounds (organic compounds of C, H, and O) are more especially destroyed by aerobic bacteria, which when present in water are obliged to obtain the oxygen which they require from the organic matter which is present, thus decomposing it. Quarternary organic substances (that is, such as contain nitrogen) are gradually decomposed by various anaerobic and aerobic bacteria, being first transformed into albuminoids, peptones, and amino compounds, and these then into ammonia, nitrites, nitrates, methane, N, H, and CO_2.

It is thus not easy to provide for the purification of the immense quantities of water which accumulate in the sewers of populous cities. One need only remember that Paris with its system of "tout à l'égout" daily produces 1,000,000 cu. metres of sewage water which cannot be passed into the watercourses without having undergone purification, because each litre of this water contains 1·250 grms. of dry residue, two-thirds of which consists of mineral matter and one-third of organic matter. London separates weekly from 80 to 100 tons of bulky detritus and floating bodies in its sewage water, and thus also Milan [1] and all important cities have to devise some method of purifying the water from their sewers. During the last quarter of a century the favourable results obtained in Paris and Berlin by a simple and very economical system of purification have commenced to be collected. The sewage water is distributed over immense surfaces of cultivated ground, or simply of ploughed land, which retain the fertilising principles, and the water is collected at a depth of a few metres in enormous drainage tubes and is clear and relatively pure. The City of Berlin has already devoted to this purpose 11,000 hectares (26,800 acres) of land, and in

[1] In 1904 the sewers of Milan collected the refuse of 150,000 inhabitants, the new drainage works being still incomplete, and this was distributed over 2800 hectares of ground (6830 acres), of which 2000 formed a sewage farm. When the drainage scheme is complete, an area of irrigated ground of 1 hectare (2·44 acres) will be used per 300 inhabitants. In 1902, however, Menozzi recommended the employment of 1 hectare of ground for every 90 inhabitants, and not to exceed 150 inhabitants, in order to unite the maximum hygienic advantage with the greatest agricultural profit. In 1907, 5000 hectares (12,200 acres) of land were already used for the deposition of the Milan sewage.

The farms which are irrigated with the sewage water to-day give eight or even nine crops per year. It is found advantageous to interrupt the irrigation for a few days occasionally in order to give the bacteria time to decompose the substances deposited on the surface and in the interior of the soil. Rigorous inquiries conducted in various countries and also in Milan show that the regions in which sewage farms are placed have not been subject to any epidemics proceeding from this cause. Even the animals fed on the fodder from these meadows do not suffer any ill results (experiments conducted in Berlin in 1907). The ammonia, hydrogen sulphide, suspended matter and alkaline reaction which are always found in sewage water are destroyed by this purification, and even the organic nitrogen and phosphoric acid are markedly diminished. Effluents containing 10,000,000 of bacteria per c.c. contain less than 400,000 after the third day of culture.

Paris a smaller quantity, 3700 hectares (9000 acres) under vegetables and 1800 hectares (4440 acres) of meadow, are employed, but these are subjected to more intense cultivation, so that 40,000 cu. metres of water are passed per year over each hectare (2·44 acres) of land. But in order to avoid saturation or obstruction of the soil, the irrigation is interrupted during twelve hours in the twenty-four, and for some days in the week, in order to allow the chemical-biological phenomena to take place more rapidly, because on these phenomena, in which not only chemical and mechanical processes but more especially the life processes of the aerobic bacteria take part, the proper purification of the sewage water depends. Pucch showed in 1908 that even as much as 600,000 cu. metres of water per annum can be passed over each hectare of land.

A new process, called the biological process, which has greatly extended during the last few years, is nothing else than an improvement of that already described, and the decomposition of the noxious substances is carried out progressively by relying upon various

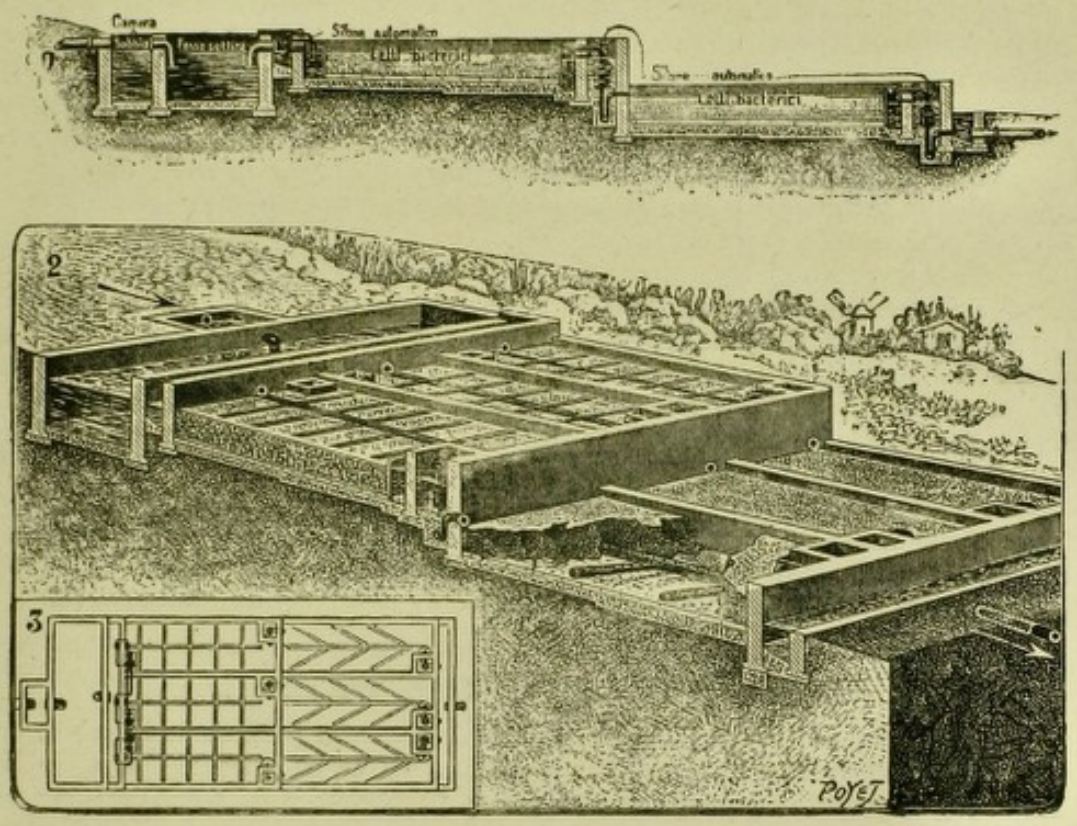


FIG. 82

species of micro-organisms at various periods. In this way these co-operate in a marvellous manner to perform their purifying work. We give a sketch of an installation visited by the writer in 1902 at Grünewald, a suburb of Berlin, erected by the Städtereinigungs Gesellschaft of Wiesbaden, to purify the effluent sewage water from one part of the quarter and the large quantities of washings from the cattle waggons in the adjacent railway station before these are turned into the outlet canal.

The water enters by the pipe *O* into a sand-filter, and then into a reservoir of masonry sunk into the ground and covered by a vault and divided into three chambers (septic tanks, Fig. 82: section, aspect, and plan). On passing slowly from the one portion into the other, the suspended organic matter in the water is deposited and gradually putrefies through the action of the anaerobic bacteria, becoming soluble and thus more easily oxidisable. In these septic tanks only very small quantities, if any, of deposit are left.

The water is then distributed alternately to a lower level by means of automatic syphons and perforated tubes on to bacterial or oxidising beds formed of tanks of masonry, at the bottom of which are perforated drainage tubes on which lies the first layer of 30 cms. of gas coke in large pieces, then 20 cms. of medium-sized pieces, and then a third layer of 50 cms. of small coke (5 to 30 mm. diameter). At this point the perforated distributing tubes are placed, and are covered or protected by a layer of 30 cms. of coarse coal cinders.

The water which fills one of the bacterial beds remains stagnant for two or three hours, after which it is removed by means of a syphon on to a lower bed constructed in the same manner. The other upper bed is then at once filled with new water, whilst the first remains empty, and thus aerobic bacteria multiply with the help of the atmospheric oxygen, nitrifying the nitrogenous organic and ammoniacal matter retained by the coke so that this is destroyed. Thus the bacterial beds do not become obstructed and do not lose their activity. The water which issues from the first upper bacterial beds is almost clear, and when it is removed from the lower beds after about one and a half hours it is clear, colourless, and odourless; whilst the sewage water before the purification is blackish, turbid, and fœtid. The water thus purified is no longer able to undergo putrefaction.[1]

Each time that the water is removed from the bacterial beds, they must be left empty in contact with the air for one or two hours, in order to revive the activity of the oxidising bacteria, and the work thus alternates continuously from the one bacterial bed to the other. In England and America bacterial beds which work continuously are also much used. In these the water is distributed in the form of a very fine spray, and it is thus extensively aerated, so that a greater effect is obtained for the same surface of the bed. These plants, however, are more costly and require continual repairs to the distributing apparatus.

New bacterial beds only acquire their full activity after some weeks in summer, or some months in winter. During the last few years less importance has been attached to the action of such septic tanks. It has also been found that nitrifying bacteria develop quite well even on beds of peat.

In order to ascertain whether a sewage water has been purified by a biological process and has lost its tendency to putrefy (that is, to evolve an unpleasant odour and hydrogen sulphide), Spitta and Weldert in 1906 proposed the treatment of a small sample with indonaphthol blue: if the water has been well purified it does not decolorise this latter in five or six hours; and if it is impure it decolorises it even before hydrogen sulphide is formed. According to Fendler and Stüber (1909) the test is carried out in the following manner: 20 c.c. of the water under examination are treated with 1 cm. of HCl, 0·3 c.c. of a 1 per cent. solution of paraminodimethylaniline sulphate and 0·3 c.c. of a 1 per cent. hydrochloric acid solution of sublimed ferric chloride (hydrochloric acid of sp. gr. 1·125); as soon as hydrogen sulphide is formed even to the extent of 0·5 mgrm. per litre, the blue colour immediately appears. Hydrogen sulphide may also be detected by means of lead acetate paper.

DISTILLATION OF SEA WATER

During short voyages vessels carry fresh water for drinking purposes in barrels of wood, or better still, in iron tanks. But after some days the water putrefies; so that during longer voyages, and in battleships, it is necessary to produce it on board from sea water by distilling this in apparatus which occupies little space and utilises the heat efficiently. It is impossible to use the condensed water from the engines for human consumption, because it contains much contamination from the evil-smelling oil with which the pistons are lubricated. As distilled water contains no dissolved air and is tasteless, it is advisable to aerate it by suitable means. The vessels of the German Navy carry plants which distil 1250, 2400, or 4000 litres per twenty-four hours, and are represented diagrammatically in Figs. 83 and 84.

They have two cylinders, *A* and *B*, of about 0·4 metre diameter. The heating and distillation of the sea water contained in *A* are carried out by a group of tubes immersed in the water itself in which steam circulates under pressure. This steam passes in through the tube *d* from suitable boilers, whilst the condensed steam in *e* passes into the condenser and water-separator *g*. The steam from the sea water which is evolved in *A* passes a perforated copper diaphragm, *a*, and then another one, *c*, before entering the delivery tube *m*, so that any small drops of water and traces of salt carried over by the steam are retained

[1] Exact experiments conducted under the auspices of the Berlin Municipality have shown that the sewage water contained 70 mgrms. of suspended organic matter per litre, and that after purification it did not contain even 1 mgrm. Before purification it contained 30 to 40 mgrms. of ammoniacal nitrogen, and afterwards only 0·07 mgrm. The dissolved organic matter before purification reduced from 126 to 147 mgrms. of potassium permanganate per litre, whilst after purification only 18 to 22 mgrms. were required. The number of bacteria, which at first averaged 1,000,000 per c.c., was afterwards about 45,000. The quantity of nitrates was increased in the process through nitrification by the aerobic ferments.

In the case of epidemics it is advisable to subject such water to sterilisation by means of ozone (*see* Ozone) in order to completely destroy the pathogenic bacteria. This can be carried out at a cost of about one-third of a penny per cubic metre in the case of large installations, or even more economically by means of small quantities of calcium hypochlorite.

The steam condenses in the group of tubes *m* of the refrigerator *B*, and the water is collected in *p*, together with the hot water proceeding from the condenser *g*, through the tube *v*.

The water thus condensed is completely cooled by the other group of tubes, *o*, and issues from the lower tube *r* in order to be used or to be passed through a carbon filter. The water from the cooler enters cold from the tube *i*, and escapes hot from the tube *k*, after which it serves to increase the water supply in *A* as fast as it is distilled. The air which is developed by the water in the refrigerator escapes from the tube *t*, and is conducted into *A*, where it mixes with the vapours of the distilled water and remains dissolved in them after condensation. The water thus obtained no longer has the disagreeable taste of boiled non-aerated water.

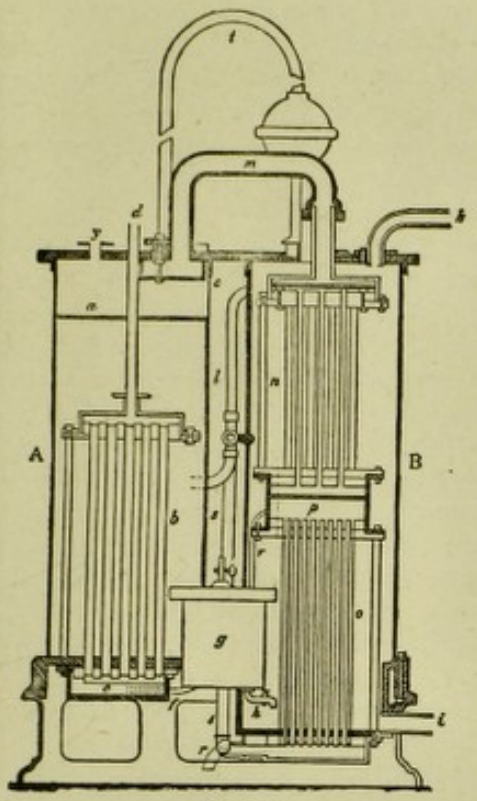


FIG. 83.

Pamphlette (Ger. Pat. 47,219 of 1888) distils sea water under reduced pressure and aerates it simultaneously.

H. Ferguson (Ger. Pat. 53,397 of 1889) employs steam dried before condensation, as otherwise the water has no taste.

DISTILLED WATER

For laboratory use and also for certain industries chemically pure water is required and is obtained by distilling ordinary water with suitable precautions.

The distillation is carried out in tinned copper boilers, furnished with a special still-head and with a serpentine cooler of block tin. Violent boiling is avoided in order to prevent the steam from carrying over impurities. The first portion of the distillate is rejected because it contains carbon dioxide and ammonium carbonate, which are recognised by the turbidity which they produce with a solution of lead acetate. If the water contains magnesium chloride, a little lime is added before distillation in order to prevent hydrochloric acid from distilling. In this case, however, the first portion of the distillate is rejected because it contains ammonia from the ammoniacal salts: the remainder of the distillate is pure water. But it is necessary to leave the last portion of the water (about a quarter) undistilled, because certain organic substances commence to decompose, yielding impure distilled water.

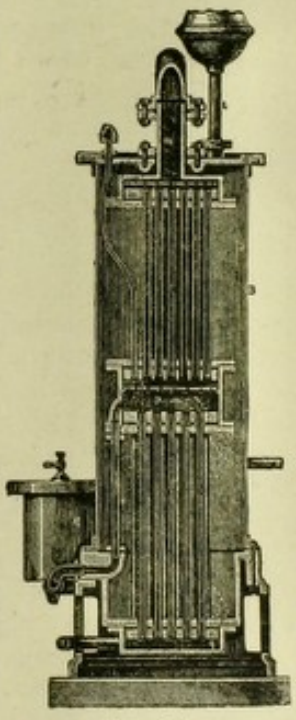


FIG. 84.

Stas added 4 to 5 per cent. of a concentrated solution of potassium permanganate to the water. He then let it stand for twenty-four hours and added a further 1 to 2 per cent. of potassium manganate solution, and sometimes a further quantity of fairly concentrated potassium hydroxide solution (in order to obtain a slower decomposition of the permanganate) before distilling. At the commencement of ebullition the heat supply was moderated because much foam was at first formed. After the twentieth part of the water had passed over he commenced to collect pure distilled water free from organic matter. In order to obtain water absolutely free from inorganic matter, the still-head should be provided with diaphragms which retain the particles of water and salt carried over by the steam. Distilled water has at first a special odour which it loses on standing in the air or filtering through wood-charcoal which has been previously heated to redness. It should leave no trace of residue on evaporation, should not become turbid with silver nitrate or lead acetate, and, in fact, should not give any chemical reaction which points to the presence of impurities. These tests are made on water after boiling, to remove carbon

dioxide which may have been absorbed from the air, and which reacts with silver and lead salts.

In the apparatus illustrated in Fig. 85, we see the boiler *a*, which is filled to two-thirds of its capacity with hot water coming from the upper part of the receiver *f* through the cock *c*. The water is heated by indirect steam under pressure, which circulates in a coil, *g*, terminating in a throttle-valve under the boiler. The steam which distils escapes through *c* and is made to follow a tortuous path before it arrives at the coil of the condenser *f*. By this means the impurities and water-spray carried up by the boiling liquid are retained. The boiler is occasionally emptied through the lateral cock, so that no deposit may be formed.

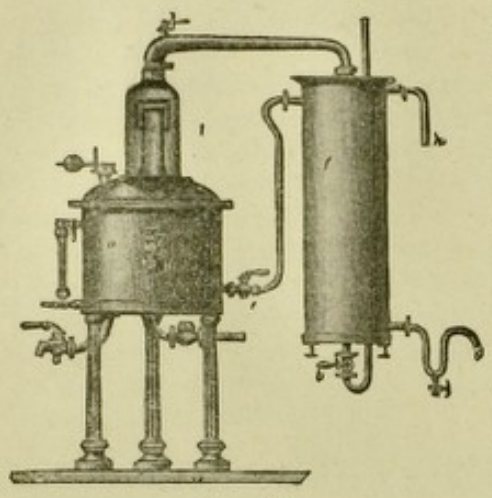


Fig. 85.

The condenser water enters from the cock *b* below and escapes above where it is very hot from the tube *h*. The pure distilled water issues cold from the tube *g*. By means of a similar plant on a large scale as much as a thousand litres and more of distilled water are produced per day.

In chemical laboratories an apparatus similar to that illustrated in Fig. 86 is often used, in which steam from a water-bath is used which heats a steam oven with double walls for drying chemical preparations. The heat supply takes the form of an ordinary stove which is heated with coal or wood.

NATURAL MINERAL WATERS. It is impossible to explain what may be called a mineral water to-day. The current definition is debased by the influence of other than scientific factors. Commercialism, unscrupulous doctors, and complacent or interested chemists, all take part in the trade of the miracle-mongers and agree to deceive once more that larger part of the world which always consists of fools. In the past those waters were always called mineral waters which were not polluted and contained an excess of mineral salts, at least 1 grm. per litre; or which contained certain substances, such as arsenic, lithium, iodine, and CO_2, to which definite therapeutic effects were attributed. To-day waters are considered to be mineral waters when they only contain $\frac{1}{2}$ grm. per litre of mineral residue, and alchemistic traditions have been revived by attributing to these a definite and specific therapeutic action. If in the valuation of mineral waters a rigorous system were to be followed, including positive and indisputable evidence of their medical effects, then very few of the innumerable waters of to-day would survive.

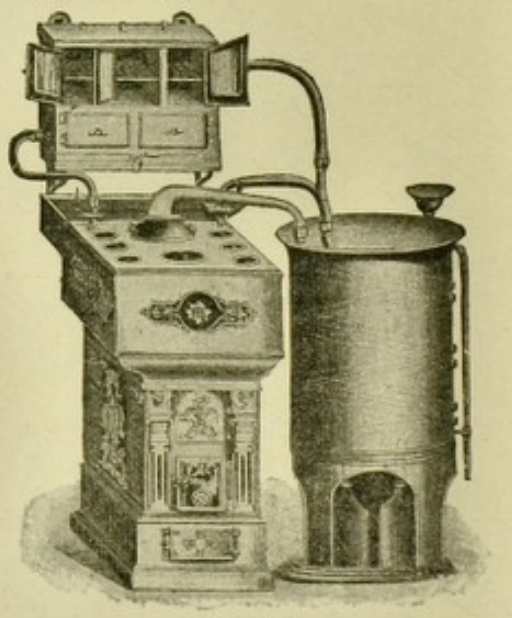


Fig. 86.

After these considerations we may say that the composition of the so-called natural mineral waters is very varied and that in many cases their temperature is very high.

Among the many possible classifications we may choose the following, not taking into account the factor of radio-activity which however appears to be present to a greater or less extent in almost all mineral waters, and the effects of which are still somewhat doubtful, although an explanation has thus been sought for the therapeutic deficiency of waters containing small amounts of salts.

We must remark that to-day it is believed to be possible to distinguish natural mineral waters from artificial imitations by means of their different electric conductivity and of the radio-activity of some of them. But both factors can also be imparted artificially.

I. **Alkaline Mineral Waters.** These contain much soda and CO_2 and few alkaline earths, Na_2SO_4, and NaCl.[1]

[1] These are then divided into the following varieties:

(*a*) *Simple Acid Waters.*—These contain little solid residue and not less than 400 c.c. of CO_2 per litre (Heppingen, Apollinaris, Wernasser Springs, Sinneberger, Maria at Marienbad).

II. **Glauber Salt Waters** with much Na_2SO_4, together with Na_2CO_3 (Karlsbad, Bertrich, Marienbad, Salzbrunn, salt springs of Franzensbad, &c.).

III. **Chalybeate Waters.** These contain at least 0·06 grm. of iron salts per litre.[1]

IV. **Salt Water** containing much NaCl and other chlorides and few sulphates and carbonates.[2]

V. **Bitter Waters** containing $MgSO_4$ and Na_2SO_4. These are found at Pülna, Saidschutz, Sedlitz, Birmanstorf, Mülligen (Switzerland), Friedrichshall.

VI. **Sulphuretted Waters.** These contain sulphides and smell of H_2S: Stackelberg, Bagnères de Luchon, St. Sauven, Tabiano, Albano, &c.

VII. **Springs which are simply Hot: Thermal and Indifferent.** These contain little dissolved material but have elevated temperatures (more than 24°). These temperatures are at Plombière, 19° to 65°; Tropuszko, 49° to 55°; Warmbrunn, 35° to 40°; Ragaz, 35°; Johannisbad, 29°; Wiesbaden, &c.

Certain mineral waters included in I. and VI. are hot, for instance, those of Vichy, which have a temperature of 32·3°; Karlsbader Sprudel, 74°; Kochbrunner, 69°.

Some waters contain special metals, for example, that of Los Banctos in Chili contains 0·322 grm. of LiCl, and that of Salsomaggiore 0·735 grm. Certain waters contain bromine and iodine (*see* preceding Note). The water of Roncegno contains notable quantities of arsenic (0·124 grm. As_2O_5 per litre).

Other waters contain a large amount of silicates.

All these mineral waters are consumed to a great extent on the spot in delightful spas, which contribute more than a little to the therapeutic efficiency of the treatment; and a part is placed on the market in sterilised and well-closed bottles, and then forms those much-extolled table waters which are as much the subject of the play of fashion as are the large bonnets of the ladies!

A large trade in mineral waters, natural and artificial, is conducted in Italy and to a still greater extent in France and in Germany. In 1905, 9807 tons were imported by Germany of the value of £140,000 and 47,873 tons were exported of the value of £359,050. In 1904 Italy imported 2662 tons for £32,000 and exported 1700 tons for £16,700. In 1908 3304 tons were imported for £42,296 and 4231 tons exported for £40,620.

Two-thirds of the Italian imports come from Austria-Hungary.

ARTIFICIAL MINERAL WATERS. These are imitations of the better quality natural mineral waters, but are distinguished from these by lack of radio-activity, by their different electric conductivity and cryoscopic behaviour (*see* p. 85). This, perhaps, also explains their different therapeutic value. But as we have already said one has now succeeded in imparting these properties artificially.[3] All types of mineral waters are manu-

(*b*) *Acid-Alkaline.* These contain much Na_2CO_3 and CO_2 and few other salts (Vichy, Mont Dore, Neuenahr, Chaudes-Aigues, Biliu, Preblau, &c.).

(*c*) *Acid-Alkaline Muriatic.* These contain Na_2CO_3 and NaCl (Ems, Selters, Gleichenberg, Wellbach, Luhatzschowitz (iodine and bromine), Krankenheil, &c.).

[1] (*a*) *Pure Acid Chalybeate.* These contain few salts and much CO_2 (Schwalbach, Spaa, Altwaser, Brückenau, Königwerth (Carolina springs at Marienbad), Frejenwalde, Recoaro, &c.).

(*b*) *Saline Alkaline Acid Chalybeate.* These contain $FeCO_3$ and Na_2CO_3, Na_2SO_4 and CO_2 in large amounts (Franzensbad, Elster, Cudowa, Flinsberg, &c.).

(*c*) *Saline Acid Chalybeate.* These contain $FeCO_3$, $CaCO_3$ and $CaSO_4$ (Pyrmont, Driburg, Griesbach, St. Moritz, Charlottenbrunn, Contrexéville, &c.).

(*d*) *Chalybeate Waters containing $FeSO_4$.* These are found at Alexisbad, Muskau, Mitterbad, and Ratzer in Tyrol, Parad in Hungary, &c.

[2] (*a*) *Simple Saline Waters with little NaCl* (Kissengen, Homburg, Kronthal, Neuhaus).

(*b*) *Saline Waters containing much NaCl.* These are found at Nauheim, Soden, Reichenhall, Wittekind, Sulza, Frankenhausen, and Hall near Innsbruck-Salzhausen.

(*c*) *Bromo-Iodo Saline Waters.* These contain much I and Br in the form of iodides and bromides of Na, K, Mg (Kreuznach, Elmen, Dürkheim, Hall in Austria, Salzbrunn, Wildegg, Bassen, Salice, Salsomaggiore, Abano, &c.). The bromo-iodo-saline water of Salsomaggiore is collected from artesian wells 700 metres deep. Its temperature is 14° and it has a density of 16° Bé. It contains 178·88 grm. of dry residue per litre consisting of 154 grm. NaCl, 0·735 LiCl, 0·637 NH_4Cl, 15·848 $CaCl_2$, 0·255 $SrCl_2$, 5·584 $MgCl_2$, 0·033 $FeCl_2$, 0·059 $AlCl_3$, 0·0057 $MnCl_2$, 0·304 $MgBr_2$, 0·066 MgI_2, 0·012 MgB_4O_7, 0·078 $Fe(HCO_3)_2$, 0·603 SO_4Sr, 0·023 SiO_2 (Nazini and Anderlini 1898); it is one of the richest waters in bromine and iodine in the world, and the richest in the world in strontium and lithium.

[3] The unit of measurement of the radio-activity of mineral waters was proposed by Mache in 1904. The quantity of emanation from 1 litre of the water was determined by passing through it a definite volume of air, in which an electroscope at a definite voltage was placed. The rapidity of decrease of the voltage during one hour was then determined. This diminution of voltage, after suitable corrections, was re-calculated into electrostatic units and then multiplied by 1000. If, for example, the quantity in electrostatic units corresponded to 0,000,000,000,33 amps., the unit proposed by Mache would be a thousand times smaller. The Fontactoscope is an apparatus which may be definitely used for these determinations at the spring on the spot.

Artificial mineral waters are rendered radio-active by immersing an insoluble radium salt in them; for example, the sulphate of radium. The most active mineral waters are those of the ancient Roman fountain in the island of Ischia (3800 units); those of Joachimstal in Bohemia, which show 14,000 units; of Baden-Baden, with 10,000

factured on a very large scale, and apart from their therapeutic properties, a guarantee of the purity of the substances employed is necessary.

The first scientific factory for mineral waters was founded on a scientific basis in 1821 by Dr. Struve at Dresden, who recognised the importance of CO_2 for keeping salts in solution which would otherwise be less soluble or quite insoluble in water. The preservative action of CO_2 was known to him, and to-day the dissolved air is always expelled from the water in order that it may keep better. The pessimistic objections to artificial mineral waters have now disappeared, and when these are properly prepared the same effect can in many cases be produced as with a natural spring. After the year 1880 the manufacture of such waters underwent extraordinary developments by the application of liquid carbon dioxide ; but even of the artificial waters it must be said that their success is often merely due to commercial speculation based on advertisement.

For the preparation of table water as a mere beverage, a good potable water suffices, to which a little sodium chloride or carbonate is added, after which it is saturated with carbon dioxide under pressure.

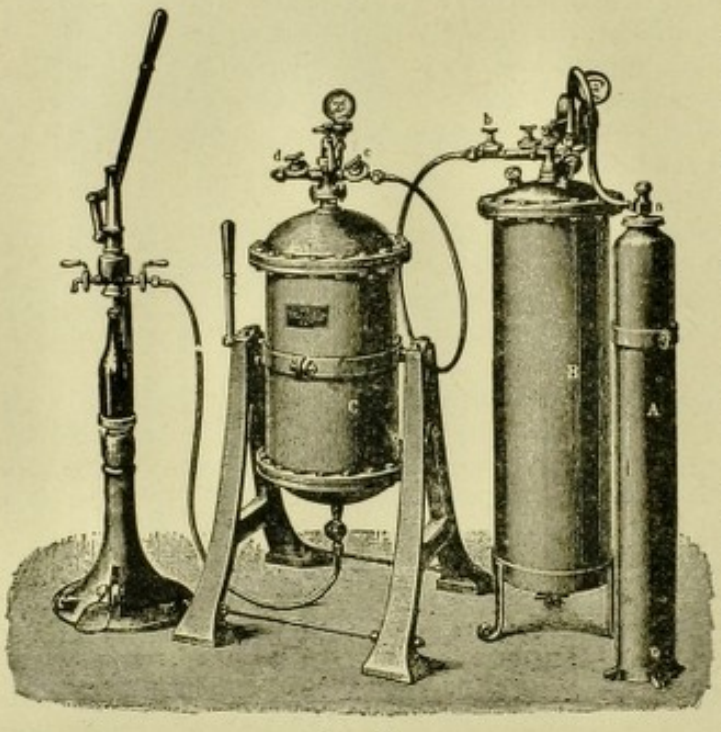


FIG. 87.

For the preparation of medical mineral waters it is necessary to employ pure distilled or sterilised water, which is mixed with the required salts and saturated with carbon dioxide at a pressure of five atmospheres. It is then placed in sterilised bottles with pure sterilised stoppers and kept at a pressure of 1½ to 2 atmospheres.

The carbon dioxide is prepared from magnesite or marble, and occasionally from bicarbonates, which are treated with commercial sulphuric acid, and it is then washed with water, ferrous sulphate, sodium bicarbonate, and sometimes with permanganate solution (in order to remove odorous organic compounds).

To-day, however, the use of liquid carbon dioxide has become general, as this is purer and more convenient, and is already under pressure (*see below*, Preparation of Liquid Carbon Dioxide).

A simple type of apparatus for the saturation of mineral waters or saline solutions with carbon dioxide is illustrated in Fig. 87. *A* is the cylinder of liquid carbon dioxide, and by means of the valve the expansion cylinder *B* is filled from this with gaseous CO_2, until a pressure of five atmospheres is indicated. The CO_2 is then passed through the cocks *b* and *c* into the mixed salts and water contained in *C*, which it saturates ; the absorption is accelerated and increased by violently oscillating the vessel *C* or by the use of an automatic agitator inside which is actuated from without. If a pressure regulator is attached to the cylinder *A*, the expansion cylinder *B* may be dispensed with. In the figure we see how the mineral water is introduced into the bottles by means of a special cock which simultaneously drives in the stopper.

In many establishments sterilised water is employed instead of using ordinary drinking water.

Water saturated with compressed oxygen is also being gradually introduced to-day.

units ; whilst those prepared artificially for drinking purposes show 10,000 units, and those used for bathing purposes show as much as 200,000 units.

ICE AND FREEZING MIXTURES

We have already studied the behaviour of water at low temperatures and have seen what happens during the separation of ice. Before speaking of natural and artificial ice, which is in general use for the production of low temperatures for varied industrial and hygienic purposes, we will say a few words on artificial methods of producing cold.

FREEZING MIXTURES. These are ordinarily formed of salts or of saline mixtures which on dissolving in water produce a strong lowering of temperature. This diminution of temperature is generally greater with the increase of the following factors: the heat of solution (that is, the heat required by the salt during solution), the solubility of the salt, and the concentration of the resulting solution, and therefore also the freezing-point of this latter; the limit of maximum refrigeration is given by the freezing-point of the saturated solution.

Mixtures of salts produce greater temperature depressions than do simple salts, because they dissolve in less water and therefore give more concentrated solutions. The saline mixtures should be well powdered, and the ice should be well pounded in order to obtain a maximum cooling effect.

With a mixture of 5 parts of HCl and 8 parts of Glauber salt (crystallised sodium sulphate) a lowering of the temperature by 28° may be obtained. With 1 part of sodium chloride and 3 parts of powdered ice or of snow, a refrigeration of 21° is obtained (if in this case the initial temperature is 0° a temperature of −21° may be obtained). With 5 parts of ammonium nitrate, 1 part of ammonium chloride, and 3 parts of water, the temperature is lowered by 30°. On mixing crystallised calcium chloride (not the fused substance) with water, the temperature is lowered by 48·5°. With 3 parts of ammonium chloride, 2 parts of potassium nitrate, and 10 parts of water, the temperature is lowered by 26°. If to this last mixture 4 parts of Glauber salt are added, the diminution of temperature amounts to 32°. With 15 parts of potassium sulphocyanide and 10 parts of water a temperature depression of 34° is obtained.

Freezing mixtures are only employed to a limited extent in laboratories and in certain small special industries. For large industrial operations natural ice, or more especially artificial ice and large freezing machines, are to-day used. Since 1870 these have been greatly improved, so that they have to-day reached a high degree of perfection.

The theoretical explanation of the behaviour of freezing mixtures is given by the following considerations: when a salt is dissolved in water—apart from the phenomena of ionic dissociation (which occur in dilute solutions, whilst we have to do with concentrated solutions)—the lowering of the freezing-point of the solvent is the greater the more salt has been dissolved (cryoscopy). The maximum lowering of the freezing-point corresponds to the freezing-point of the solid solution, and is nothing less than the multiple point (*see* phase rule, p. 115) of a system in complete equilibrium, and in this case it is also called the *cryohydric* or *eutectic* point.

Furthermore, on dissolving, the salt produces a cooling effect which is the greater the greater is its heat of solution. This rule is a deduction from Le Chatelier's principle (p. 61) or more exactly from the principle of mobile equilibrium enunciated and mathematically demonstrated by Van't Hoff in order to explain many important phenomena.

This principle says that any displacement of the factors regulating a system in equilibrium produces transformations in the system which counteract the action of the modifying factor.

In accordance with this rule of antithesis, salts which dissolve in the cold with development of heat are less soluble or little more soluble on heating, for example, sodium chloride, calcium hydroxide, calcium sulphate and sodium sulphate; whilst on the other hand bodies which dissolve in the cold with absorption of heat, for example, potassium nitrate, are more soluble hot than cold; the solubility is the greater as the absorption of heat is greater. Consequently the amount of cold produced on dissolving a salt in water is greater as its solubility is greater. We have thus shown the strict connection between solubility and heat of solution.

The heat of solution in these cases is given by the rise of temperature necessary in order to dissolve a further quantity of salt in a saturated solution. When in fact we have a system formed of a saturated solution in presence of an excess of solid salt, then on lowering the temperature a certain quantity of salt ordinarily separates, and in order to be able to dissolve a further quantity, the same quantity of heat is necessary which had been first removed. Thus the more salt dissolves in a solution, the stronger will be the absorption of heat.

If we add ice to a system formed of a solid salt and its saturated solution at 0°, the system is no longer in complete equilibrium, because the freezing-point of the solution saturated at 0° (cryohydric point) is much lower, and in order to reach it the temperature must be depressed. But this is possible if the ice melts, because on melting it absorbs heat (80 cals. per kilo). Thus if ice and salt are present in sufficient quantities to maintain the solution in a state of saturation, then as the ice melts it will gradually continue to lower the temperature until the freezing-point of the saturated solution (cryohydric point) is reached. Complete equilibrium is then attained, and then only are the ice and salt able to co-exist.

ICE, the properties of which we have already studied on p. 205 *et seq.*, is employed in breweries, spirit distilleries, paraffin works, margarine factories, chocolate works, coal-tar colour works, dyeworks, dairies, cheese factories, sugar refineries, the preparation of Glauber salt $MgSO_4$ and NaCl from solutions, and generally for many crystallisations. It is also much used on vessels and railway waggons carrying carcasses and foodstuffs in general. Refrigerating chambers are to-day also used for the preservation of dead poultry and eggs (*see* vol. ii, " Organic Chemistry ").

Thus the industrial use of ice on a large scale has developed in an extraordinary manner during the last few years. Ice which is to come in contact with foodstuffs or beverages should correspond to all the requirements of a potable water.

NATURAL ICE. During their mild winters southern countries import large quantities of natural ice from more northern climates. In North America especially a regular industry of this kind exists with suitable and perfected machinery for obtaining natural ice, especially from the frozen lakes.

By means of a kind of planing machine, about $2\frac{1}{2}$ cms. of the surface, which is impure, is removed ; a traction-engine is then employed, which carries several circular saws on an axis, and these saw through the mass in directions at right angles, to form large blocks of ice containing individual subdivisions which still adhere slightly (about 100 subdivisions to each block). Large cubes are thus separated which can be broken up with chisels and carried to the coast for transportation to South America and even to Australia.

There are a very few similar plants of less importance in Europe. That of the Norddeutsche Ice Works in Berlin produced 30,000 tons of ice in the winter of 1871.

Norway supplies large quantities of ice, which are quarried from its glaciers by working them much in the same manner as a mine. This is exported to England in large quantities at a price varying from 2*s.* to 2*s.* 6*d.* per ton at the port of shipment. In 1901 346,000 tons were exported, and 285,000 tons in 1902.

In France more than one million tons of ice are consumed annually, of which the bulk is natural (850,000 tons), 60,000 tons of which are imported from Norway to the value of more than £40,000 at their destination.

Ice was at one time stored in cellars or ice-houses underground, which were costly and inconvenient. To-day ice-houses are built above ground with double wooden walls between which insulating material is placed such as sawdust, peat, or, still better, rice chaff. Double walls of masonry also suffice, and in that case the insulating layer is formed of air. The doors are double, with a northern aspect, and the ice rests on a perforated false floor so that it may not be in contact with the water produced on melting, which, if not separated and removed by a syphon tube, would accelerate the melting of the ice. All access of air from outside is avoided as far as possible in order to preserve the ice, because the external air is always warmer than that inside the ice-house.

ARTIFICIAL ICE. Machines for the production of ice or artificial cold are based on the principle of the absorption of heat which occurs on rapidly evaporating a cold and easily volatile liquid, for example, ether boiling at 35°, ammonia at −33·5°, sulphur dioxide at −8°, carbon dioxide at −78°, and even water (Carré's machine).

Another type of machine, on the other hand, is based on the cooling effect produced by a strongly compressed gas when this is allowed to expand rapidly (for instance, air).

The boiling-point of a liquid is raised when this is exposed to pressure, and is lowered when the pressure is diminished. In some ice machines the heat of evaporation is abstracted from the evaporating liquid itself by preventing access of heat from without, and the liquid then becomes the colder the less the pressure and the lower its boiling-point, because a small reduction of the pressure then causes great evaporation of the liquid. The reason why the most intense degree of cooling is produced by liquid carbon dioxide is thus explained because this boils at the lowest temperature. Ammonia, methyl chloride, methyl ether, and sulphur dioxide follow in order of efficiency.[1]

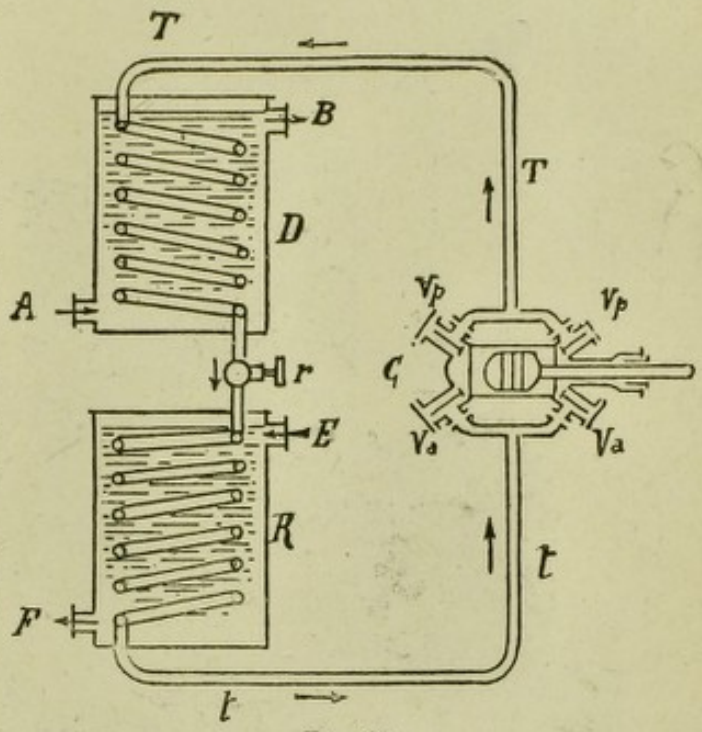


FIG. 88.

The *chemical analysis of ice* is the same as that of water, but one need not consider the ammonia which may have been absorbed from the atmosphere of the works.

Ice machines using ammonia. In actual practice ice machines make use either of ammonia, of liquid sulphur dioxide, or of liquid carbon dioxide. The machines which are most used are those of Linde using ammonia, which are constructed of the following parts, represented diagrammatically in Fig. 88. The compressor *C* is a pump with inlet valves, *Va*, and outlet valves, *Vp*. The necessary quantity of ammonia is first introduced into the machine by temporarily uniting the valve *Va* with a bomb of pure liquid ammonia free from water, which is placed on the market by various works. The gasified ammonia is gradually compressed by the compressor *C* into the tube *T*, which terminates in a very long spiral surrounded by water which circulates continuously in the tank *D*, called the condenser, in order to cool the ammonia which is heated by the compression. In this way liquid ammonia accumulates in the lower part of the coil of the condenser and is gradually

[1] *The Theory of the Ice Machine.*—The refrigerating power of a machine is given practically by the number of *frigories* which it produces per hour, that is, by the number of calories which it abstracts from the bodies to be cooled. The *frigorie* is nothing else than the negative calorie. The yield of the freezing machine is expressed by the relation between the work which it consumes and the heat abstracted from the substances to be cooled. For a perfectly reversible machine working between the temperature limits T_1 and T_2, the yield is the greater the smaller the difference between these limiting temperatures. For the production of ice it would therefore be best if the lower limiting temperature were not much inferior to 0°, apart from the mechanical difficulties of an easy interchange of heat between the water to be frozen and the brine which circulates in the apparatus. The quantity of heat Q_0 in calories abstracted from a kilo of water at $+ t^\circ$ in order to transform it into 1 kilo of ice at $- t_1$ is given by the following formula: $Q_0 = (79 + t + ct_1)$, where 79 is the heat of fusion of ice, or the amount which must be absorbed from the water in order to freeze it, and c is the specific heat of ice. Thus, starting from water at + 17° in order to obtain ice at −8°: $Q_0 = 79 + 17 + (8 \times 0{\cdot}5) = 100$ calories. We must take into account the interchange of heat between the surrounding atmosphere and the whole of the machinery which may be calculated for each machine and is proportional to the rise of temperature, $T_2 - T_1$; finally, we must take into account the practical yield, which is smaller to a more or less extent than the theoretical yield according to the perfection of the machinery and to the insulation and the size of the machines. Machines of a very large capacity give the best yields.

allowed to enter through the cock *r* into the refrigerating coil *R*, which is in connection with the inlet valve *Va* of the compressor *C*, by means of the tube *t*. The liquid ammonia instantly evaporates on entering *R* under the exhausting action of the pump, producing considerable cold. The coils of *R* are surrounded by brine (water and calcium chloride) which is strongly cooled and serves to freeze water which is contained in suitable moulds of sheet iron, which are immersed in this very cold solution. Work may naturally be continued for a long time with the same quantity of ammonia, because this is exhausted from *R* at the same time as it is compressed in *D*. In Fig. 89 the freezing machine of Linde is illustrated as it is used in many factories. The compressor is worked by a motor with a large flywheel. Vertical agitators are used in the condenser and refrigerator, being worked by cog-wheels, so that the temperature of the coils may be rapidly communicated to the liquids. The coils consist of very close spirals and are made of iron in one single piece without any seam, in such a way as to resist strong pressure. There are few works in Europe which construct them satisfactorily. In the condenser common water circulates at a temperature of 10° to 20°, and in the refrigerator a 30 per cent. aqueous solution of calcium chloride is employed, which does not freeze even at 12° below zero.

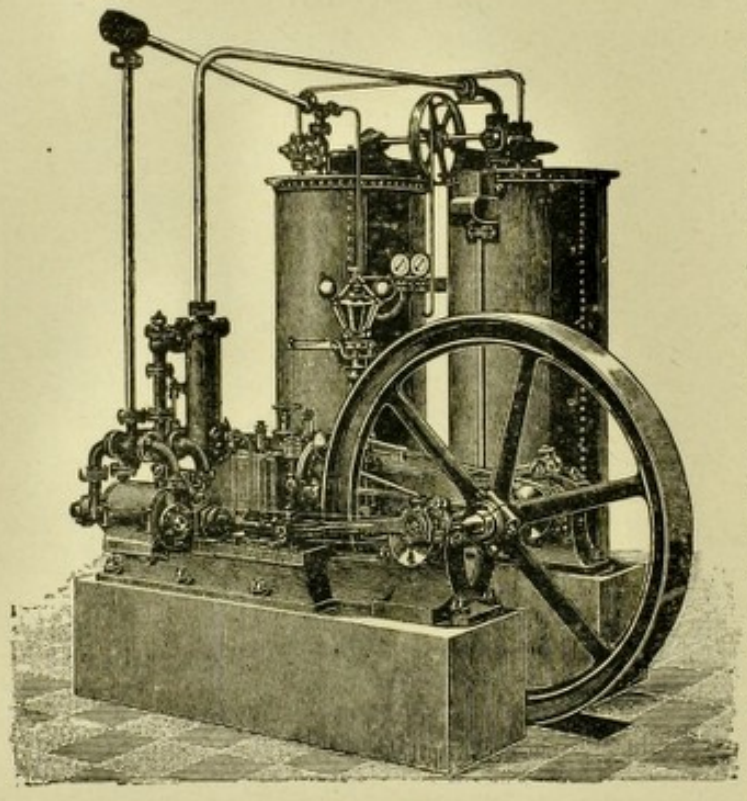


Fig. 89.

This brine is cooled by the ammonia which evaporates in the refrigerating coil and is pumped into a tank at the side, called the freezing-tank, which should not be far from the machine, and which is not shown in the figure. In this tank the boxes or moulds of sheet iron containing the drinking water which is to be frozen are placed. The brine continuously circulates between the freezing tank and the refrigerator.

A light rod moves automatically in the middle of each box containing the water, in order to facilitate the escape of the air dissolved in it, so that transparent ice may be obtained ; otherwise the small air-bubbles render the ice opaque. These rods are removed a few moments before the water in the centre of the box is also frozen. The impurities in the water collect in the centre of the ice-block, because this is the portion to be frozen last.

Large plants contain automatic contrivances which lift out and remove ten boxes at once when the ice blocks are completely formed, and refill the boxes with fresh water.

These Linde machines are constructed in all sizes for the production of from 50 kilos to 2000 kilos of ice per hour.[1] During the last twenty-five years more than 6000 Linde machines have been constructed.

[1] The cost of a Linde machine, including erection—exclusive, however, of the motor—would be approximately as follows :

	£
For the production of 100 kilos per hour with 6 h.p.	600
,, ,, 500 ,, ,, 20 ,, ...	1600
,, ,, 1000 ,, ,, 40 ,, ...	2920
,, ,, 2000 ,, ,, 65 ,, ...	4400

From plants producing 5 tons per day the ice costs about 8*s*. per ton.
,, ,, 40 ,, ,, ,, 3*s*. 3*d*. per ton.

In ice factories employing machines working with ammonia, safety apparatus should be provided in case of escape of ammonia or of explosion. Safety-masks and respiratory apparatus are required for the workmen who may

There are also many other types of ice machines, and those of Pictet which use sulphur dioxide are important, and still more so those improved machines of Pictet which use a special liquid composed of a mixture of sulphur dioxide and liquid carbon dioxide boiling at $-19°$. These machines are more especially used in France.

If instead of producing ice it is desired to cool localities, the brine is circulated in numerous winged tubes such as are employed for heating.

Freezing machines using dry air. The first to propose the utilisation of the expansion of compressed gases for the production of cold was Herschel in the first half of the nineteenth century. In 1852 Smyth and Nesmond constructed the first machine which utilised this principle for producing ice. It was improved in 1862 by Kirk, but it only became practical through the work of Windhausen in 1869. He improved it still further, and to-day it is constructed in very large sizes, which serve especially for the refrigeration of large air spaces, and magazines for foodstuffs.

Later on, in the chapter on Liquid Air, we will discuss the calculations and formulæ which show the amount of cooling produced by the expansion of compressed air, and we will then see that the reduction of temperature is about a quarter of a degree for each atmosphere, resulting from the difference of pressure before and after expansion. This datum is only of practical

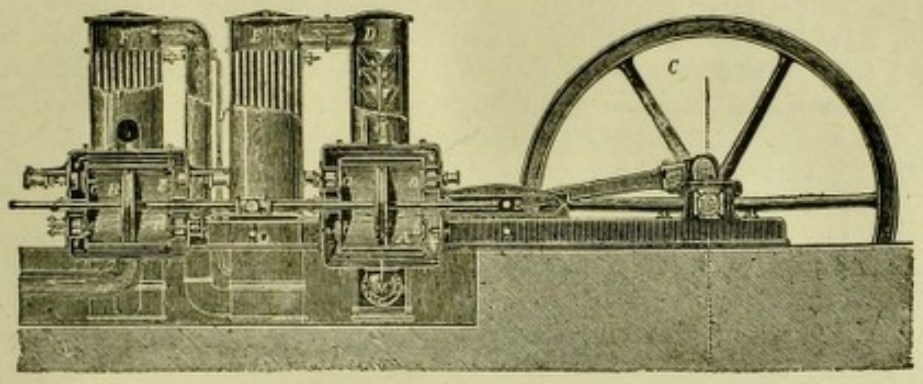


FIG. 90.

value for temperatures near zero, and for pressures which are not very large; whilst for temperatures much lower than zero the cooling is much less than a quarter of a degree per atmosphere.

We will clearly explain the principles on which the refrigerating machines of Windhausen which use air are based. One of the most largely used types of this machine is reproduced in Fig. 90. The cylinder A is the compressor and B the exhauster. The pistons of both cylinders are connected to a common piston-rod moved by a flywheel, C. The air enters through the valves a, which open inwards alternately in accordance with the movements of the piston. The strongly compressed air escapes alternately by the valves b, which only open when a certain pressure is reached. The air thus compressed issues through a large tube and then rises in a cylinder, D, containing several funnels of sheet metal, which serve to cool it, and to condense the moisture which it contains, so that it arrives fairly dry in the exhauster B by means of the valves c, after having traversed the groups of pipes contained in the cylinders E and F, in which a continuous current of fresh water circulates. The water circulates in an opposite direction to the air, entering at the lower part of the cylinder F, passing out from the upper part of this cylinder, descending to the base of the cylinder E, and passing out from the upper part. The air entering the cylinder B overcomes a certain weight on the valve e, which opens towards the interior, then expands and becomes strongly cooled even down to $-40°$, and issues

have to be employed for rescue or repairing operations. Explosions have sometimes occurred which have been explained by excessive compression (up to 40 atmospheres), which produces so much heating as to cause, under certain conditions, a partial decomposition of the ammonia into H_3 and N, thus doubling the volume of the decomposed ammonia. If a flame is present in localities in which this occurs, explosions may be caused by the ignition of the detonating mixture of hydrogen and air.

through the valve *d*, whence it is conducted into the places where the cooling is to take place, or into the boxes where ice is made. In this latter case it may be recovered in order to be brought back into circulation, as it is always dry and already considerably cooled.

Machines using carbon dioxide. These are widely diffused, as might be supposed according to the theoretical advantages which they possess, when compared with those using ammonia. CO_2 does not attack the metallic portions of the machine; it is less poisonous and dangerous than ammonia in case of gas escape. However, such leakages, whilst they are easily noticed by means of the odour in the case of ammonia, are not so easy to detect in machines using CO_2.

In order to obtain an equal refrigerating effect, machines using CO_2 theoretically require a space six times smaller than those using NH_3, and sixteen times smaller than those using sulphur dioxide: so that smaller and less costly machinery should be required. Practically, however, it is not possible to reduce the proportions of machinery to these limiting values. During the last few years the compressors have been greatly improved, and these machines to-day tend to replace those mentioned above.

USES OF ICE. The refrigerating industry has to-day acquired an extraordinary importance and numerous industries are connected with it (*see* p. 230).

Through the use of refrigerating machines on board ship, England was able to import in 1900 the following products from far distant regions: 6,434,000 frozen sheep from Australia, New Zealand, and South America; 60,000 tons of frozen and refrigerated beef from America and Australia; 65,900 tons of butter from Australia, New Zealand, the United States, and Canada; 167,000,000 eggs from Morocco, Egypt, United States, and Russia; and to these must be added enormous quantities of fresh fruit, salmon, game, &c. The total value of these important products for 1900 was £26,600,000; and in 1907 it rose to £36,000,000. In the United States 12,000,000,000 tons of foodstuffs are preserved by cold each year. The preservation and transportation of fruit are often carried out by freezing it to $-4{\cdot}5°$ during transport and in the warehouses before consumption.

The English companies pay £3 8*s*. per ton for the transport of frozen meat from Buenos Aires to London, whilst the transport to Genoa costs £8 16*s*. per ton.

Until a few years ago only three public slaughter-houses in France were provided with refrigerating machinery, whilst in Germany there were 270. In France in 1902–1903 there were 1077 ice machines, of which 55 per cent. were worked with ammonia, 27·8 per cent. with sulphur dioxide, 11 per cent. with carbon dioxide, and 7·6 per cent. with methyl chloride.

In the United States 4,500,000 tons of artificial ice are produced annually, together with 20,000,000 tons of natural ice.

HYDROGEN PEROXIDE: H_2O_2

This substance was first produced by Thénard in 1818 by the action of HCl on barium peroxide.

It is formed in the atmosphere by powerful electrical discharges or heavy snowfalls. Snow may contain as much as 1 mgrm. of hydrogen peroxide per kilo.

It is formed in very small quantities during the combustion of hydrogen and hydrocarbons. It is also produced wherever ozone is found in the presence of water; also on burning hydrogen in air, and thus also during the slow combustion of ether. A hot platinum spiral becomes red hot in contact with ether vapour and then forms H_2O_2. Some metals (Cu, Fe, Pb) form a little H_2O_2 when agitated with H_2SO_4 and air.

PROPERTIES. Pure concentrated hydrogen peroxide decomposes easily into $H_2O + O$, developing heat (97 Kj = 23,180 cals.), and decomposes with a powerful explosion if it contains impurities. Sometimes a violent shock or even contact with dust in the air and with impurities is sufficient to cause its decomposition and explosion, so that it is not wise to store pure hydrogen peroxide (*see below*).

H_2O_2 is an energetic oxidising agent and decolorises dyestuffs, liberates iodine from iodides, transforms sulphurous into sulphuric acid, and sulphides into sulphates. It also transforms oxides of Ca, Ba, Sr, into peroxides. With H_2S it separates sulphur and forms H_2O.

Some very finely powdered metals (Au, Pt, Ag, &c.) evolve oxygen in contact with H_2O_2 without alteration of the metal itself. Manganese dioxide, MnO_2, is reduced in presence of an acid and of H_2O_2, liberating half its own oxygen together with one atom of oxygen from the H_2O_2. Certain rather unstable metallic oxides of Ag, Au, and Pt are also reduced with evolution of their own oxygen united to that liberated by the H_2O_2. In a similar manner potassium permanganate is reduced to manganous oxide, which forms manganous sulphate in presence of H_2SO_4 with decolorisation of the permanganate and evolution of oxygen. With chromic acid chromium oxide is obtained. H_2O_2 reacts with sodium hypochlorite, producing water, oxygen, and sodium chloride. We thus see that hydrogen peroxide is also able to effect energetic reductions due to the avidity with which the atomic oxygen of the hydrogen peroxide combines when liberated with another atom of oxygen of an oxidised substance, thus being transformed into the more stable molecular oxygen, O_2.

The size of the molecule of hydrogen peroxide has been measured by cryoscopic determinations.

CHARACTERISTIC REACTIONS OF H_2O_2. Hydrogen peroxide decolorises indigo solution alone, and still more rapidly in presence of a little ferrous sulphate. With starch paste and potassium iodide a blue coloration is obtained due to the liberation of iodine, and this reaction is also more sensitive in presence of a trace of ferrous sulphate.

The following is a very sensitive reaction : solutions of ferric chloride and potassium ferricyanide (red prussiate) are mixed, and a very small quantity of hydrogen peroxide is then added. The ferricyanide is reduced to potassium ferrocyanide, which immediately forms Prussian blue with the ferric chloride. With very minute traces of hydrogen peroxide the coloration is green.

A colourless solution of titanium dioxide in concentrated sulphuric acid is coloured orange-yellow by minimal traces of H_2O_2, through the formation of titanium peroxide. (*Translator's note.*—The original text says titanic anhydride, which is obviously a slip.) Vanadium gives a similar reaction.

The reaction with benzidine which we have already described in discussing ozone (p. 185) is very sensitive and characteristic for hydrogen peroxide and is carried out in the following manner : To 10 c.c. of a very dilute solution of H_2O_2 (even one drop in 400 c.c. of water) a drop of a 10 per cent. copper sulphate solution, and then, drop by drop, a saturated alcoholic solution of benzidine are added, until a slight turbidity is formed. The liquid is then shaken, when a deep blue precipitate is formed which is characteristic of H_2O_2 (Arnold and Mentzel, 1902).

The following is a fairly sensitive reaction : hydrogen peroxide is acidified in a test-tube, ether is added and then one or two drops of a dilute solution of potassium bichromate or chromic anhydride ; on shaking, the new chromium compound thus formed (perchromic acid) dissolves in the ether, giving a blue colour, which, however, very quickly disappears.

Recently (1909) Charitschkoff found that even very small traces of hydrogen peroxide (0·03 per cent.) redden a piece of dry paper impregnated with a benzene solution of the cobalt salt of naphthenic acid (ozone does not react directly).

APPLICATIONS. Hydrogen peroxide is used for bleaching fine fabrics, especially woollen and silken fabrics, and ostrich feathers, ivory, &c. It is first made feebly alkaline with ammonia, and the textile fabrics to be dyed are then immersed for twelve hours in a cold bath containing 5 to 10 per cent. of commercial hydrogen peroxide. If the solution is heated bleaching takes place in an hour, but then the bath which remains is very weak, whereas cold baths still contain much H_2O_2 after use, and can be used for successive operations by replenishing them with a little H_2O_2. A more gradual reaction with

less loss of oxygen is obtained by the use of hydrogen peroxide dissolved in a 10 per cent. sodium acetate solution. Baths which have been used are preserved by acidifying them weakly with sulphuric acid. H_2O_2 also decomposes any residual SO_2 and Cl in fabrics which have been bleached by other means. It imparts to hair a beautiful yellowish golden colour, and is used for that purpose by women.

It is a good depolariser for galvanic batteries and a good antiseptic. It is also used for cleaning old blackened paintings, because it transforms the black lead sulphide (formed from white lead and hydrogen sulphide) into white lead sulphate.

Commercial hydrogen peroxide of a strength of 10 to 12 vols. costs from about £10 to £12 per ton.[1]

In Italy 60 tons of hydrogen peroxide were manufactured in 1893, and in 1903 the production had already risen to 1370 tons, and in 1907 to 1800 tons, valued at £17,040. But in 1903 the production decreased to 1470 tons. In 1908 Germany exported 304 tons, and about 446 tons in 1909.

PREPARATION. H_2O_2 is formed by adding barium peroxide to cold mineral acids, and sulphuric acid is used by preference because it forms insoluble barium sulphate easily separated from the hydrogen peroxide which is dissolved in the water. By employing HCl, on the other hand, soluble barium chloride is formed which is difficult to separate.

$$BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4.$$

It may also be produced by the action of carbon dioxide under pressure in presence of water.

$$BaO_2 + H_2O + CO_2 = BaCO_3 + H_2O_2.$$

A pure aqueous solution of hydrogen peroxide is obtained in practice by the action of sulphuric acid on the hydrate of barium peroxide in the following manner: Barium peroxide is finely powdered and added to a definite quantity of dilute HCl until this is almost completely neutralised ; it is then filtered and the clear cold liquid is treated with baryta water until all the silica and the other metallic oxides are precipitated. The liquid is again filtered and all the barium peroxide then precipitated as hydrate by adding excess of baryta water. It is collected on a filter, washed, and the moist hydrate then added little by little, with continuous agitation, to dilute sulphuric acid (1 : 5 H_2O), which is kept at a temperature below 10° by the addition of ice. Dilute hydrofluoric acid is now sometimes used instead of sulphuric acid, in which case the work is carried out in leaden vessels. When the acid (HF or H_2SO_4) is thus completely neutralised, the whole is stirred for some hours, allowed to settle and then filtered. If the exact elimination of all the acid which remains in solution is desired, this is achieved with a little barium peroxide and the liquid is again filtered. A little acid is, however, always left in commercial H_2O_2, because it preserves its strength for a longer time with this addition. It has recently been found that its strength is still better preserved by the addition of a very small quantity of tannin instead of sulphuric acid (Ger. Pat. 196,370 of 1907). E. Merck (1909) obtained good results with traces of barbituric acid. The liquid ordinarily maintains its strength satisfactorily on being stored in glass vessels internally coated with paraffin. It contains about 3 per cent. of H_2O_2, and is sold at a strength of 10 to 12 vols., which means that 1 litre of hydrogen peroxide develops from 10 to 12 litres of oxygen.

Concentrated H_2O_2 may be obtained from this solution by distilling it at 75°, after having first separated all traces of alkali, metallic salts, or suspended matter. Hydrogen peroxide of 50 per cent. strength is thus obtained, and on redistilling it *in vacuo* at a pressure

[1] The strength of hydrogen peroxide is determined by acidifying it strongly with sulphuric acid, diluting 5 c.c. with 50 c.c. of water, and then adding from a graduated burette a solution of potassium permanganate of known strength $\frac{N}{10}$ (namely, 3·17 grms. permanganate per litre), with stirring until the last drop of permanganate is no longer decolorised. The calculation is then based on the following equation, which shows that 1 c.c. of $\frac{N}{10}$ solution of permanganate corresponds to 0·001701 grm. of H_2O_2 or to 0·5594 c.c. of oxygen.

$$5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = 5O_2 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

On multiplying the percentage weight of H_2O_2 by 3·29, one obtains the strength expressed in volumes of oxygen, that is, the number of litres of oxygen which 1 litre of the solution is capable of liberating. If the hydrogen peroxide has a strength of 3 per cent. by weight of H_2O_2, its strength expressed in volumes will be 9·87, that is, in round figures, it has a strength of 10 vols.

of 5 to 7 cms. of mercury the water first passes over and is then followed by pure concentrated hydrogen peroxide. This may also be obtained from the 50 per cent. H_2O_2 by extracting it with ether. From the ethereal solution the ether is separated by distillation and the hydrogen peroxide which remains is in turn distilled at reduced pressure. A clear heavy liquid is thus obtained of sp. gr. 1·49 which boils at 69° at a reduced pressure of 26 mm. and smells like nitric acid. It is soluble in water, alcohol, and ether, and contains up to 99 per cent. of H_2O_2. The concentration of hydrogen peroxide by means of a strong current of air at temperatures of 50° to 60° has recently been described (Ger. Pat. 219,154), the H_2O_2 being then distilled of 100 per cent. strength at a temperature of 60° to 80°, still in the current of air.

Merck prepared pure hydrogen oxide by adding a calculated quantity of sodium peroxide in small quantities to a given volume of 20 per cent. sulphuric acid which was kept cool. Two-thirds of the sodium sulphate immediately separated as crystals; the liquid was then filtered and distilled *in vacuo*. The remainder of the sodium sulphate was left in the retort and did not decompose the H_2O_2. Merck also prepares pure H_2O_2 by treating barium peroxide with CO_2 in presence of water (Ger. Pat. 179,771 of 1905–1906).

Staedel obtains very pure crystallised H_2O_2 of 100 per cent. by cooling the ordinary concentrated 96 per cent. product by means of a freezing mixture of ether and liquid carbon dioxide, thus producing a temperature of 80° to 100° below zero. On then taking a minimal quantity of this solidified H_2O_2 and placing it in 96 per cent. hydrogen peroxide cooled to −8°, a mass of transparent crystals of chemically pure H_2O_2 immediately separates. This product melts at −2°. In contact with platinum black or manganese dioxide it explodes with great violence. It instantly sets fire to magnesium powder, carbon, wool, &c., but does not react with reduced iron.

Very pure hydrogen peroxide of 10 per cent. strength is easily obtained by dissolving 170 grms. of sodium perborate and 60 grms. of citric acid in one litre of water.

HYDROGEN SULPHIDE (OR HYDROSULPHURIC ACID): H_2S

This body is found free in nature, especially in volcanic gases and in some sulphuretted waters. In Italy such waters are found at Abano, Tabiano, &c. It is formed during the putrefaction of organic matter containing sulphur (albuminoids). This explains its presence in rotten eggs, closets, and latrines. During the putrefaction of organic matter sulphates, for instance, calcium sulphate, are also reduced, generating sulphides and hydrogen sulphide.

PHYSICAL PROPERTIES. Hydrogen sulphide is a colourless gas with a strong smell of rotten eggs, of density 1·19. If breathed in large quantities it acts as a soporific and a powerful poison, and if the pure gas is breathed it rapidly produces death (*see* Note, p. 190). It liquefies at a pressure of 17 atmospheres, or a temperature of −74°, yielding a colourless liquid of sp. gr. 0·9, which solidifies at −91°. One volume of water dissolves 3 to 4 vols. of H_2S gas.

CHEMICAL PROPERTIES. It burns with a bluish flame, giving sulphur dioxide: $H_2S + 3O = H_2O + SO_2$.

With a limited quantity of air, and if the flame of H_2O is cooled by introducing a cold body into it, the hydrogen alone is burned and the sulphur is deposited. The utilisation of the sulphur contained in the by-products of the Leblanc soda industry is based on this reaction. The aqueous solution of H_2S becomes turbid in contact with air by the deposition of very fine insoluble sulphur, $H_2S + O = H_2O + S$; therefore, in order to preserve aqueous solutions of H_2S without alteration it is necessary to completely fill the bottles or close them hermetically.

The halogens react similarly to air, as we have seen in the preparation of hydriodic acid: $H_2S + I_2 = 2HI + S$.

H_2S is a good reducing agent, easily abstracting oxygen from other substances and reducing them to less highly oxidised compounds. This occurs

with chromic and nitric acids. Thus on pouring a little fuming nitric acid into a cylinder containing dry H_2S, this catches fire with a slight explosion. In presence of porous materials H_2S is slowly oxidised in the air with the final formation of sulphuric acid. On the other hand, it is capable of reducing sulphuric acid, and for this reason this acid is not suitable for drying H_2S.

Being a reducing agent, it reduces solutions of potassium permanganate which transforms it into sulphuric acid. It decomposes with sulphur dioxide at the ordinary temperature, the sulphur of the H_2S and of the SO_2 being separated :

$$SO_2 + 2H_2S = 2H_2O + S_3.$$

This reaction explains the powerful deodorising action of sulphur dioxide in places smelling of H_2S. All that is necessary in order to eliminate such odours is to burn a little sulphur. The removal of the taste and smell of sulphur from wines by means of burning sulphur is due to the same cause. In many industries H_2S is separated from other gases by passing the mixture over hydrated ferric oxide or through alkaline solutions of ferric salts.

H_2S is a very weak acid which only reddens blue litmus paper weakly, and forms two categories of salts with bases, namely, sulphides and hydrosulphides.

$KOH + H_2S = H_2O + KSH$ (potassium hydrosulphide or monopotassium sulphide)

$PbO + H_2S = H_2O + PbS$ (lead sulphide).

Almost all the metals form sulphides with H_2S with liberation of hydrogen, *e.g.* $Pb + H_2S = PbS + H_2$.

The sulphides, then, are salts or hydrosulphuric acid. They have characteristic colours varying with the nature of the metal. Thus zinc sulphide is white; cadmium sulphide, yellow; antimony sulphide, orange-red; lead sulphide, blackish brown; stannous sulphide, brown; stannic and zinc sulphides, yellow, &c. Since, also, many metallic sulphides are insoluble in water and in acids, one may thus obtain precipitates from salts of other acids by treating them with hydrogen sulphide, which is therefore a valuable reagent in analytical chemistry. Very small traces of hydrogen sulphide may be detected by paper impregnated with lead acetate, which is immediately blackened.

Hydrogen sulphide is a weakly exothermic compound :

$$H_2 + S = H_2S \text{ gas} + 11 \text{ Kj and } H_2S + \text{aq.} = H_2S \text{ sol.} + 19 \text{ Kj},$$

that is, 30 Kj. (7170 cals.) in all. The heat of formation being very small, one can understand how it is that it is formed with difficulty from the elements H and S, and why it decomposes easily on heating (into H and S), and also why it is a weak acid.

It is a dibasic acid because its two hydrogen atoms may be replaced by one atom of a divalent metal or by two atoms of a monovalent metal. The behaviour of the dilute aqueous solution of its salts is, however, apparently abnormal, as is that of all weak dibasic or polybasic acids, and potassium or sodium sulphides in aqueous solution show an alkaline reaction on account of the hydrolytic dissociation which is explained in the following manner :

The ions of H_2S in aqueous solution should be $H_2^{\cdot}$ and S'' ; where S'' represents the divalent anion of H_2S. In reality, however, the total dissociation is preceded by another phase, namely, $H_2S = H^{\cdot} + HS'$, where the anion HS' is monovalent and has a weakly acid reaction, in common with those of weak dibasic acids in general, which in aqueous solution are mainly dissociated in accordance with this second phase. The acid action is always due to the cation $H^{\cdot}$, whilst only a small portion of the monovalent anion is finally dissociated into the divalent anion : $HS' = H^{\cdot} + S''$. Thus, in aqueous solutions of H_2S there are many HS' and $H^{\cdot}$ ions and few S'' ions.

In the case of more energetic acids, on the other hand, the second phase of the dissociation preponderates. These considerations on ionic dissociation also explain the general behaviour of the two categories of salts of dibasic acids.

In the case of hydrogen sulphide, we have, for example, monosodium sulphide, NaHS (or sodium hydrosulphide, also called the acid sulphide or secondary sulphide of sodium), and disodium sulphide, Na_2S, also called the primary sulphide or neutral sulphide or normal sulphide of sodium. In aqueous solution the acid sulphide should show an acid reaction. Actually it shows neutral reaction because the weak anion SH' is only very slightly dissociated into S'' and H; and, therefore, there are very few $H^{\cdot}$ ions showing acid action, and even this dissociation is much diminished because SH' becomes saturated with reformation of non-dissociated H_2S by minimal quantities of $H^{\cdot}$ cations of the water itself (which under such conditions is very slightly dissociated into $H^{\cdot}$ and OH'), and thus free hydroxyl ions of the water, which produce an alkaline reaction, remain, saturating and paralysing the weak acid action of the few remaining free $H^{\cdot}$ ions, and the aqueous solutions of these monometallic sulphides (NaHS) thus show neutral reaction. The dimetallic or primary sulphides of these weak acids, on the contrary, show a markedly alkaline reaction in aqueous solution, because the two ions of the disodium sulphide, S'' and $Na_2^{\cdot\cdot}$, do not remain dissociated in this manner, as the anion S'' is readily hydrolised by water, being transformed as follows: $S'' + H_2O = HS' + HO'$, and the SH' is further transformed in part into H_2S, and thus the alkaline reaction of hydroxyl (OH') which gradually increases turns red litmus paper blue. As a matter of fact the so-called neutral salts of weak acids, even of monobasic acids such as sodium hypochlorite, &c., show an alkaline reaction on account of pronounced *hydrolytic dissociation* in aqueous solution (p. 97).

APPLICATIONS. Hydrogen sulphide is used in analytical laboratories, and also industrially for the purification of hydrochloric and sulphuric acids, &c.

PREPARATION. Hydrogen sulphide is formed in small quantities by passing hydrogen through boiling sulphur; or by mixing hydrogen and sulphur vapour at 500° in presence of porous bodies, such as pumice or bricks.

It is also formed by heating certain metallic sulphides to redness in presence of hydrogen: $Ag_2S + H_2 = H_2S + Ag_2$.

It is ordinarily prepared in the laboratory by acting on the metallic sulphides with an acid. Sulphuric acid or hydrochloric acid is commonly used with iron sulphide at the ordinary temperature in similar apparatus to that which is used for the preparation of hydrogen (p. 131).

$$FeS + SO_4H_2 = SO_4Fe + H_2S\,;\quad FeS + 2HCl = FeCl_2 + H_2S.$$

In this case the gas contains hydrogen proceeding from the action of the acid on the metallic iron which is always present as an impurity in the sulphide.

Pure hydrogen sulphide is obtained by heating antimony trisulphide with concentrated hydrochloric acid.

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

The sulphide is placed in a flask closed with a stopper carrying a thistle funnel for the introduction of the acid and a delivery tube for the gas, as in the preparation of chlorine (p. 142). The H_2S which is formed is first washed in water and then collected by displacement in cylinders filled with water.

Pure H_2S is also obtained by decomposing barium sulphide with pure hydrochloric acid: $BaS + 2HCl = BaCl_2 + H_2S$.

HYDROGEN PERSULPHIDE: H_2S_5

Just as hydrogen peroxide is formed by the action of acids on metallic peroxides, so by acting on certain metallic persulphides or polysulphides with acids, hydrogen persulphide is formed, but only the sulphide, H_2S_5, whatever may be the reacting polysulphides (Na_2S_2, Na_2S_3, Na_2S_4, Na_2S_5); probably because the other hypothetical hydrogen persulphides decompose, giving H_2S and H_2S_5.

$$4Na_2S_2 + 8HCl = 8NaCl + 4H_2S_2\,;\quad 4H_2S_2 = 3H_2S + H_2S_5\,.$$

This persulphide is an easily volatile, limpid yellow oil of sp. gr. 1·71. It decomposes easily in presence of moisture, giving sulphur and H_2S_5.

Bloch and Hohn (1908) prepared the persulphides S_3H_2 and S_2H_2, the existence of which was also confirmed by Bruni and Borgo (1909).

HYDROGEN SELENIDE : H_2Se

This is obtained from the elements at 400°, or better still from iron selenide, FeSe, with hydrochloric acid. It is a colourless gas with a repugnant odour. It is a weak acid and more poisonous than H_2S. Pure selenium is liberated from its solutions by contact with the air. It precipitates many heavy metals in the form of *selenides*.

Selenious chloride, Se_2Cl_2, is also known, and so is selenium tetrachloride, $SeCl_4$, which is a solid, sublimes unchanged, and is more stable than sulphur tetrachloride.

HYDROGEN TELLURIDE : TeH_2

This gas is obtained mixed with oxygen by the action of hydrochloric acid on zinc telluride : it is a very poisonous, evil-smelling, colourless gas, and easily dissociates. It precipitates the salts of heavy metals from solution in the form of tellurides.

$TeCl_2$ and $TeCl_4$ are also known ; the latter boils unaltered at 380°. Analagous compounds with Br, I, F, are also known.

HALOGEN COMPOUNDS OF SULPHUR

SULPHUR MONOCHLORIDE : S_2Cl_2. This is the most stable of these halogen compounds, and is obtained by passing dry chlorine over molten sulphur. It is a reddish-yellow liquid which fumes in the air and irritates the eyes. It has a specific gravity of 1·69 and boils at 138°.

It readily dissolves sulphur (66 per cent.) and the heavy solution is used for the vulcanisation of india-rubber.

It decomposes with water as follows :

$$2S_2Cl_2 + 2H_2O = SO_2 + 3S + 4HCl.$$

SULPHUR DICHLORIDE : SCl_2. This compound is obtained by saturating the monochloride with chlorine at 6° to 10° and then driving off the excess of chlorine with CO_2 :

$$S_2Cl_2 + Cl_2 = 2SCl_2.$$

It is a reddish-brown liquid of sp. gr. 1·62, which boils at 64°, when it is partially decomposed into Cl_2 and S_2Cl_2 ; it is decomposed by water.

SULPHUR TETRACHLORIDE : SCl_4 (*bromides* and *iodides*). This chloride is only stable below 0° ; it is obtained by saturating sulphur chloride with chlorine at − 20°.

SULPHUR BROMIDE : S_2Br_2, is also known. It is a red liquid which boils at 190° to 200°.

Iodides of sulphur are not well known, but in 1900 Moissan appears to have prepared from its elements sulphur hexafluoride, SF_6, which is an almost inactive gas.

OXY-COMPOUNDS OF S, Se, Te

Whilst only two oxidised compounds of selenium and tellurium are known, namely, the dioxide and trioxide (SeO_2, SeO_3 ; TeO_2, TeO_3), four oxygen derivations of sulphur are known.

S_2O_3	SO_2	SO_3	S_2O_7
Sulphur sesquioxide	Sulphur dioxide or sulphurous anhydride	Sulphur trioxide or sulphuric anhydride	Sulphur heptoxide or persulphuric anhydride

Excepting sulphur sesquioxide, all these other oxides, which are also called anhydrides, generate the corresponding dibasic acids with one molecule of water. These acids give two series of salts : acid salts and neutral salts.

But there are also other oxy-acids, which only exist in the form of salts, and of which the corresponding oxides or anhydrides are not yet known.

$S_2O_3H_2$, thiosulphuric acid (sometimes called hyposulphurous acid)
$S_2O_4H_2$, hydrosulphurous acid (the true hyposulphurous acid)
SO_3H_2, sulphurous acid
SO_4H_2, sulphuric acid
$S_2O_6H_2$, dithionic acid (hyposulphuric acid)
$S_3O_6H_2$, trithionic acid
$S_4O_6H_2$, tetrathionic acid
$S_5O_6H_2$, pentathionic acid
$S_2O_5H_2$, disulphurous acid
$S_2O_7H_2$, disulphuric acid
$S_2O_8H_2$, persulphuric acid
$S_2O_9H_2$, oxypersulphuric acid (Caro's acid)

SULPHUR DIOXIDE : SO_2

Sulphur dioxide is found free in considerable quantities in nature, in certain volcanic emanations, and being an exothermic compound it is readily formed together with a trace of SO_3 by burning sulphur in the air : $S + O_2 = = SO_2 + 71{\cdot}6$ cals., and 1 kilo of sulphur develops 2165 cals. on burning. The formation of SO_2 by burning solid sulphur occurs without change of volume, that is, from 1 vol. of O_2 1 vol. of SO_2 is obtained, and from this its composition may also be deduced, because if SO_3 were to be formed then from 3 vols. of O_2 one would obtain 2 vols. of SO_3. SO_2 is manufactured industrially by roasting certain metallic sulphides, especially pyrites (sulphides of iron, copper, &c.), in special furnaces : $CuS + 3O = CuO + SO_2$, and also :

$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2 + 419{\cdot}8 \text{ cals.},$$

that is, 105 cals. for each molecule of SO_2 (*see* Note, p. 164).

The SO_2 from large copper smelting plants is sometimes utilised for the manufacture of sulphuric acid in lead chambers, but cannot be used for the manufacture of catalytic sulphuric acid, because the catalyst soon becomes covered by powdered zinc oxide and the excessive amount of moisture renders the acid very dilute.

A regular development of SO_2 is conveniently obtained in the laboratory by heating one part of mercury or of copper turnings with three parts of strong sulphuric acid in a flask.

$$Cu + 2SO_4H_2 = CuSO_4 + 2H_2O + SO_2.$$

Pure sulphur dioxide is also obtained by decomposing sulphites and disulphites with mineral acids, or by reducing sulphuric acid by heating it with charcoal in a flask : $2SO_4H_2 + C = 2SO_2 + CO_2 + 2H_2O$.

Since CO_2 is formed together with SO_2 in this manner and is difficult to separate, this method is only employed when a dilute aqueous solution of SO_2 is to be prepared, in which case the gaseous mixture is passed through water in which the CO_2 is only slightly soluble.

SO_2 has also been prepared industrially by decomposing sulphuric acid by heat (Debray and Deville, p. 179) in order to thus manufacture sulphur trioxide (*see below*).

PHYSICAL PROPERTIES. Dry sulphur dioxide is a colourless gas of suffocating, disagreeable, and penetrating smell ; it gives white fumes in moist air ; it is harmful for respiration and to vegetation, and is employed as an antiseptic in various industries (beer, wine, meat, &c.).

It is readily liquefied by cooling it with ice and salt, or at a pressure of three atmospheres only.

In the liquid state it is colourless and fairly mobile, has a specific gravity of 1·53 at 0°, boils at −8°, and solidifies at −76°. It absorbs much heat on evaporation, and on this account it is employed in ice factories for the production of cold (*see* Ice).

On pouring liquid SO_2 on to mercury and accelerating the evaporation by means of a jet of air, the mercury is solidified (− 40°).

One volume of water at 0° dissolves 80 vols. of SO_2 and at 15° about 50 vols. with evolution of heat. Therefore in order to obtain more concentrated solutions it is necessary to cool the water, because the gas is less soluble in hot water, and at a certain temperature all the SO_2 is liberated. At a temperature of 20° the saturated solution contains 8·6 per cent. by weight of SO_2 and at 40° only 6·1 per cent.; at 15° the saturated solution of specific gravity of 1·056 contains 11 per cent. of SO_2.[1] Alcohol at 0° dissolves 54 per cent. of SO_2 and at 26° only 26·5 per cent. On solution in water sulphur dioxide forms sulphurous acid: $H_2O + SO_2 = SO_3H_2$, but this acid has not yet been isolated as such.

On dissolving in water SO_2 develops 32 Kj (7700 cals.).

CHEMICAL PROPERTIES. On heating with oxygen or air in presence of platinum sponge, or platinised asbestos, iron oxide, or certain other catalytic substances, SO_2 is completely oxidised, giving sulphur trioxide: $SO_2 + O = SO_3$. The aqueous solution is also slowly oxidised in the air giving sulphuric acid: $SO_2 + O + H_2O = H_2SO_4$, and more easily by the action of the halogens: $SO_2 + 2H_2O + I_2 = SO_4H_2 + 2HI$, so that the iodine solution is decolorised.

Sulphur dioxide is a good reducing agent, because it removes oxygen from many substances, being itself oxidised, and thus decolorises solutions of potassium permanganate yielding manganous salts:

$$2KMnO_4 + 5SO_2 + 2H_2O = K_2SO_4 + 2MnSO_4 + 2H_2SO_4.$$

The natural colouring matters are also decolorised by SO_2, for instance, those of many flowers, of wine, of wool, and of raw silk, which are bleached in this manner. Leuco-compounds are formed in this way which are not very stable, but which are soluble in dilute sulphuric acid and liable to re-oxidisation by the air. Therefore bleaching by this means is not very durable if these products are not removed by washing with water or dilute sulphuric acid.

SO_2 may be reduced in turn by more energetic reducing agents, such as H_2S, with separation of sulphur: $SO_2 + 2H_2S = 2H_2O + 3S$. The gas does not maintain combustion and may therefore be used to extinguish fires.

Traces of SO_2 are detected by treating even very dilute solutions with a few crystals of potassium iodate and then a few drops of HCl, and shaking with a little chloroform; this dissolves the liberated iodine and acquires a violet colour.

[1] In the case of pure aqueous solutions the amount of SO_2 present may be determined with the help of the following table, which applies to a temperature of 15·5°:

density 1·0056 = 1% SO_2	density 1·0275 = 5% SO_2	density 1·0474 = 9% SO_2
,, 1·0113 = 2% ,,	,, 1·0328 = 6% ,,	,, 1·0520 = 10% ,,
,, 1·0168 = 3% ,,	,, 1·0377 = 7% ,,	,, 1·0560 = 11% ,,
,, 1·0221 = 4% ,,	,, 1·0426 = 8% ,,	,, 1·0668 = 13% at 11°

The strength of the aqueous solution is determined with greater exactitude, even when other substances are present, by means of a titrated iodine solution, into which the solution of SO_2 is dropped with continuous stirring, $SO_2 + 2I + 2H_2O = H_2SO_4 + 2HI$, and by then also determining the total acidity with $\frac{N}{10}$ solution of sodium hydroxide in presence of phenolphthalein as indicator. In this way any sulphuric acid which may have been present in the solution of SO_2 is also determined, whilst the amount of the latter is found from the amount of iodine used, by means of the above equation.

The strength of liquid anhydrous sulphurous acid is determined by first weighing a given quantity in a weighed pipette with two stop-cocks, and then allowing the SO_2 as it evaporates to bubble through an $\frac{N}{10}$ solution of iodine, previously passing it through two weighed calcium chloride tubes in order to absorb the moisture, which is weighed separately; the excess of iodine is titrated back with a solution of $\frac{N}{10}$ sodium thiosulphate, and the result calculated by remembering that 1 c.c. of $\frac{N}{10}$ iodine solution corresponds to 1·0946 c.c. of dry SO_2 at 0° and 760 mm. Anything which remains in the pipette after this has been heated to 70° to 80° is sulphuric acid and tar, which, after weighing, is removed with hot water and the sulphuric acid titrated. The tar may also be finally extracted with ether and weighed after evaporating the ether.

APPLICATIONS OF SO_2. The greater quantity of SO_2 which is produced is used directly on the spot for the manufacture of sulphuric acid. It is also used in paper works for the bleaching of straw and of wood ; in alum factories ; for the preservation of fruit, beer, wine, meat, dextrine, sugar, and syrups, being a good disinfectant, and also for the extraction of calcium phosphate from bones in the manufacture of glue. It is also used for bleaching wool, silk, and straw hats. It is used in sugar refineries because it has very little inverting action on the sugar ; it is also employed in certain tartaric acid factories, &c. Its use has recently been proposed for the interruption of the fermentation of grape juice in wine manufacture.

The main consumption of liquid SO_2 takes place in Pictet's ice machines and in the manufacture of cellulose. It has the property of dissolving oils and fats under pressure, but is unable to compete in this respect with benzine and carbon disulphide. Liquid SO_2 is now used for the rapid disinfection of ships and for destroying the rats which infest them. It will probably acquire great importance in the future through its use in connection with steam-engines patented by Behrend and Zimmerman, serving to increase the efficiency of the steam-engines by utilising the heat which would otherwise be lost, by the evaporation of liquid SO_2 and the production of strong pressure in the motor, supplementary to the engine itself. When it has been thus utilised the SO_2 is again liquefied in a condenser with cold water and re-utilised.

STATISTICS AND PRICES. Liquid sulphur dioxide comes on to the market to-day in steel cylinders at about £1 5*s.* 7*d.* to £1 9*s.* 7*d.* per 100 kilos. The empty steel bombs, tested to thirty atmospheres, cost £4 of a capacity of 100 kilos ; or £1 10*s.* 4*d.* of a capacity of 10 kilos. But these bombs are let out on hire by the manufacturers, who after three months demand a rent of 1*s.* to 2*s.* per month.

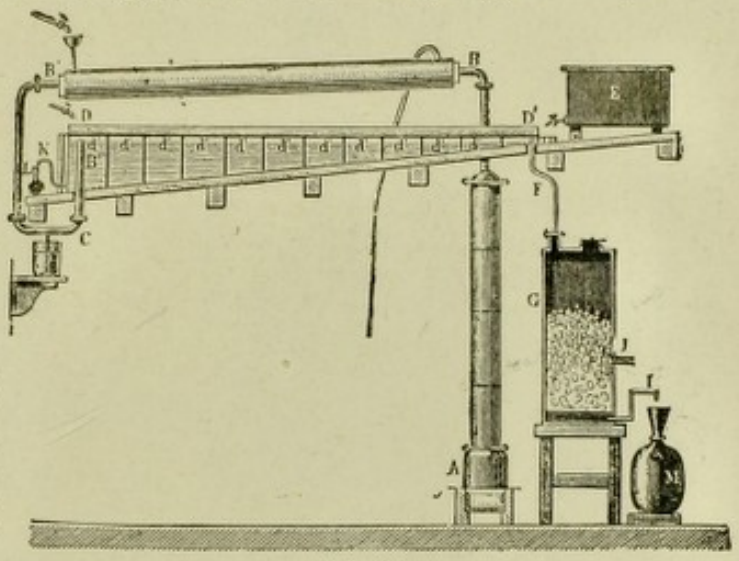


FIG. 91.

According to law (in Italy) the bomb may not contain more than 1 kilo of SO_2 per litre total capacity, so that a space of SO_2 vapour may be left, and explosions due to large variations of temperature thus avoided.

In the mines of Oppeln (Prussia) in 1893 1600 tons of liquid SO_2 were produced. Very large quantities are prepared in the factory of W. Grillo of Hamborn. In Italy 13 tons of liquid SO_2 were produced in 1902, and in 1904 50·7 tons were imported, of the value of £1217. In 1906 34·4 tons were imported at £14 per 100 kilos, and in 1908, about 51·3 tons of the value of £1088. The cost of production is about 4*s.* per 100 kilos, and the sale price for large quantities was £5 12*s.* per ton in 1899 in tank-waggons at the works. In Italy it is sold in steel cylinders containing 25 or 50 kilos at 5·8*d.* per kilo ; in order that a factory making liquid sulphur dioxide may be profitable it must produce at least 8 to 10 tons per day.

INDUSTRIAL PREPARATION OF SO_2. The preparation of SO_2 gas for the manufacture of sulphuric acid, which constitutes the main consumption of sulphur dioxide, will be described later in speaking of that acid. We will confine ourselves now to the preparation of concentrated aqueous solutions of SO_2 and of pure liquefied SO_2, which is employed in many industries.

A concentrated aqueous solution of sulphur dioxide is obtained by the direct combustion of sulphur, making use, for example, of the apparatus of Hatschek, which has been applied in many industries.

The sulphur is burned on iron plates or pans arranged in a chamber, *A*, Fig. 91, which is surmounted by a lead chimney some metres in height in order to obtain a sufficient draught. The SO_2 passes along the refrigerator *BB'*, where the small quantities of sulphuric acid which are formed are condensed. These collect in a suitable vessel with a hydraulic

seal in the lower part of the tube *C*. The SO_2 gas, on the other hand, passes into the upper part of the condenser *d'*, formed of a wooden box lined with lead and covered by a shallow pan, *D*, along which water runs continuously, cooling the gas. The condenser is divided into several compartments with vertical walls which join each side of the condenser alternately in such a manner that the water which enters continuously at *E* and escapes saturated with SO_2 from the tube *K* is forced to traverse a zigzag path in the opposite direction to the gas which continuously passes over its surface. The chamber greatly diminishes in volume because the SO_2 gas diminishes in quantity as it is absorbed. The aqueous solution of SO_2 escapes from the tube *L*, and the non-absorbed SO_2 is absorbed by water passing through the tube *F* into the large vessel *G*, which contains soda crystals, which with SO_2 form sodium sulphite or bisulphite (*see* Part III).

Theoretically 4 cu. metres of air are required per kilo of sulphur ; in practice about $5\frac{1}{2}$ cu. metres are employed. In order that the work may be carried on continuously in the hot furnace, molten sulphur may gradually be added.

This method is economical, but it does not yield very concentrated solutions, and the decomposition of sulphuric acid by carbon is in many cases preferred. H_2SO_4 of 62° Bé.

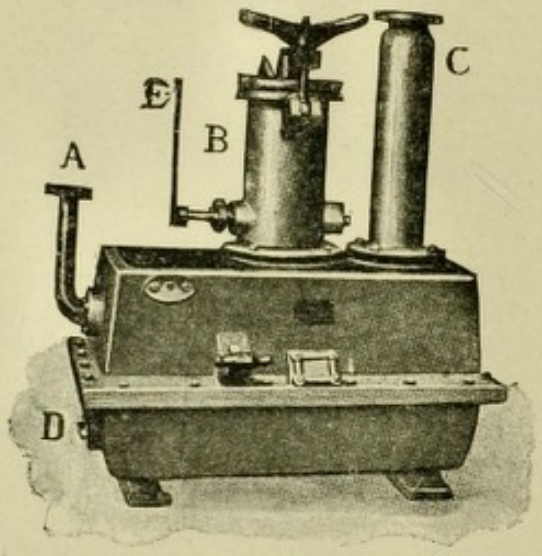


Fig. 92.

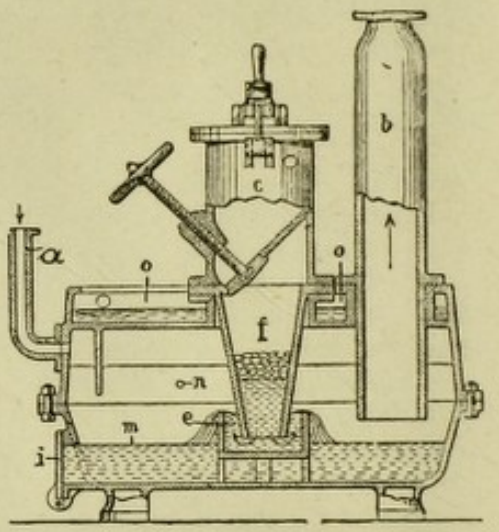


Fig. 93.

(sp. gr. 1·75) is employed : $2H_2SO_4 + C = CO_2 + 2SO_2 + 2H_2O$; if the acid is more concentrated CO is also formed : $H_2SO_4 + C = SO_2 + H_2O + CO$, and if it is very dilute H_2S is formed : $H_2SO_4 + 2C = H_2S + 2CO_2$. The operation is carried out in a very simple apparatus ; a species of stoneware receiver (*see* p. 162) with two necks containing wood-charcoal is immersed in a sand-bath placed over a furnace. Sulphuric acid is allowed to drop slowly on to the carbon and this is heated. The SO_2 gas is condensed in three successive receivers which communicate and contain water. In the first the sulphuric acid carried over by the gas is retained ; in the second and third the concentrated solution of SO_2 is formed and is removed from cocks which are fitted into the base of the receivers.

A very convenient and much used apparatus which is suitable for either small or large quantities of sulphur (from 10 to 50 kilos) is that illustrated in Fig. 92. The two superposed halves of this furnace are made of cast iron and are united by bolts. In the interior is a pan which receives the sulphur from the cylinder *B*, which is furnished with a revolving plate which can be turned by the handle *E* in such a way as to be able to charge the cylinder *B*, even during working. When the mouth of *B* is closed the sulphur can be discharged into the interior of the furnace by turning the handle *E*. By opening the aperture *D* momentarily the combustion can be started by means of a red-hot iron rod, and this hole is then closed and a regular current of air passed through *A* from a compressor or pump in order to burn the sulphur. The sulphur dioxide escapes through the tube *C*, and is conducted to the absorption or condensing apparatus.

In order to avoid too great a rise of temperature in the interior of the furnace, which would damage the pan and cause the sulphur to distil, the whole apparatus is completely immersed in a box through which cold water runs. A furnace which burns 100 kilos of

sulphur in twenty-four hours costs about £24. Various improvements on this furnace will be found described in Ger. Pat. 196,371 of 1907–1908, and its section is illustrated in Fig. 93. The sulphur is lighted through the aperture *n*, and during combustion the furnace is fed with sulphur in pieces through *c* into a funnel, *f*, which continuously allows molten sulphur to accumulate in the pan *e*. As the sulphur melts, it overflows into the furnace at *m*. Cooling is effected by passing water over the cover *o*, and air is passed in under pressure in order to burn any sublimed sulphur in the delivery tube *b*.

PREPARATION OF LIQUID SULPHUR DIOXIDE. In 1878 R. Pictet prepared liquid sulphur dioxide for his ice machines by allowing a continuous stream of strong sulphuric acid to pass on to molten sulphur which was placed in a cast-iron retort and heated to 400° : $2H_2SO_4 + S = 3SO_2 + 2H_2O$.

The strong sulphuric acid simultaneously serves to dry the SO_2 and to retain the sublimed sulphur which is carried over by the gas ; this is passed through a loose filter of cotton wool. The gas is then cooled to $-10°$ and compressed in order to obtain the liquid. R. Pictet also proposed to separate pure SO_2 from dilute aqueous solutions by separation of the water by freezing. Certain French works use the Melsens-Pictet process.

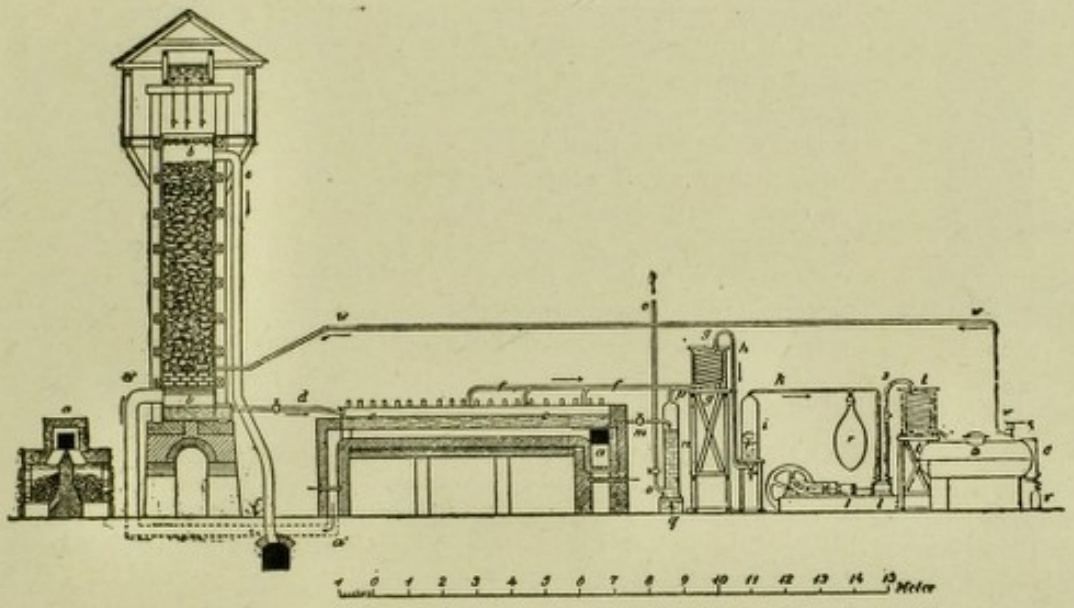


Fig. 94.

The gases obtained in the combustion of pyrites contain less than 9 per cent. by volume of SO_2 and give very dilute solutions with water containing about 2 per cent. by weight of SO_2, whilst by the above-described process the solutions contain from 10 to 12 per cent. by weight. The process of Hänisch and Schroeder patented in 1883 and perfected later (Ger. Pat. 52,025 of 1889) is of more industrial importance.

Hänisch and Schroeder prepare liquid sulphur dioxide even from gases containing 4 per cent. per volume of SO_2 only.

The complete plant is illustrated in Fig. 94. The very hot gases proceeding from the pyrites burner *a*, to the left of the figure, are passed through suitable flues, which are not indicated in the figure, under a lead basin, *e*, which contains an aqueous solution of SO_2 which is being evaporated. The somewhat cool gases then pass through the tube *a'* into the lower part of the lead tower *b*, which is filled with coke and in which they rise and meet a fine spray of water which falls from the top and dissolves all the SO_2. The other gases, *O* and *N*, pass to the chimney through the pipe *c*. The dilute aqueous SO_2 solution collects in the pan *b*, at the base of the tower, and passes thence through the tubes *d* into the evaporating pan *e*. The mixture of water vapour and SO_2 which is formed enters the bottom of the condensing tower *g* through the tube *f*. The condensing tower is to-day built differently from the one indicated in the figure ; and it, together with the other small tower, *n*, is replaced by a much more effective tower which will be described below. In any case moist SO_2 vapour alone escapes from the top of the tower through the tube *h*, and is dried in the cylindrical vessel *i*, through which a spray of strong sulphuric acid continuously falls. The dry SO_2 gas is absorbed and compressed by the pump *i*, and then enters the

spiral *t*, surrounded by cold water in which it is liquefied and accumulates in the iron receiver *u*. The iron cylinders *v*, in which the liquid SO_2 is sold, are filled by means of suitable cocks, as is seen in the figure, and the air which escapes from the cylinders enters the vessel *u*, and together with a small amount of SO_2 vapour passes into the pipe *w*, provided with pressure-valves, and from there is carried to the base of the tower *b*.

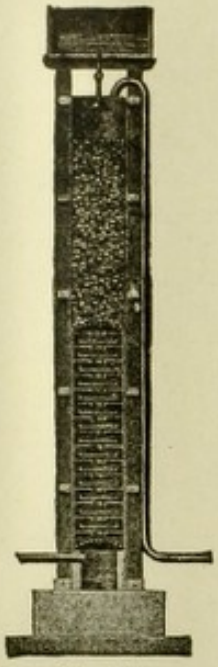


Fig. 95.

In order that the whole plant may be maintained at a fairly constant pressure which is not unduly affected by the action of the pump, a large india-rubber bag, *r*, is interposed between the pump and the rest of the plant, and serves to lessen the oscillations of pressure.

Hänisch and Schroeder separate the SO_2 in the tower *g* by means of a very ingenious principle. This tower to-day takes the form indicated in Fig. 95. A very hot mixture of steam and SO_2 enters the lower part of the lead tower, the lower half of which is filled with clay or stone plates in order to lengthen the passage of the gas, and the upper part of which contains coke. A very fine spray of cold water falls from the top of the tower in such quantity that it just serves to condense the water vapour, which then gives up its entire heat of evaporation (536 cals.) to the condensed water and maintains it at a temperature of about 100°. But at this temperature the water cannot retain more than 0·1 to 0·5 per cent. of SO_2, and almost pure water collects at the bottom of the tower, whilst pure SO_2 only mixed with a very small quantity of water vapour escapes from the top and is completely dried with H_2SO_4 in the cylinder *i*, shown in the preceding figure. As we see, in the older plant the condensed water enters the cylinder *n*, through which a jet of steam is passed, which proceeds from *o* and carries over the last traces of SO_2. When the new condensing tower is used this operation is unnecessary.

A proposal has been made (Ger. Pat. 160,940) to absorb the SO_2 from very dilute but dry gaseous mixtures by means of dicalcium phosphate :

$$2PO_4HCa + 2SO_2 + 2H_2O = \underset{\text{monocalcium phosphate}}{Ca(PO_4H_2)_2} + \underset{\text{calcium disulphite}}{(SO_3H)_2Ca}.$$

On then heating this product to 100° all the SO_2 is driven off from the bisulphite, and the dicalcium phosphate is regenerated.

SULPHUROUS ACID : H_2SO_3

The acid is not known in the free state, but is supposed to exist in aqueous solutions obtained by saturating water with SO_2. With time, and in the light, the solution decomposes with separation of sulphur and formation of sulphuric acid : $3SO_2 + 2H_2O = 2SO_4H_2 + S$.

On the other hand, the salts derived from this acid are well known (Part III), such as acid sodium sulphite $NaHSO_3$ (also called bisulphite) and the normal sulphite Na_2SO_3, both of which evolve SO_2 copiously when treated with mineral acids :

$$SO_3Na_2 + 2HCl = 2NaCl + H_2O + SO_2.$$

The constitutional formula of sulphurous acid is supposed to correspond to one or other of the two following isomers : $O=S\begin{matrix}\diagup OOH\\ \diagdown H\end{matrix}$ or $O=S\begin{matrix}\diagup OH\\ \diagdown OH\end{matrix}$

Certain organic derivatives correspond to the second formula, and certain inorganic salts to the first asymmetric formula.

Sulphurous acid is a weak acid which is not able to completely saturate energetic bases, so that the normal sulphites show a weakly alkaline reaction, whilst the bisulphites or acid sulphites show a weakly acid reaction ; and this is easily explained by the ionic theory, on account of the hydrolysis which occurs in aqueous solution, as has been explained at length for the salts of sulphydric acid (*see* pp. 238–239). Thus disodium sulphite, which might

be expected to show a neutral reaction, actually shows an alkaline reaction in aqueous solution, because it is hydrolised and alkaline hydroxyl ions are formed :

$$Na_2{}^{\cdot\cdot}SO_2{}^{\prime\prime} + H_2O = Na^{\cdot}HSO_3{}^{\prime} + Na^{\cdot}OH^{\prime}.$$

HYDROSULPHUROUS ACID : $H_2S_2O_4$

Schönbein already observed in 1852 that iron and zinc dissolve in an aqueous solution of sulphurous acid without development of hydrogen, and that the yellow liquid which results has a strongly reducing and bleaching action, much greater than that of SO_2, especially for indigo, and that it is easily decomposed with separation of sulphur and sulphurous acid. The solution in question contains hydrosulphurous acid, the composition of which is known from that of its salts.

The salts, called *hydrosulphites*, are stable, and are largely used in various industries, sometimes under the name of hyposulphites (*see* Part III).

SULPHUR SESQUIOXIDE : S_2O_3

This substance is obtained as a blue mass, which is first liquid and then solidifies, on dissolving sulphur in liquid sulphur trioxide. It is readily decomposed into SO_2 and sulphur. It decomposes violently with water, forming $SO_2 + S + H_2SO_4$ and polythionic acids. It dissolves in fuming sulphuric acid to form a blue liquid. It is used in the manufacture of aniline colours (naphthazarine).

SULPHURIC ACID : H_2SO_4

At the end of the eighteenth century Gebir knew and prepared sulphuric acid, which he obtained by distilling alum and iron sulphate.

About the year 1450 Basil Valentine obtained it by burning sulphur in presence of nitre. Angelo Sala obtained it in 1613 by burning sulphur in presence of steam and an excess of air, and in 1620 Lefèvre and Lémery perfected Sala's method by employing nitre, as is still done to-day.[1] It is found free in nature in certain rivers in America (Rio Canea and Rio Vinagre) which carry down to the sea daily 37,000 kilos of sulphuric acid and 31,000 kilos of hydrochloric acid. The mineral waters of Levico in Trent, which are used for baths, contain as much as 8·33 grms. of free sulphuric acid per litre.

It is also found in certain Sicilian snails called Aplisia : the juice which issues from the aperture of their shells produces a strong effervescence with marble, as it contains as much as 4 per cent. of free sulphuric acid.

It is much diffused as calcium sulphate in the minerals (gypsum $SO_4Ca.2H_2O$ and anhydrite SO_4Ca).

PHYSICAL PROPERTIES. The sulphuric acid which is obtained in lead chambers (*see below*) contains about 63 per cent., and in order to concentrate it, it must be distilled. It is impossible, however, to obtain by distillation an acid containing more than 98·5 per cent. of H_2SO_4, because even on distilling a 100 per cent. acid obtained by other means an acid of 98·6 per cent. is always obtained, the rest being water formed by the decomposition of the acid, which has a specific gravity of 1·842 at 12°. In order to separate this final portion of water, the acid is cooled to −10° and a few crystals of purest frozen sulphuric acid are then added. This causes the crystallisation of sulphuric acid free from water from the remaining liquid from which it is separated by means of a centrifuge (Lunge). The acid so obtained is the so-called sulphuric acid monohydrate ($SO_3 + H_2O$). This contains 100 per cent. of H_2SO_4, has a specific gravity of 1·838 at 15°, and is thus less dense than the distilled acid, although it is more concentrated.

The monohydrate already yields vapours of SO_3 and water at 40°. It commences to boil at 290°, and at 338° gives in this way an acid containing

[1] *Sala* was a medical man and chemist of Vincentio who lived at the Court of Mecklenburg and introduced the use of silver nitrate into medicine.

1·5 to 2 per cent. of water. At 416° it dissociates completely into SO_3 and H_2O. The acid of 50° Bé. commences to boil at 147°, acid of 60° Bé. at 200°, and acid of 66° Bé. (98·5 per cent.) has both specific gravity and boiling-point (338°) higher than that of the monohydrate.

The concentrated acid is a dense oily liquid ; when it contains 15 per cent. of water a crystalline hydrate, $SO_4H_2 + H_2O$, separates at 0°. This melts at + 8° ; the hydrate, $SO_4H_2 + 2H_2O$, is also known. Acid of 60° Bé. easily freezes in winter and bursts the carboys in which it is contained ; if it is somewhat more or somewhat less concentrated it does not freeze.

On mixing with water much heat is evolved with contraction of the total volume (8 per cent. of contraction with 27 per cent. H_2O), and in order to prepare the mixture one should always pour the acid slowly into the water, with thorough stirring, and not the water into the acid, in order to avoid spurting of the acid caused by the large quantity of heat which is immediately developed.

On mixing 1 mol. (98 grms.) of sulphuric acid monohydrate with 1 mol. of water (18 grms.) 26·2 Kj. (6262 cals.) are developed, with 10 mols. of water 63 Kj., with 100 mols. (that is, 1800 grms. of water) 70·5 Kj., and with 1000 mols. 74·5 Kj. (that is, 17,800 cals.) are formed in consequence of the formation of a progressive series of hydrates and of the contraction of volume (*see* p. 27).

On the other hand, on mixing concentrated sulphuric acid with snow, a very high degree of cold is produced, because the heat of solution of the acid is lower than the heat of fusion of the snow.

The specific heat of the monohydrate is 0·3315, that of the dilute acid (1 to 2 of water) is 0·725, whilst that of 1 to 20 of water is 0·955, that of water being 1.

The heat of formation of H_2SO_4 is 596 Kj. (= 142,500 cals.).

The vapour tension of the water in 40 per cent. acid is 3 mm. of mercury at 20°, 25 mm. at 60°, and 143 mm. at 100°. In acid containing 20 per cent. of water the vapour tension is 1 mm. at 20°, 1·6 at 60°, and 10 mm. at 100° ; finally acid containing 2 to 10 per cent. of water shows no vapour tension of water even at 100°. At concentrations above 98·5 per cent. of H_2SO_4, the tension is mainly due to vapours of SO_3.[1]

CHEMICAL PROPERTIES. Concentrated sulphuric acid has so much affinity for water that it abstracts hydrogen and oxygen from many organic substances, and thus chars them. It is especially used at concentrations above 60° Bé. for drying gases. Its vapours are already dissociated into

[1] TABLE OF THE VAPOUR TENSION OF WATER IN SULPHURIC ACID

Specific gravity of the acid	Per cent. H_2SO_4	Temperature									
		10°	20°	30°	40°	50°	60°	70°	80°	90°	95°
		Vapour tension in mm. of mercury									
1·342	44	4·4	8·5	15·5	28·1	48·3	—	—	—	—	—
1·380	48	3·7	7·1	13·4	23·9	40·1	69·0	107·2	—	—	—
1·418	52	3·0	5·8	10·9	18·9	31·5	54·0	84·5	131·2	207·9	251·5
1·459	56	2·2	4·3	8·1	14·2	24·1	41·6	65·0	100·9	160·0	195·0
1·502	60	1·6	3·0	6·1	10·0	16·9	28·7	46·1	72·3	118·7	146·0
1·547	64	1·2	2·2	4·0	6·5	10·9	18·7	30·3	48·0	83·7	105·0
1·592	68	0·9	1·5	3·0	4·5	7·2	12·3	19·4	31·4	56·0	72·0
1·638	72	0·7	1·0	2·0	3·2	4·8	7·5	12·0	20·0	33·7	43·4
1·687	76	0·4	0·5	1·4	2·1	3·0	4·8	7·5	11·8	18·5	22·0
1·733	80	0·2	0·3	0·8	1·3	1·9	2·9	4·1	6·2	9·3	11·0
1·755	82	0·1	0·2	0·5	0·9	1·4	2·0	2·7	3·9	5·6	6·8

SO_3 and H_2O. It decomposes in contact with red-hot porous substances. $SO_4H_2 = H_2O + SO_2 + O$ (p. 179). It does not dissolve platinum, gold, or lead, and when very concentrated does not even attack iron in the cold, and may therefore be transported in tank waggons of sheet iron.[1]

It is a strong acid which displaces other acids from their various salts, but at high temperatures it is displaced in turn by acids which are ordinarily weak, but more stable at such temperatures, such as boric, silicic, and phosphoric acids.

In H_2SO_4 hexavalent S is probably present $\begin{matrix} O = \\ O = \end{matrix}\!\!>\!S\!<\!\!\begin{matrix} -OH \\ -OH \end{matrix}$. It is a dibasic acid forming acid and neutral sulphates. Certain neutral sulphates, for example, that of copper, redden litmus paper. The sulphates in general are insoluble in alcohol, and the alkali sulphates remain unaltered even at the highest temperatures, whilst the others decompose, forming metallic oxides + SO_2 + O.

Sulphuric acid is poisonous ; magnesia is used as an antidote, but if the acid is concentrated it immediately attacks the mucous membrane of the stomach.

We give on p. 251 a table of densities of sulphuric acid at all concentrations. It should be noted that beyond 65° Bé. (90 per cent. H_2SO_4) it is practically impossible to determine the concentration by means of the density, because this latter varies so slightly, and the strength should then be determined by means of direct analysis.

APPLICATIONS OF SULPHURIC ACID. This acid, like soda, is used for such various purposes that the extent of its production is a certain indication of the industrial and civil development of the various nations. About two-thirds of the consumption of chamber acid is used for the production of artificial manures (superphosphates). Further quantities are used in the manufacture of stearine, oleine, and soaps, in the tinning and "galvanising" of iron, in the dyeing of wool and silk, for the production of sodium sulphate, and thus of soda, by the Leblanc process, for the production of hydrochloric and nitric acids of SO_2, CO_2, the sulphates of copper and iron, of alum, boot blacking, &c. It is also used in the manufacture of tartaric and citric acids. The more concentrated acid (66° Bé.) is used in the manufacture of nitroglycerine and various other explosives, of artificial dyestuffs, in the manufacture of petroleum and mineral oils, parchment, paper, &c.

STATISTICS OF PRODUCTION OF H_2SO_4.

England	in 1888	produced	800,000	tons	(calculated at 60° Bé.)	
,,	1900	,,	992,000	,,	,,	,,
,,	1905	,,	1,400,000	,,	,,	,,
France	in 1889	,,	234,000	,,	,,	,,
,,	1905	,,	870,000	,,	,,	,,
,,	1908	,,	1,000,000	,,	,,	,,

[1] *Resistance of metals to the action of H_2SO_4.* Wrought iron is less resistant in the heat, but in the cold, on the other hand, it is not attacked by acid of greater strength than 60° Bé. ; the resistance is greater with iron, which contains little silicon, much manganese, much combined carbon, and little graphitic carbon (which is the opposite to the effect produced with regard to the resistance to alkalis). Cast iron has greater resistance than wrought iron, even at high temperatures, and is not attacked in the cold by acid of 50° Bé. if air is excluded. For the storage of oleum (fuming acid), on the other hand (*see below*), wrought-iron vessels must be used and not vessels of cast iron. Lead resists dilute acid better than concentrated acid, and therefore the acid in the lead chamber should not exceed a strength of 50° Bé.

Lead is the more resistant the purer it is, and fusible alloys have only a very slight resistance. Hard lead which contains 2 to 18 per cent. of antimony is less resistant on heating. Bismuth renders lead less resistant even if only 0·01 per cent. is present. Concentrated Glover acid attacks lead more than concentrated H_2SO_4. Mixtures of concentrated nitric and sulphuric acids, and even concentrated nitric acid (sp. gr. 1·37 to 1·42), attack lead very little in the cold, whilst dilute nitric acid dissolves lead freely even in the cold. Hydrofluoric acid attacks lead slightly at high temperatures (Glover tower) ; copper resists sulphuric acid better than lead ; hard lead is less resistant than pure lead, but develops less hydrogen, and is therefore preferred for the transport of sulphuric acid in closed vessels. Oleum attacks lead more than concentrated H_2SO_4.

Japan in	1900	produced	60,000	tons	(calculated at 60° Bé.)	
,,	1905	,,	64,000	,,	,,	,,
Germany in	1882	,,	287,000	,,	,,	,,
,,	1901	,,	857,000	,,	,,	,,
,,	1905	,,	1,200,000	,,	,,	,,
,,	1908	,,	1,600,000	,,	,,	,, ($\frac{1}{10}$ catalytic)
United States in	1905	,,	1,090,000	,,	,,	,,

In 1905 Germany imported 33,874·6 tons of sulphuric acid at £2 5*s.* per ton, being £76,160, and exported 48,754·5 tons of the value of £109,600. In 1908 the exports rose to 60,000 tons, and the imports also rose. In 1909 the exports were 64,000 tons and the imports 74,400 tons.

In 1905 the United States produced 92,000 tons of sulphuric acid from zinc sulphide. In 1908 there were 15 works which used crude sulphur with a yield of 432 per cent. of sulphuric acid at 50° Bé. ; and 105 works, which worked with iron pyrites, with a yield of 211 per cent.

						£
In Italy in	1879	13 works	produced	10,000 tons	at 52° Bé., value	45,720
,,	1890	20	,,	60,000	,, ,,	120,000
,,	1901	30	,,	235,000	,, ,,	357,600
,,	1903	—	,,	263,018	,, ,,	397,868
,,	1905	—	,,	302,100	,, ,,	400,908
,,	1908	90 (?)	,,	524,210	,, ,,	840,000

About 80 per cent. of all the sulphuric acid produced in Italy is used in manure factories, the larger number of which are connected with the sulphuric acid factories. Six per cent. is used for copper sulphate, 3½ per cent. for the manufacture of nitric and hydrochloric acids, 4½ per cent. in the preparation of sulphates of aluminium, ammonium, manganese, barium, zinc, &c. ; 6½ per cent. are used for all other purposes. In 1908 Italy exported 200 tons of sulphuric acid valued at £600.

In 1880 the world's production was 1,850,000 tons, in 1892 2,818,000 tons, in 1902 4,450,000 tons, and in 1909 8,000,000 tons (calculated at 60° Bé.).

The price of sulphuric acid varies somewhat ; crude lead chamber acid at 52° Bé. is sold at about £1 8*s.* per ton ; that at 60° Bé. at about £2 8*s.* per ton, at 65° to 66° Bé. at £3 4*s.* per ton.

PREPARATION OF H_2SO_4. The formation of this acid by decomposition of certain metallic sulphates is of theoretical interest :

$$Ag_2SO_4 + 2HCl = 2AgCl + H_2SO_4.$$
$$CuSO_4 + H_2S = CuS + H_2SO_4.$$

H_2SO_4 was first prepared on a large scale by heating iron sulphate and condensing the gas in a little water, thus using the sulphur trioxide only : $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$.

Attempts were also made to obtain it by the interaction of chlorine, SO_2, and water, as was explained on p. 165. Sulphuric acid has recently been obtained (1910) by the action of ultra-violet rays on moist SO_2 (*see* Ozone). The preparation of H_2SO_4, by passing the mixture of H_2S and SO_2 (as obtained in the recovery of sulphur in the Leblanc soda works by the Chancel-Claus process, *see* Part III) over a catalytic mass of platinum at 540°, has also been proposed (Ger. Pat. 157,589). In 1909 H. Trey (Ger. Pat. 207,761) obtained sulphuric acid by heating calcium sulphate with silicious sand to 1250°–1400° ; the sand contained 0·5 per cent. of iron oxide, which acts as a catalyst. The mixture of $SO_2 + O$ which is formed may also be used for the catalytic preparation of SO_3 (*see below*) ; the silicious residue from this process may be utilised in glass factories. This process has already been applied in a large works. According to a United States patent (930,471 of 1909), by W. Hallock, sulphuric acid is obtained by submitting a mixture of $SO_2 + H_2O$ + air to the action of radio-active emanations.

Sulphuric acid is now prepared industrially from SO_2 obtained by burning

SPECIFIC GRAVITIES OF SULPHURIC ACID SOLUTIONS AT 15° C. (LUNGE).

Sp. gr. at $\frac{15°}{4}$ (vacuum)	Baumé degrees	100 parts by weight of pure acid contain—		1 litre of pure acid contains in kilos		Sp. gr. at $\frac{15°}{4}$ (vacuum)	Baumé degrees	100 parts by weight of pure acid contain—		1 litre of pure acid contains in kilos	
		SO_3	SO_4H_2	SO_3	SO_4H_2			SO_3	SO_4H_2	SO_3	SO_4H_2
1·005	0·7	0·68	0·83	0·007	0·008	1·495	47·8	48·34	59·22	0·723	0·885
1·015	2·1	1·88	2·30	0·019	0·023	1·505	48·4	49·12	60·18	0·739	0·906
1·025	3·4	3·07	3·76	0·032	0·039	1·515	49·0	49·89	61·12	0·756	0·926
1·035	4·7	4·27	5·23	0·044	0·054	1·525	49·7	50·66	62·06	0·773	0·946
1·045	6·0	5·45	6·67	0·057	0·071	1·535	50·3	51·43	63·00	0·789	0·967
1·055	7·4	6·59	8·07	0·070	0·085	1·545	50·9	52·12	63·85	0·805	0·987
1·065	8·7	7·73	9·47	0·082	0·102	1·555	51·5	52·79	64·67	0·821	1·006
1·075	10·0	8·90	10·90	0·096	0·117	1·565	52·1	53·46	65·49	0·837	1·025
1·085	11·2	10·04	12·30	0·109	0·133	1.575	52·7	54·13	66·30	0·853	1·044
1·095	12·4	11·16	13·67	0·122	0·150	1·585	53·3	54·80	67·13	0·869	1·064
1·105	13·6	12·27	15·03	0·136	0·166	1·595	53·9	55·55	68·05	0·886	1·085
1·115	14·9	13·36	16·36	0·149	0·183	1·605	54·4	56·30	68·97	0·904	1·107
1·125	16·0	14·42	17·66	0·162	0·199	1·615	55·0	57·05	69·89	0·921	1·128
1·135	17·1	15·48	18·96	0·176	0·215	1·625	55·5	57·75	70·74	0·938	1·150
1·145	18·3	16·54	20·26	0·189	0·231	1·635	56·0	58·43	71·57	0·955	1·170
1·155	19·3	17·59	21·55	0·203	0·248	1·645	56·6	59·10	72·40	0·972	1·192
1·165	20·3	18·64	22·83	0·217	0·266	1·655	57·1	59·78	73·23	0·989	1·212
1·175	21·3	19·69	24·12	0·231	0·283	1·665	57·7	60·46	74·07	1·007	1·233
1·185	22·5	20·73	25·40	0·246	0·301	1·675	58·2	61·20	74·97	1·025	1·256
1·195	23·5	21·78	26·68	0·260	0·319	1·685	58·7	61·93	75·86	1·043	1·278
1·205	24·5	22·82	27·95	0·275	0·337	1·695	59·2	62·64	76·73	1·062	1·301
1·215	25·5	23·84	29·21	0·290	0·355	1·705	59·7	63·35	77·60	1·080	1·323
1·225	26·4	24·88	30·48	0·305	0·373	1·715	60·2	64·07	78·48	1·099	1·346
1·235	27·4	25·88	31·70	0·320	0·391	1·725	60·6	64·78	79·36	1·118	1·369
1·245	28·4	26·83	32·86	0·334	0·409	1·735	61·1	65·50	80·24	1·136	1·392
1·255	29·3	27·76	34·00	0·348	0·426	1·745	61·6	66·22	81·12	1·156	1·416
1·265	30·2	28·69	35·14	0·363	0·444	1·755	62·1	66·94	82·00	1·175	1·439
1·275	31·1	29·62	36·29	0·377	0·462	1·765	62·5	67·65	82·88	1·194	1·463
1·285	32·0	30·57	37·45	0·393	0·481	1·775	63·0	68·49	83·90	1·216	1·489
1·295	32·8	31·52	38·61	0·408	0·500	1·785	63·5	69·47	85·10	1·240	1·519
1·305	33·7	32·46	39·77	0·424	0·519	1·795	64·0	70·45	86·30	1·265	1·549
1·315	34·6	33·41	40·93	0·439	0·538	1·805	64·4	71·50	87·60	1·291	1·581
1·325	35·4	34·35	42·08	0·455	0·557	1·815	64·8	72·69	89·05	1·319	1·621
1·335	36·2	35·27	43·20	0·471	0·577	1·821	65·0	73·63	90·20	1·341	1·643
1·345	37·0	36·14	44·28	0·486	0·596	1·823	65·1	73·96	90·60	1·348	1·651
1·355	37·8	37·02	45·35	0·502	0·614	1·825	65·2	74·29	91·00	1·356	1·661
1·365	38·6	37·89	46·41	0·517	0·633	1·827	65·3	74·69	91·50	1·364	1·671
1·375	39·4	38·75	47·47	0·533	0·653	1·829	65·4	75·03	91·90	1·372	1·681
1·385	40·1	39·62	48·53	0·549	0·672	1·831	65·5	75·35	92·30	1·380	1·690
1·395	40·8	40·48	49·59	0·564	0·692	1·833	65·6	75·72	92·75	1·388	1·700
1·405	41·6	41·33	50·63	0·581	0·711	1·835	65·7	76·27	93·43	1·400	1·713
1·415	42·3	42·17	51·66	0·597	0·730	1·837	65·7	76·90	94·20	1·412	1·730
1·425	43·1	42·96	52·63	0·612	0·750	1·839	65·8	77·55	95·00	1·426	1·748
1·435	43·8	43·75	53·59	0·628	0·769	1·840	65·9	78·04	95·60	1·436	1·759
1·445	44·4	44·53	54·55	0·643	0·789	1·8415	—	79·76	97·70	1·469	1·799
1·455	45·1	45·31	55·50	0·659	0·808	1·8405	—	80·57	98·70	1·483	1·816
1·465	45·8	46·07	56·43	0·675	0·827	1·8395	—	81·18	99·45	1·494	1·830
1·475	46·4	46·83	57·37	0·691	0·846	1·8385	—	81·59	99·95	1·500	1·838
1·485	47·1	47·57	58·28	0·707	0·865						

iron, copper, or zinc pyrites; the copper and zinc are then utilised as is explained in Part III Copper Sulphate, &c.).

$$2FeS_2 + 11O = Fe_2O_3 + 4SO_2 + 419{\cdot}8 \text{ cals.}$$

Once this reaction has been started further heat is no longer required, because sufficient heat is evolved during combustion to continue the burning of the pyrites.

The gas which is produced by burning the pyrites in suitable ovens (*see below*) contains 7 to 8 per cent. of SO_2, the remainder being air and excess of nitrogen. Steam and oxygen furnished by nitrous fumes are added to this gas and the formation of H_2SO_4 takes place in large lead chambers (*see below*).

The phenomena which occur in the lead chambers have been the subject of a great deal of work and of many interpretations, as will be noted later.

The nitrogen of the air and the excess of air, when they issue from the lead chamber, carry with them considerable quantities of N_2O_3 (red vapours) which are utilised by absorbing them with concentrated sulphuric acid in the so-called Gay-Lussac towers. The so-called "nitrous" acid, which is a solution of nitrosylsulphuric acid (also called Weber's acid) in sulphuric acid, is thus obtained:

$$2SO_4H_2 + N_2O_3 = \overline{\underline{2SO_2}}\begin{matrix}ONO\\OH\end{matrix} + H_2O.$$

The nitrogen oxides are recovered from this acid in the Glover tower, through which the current of SO_2 which proceeds from the ovens is passed (*see below*).

The sulphuric acid which collects on the floor of the lead chamber contains about 63 to 65 per cent. of H_2SO_4. We will explain later how this is concentrated when necessary.

THEORY OF THE FORMATION OF H_2SO_4 IN THE LEAD CHAMBER. In 1884–1885 Lunge and Naef[1] showed experimentally, by analysing the gases in the lead chamber of a large works, that in the first chamber excess of NO is present compared with the NO_2, and that the gases are only slightly coloured; in the succeeding chambers about equal quantities of NO and NO_2 are always present. But neither in any of the chambers nor in the acid which is formed was excess of NO_2 present, nor was nitric acid found, and thus they believe that the reaction is not caused by the peroxide N_2O_4, but always by the trioxide N_2O_3, with intermediate formation of crystals of nitrosylsulphuric acid, which give H_2SO_4, with steam, regenerating N_2O_3:

$$(1) \qquad 2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2\begin{matrix}OH\\ \diagup\diagdown\\ ONO\end{matrix};$$

[1] A theory had already been propounded by Clément and Désormes in 1806, and was developed by Davy in 1812, which supposed the following reactions to occur: $2SO_2 + 3NO_2 + H_2O = NO + 2SO_2(OH)(ONO)$ (crystals). The NO is transformed into NO_2 by the oxygen of the air, and the crystals form H_2SO_4 with steam and air regenerating nitrogen peroxide: $2SO_2(OH)(ONO) + H_2O + O = 2SO_4H_2 + 2NO_2$. This theory was partially upheld later by Gmelin (1852), Winkler (1867), and Lunge (1884–1903), with certain modifications concerning the formation of nitrosylsulphuric acid.

In 1835 and 1844 Berzelius, who was followed for some years by many other chemists, maintained that the formation of crystals was not necessary and that the reaction occurred by the direct interaction of nitrogen peroxide (NO_2 or N_2O_4)SO_2 and water: $SO_2 + NO_2 + H_2O = H_2SO_4 + NO$, and that the NO reacted with the oxygen of the air to re-form NO_2. He supposed confusedly that a mixture of N_2O_3 and N_2O_4 was present in the chamber which gave rise to the formation of sulphuric acid. Peligot also, in 1844, did not admit that crystals were formed, and attributed the oxidisation of the SO_2 to the direct action of nitric acid and of regenerated nitrogen peroxide N_2O_4, which with water again formed nitric acid: $SO_2 + 2NO_3H = SO_4H_2 + N_2O_4$.

In 1867 R. Weber showed that the theory of Peligot was untenable because HNO_3 in contact with SO_2 forms H_2SO_4 slowly, whilst the reaction is easy with nitrous acid (HNO_2 or N_2O_3), especially if this is dissolved in water or dilute H_2SO_4, even without the formation of crystals: $SO_2 + N_2O_3 + H_2O = 2NO + H_2SO_4$. In 1867 C. Winkler maintained, on the other hand, that nitric oxide, which is formed in the reaction, is transformed into NO_2 or N_2O_4 by the oxygen of the air, and that this forms a white cloud of crystals of nitrosylsulphuric acid in contact with SO_2 and water vapour. This cloud is deposited, and in contact with the hot dilute sulphuric acid of the chamber decomposes into H_2SO_4 and NO, which latter is evolved as gas and again takes part in the cycle of reactions.

(2) $2SO_2 \begin{matrix} OH \\ ONO \end{matrix} + H_2O = 2H_2SO_4 + N_2O_3.$

In order to explain why the excess of NO is present in the first chamber where the reaction is more energetic and the temperature higher, Lunge suggested later that a direct action also occurred between nitrosylsulphuric acid and SO_2, an excess of NO being thus generated according to equation (3).

(3) $2SO_2 . OH . ONO + SO_2 + 2H_2O = 3SO_4H_2 + 2NO.$

He supposed that the nitrogen oxide thus formed in its turn renders the process in the first chamber more active by directly transforming SO_2 into nitrosylsulphuric acid, with the help of air and water vapour :

(4) $2SO_2 + 2NO + 3O + H_2O = 2SO_2(OH)(ONO).$

The reactions which occur in the lead chamber are in part reversible, and in order to explain them according to the law of masses, it is necessary that there should be certain relations between the reacting substances in order that the reaction may proceed in a given sense. Thus, if air or nitrous vapours are present in abundance the reactions (1) and (4) preponderate, whilst if there is a relative excess of SO_2 the reaction (3) will preponderate, and the gases are lighter in colour through the formation of colourless NO. This does not matter in the first chamber because NO is able to give the reaction (4), but it is harmful if it occurs in the last chamber, and NO is then lost, because it is not absorbed by H_2SO_4 in the Gay-Lussac tower. N_2O_3 should, therefore, abound in the last chamber (reaction (1)), so that all the SO_2 may be utilised. The vapours in the last chamber should be strongly yellowish brown in colour (N_2O_3). In general, then, the process in the chambers is regular and good if oxygen and nitrous vapours are abundantly present, otherwise SO_2 is lost, and if excess of air alone be present this is incapable of oxidising SO_2 and transforming it into H_2SO_4. During normal working not more than 0·5 per cent. of the sulphur burned in the ovens should be present in the final gases in the state of SO_2.

The equilibrium between the various reactions in the interior of the lead chambers is very complex, and depends upon three principal factors, namely, the quantitative relation between the reacting substances, the temperature and the volume of the lead chamber. The formation and decomposition of nitrosylsulphuric acid is closely connected with the vapour tension inside the chamber, and thus depends on temperature, and on the concentration of the sulphuric acid in the chamber itself, as well as on that of the condensed liquid, which is suspended in droplets as a mist. It is necessary to remember that the solution of N_2O_3 in H_2SO_4 (nitrosylsulphuric acid) has lesser vapour tension, and is therefore the more stable, the greater is the concentration of the acid and the lower the temperature, whilst the tension of the N_2O_3 increases with dilution of the acid, that is, by the action of water, and with elevation of the temperature, that is, the nitrosylsulphuric acid then re-generates N_2O_3 and H_2SO_4. In order to deduce *a priori* the state of affairs in the lead chamber, one must consider the temperature, the concentration of the acid which collects in the chamber, the quantity of water vapour, &c.

Lunge, Hurter, and Sorel have been able to demonstrate experimentally that in the lead chamber the process of sulphuric acid formation corresponds very well to that theoretically derived from the tension of H_2SO_4 vapours (in liquid or in drops).

Of late years it has been found that the so-called blue acid, H_2SNO_5 (sulphonitronic acid discovered by Sabatier), may be formed in Gay-Lussac towers, when an excess of nitrosylsulphuric acid has been formed, or when the temperature is higher than 30°, in presence of the coke which fills the tower. This acid decomposes to form sulphuric acid with loss of NO. Raschig maintains that this acid is always formed as an intermediate product in the production of sulphuric acid, and Lunge admitted in 1907 that the reaction (1) occurs in two phases : (1*a*) $SO_2 + NO_2 + H_2O = H_2SNO_5$, and (1*b*) $2H_2SNO_5 + O = H_2O + 2HSNO_5$ (nitrosylsulphuric acid), and that the reaction (3) also

occurs in two phases : (3*a*) $2HSNO_5 + SO_2 + 2H_2O = H_2SO_4 + 2H_2SNO_5$, and (3*b*) $H_2SNO_5 = H_2SO_4 + NO$, and then the cycle of reactions which forms sulphuric acid is completed by reaction (4*a*) $2NO + O_2 = 2NO_2$, which re-enters into reaction (1*a*).

In 1895 and 1901 Ostwald endeavoured to explain the formation of sulphuric acid in the lead chamber by attributing it to the catalytic action of N_2O_3, which, without taking any part in the reaction, was able, he supposed, to increase the velocity of reaction $SO_2 + O + H_2O = SO_4H_2$, which under ordinary conditions is very slow and almost imperceptible. In 1903, however, Lunge maintained that one cannot speak of a catalyst when the formation of intermediate products and the very great facility of reaction of these products without the intervention of the catalyst have been demonstrated.

In the case of true catalytic action there are no intermediate reactions, and the catalyst merely accelerates reactions which would take place very slowly without it, though in some cases they need several years in order to become apparent (*see* p. 68). It is maintained by some that H_2SO_4 is only formed in the chamber in contact with the leaden walls, which would thus act as catalysers, and hence the tendency to increase the surface area, as, for example, in Gilchrist's process.

The theoretical interpretation of the reactions taking place in the lead chamber is continuously under discussion, and the arguments have not yet terminated, but are being energetically carried on with much abundance of theoretical arguments and experimental results by Lunge, Raschig, and others.

In 1904 to 1908 Raschig attributed to the crystals of the lead chamber the constitutional formula SO_2 (OH) (NO_2) (nitrosulphonic acid), but he also supposed the intermediate formation in the chamber of nitrososulphuric acid, $HSNO_4$ (thus $HNO_2 + SO_2 = HSNO_4$), which, with HNO_2, forms blue acid, H_2SNO_5.

In 1904 Trautz, on the other hand, combined the various reactions of Lunge and Raschig, and arrived at the following inclusive equation : $SO_2 + 2NO + O + H_2O = H_2SO_4 + 2NO$, that is to say, he supposed that NO acts as a catalyser only, without taking part in the reaction.

From 1893 to 1910 Jurisch maintained that the reactions of Lunge and Raschig only take place when the lead chamber is behaving abnormally (that is, when there is an excess or deficiency of steam, air, or nitrous products, &c.). In the complete absence of water even nitrogen may be formed : $3SO_2 + N_2O_3 = 3SO_3 + N_2$, whilst during normal working the presence of N_2O_3 suffices to explain the continuous formation of sulphuric acid by means of a catalytic action or by continuous regeneration from NO and the atmospheric oxygen.

INDUSTRIAL PREPARATION OF SULPHURIC ACID

This industry has to-day acquired an extraordinary importance in every country, serving as the basis of many other industries, and the development of the sulphuric acid manufacture is justly used as a measure of the industrial progress of a nation. For this reason we will enter into various details in describing the most important operations and processes of this industry, which is very extensive in Italy.[1]

[1] The first sulphuric acid works was erected by Ward in 1740 at Richmond, near London. He heated a mixture of sulphur and saltpetre in iron capsules and collected the sulphuric acid vapours in glass vessels of 300 litres capacity, containing a little water. The product was concentrated by heating the glass vessels in a sand-bath, but great inconvenience was caused by the facility with which the vessels were broken. In order to avoid this trouble, Roebuck and Garbett in 1746 replaced them by receptacles or chambers of lead about two metres wide, in which a furnace in the centre produced the acid from sulphur and saltpetre. In 1766 this method was first introduced into France by Holker (at Rouen) ; in 1774 La Follie also passed a jet of steam into the lead chamber ; and in 1793 Clément and Bésormes showed the importance of a current of air in the lead chamber, which facilitated the formation of sulphuric acid and effected a notable saving of nitre and sulphur. Thus, before that time only 130 kilos of sulphuric acid were obtained from 100 kilos of sulphur, whereas to-day this yield is more than doubled. They had then already correctly interpreted the process of sulphuric acid formation, and said that the nitric acid was merely a means of fixing (by means of nitrous vapours) the oxygen of the air which transformed the SO_4

Very little pure sulphur is to-day employed as the source of sulphur. The sulphur which is obtained in the purification of lighting gas, which contains it as H_2S, is sometimes used, and so is that regenerated from the residues of the Leblanc soda industry. During the last few years Oddo has proposed the use of sulphur ores directly, but on account of certain technical difficulties and for economic reasons it does not appear to be practicable. Almost all sulphuric acid is to-day obtained from pyrites.

PYRITES. Pyrites is the material which is to far the greatest extent used to-day, especially iron pyrites, FeS_2, which theoretically contains 53·33 per cent. of sulphur. This is found abundantly in large mineral deposits in various countries, and often contains admixtures of sulphides of lead, zinc, copper, &c. In such cases, the copper, lead, zinc, gold, nickel, selenium, tellurium, thallium, &c., which it may contain, are also utilised and the sulphur is thus obtained at a lower cost.

Pyrites are most abundant in Spain, in which country there are deposits 107 kilometres long and 30 kilometres broad ; at some points their depth reaches 40 metres and they contain about 50 per cent. of sulphur (*see* section, Iron Sulphide).

In Italy the most important deposits of pyrites are in the Val d'Aosta, containing 48 to 50 per cent. of sulphur and much arsenic (and about 1 per cent. of zinc, whilst the pyrites of Brosso contain a maximum of 0·2 per cent.). There are also important mines in Libiola near Genoa, in Bergamasco, with about 0·5 per cent. of As ; in Veneto (Agorda and Vicenza), in Pallanza (30 to 35 per cent. of sulphur and up to 1 per cent. of nickel), in the Island of Elba, in Traversella, &c. ; and pyrites containing a considerable amount of copper are found in certain Tuscan mines. Pyrites containing less than 30 per cent. of sulphur burn badly. The consumption of pyrites for sulphuric acid manufacture in Italy in 1893 was about 60,000 tons, whilst the consumption of sulphur for the same purpose was 1000 tons. In 1908 Italy produced 132,000 tons of pyrites, and imported 164,400 tons, of which about half came from Spain. The world's consumption exceeded 3,000,000 tons. Pyrites are bought according to the percentage of sulphur, and for each unit of sulphur 3·7*d.* to 5·3*d.* is paid per ton. Pyrites containing 50 per cent. of sulphur at 4·8*d.* per unit thus cost £1 per ton at Genoa (customs charges not included).

The sulphur contained in pyrites as copper sulphide is not much utilised, because it partially forms calcium sulphate with calcium carbonate. That contained as zinc sulphide was formerly only utilised to one-half its extent, but it is better utilised to-day.

When 100 kilos of pyrites are burned 70 to 73 kilos of ash are obtained, which consists almost entirely of iron oxide, Fe_2O_3 (*burnt pyrites*).[1]

Pyrites containing copper are more valuable, but it is necessary to only roast them to such a point that the copper still remains in the form of sulphide, because it is thus more

into SO_3. In 1835 the first Gay-Lussac towers were installed in France for the condensation of nitrous vapours and effected a great economy of saltpetre.

In 1861 the first Glover tower was erected at Newcastle in order to regenerate the nitrous vapours condensed by sulphuric acid in the Gay-Lussac tower. Until about the year 1835 Sicilian sulphur had always been employed for the manufacture of sulphuric acid, but when the Government of Ferdinand II. of Bourbon, at Naples in 1858, conceded the monopoly of sulphur-mining to the House of Taix-Aycard and Co., of Marseilles, a concession which raised the price from 9*s.* 7*d.* to 28*s.* per ton, all Europe endeavoured to obtain sulphur from other sources, especially from pyrites ; and America alone used impure Sicilian sulphur, containing 90 per cent. of sulphur, until 1882. In 1835 Perret had already devised a furnace for roasting pyrites and obtaining the sulphur in the form of SO_2 ; and in 1852 Usiglio proposed the use of muffle-furnaces, which, however, left a residue containing 15 per cent. of sulphur. From 1848 to 1867 the furnaces were further perfected by Perret and then by Oliver constructing the burners with several grates in order to burn lumps of pyrites as well as a more finely divided product.

The first sulphuric works in Italy was constructed in 1805 and enlarged in 1815 in the Church of San Vincenzo al Prato in Milan, conceded freely by Napoleon to Francesco Fornara di Massimo d'Arona. The Sclopis works at Turin were erected about the year 1845 with lead chambers (though for many years these works produced H_2SO_4 without chambers), and a few years afterwards the important works of Candiani and Biffi at Milan were erected.

[1] The utilisation of burnt pyrites is a problem which has not been solved, and in many cases the works are more or less choked by the enormous masses of this by-product which have accumulated. In 1874 Hochberger advised the use of burnt pyrites, after sifting, for the polishing of glass and mirrors ; and it has been used for this purpose, but the consumption is absurdly small. It is also used as road metal, but even then gives very much dust. It is employed for absorbing H_2S in gas manufacture, but is not so suitable for this purpose as limonite, and requires larger plant than the latter. Buisine uses it for the preparation of sulphur, ferrous sulphate and ferric sulphate, by heating it with acid at 60° Bé. Attempts have also been made to manufacture bricks from burnt pyrites. Arnois obtained a red mineral pigment similar to colcothar by mixing it with 3 to 4 per cent. of NaCl and $CaCO_3$ and heating to redness in an oxidising furnace. Pyrites burnt in lumps still contains 1·5 to 3 per cent. of sulphur, and burnt powdered pyrites from 0·7 to 1·5 per cent. Cupriferous pyrites contains 1·5 to 3 per cent. of sulphur after burning, which is partially present as sulphide and partly as sulphate. A considerable quantity of burnt pyrites, containing comparatively little sulphur, is utilised in large metallurgical centres for the preparation of iron in blast-furnaces. It does not stand heavy freight charges, and therefore in certain centres where large quantities of burnt pyrites are obtained it may, perhaps, pay to erect a small blast-furnace for the production of iron of poor quality, which has, however, only a low value.

easily extracted. Lead, zinc, and calcium carbonate are disadvantageous in iron pyrites because they form insoluble sulphate on roasting. Calcium fluoride produces HF which damages stoneware and lead apparatus. If the pyrites contain arsenic, arsenic trioxide is formed. This is sometimes harmful, and the acid of the first chamber may contain up to 0·2 per cent. of As, and that from the Glover tower up to 0·35 per cent. Pyrites which are poor in sulphur give a smaller *relative* yield, and the cost of working is proportionately greater for the same quantity of sulphur than in the case of rich pyrites.

PYRITES BURNERS. The first burners were those of Olivier-Perret which worked badly on account of the varying size of the crushed pyrites. In the works of Maletra at Rouen and at St. Denis, separate burners are constructed for roasting pyrites in lumps and in powder. These Maletra furnaces are in general use to-day, with various modifications in all works.

The pyrites first pass through a rock-breaker (Fig. 96) which is able to treat 40 to 130 tons of pyrites in ten hours ; 86 per cent. of the product consists of pieces as large as nuts and 14 per cent. of small pieces and powder.

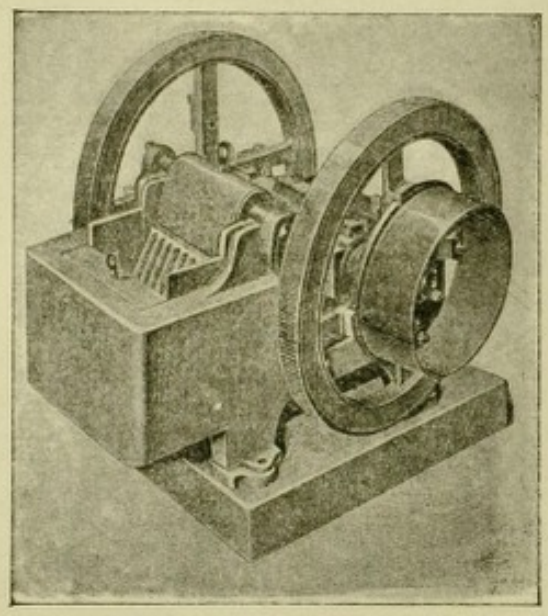


Fig. 96.

The mineral is charged into the rock-breaker on the left and falls on to the vertical grooves of a hard cast-iron plate, to which a vertical oscillatory movement is imparted by means of large flywheels, and a sort of mastication of the mineral is thus effected.

(*a*) **Pyrites Burners for Lumps.** The furnaces are constructed of brickwork and the floor is formed of a grate of removable bars on which the lumps of pyrites are distributed. The relationship between the surface of the grate, the height of the layer of pyrites, and the quantity which can be burned in twenty-four hours, has to be determined for any given quality of ore. A furnace which was employed with satisfactory results in Muspratt's works is constructed with a grate containing fifteen bars of square cross-section arranged in such a manner that their corners are opposite to one another: (◇ ◇) ; these occupy a surface of about 2 sq. metres. They are charged with a layer of pyrites 60 cm. deep, and 450 kilos are burned per twenty-four hours, the residue containing 2 per cent. of S.

As many as twelve double furnaces are arranged in one row, so that there are twenty-four furnaces in all, and these are charged every twelve hours, the mass being lighted from above by means of two pieces of red-hot coke. Before recharging the furnace the residue of burnt pyrites and cinders is made to fall by turning the square bars in such a way that the intervals are enlarged (□□).

In order to avoid fusion of the ash in the case of rich pyrites, a smaller amount is charged into the furnace. The temperature of the gas which leaves the ovens varies between 400° and 500°. The access of the air is regulated by a sliding damper which is placed under the grate.

(*b*) **Furnaces for Pyrites Powder.** Maletra furnaces are ordinarily used. These were shown in 1873 at the International Exhibition in Vienna.

They are formed by double furnaces placed back to back and joined to one another, each being formed of six hearths of fireclay 6 to 7 cms. thick, connected with one another and supported in the middle in such a way that the six hearths are each about 3 metres long and about 80 cms. wide (Fig. 97).

In twenty-four hours 30 kilos of pyrites can be burned per square metre of surface.

When the furnace is new it must be heated to a dark red heat for the first time very slowly and with very great precautions, by means of a separate hearth, which is then bricked up when the furnace has reached the necessary temperature. During this interval the furnace gases pass out through the chimney, but when the pyrites commence to burn, the communication with the chimney is closed and the gases are then turned into the

Glover tower. The first charge is composed of thin layers of powdered pyrites on each alternate hearth, and the partially roasted pyrites are made to pass gradually, by means of suitable tools, from the hearth above to the next hearth below, the hearth being then again charged. The exhausted and well-burnt residue finally arrives at the lowest hearth and contains only 1½ to 3 per cent. of sulphur, whilst in the first furnaces as much as 10 per cent. of the sulphur was lost. The burnt pyrites finally fall into the cooling-box or directly into small iron waggons placed below, and are then removed.

When regular working is established the upper hearth of each furnace is charged with 150 kilos of pyrites, and each furnace burns 600 kilos per twenty-four hours. The sulphurous gases leave the furnace at a temperature of about 400° and first pass into large flues or chambers, where the dust which is carried over is almost completely deposited. These dust chambers are so constructed that the gases are forced to pursue a zigzag path by means of transverse walls; and if the pyrites contain much arsenic the gases must also be passed through very long wide flues, where the As_2O_3 is deposited.

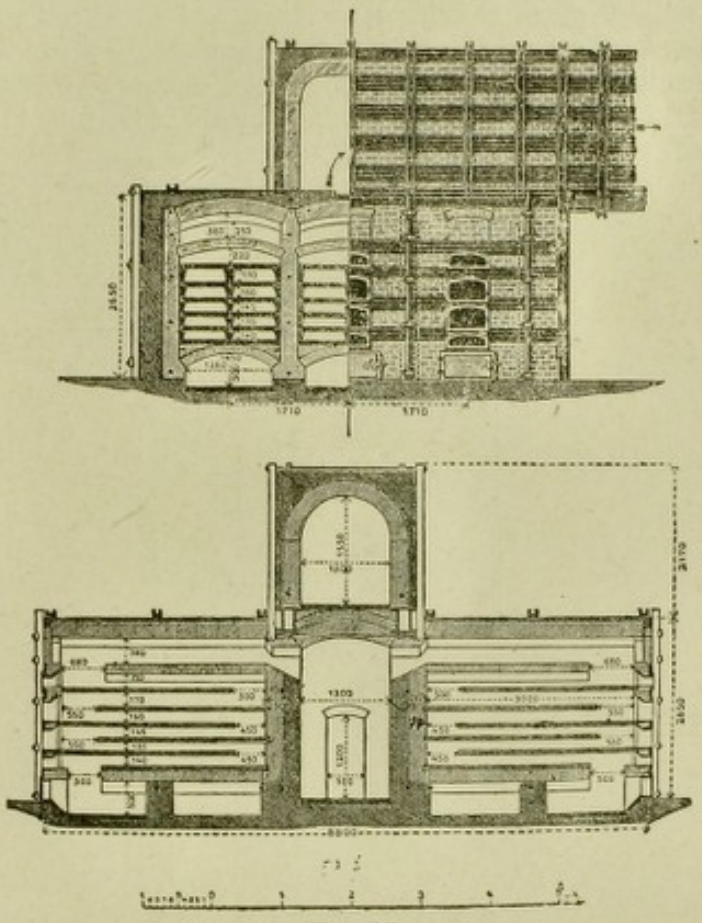


FIG. 97.

In Germany, where zinc blende is very abundant, special large muffle-furnaces are constructed in order to utilise the sulphur which it contains.

If molten slag is formed on the hearth, this must be immediately removed from the furnace, as otherwise it increases in quantity and causes loss of sulphur (up to 10 per cent.).

The gases which are formed in these pyrites burners are ordinarily composed of 7·5 to 8 per cent. by volume of SO_2, 10 to 11 per cent. of oxygen (of which about 4 per cent. is further utilised to transform the SO_2 into SO_3, and the other 6 to 7 per cent. is in excess), and 80 to 81 per cent. of nitrogen. The furnace gases are hot and cause a draught in the direction of the lead chambers, in which, in spite of the condensation of the sulphuric acid, there is always a slight pressure which is increased by the steam-jets. If the chambers are not perfectly gas-tight losses easily occur, as jets of gas escape at the damaged points.

(*c*) **Rotary Mechanical Furnaces for Burning Pyrites.** These are more expensive than Maletra furnaces and require motive power, and also produce some dust. They have, however, the advantage that they can be fed much more regularly without the necessity of the entry of a large excess of air; and they also greatly economise manual labour, which is of special advantage where this is very dear.

These furnaces were introduced industrially after the year 1870 by the brothers Macdougall of Liverpool, but presented so many inconveniences that they have since been repeatedly modified and have been abandoned by some works. Since 1891, however, the improvements introduced have been so marked that they have gradually replaced, with advantage, the Maletra furnaces.

A mechanical furnace which has yielded good results is that used by Frasch since 1890, especially for the treatment of the metallic sulphides which are obtained in the purification of petroleum. (Sulphur is separated from petroleum during distillation in presence of a mixture of much copper oxide, lead oxide, and iron oxide) (*see* vol. ii, "Organic

Chemistry "). Fig. 98 shows such a furnace of five metres diameter, formed of several vaulted planes on which toothed arms of cast iron fixed to a central vertical shaft rotate. A continuous current of cold water passes in at the bottom of this shaft through the internal tube $K'D$ from the reservoir placed above the furnace. This water also circulates in the lateral arms in such a manner that all parts of the iron are cooled, whilst in other mechanical furnaces they are always worn out. The hot water which escapes at the top of the tube k is utilised in the boilers. The sulphide is added in lumps through the aperture, n, and on the highest hearth it is moved by the arm, H, which carries teeth at a certain angle, from the circumference towards the centre where it passes through an aperture which carries it to the second hearth in which the revolving arm carries teeth inclined in the opposite direction, so that the mineral is carried from the centre to a suitable opening at the circumference, where it falls on to the third hearth, and so on in the following hearths. An adjustable current of air enters through the lower apertures, i and r, and causes the combustion of the sulphides.

The SO_2 gas and air pass out at the top of the tube P, and deposit all the dust in chambers, M, M', and M'', where they are forced to pursue a lengthy zigzag path before arriving at

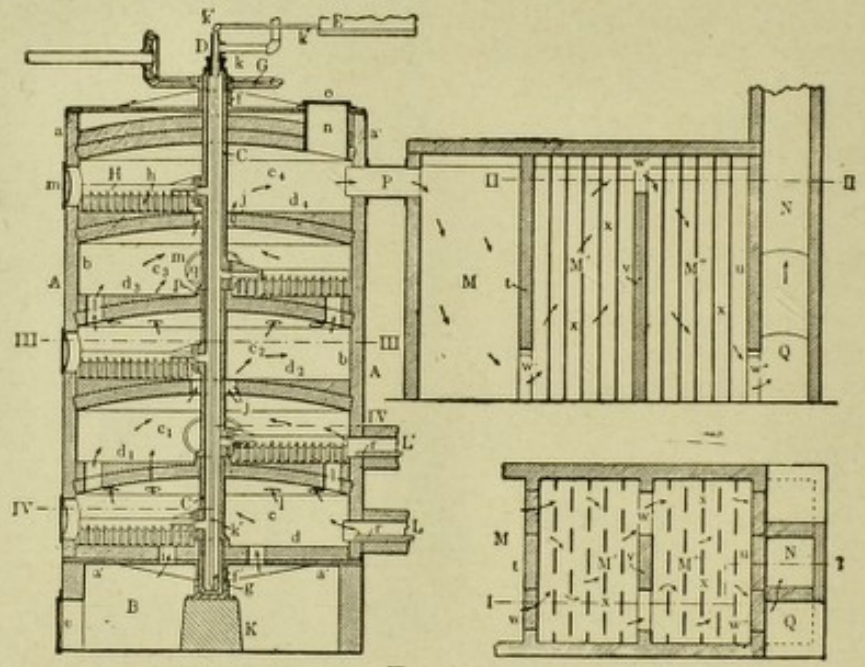


FIG. 98.

the tube Q, which conducts them to the Glover tower. The burnt pyrites are completely discharged through the apertures i. The working of these furnaces appears to be satisfactory, and about thirty were at work in the year 1902.

Herreshoff, on the other hand, constructs similar furnaces in which cold air circulates instead of water. Kauffmann has recently modified these mechanical furnaces still further. In 1901 thirty works in America, Germany, and England introduced many of these furnaces, some of which burn five tons of pyrites in twenty-four hours. In order to work seventy of these automatic burners in one works, only two operatives are required. More than fifty of these furnaces have also been introduced into Italy; and in Europe about 300 were at work in 1906.

INCLINED, CYLINDRICAL, ROTARY FURNACES, into which pyrites continually enter at one end and air for the combustion at the other, were suggested by Ducco in 1906, and after various modifications and experiments made in the works of Rifredi, near Florence, they have also been employed in certain other Italian works. The internal surface of these Ducco burners is formed with spiral grooves which facilitate descending movements of the pyrites without the production of much dust: there is an ingenious device for feeding in the pyrites continuously.

SULPHUR BURNERS. By starting from crude sulphur in the manufacture of sulphuric acid a greater expense is incurred than when pyrites are used. However, certain advantages are obtained in some cases which cannot be obtained with pyrites. It is of

advantage that the gases arriving in the lead chamber should contain a high percentage of SO_2, that is, that they should be diluted as little as possible with inert gases, and this object is attained by burning sulphur, whilst when pyrites are burnt the gases are mixed with air and with much nitrogen formed from the air which has been deprived of oxygen by oxidisation of the iron in the pyrites ; they are thus more dilute ; and in order to obtain an equal production of sulphuric acid lead chambers about 25 per cent. larger are required and the burners are also more costly. Sulphur also yields a purer acid, free from iron and arsenic.

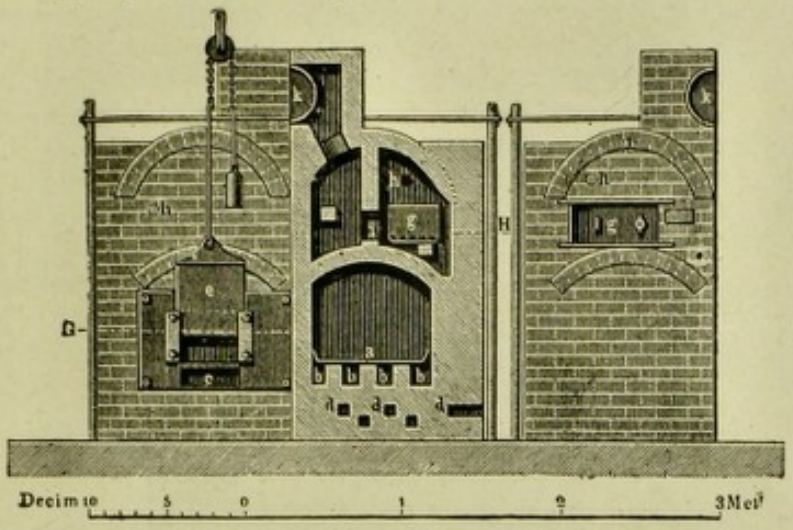


FIG. 99.

The combustion of sulphur is difficult to regulate, because when once it has been started so much heat is developed that the sulphur distils and then enters the lead chamber yielding a turbid sulphuric acid.

The best of these furnaces is the double one described by Lunge and shown in Fig. 99. The sulphur is charged on to iron trays with up-turned rims, *a*, supported in the interior of the brickwork furnace by supports which form the flues, *b*, through which cold air enters from the openings, *d*. This air cools the trays, thus regulating the heat supplied by the burning sulphur, and escapes hot through the aperture, *c*, after which it is utilised as a source of heat. The hot fumes from the burning sulphur pass through the aperture, *h*, into the chamber, *g*, where they heat vessels containing sodium nitrate and sulphuric acid for the production of nitrous vapours. The distilled sulphur is here burnt, and the whole of the gases pass through the tube, *i*, into the leaden tube, *k*, leading to the lead chamber, which is common to two adjoining furnaces. Air may be admitted through the aperture, *h*, in order to secure the complete oxidisation of the sulphur vapours. In these furnaces 150 kilos of sulphur are burned in twenty-four hours per square metre of trays. For every two furnaces, which are charged alternately, there is one pipe, *k*, which carries the gaseous mixture into the first lead chamber.

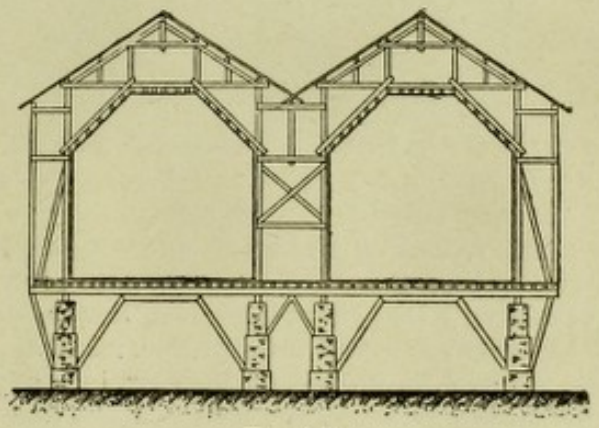


FIG. 100.

As we have already stated, Oddo has recently proposed (1907 and 1910) to burn sulphur ores directly in somewhat modified mechanical Herreshoff furnaces. He proposed to form briquettes of 5 parts of "sterro" (which contains 40 per cent. of sulphur on an average) with 1 part of crude sulphur, rendered compact in presses heated in furnaces to 140°. The resulting material containing 50 per cent. of sulphur would thus cost about £1 4*s*. per ton at the port of Genoa. It cannot be denied that pyrites of the same strength only cost £1, and have in the past cost less than 16*s*. The other small advantages accruing to sulphuric acid manufacturers using this conglomerate of Oddo do not appear sufficient to induce them to abandon the use of pyrites. This would only be possible if the sulphur-containing agglomerates were placed on the market at a price lower than or equal to that of pyrites. If its use were to become very general, then it would be possible to place it on the market at lower prices.

LEAD CHAMBERS. The gases pass to the lead chamber by means of a leaden tube 60 to 80 cm. in diameter at a temperature of 60° to 90° ; in some works the temperature of the gas may even be 100°, a temperature which is easily reached in furnaces burning sulphur, whilst gases from pyrites furnaces at 300° to 400° cool down during their passage

through the Glover tower, and where this is lacking are cooled by a jet of water or by being used to heat lead pans containing sulphuric acid for concentration. The lead chambers are supported on pillars at a height of from two to three metres above the ground, so that the ascending current of hot gases from the furnaces may be utilised, and in order that any leakage of the condensed acid through the chamber floor may always be noticed (Fig. 100). At the bottom a firm wooden framework carries the base of the chamber which consists of closely fitting wooden planking 3 cm. thick, firmly bolted together and impregnated and covered with water-glass ; the floor of the chamber rests on this platform and is formed of soldered leaden plates of a thickness of about 3 mm. This leaden floor has turned-up sides, 50 cm. or more high, and holds the acid which is formed. The walls and roof are supported by a firm wooden framework to which they are fixed by strips of lead to which they are soldered. The vertical walls do not touch the bottom, but hang at a distance of 1 to 2 cm. above it, so that the bottom of the chamber is closed by a kind of hydraulic seal formed of the condensed acid.

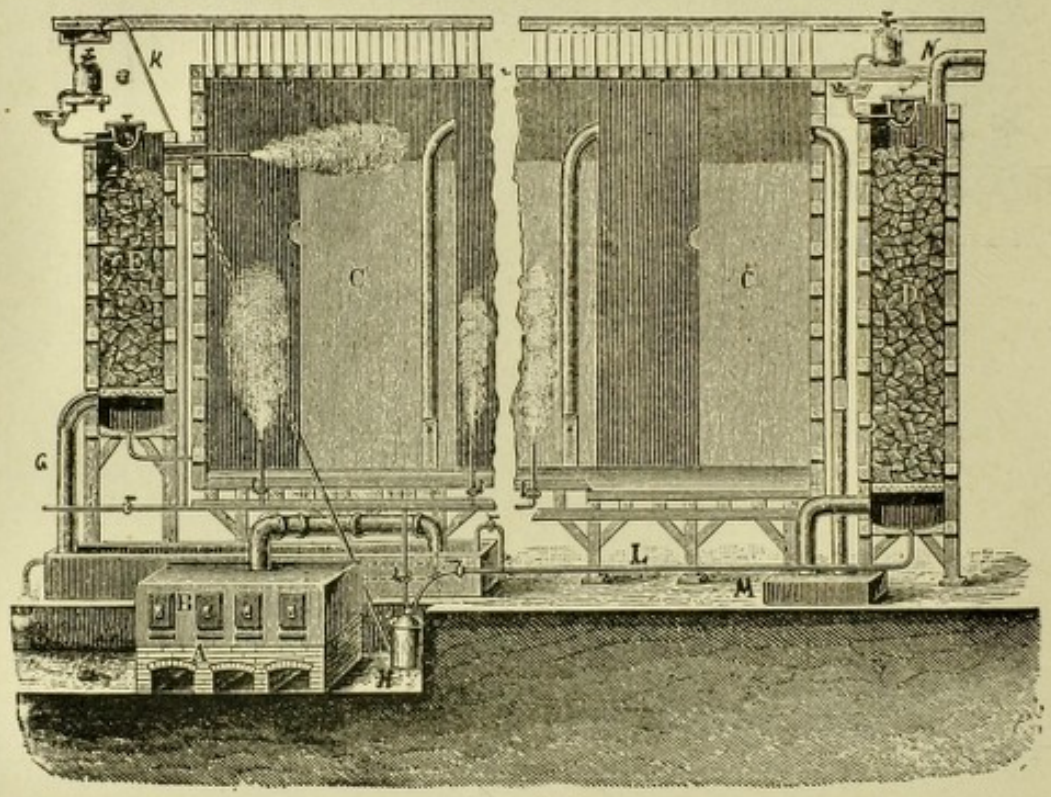


FIG. 101

The volume of the lead chambers must be large, because the yield is better when the reacting gases are well mixed, and since 8140 litres of reacting gases are formed per kilo of sulphur in the pyrites, the volume is so reckoned that 1½ kilos of pyrites burnt in twenty-four hours correspond to about 1 cu. metre in the lead chamber.[1]

A system of three or four chambers is generally used. The first is the largest and collects the greater portion of the acid ; the last (the tail chamber) is the smallest, and is mainly used for cooling and drying the gas. The draught in the chambers is produced by the hot gases which pass into the Glover tower, by the condensation which occurs in the chambers, and by the absorption of gas in the Glover tower.

Sufficient steam must be passed into the lead chambers to transform all the SO_2 of the burning sulphur into sulphuric acid, and to yield an acid in the first chamber of 50° to 52° Bé., that is, about 2 kilos of steam per kilo of sulphur. When Glover towers are used 60 per cent. of steam is sufficient.[2]

[1] This chamber lasts for fifteen to twenty years, according to the intensity with which it is worked. Good results are obtained with chamber systems of 4000 cu. metres, in connection with which about 7 tons of pyrites are burned in twenty-four hours. Each cubic metre of volume of such a chamber requires about 200 to 250 kilos of lead plates of 3 mm. thickness.

[2] In order to economise fuel, the use of a fine water-spray instead of steam-jets in the lead chamber has been proposed, and its application has in general produced favourable results. The water and the dry steam are introduced at the top of the first chamber by six to eight jets in close proximity to the Glover tower.

The *nitrous fumes* are produced in the *nitre pots* which are placed between the dust flues and the Glover tower, and are heated by the gases from the pyrites burners. The reagents consist of equal weights of nitrate and of H_2SO_4 at 50° Bé. They are contained in small lead vessels, and a residue of sodium disulphate is obtained.

In some cases instead of the employment of nitre pots nitric acid is dropped directly with the nitrous sulphuric acid into the Glover tower. In Fig. 101 an old plant is shown which would have to be modified in various respects to-day.

The gases pass from the burners, *A*, into the dust flues, and then through the pipe, *G*, into the Glover tower, *E*, and thence at the top into the lead chamber, *C*. They pass out from the opposite end of this chamber below and ascend by a tube into the upper part of a second chamber, and so on through a third chamber or more. They pass into the vessel, *M*, from which they enter the Gay-Lussac tower, *D*, from the top of which a spray of sulphuric acid passes from *N* and dissolves the nitrous fumes. This acid passes through the tube *L* to the pulsometer, *H*, which raises it through the tube *K* to the top of the Glover tower where the nitrous vapours are regenerated.

In ordinary lead chambers, working regularly, 2½ to 3½ kilos of H_2SO_4 calculated at 100 per cent. can be produced per cubic metre in twenty-four hours, and correspond to 4 to 5½ kilos of sulphuric acid of 50° Bé.

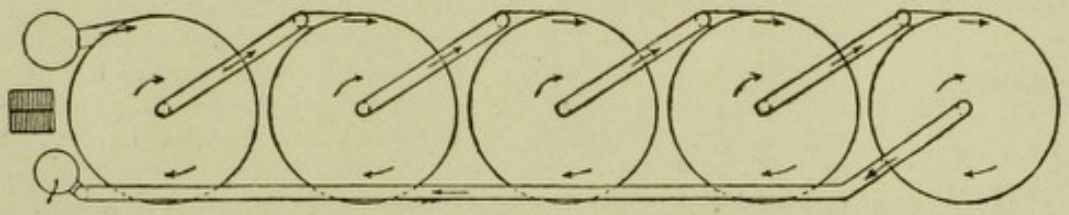


Fig. 102.

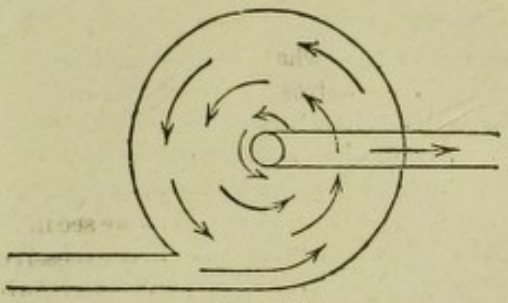


Fig. 102*a*.

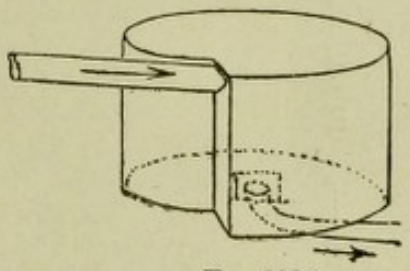


Fig. 102*b*.

TANGENTIAL LEAD CHAMBERS. In 1882 Abraham stated that the gases entering the ordinary lead chamber pursue a spiral path. In 1898 Th. Meyer (Ger. Pat. 301,376) observed that if the gases are made to enter tangentially at the base of a cylinder and are made to issue from the top through an aperture in the centre of the cover, the gas in the interior of the cylinder pursues a spiral course, and the same thing occurs if the gas enters tangentially at the top and issues at the base through a central aperture as indicated in Fig. 102 (*a*). In ordinary lead chambers the gases have a tendency to pursue a rectilinear path and do not mix much. Therefore it is necessary to construct very large chambers which are very costly. If, on the other hand, the chambers are constructed of a cylindrical shape and the gases enter tangentially at the top and issue through a hole in the centre of the floor (Fig. 102 (*b*)) contact between the gases is so intimate and rapid that the same quantity of sulphuric acid may be produced with two-thirds of the volume of the ordinary lead chamber, and thus with a correspondingly less expense for plant. In the cylindrical lead chambers 172 kilos of 3 mm. lead sheet are used per cubic metre, whilst in the ordinary rectangular chambers at least 200 kilos are required. In 1903 tangential lead chambers of a combined capacity of 40,000 cu. metres had already been constructed in various works and produced 160 tons of H_2SO_4 per day. Each cubic metre of the chamber produces 4 kilos of H_2SO_4, and in some cases even 6 kilos, in twenty-four hours.

Fig. 102 indicates diagrammatically a system of five tangential chambers in a sulphuric acid factory. The shaded square on the left indicates the pyrites burners and above this is the Glover tower and below the Gay-Lussac tower, which receives the gas which is

passed through the five chambers. The temperature in the first chamber is regulated by means of a group of lead tubes which pass from the top to the bottom of it, and through which cold water circulates, which is used to feed the boilers. More recently this bundle of tubes has been replaced by a large central ring open above and at the base, through which air circulates, so that the true chamber is formed by the interval between the external cylinder and the internal cylinder which forms the ring. In 1906 Th. Meyer (Ger. Pat. 186,164) improved the system by increasing the size of the first chamber and making the next one or two chambers gradually smaller, introducing the gas tangentially at two points at different heights in each chamber in order to obtain more complete admixture.

An important modification of the form of the lead chamber has also been introduced industrially by F. J. Falding of New York (U.S. Pat. 932,771 of 1909). He uses a single lead chamber which is one and a half times higher than it is broad. The gases from the Glover tower enter at the top and pass out at the base ; but since they are still very hot they are cooled in a cylindrical tower before being passed into the Gay-Lussac tower. By Falding's system 40 per cent. of lead is saved for a given yield. With a single Glover tower several of these vertical chambers may be fed at once. But it should be noted that in 1908 O. Guttmann had already proposed and described lead chambers similar to those patented by Falding.

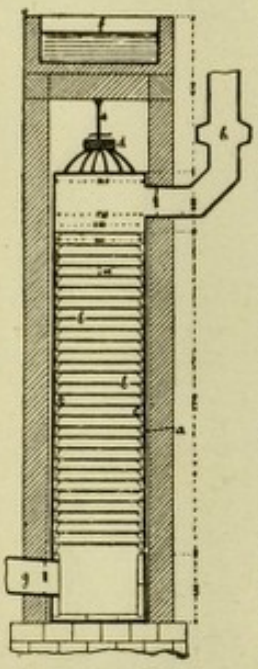


Fig. 103.

PLATE TOWERS OF LUNGE AND ROHRMANN. For the purpose of increasing the intimate contact of the gases and obtaining a more rapid production of acid Lunge in 1887 suggested the replacement of lead chambers by towers formed of close-fitting plates of perforated earthenware. These towers were gradually improved and in 1903 23,000 plates were in use altogether in various works, producing 150 tons of H_2SO_4 per day. 100 cu. metres in these towers produce as much as 750 cu. metres of tangential chambers, or 11,000 cu. metres in rectangular chambers.

The prime cost of these towers is somewhat high, and for an equal production of acid towers of 100 cu. metres would cost about £800, whilst 750 cu. metres of tangential lead chambers would cost about £560.

Plate-towers have also been proposed for the diminution of the volume of the lead chambers by interposing them between one chamber and another. They may also replace Gay-Lussac towers, as we see in Fig. 103. The practical advantages of these towers have been excessively exaggerated by some and much depreciated by others. As towers interposed between the chambers they increase the resistance to the current of gas, and this is remedied by means of a hard-lead aspirator at the tail end of the chamber. The yield from these towers is especially high if they are fed from above with nitrous sulphuric acid. Large economies of space are effected by the use of these towers and the supervision is rendered easier. In England these interposed towers are somewhat common, but the replacement of steam by water-sprays has not been found advantageous, perhaps because steam is very cheap in England.

In Fig. 104 are shown drawings of a works, both in section and in plan, for the production of eleven tons of H_2SO_4 per day. The lead chamber, B, is 7·25 metres high, 8·4 metres wide, and 25 metres long, and receives the furnace gases through two Glover towers, G and A. The gases then pass through five plate-towers, as is seen on the plan in the figure, and are collected by the aspirator, Z, which passes them through a small plate-tower which acts as a Gay-Lussac tower, L_1, and then through a large Gay-Lussac tower, L_2.

Gilchrist proposes the replacement of lead chambers by towers traversed horizontally in all directions by a large number of lead tubes which pass from one portion to another, and into which cold air is injected in order to regulate the reaction. Such towers have been applied in America.

GAY-LUSSAC TOWERS. These towers were suggested by Gay-Lussac in 1827 and were applied for the first time at Chauny in 1835. In Germany they are constructed with stoneware tubes of 80 cm. diameter and 80 cm. high, superposed to a height of 12 metres. These towers are to-day constructed entirely of lead and about 2 metres above the ground, in the form of cylinders 12 to 13 metres high and 2½ to 3 metres in diameter, supported by vertical beams, and dip almost to the bottom of a lead receiver, which is turned up at the sides to a height of about 15 cm., so that a hydraulic seal is formed by the acid

which collects. The tower is filled inside with acid-resistant bricks or stones, and at a height of a metre this subdivided material is supported by a strong grating of lead. The gases from 4000 cu. metres of lead chambers can be handled in such a tower of 55 cu. metres capacity.

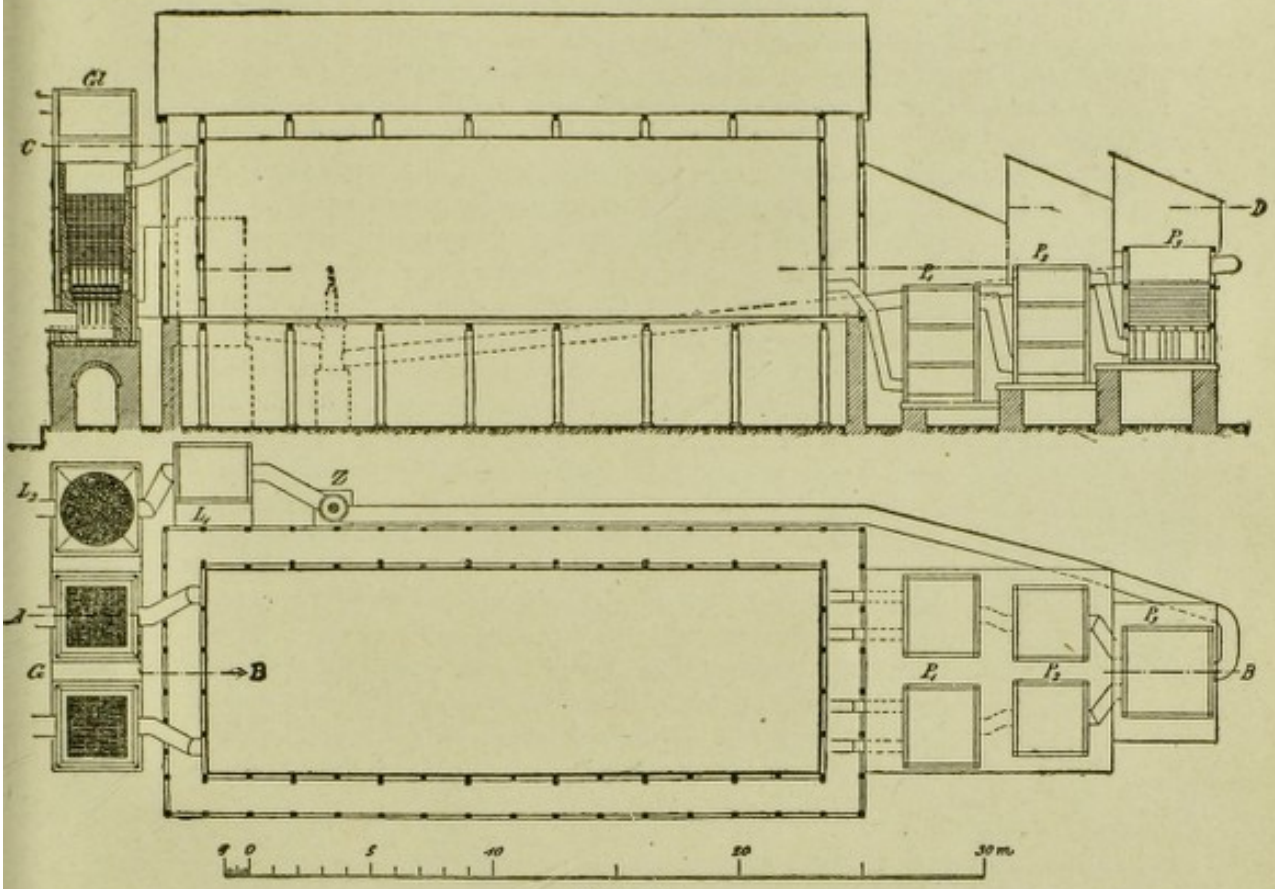


FIG. 104.

The towers were at one time filled with lumps of coke, but these caused loss of nitrate and other inconveniences (obstructions, &c.).[1]

To-day, however, they are filled to one-third of their volume with small cylinders or clay spheres which are close-packed; they are followed above by a layer of hard

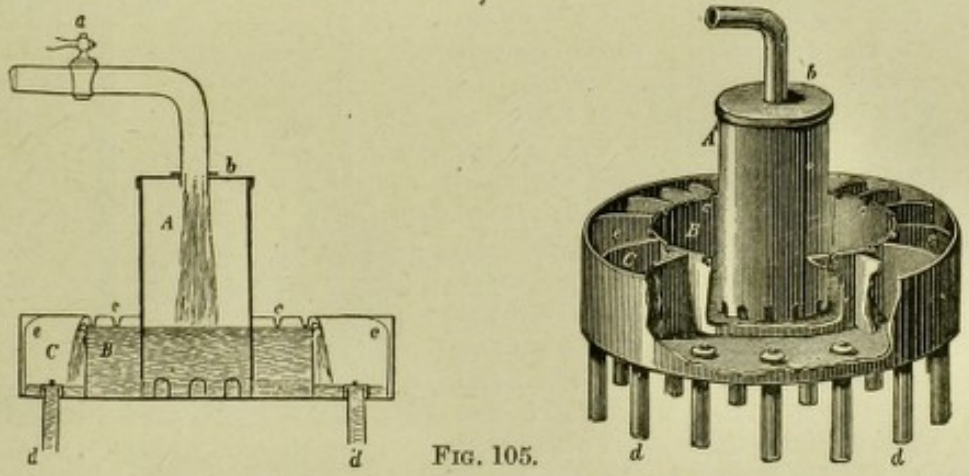


FIG. 105.

compact coke. Nitrous gases enter at the bottom from the last lead chamber, and concentrated sulphuric acid of 60° to 62° Bé. falls from above, being subdivided into thin continuous streams by means of the apparatus indicated in Fig. 105, which also forms the roof of the tower, being closed by grooves forming a hydraulic seal; the acid

[1] When sulphur is burnt the tower need only be 8 metres high. With pyrites furnaces the height varies from 12 to 18 metres, according to the size of the chambers. The volume of the Gay-Lussac tower when it is fed with an acid of 61° Bé. should be about 1½ per cent. of the volume of the lead chambers; and if an acid of 60° Bé. is used, its volume should be 2 per cent. of that of the chambers. Towers of medium cross-section have sides about 2 metres wide.

spray dissolves the nitrogen oxides contained in the gases which issue from the lead chamber and forms the so-called nitrous sulphuric acid, which is a solution of nitrosylsulphuric acid, $SO_2\begin{cases}ONO\\OH\end{cases}$ in sulphuric acid.

About 500 litres of sulphuric acid of 62° Bé. are passed through the Gay-Lussac tower for every ton of pyrites which is burnt, and at the base of the tower a nitrous sulphuric acid of 59° to 60° Bé. collects, containing 7 to 8 per cent. of nitrosylsulphuric acid (= 2·4 per cent. N_2O_3), and is titrated with a solution of potassium permanganate. The absorbing power for nitrous fumes appears to be greatly increased, in fact, more than doubled, if an acid of 54° to 56° Bé. is used for absorption (Heinz and Petersen ; Ger. Pat. 217,723 of 1908). Plate-towers are also used to-day instead of Gay-Lussac towers.

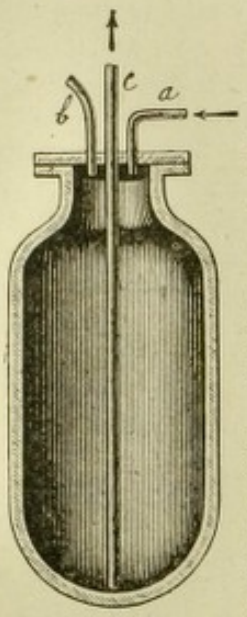


Fig. 106.

The acid for use in the Gay-Lussac towers is collected in receivers of lead, stoneware, or cast iron (pulsometers, acid elevators, pressure pots, acid eggs, or Montejus), from which it is raised by means of air from a pressure-pump through stoneware or leaden pipes.

These elevators are known in various forms, and to-day those are preferred which work automatically. The simplest non-automatic type is illustrated diagrammatically in Fig. 106 and consists of a vertical cylinder of cast iron or lead into which the acid enters through the tube *a* which communicates with a large reservoir. When the cylinder is full the cock on this tube is closed and that conveying the compressed air is opened ; this then acts on the surface of the acid and forces it to rise to the desired height up the tube *c*, which reaches to the bottom of the cylinder. When the cylinder is empty the operations are recommenced as at first by again filling the pot with acid. In order to prevent the acid from accidentally getting into the air-tube and pump, the air-tube reaches the cylinder at a height of three or four metres from the acid, and there is always a cock attached to the cylinder by which the air pressure may be relieved when operations are to be stopped. An automatic pulsometer or acid elevator is shown in Fig. 107. The acid which is to be raised is kept in the reservoir, *h*, and descends into the cylinder, *b*, by raising the valve, *i*, and entering the elevator through the tube *g*. The air displaced by the acid passes through the small U-tube *f* and escapes through tube *d*. If the cock of the tube *e* is opened, then before the pulsometer is full the compressed air which passes in through the tube *e* escapes through the tubes *f* and *d*, but when the acid reaches a level higher than *m* the tube *f* is filled and the air compression closes the valve, *i*, and prevents any further arrival of acid ; whilst that contained in *b* rises up the tube *d* to the height required as long as the pressure lasts. When the vessel, *b*, is empty, or almost empty, the compressed air is again able to escape through *f* and *d*, and the pressure which had shut off the valve, *i*, ceases, so that acid enters and the operations proceed afresh. The cylinder, *b*, can be filled and emptied about thirty to forty times an hour. The Schütze acid elevator is very useful for economising compressed air (and therefore motive power) and works still more automatically than the others. It is therefore much used because a maximum economy of compressed air is obtained. Whilst the liquid to be elevated enters through the valve *A* (Fig. 108)

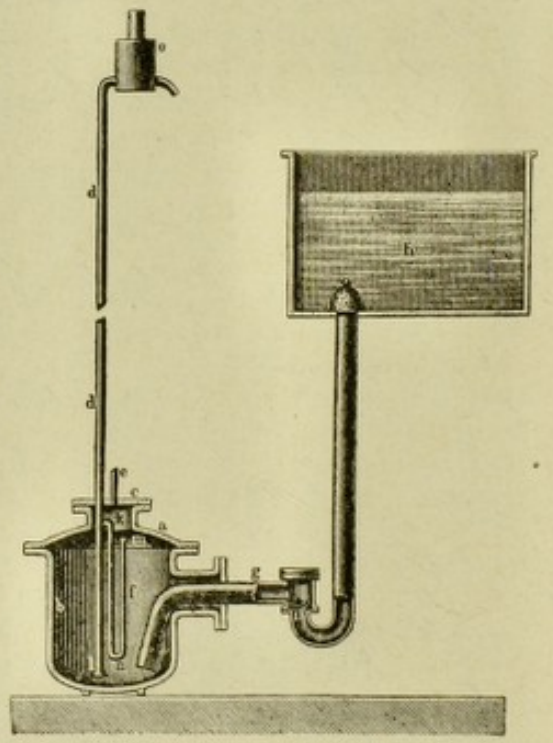


Fig. 107.

the air at first contained in the receiver escapes through the valve *D*. When the liquid reaches the upper ball, B_1, of the float, *C*, this rises and its upper arm closes the outlet valve *D*, at the same time opening the valve *E*, which gives access to compressed air, and the liquid then rises through the tube, *G*, to the desired height. When the level of the acid in the receiver has dropped to the lower ball, *B*, of the float this drops and closes the valve *E*, and the remaining air pressure suffices to completely empty the receiver. Then only the escapement valve *D* re-opens, so that all pressure ceases, and the receiver is again filled quite automatically by the acid which enters from *A* by lifting the ball-valve *A*, which was closed whilst there was air pressure in the receiver. During the filling of the receiver the upper part of the tube, *G*, remains full, because the ball of the valve *G* drops.

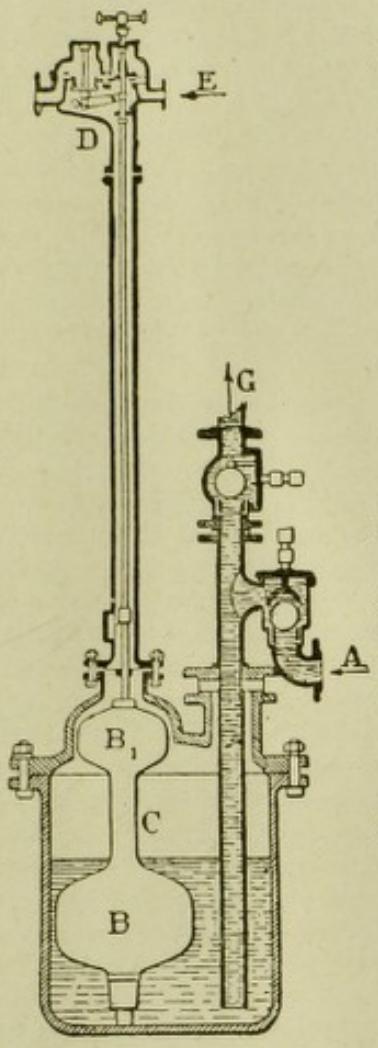


Fig. 108.

Forty-five pulsations (fillings of the receiver) may be obtained per hour. In order to raise a liquid of density 1·8 to a height of 10 metres the air must have a pressure of about 2½ atmospheres. This apparatus may be used for any liquids, and for acids it is constructed of cast iron which may be lined with lead, or in the case of hydrochloric acid it is made of stoneware, and in the case of fatty acids, of copper.

We will describe another apparatus for raising liquids which is often used industrially, and which we have already mentioned in the chapter on the extraction of sulphur from the interior of the earth by the Frasch system (p. 199). This is the so-called *Mammoth pump*. With an equal air pressure a heavy liquid may be raised to a greater height than with an ordinary pump, if the column of liquid to be raised is rendered lighter by emulsifying it with air or sometimes even with water. If the sulphuric acid in the tank *E* (Fig. 109) is to be lifted into the receiver, *L*, it is first passed into a U-shaped tube, *G*, at a lower level than the tank ; at the lower part of this U-tube there enters on the left a tube, *A*, from which a very fine jet of compressed air is blown, which emulsifies the liquid and raises it to the tank *L* by the long tube, *BK*. At the top the air separates from the liquid and is set free.

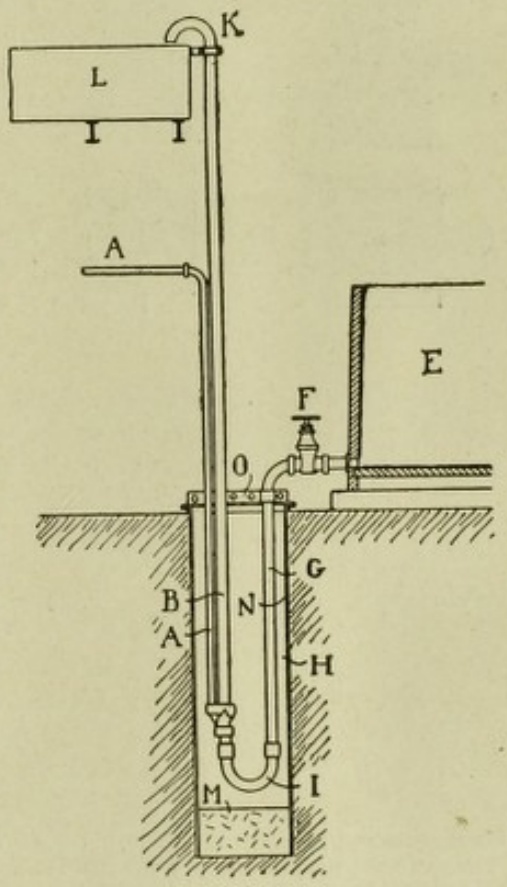


Fig. 109.

The **Glover tower** serves three important purposes : firstly, it cools the furnace gases down to 60° to 100° ; secondly, it concentrates the chamber acid of 50° to 53° Bé. up to 60° to 62° Bé. ; thirdly, it denitrifies the acid proceeding from the Glover tower, and at the same time washes the furnace gases. It consists of a cylindrical leaden tower about 3 metres in diameter and 8 to 10 metres high (Fig. 110), supported by an external framework of wood or cast iron and protected inside to two-thirds of its height by a lining of acid-resistant bricks. It is then filled with bricks of the same material or with small cylinders or spheres of clay which lie on perforated

horizontal planes of earthenware which are supported by small pillars at the base of the tower ; the base is united to the cylindrical portion and rests on stones contained in a vessel in which water circulates in order to cool the base of the tower. The tower is raised two or three metres above the ground in order to allow room for the spiral coolers which cool the acid issuing from the base which is still very hot (up to 150°).

In the upper part of the tower there are two lead vessels, one of which contains nitrous sulphuric acid, comprising two-thirds of the whole acid used, and of a strength of 56° to 60° Bé., and containing $2\frac{1}{2}$ to 3 per cent. of N_2O_3, and the other sulphuric acid from the chambers. The two supplies of acid are slowly distributed as a spray by arrangements similar to those shown in Fig. 105, p. 263. They mix in the tower and descend against the current of hot SO_2 gases coming from the pyrites burners, through an earthenware pipe incased by metallic sheeting. The nitrous vapours are liberated and escape into the top of the tower together with SO_2 and air, passing out through a leaden tube which conducts them to the upper part of the first lead chamber. At the base of the tower concentrated sulphuric acid, up to 63° Bé., collects and is free from nitrous compounds.[1]

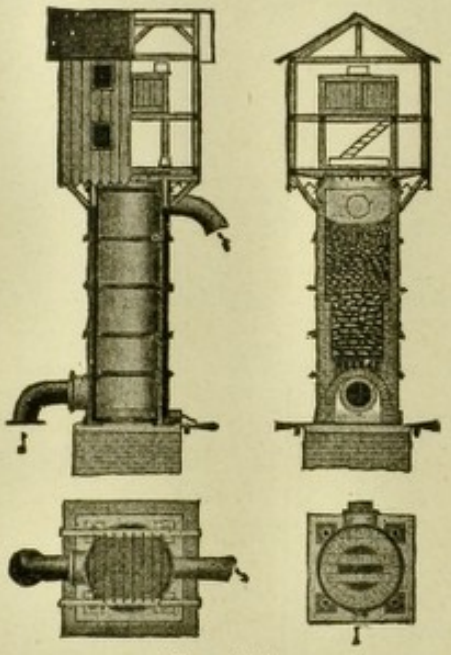


Fig. 110.

It is not advisable to concentrate the acid in the Glover tower to a strength above 63° Bé. because the leaden walls of the tower are otherwise attacked. Ordinarily acid of 60° to 61° is obtained and passes out of the tower at a temperature of 125° to 145°, after which it is cooled with water which passes through lead coils before being collected in tanks of cast or wrought iron. About 40 per cent. of the water vapour required in the lead chambers is furnished by the Glover tower. In order to produce 150 kilos of sulphuric acid of 53° Bé. without the Glover tower, 22 kilos of coal are necessary for steam production, whilst when the Glover tower is used only 13 kilos are required for this purpose.[2]

Hegeler and Heintz (Fr. Pat. 341,257 of 1904) appear to have succeeded in obtaining sulphuric acid of 66° Bé. directly in the Glover tower by regulating the temperature by suitable means, so that the leaden walls of the chamber are not attacked, and by forcing the "nitrous" acid back to the base of the tower by means of a pump in order to produce more SO_3 and thus more sulphuric acid.

The reactions which occur in the tower are, according to M. Neumann (1906), the following: In the lower part of the tower, where the temperature is higher, there is a reducing action (I), and in the upper part where the temperature is lower an oxidising action (II):

$$\text{(I)}\quad (\alpha)\quad 2SO_2\begin{matrix}\diagup\ O.NO\\ \diagdown\ OH\end{matrix} + H_2O = 2H_2SO_4 + N_2O_3$$

$$(\beta)\quad N_2O_3 + SO_2 + H_2O = H_2SO_4 + 2NO$$

or altogether:

$$(\beta + \alpha)\ 2SO_2\begin{matrix}\diagup\ ONO\\ \diagdown\ OH\end{matrix} + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

[1] For a system of lead chambers of 4000 cu. metres capacity, a Glover tower of about 70 cu. metres is required, or less, unless all the chamber acid is to be concentrated to 62° Bé. ; ordinarily the capacity of the Glover tower is 2 per cent. of that of the lead chambers. 4000 kilos of Spanish pyrites burnt in twenty-four hours yield 2040 kilos of acid of 53° Bé., and if this is all passed into the Glover tower 1670 kilos of 62° Bé. are obtained. Ordinarily, however, a part of the acid is used at a strength of 50° Bé. The work of the Glover tower is not remunerative if the gas from the furnaces has a temperature below 250°, as in the case of sulphur furnaces. For each 100 kilos of sulphur burned, or the corresponding quantity of pyrites, the Glover tower receives 800 to 1500 kilos of acid (two-thirds of which is nitrous), according to the temperature of the gas which escapes from the burners, less being required when it is hotter.

[2] *Steam Boilers.* For the production of steam for the chambers and acid pumps, two small boilers are employed by preference, because whilst one is working the other can be cleaned, and the manufacture thus continues without interruption. It is calculated that for 1000 cu. metres of chamber volume the consumption of coal for the boilers should be 350 kilos on the average per twenty-four hours.

Whilst the reaction (α) causes evolution of heat, the action (β), in accordance with which the N_2O_3 is reduced to NO, absorbs heat, and, therefore, in order to facilitate the formation of sulphuric acid (3 mols.) in the Glover tower it is necessary to maintain the lower portion of the tower at a high temperature (150° to 160°), which is also necessary in order to decompose the nitrous sulphuric acid. In the upper part of the tower where the gases are liberated together with NO, the following reactions occur :

(II) (γ) $2NO + O = N_2O_3$

(δ) $2SO_2 + N_2O_3 + O_2 + H_2O = 2SO_2\begin{matrix}\diagup OH \\ \diagdown ONO\end{matrix}$

or altogether :

($\gamma + \delta$) $2SO_2 + 2NO + O_2 + H_2O = 2SO_2\begin{matrix}\diagup OH \\ \diagdown ONO\end{matrix}$.

These two reactions are exothermic and are facilitated by gradual abstraction of the evolved heat, so that some nitrosylsulphuric acid may be produced in addition to that already formed and yields sulphuric acid in the lower part of the tower.

Neumann himself (Ger. Pat. 169,729) proposed the production of the greater part of the sulphuric acid by means of a series of three or four communicating Glover towers cooled above and heated below by means of the hot gases from the pyrites burners during their passage to the first tower ; in the last tower, where the gases are poor in SO_2 and O, a higher temperature (200°) is maintained which also facilitates the reaction.

The firm of Niedenführ to-day construct Glover towers in which the gases are cooled in the middle of the tower and escape without cooling the nitrous sulphuric acid which descends (Ger. Pat. 206,877) ; the substitution of all the lead chambers by a number of Glover towers has even been proposed (Ger. Pat. 217,036).

A small portion of the nitrous products is lost, and in order to reduce this loss to a minimum two parts of nitrous sulphuric acid to one part of lead-chamber acid are passed through the Glover tower. When the temperature in the lower part of the Glover tower is excessively high, the reduction of the nitrogen oxides may lead to the formation of elementary nitrogen, thus causing losses and, therefore, a larger consumption of nitrate.

REGULATION OF THE PROCESSES IN THE LEAD CHAMBERS. If 1·9 kilos of Spanish pyrites are to be burnt per cubic metre of chamber space per twenty-four hours, it is necessary to regulate the draught so that the furnace gases contain about 7·5 per cent. by volume of SO_2, and that the final gases which escape from the chamber contain from 6½ to 7½ per cent. by volume of oxygen.[1]

The entry of the vapours is regulated in such a way that the acid which is formed in the chamber is maintained at a definite concentration of 50° to 53° Bé., but that in the last chambers in which no steam is injected, and in which the gases are poor and partially exhausted, is sometimes only at 40° Bé. The acid which falls from the roof and the walls varies rather rapidly in concentration with the variation in the amount of steam, and is ordinarily more concentrated by 2° to 3° Bé., so that an excess or deficiency of steam may be detected by frequently titrating this acid which is collected through suitable apertures and channels constructed along the internal walls of the chamber.

The temperature inside the lead chamber increases or diminishes with increase or diminution of nitrate, and if the temperature of the vapours which enter the chamber is 70° to 90°, then the most suitable mean temperature in the first chamber is about 65°, whilst in the second chamber it is 55°, and in the third about 35°, although in some works to-day temperatures of about 100° in the first chamber are advantageously employed. But the lead is then more rapidly attacked, especially if the quantity of nitrous fumes is not very carefully regulated. The gases are led from the last chamber through a long leaden tube to the base of the Gay-Lussac tower which is placed close to the Glover tower.

[1] In order to start work in lead chambers the pan is filled with sulphuric acid of 45° to 50° Bé., so that a hydraulic seal is obtained with the vertical walls. SO_2 and nitrous fumes are then introduced until the gases in the last chamber have a yellowish-brown colour. For this purpose 12 to 15 per cent. of nitrate are required compared with the weight of sulphur which is burned, and if very intense working takes place as much as 20 per cent. may be required. On the second day air and steam are also introduced, and on the third day regular work may be started in all the chambers. In the first chamber there should always be a slight excess of pressure, while from the second and third this should almost disappear, or there may even be a slight vacuum in the third. Gases from sulphur burners should contain about 11 per cent. of SO and those from pyrites burners about 7·5 per cent.

The colour of the vapours in the first chamber should be very pale and should gradually change as one gets further from the point of entry, through the whole chamber system, acquiring a more and more intense yellowish-brown colour, and should enter the Gay-Lussac tower with a markedly reddish-brown colour. The gases which escape from this tower should be colourless.

The acid which collects at the base of the chamber is removed from time to time, but to an extent of not more than 10 cm. each time, a layer of at least 20 to 30 cm. being always left.

The most important control of the progress of the reactions in the lead chambers is effected by watching the work of the towers, which for convenience should be placed close together (*see* Fig. 104, p. 263), and by analysing the gases which escape by a suitable analytical process. The SO_2 of the furnace gases is titrated with a solution of $\frac{N}{10}$ iodine by Reich's method.

An analysis of the gas proceeding from the Glover tower gave the following results:

SO_2	O	NO	N_2O_3	N_2O_4	N
6·9%	10·9%	0·113%	0·036%	—	92·05%

At the outlet of the last (fourth chamber), the composition was:

—	7·3%	—	0·182%	0·121%	92·57%

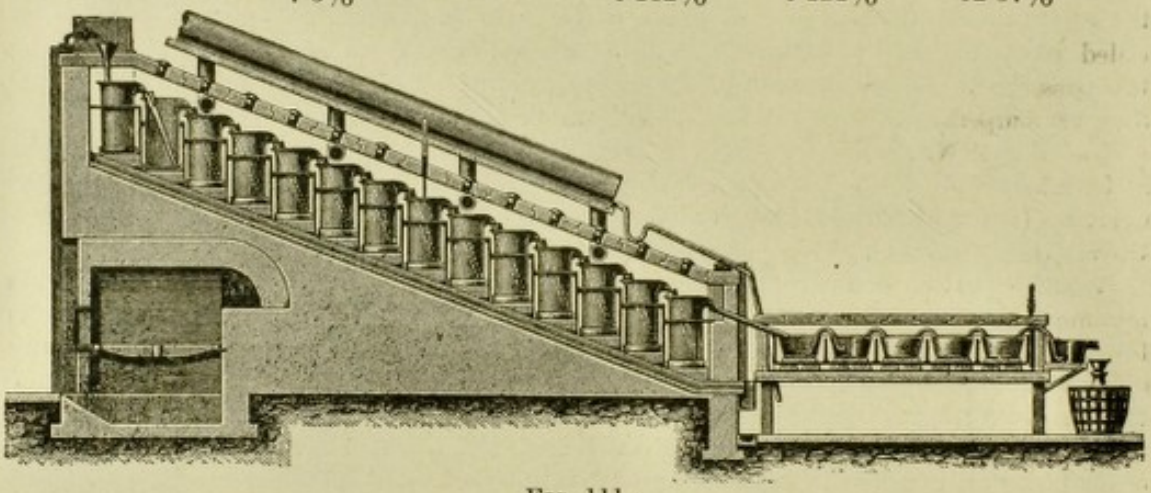


Fig. 111.

75 per cent. of the sulphur dioxide contained in the gases escaping from the Glover tower is transformed into sulphuric acid in the first chamber, 20 per cent. in the second, and 4½ per cent. in the third. The exhausted gases which escape from the Glover tower are observed by means of a window placed in the pipe which conducts them to a suitable chimney in which the draught through the whole of the lead chambers may be suitably regulated by means of automatic valves, an aspirator being used when required. Naturally the gases which issue from the chimney must not contain SO_2 or any nitrous vapours.

CONCENTRATION OF H_2SO_4. The sulphuric acid from the chambers of 50° to 52° Bé. (65 per cent. H_2SO_4) is not concentrated in the Glover tower, as otherwise it would become dirty, but is evaporated in leaden pans up to a strength of 60° Bé. (78 per cent. H_2SO_4). Any further concentration is conducted in vessels of cast iron and not of lead, because at such temperatures the lead becomes soft and is then attacked. The rims of these vessels are made of lead so that they may resist the action of the acid vapours which are evolved. So-called English sulphuric acid of 64° Bé. (86 per cent. H_2SO_4) is thus obtained. With three leaden pans 2 metres long, 1 metre wide, and 30 cm. deep, 3 tons of sulphuric acid of 52° to 53° Bé. may be concentrated up to 60° in twenty-four hours, with a consumption of half a ton of coal. They are heated by means of the hot gases from the burners, which traverse the surface of the acid, or if a purer acid is required, the heating may take place below the pans, which in this case rest on iron plates. In some localities the concentration is effected by means of high-pressure steam which circulates in leaden coils immersed in the acid.

In some smaller works, especially in England, acid of 66° Bé. (which is really 65·7° Bé. containing 93·5 per cent. of H_2SO_4; sp. gr. 1·837) is made by concentrating in large glass

retorts, 90 cm. high and of 50 cm. diameter, which are heated by gas in suitable furnaces, and an acid containing 91 to 92 per cent. of H_2SO_4 is thus obtained. In order to obtain 94 to 96 per cent. acid, iridio-platinum pans containing 10 per cent. of iridium are still used. Gilded platinum pans are still better as they are much less attacked, but these sometimes cost more than £4000.

These plants have now lost their importance, and are being gradually sold, because acid of a high degree of concentration is to-day easily and economically prepared by adding fuming sulphuric acid (oleum) to dilute chamber acid, or for a more economical process of preparation 93 per cent. acid may be used. This change is also due to the fact that during the last few years the price of platinum has risen very greatly to more than £240 per kilo. Alloys of 90 per cent. of gold with 10 per cent. of platinum have even been resorted to. For very large plants the Negrier process (1892) has given good results. The necessary plant is shown in Fig. 111 and consists of a series of porcelain capsules or vessels disposed two by two along a kind of staircase in a furnace, resting on asbestos sheets and surrounded by sand. A current of hot air passes from the base to the top of the staircase, whilst the acid descends slowly from the top to the bottom from vessel to vessel, gradually becoming more concentrated and finally passing through a coil where it is cooled. The steam

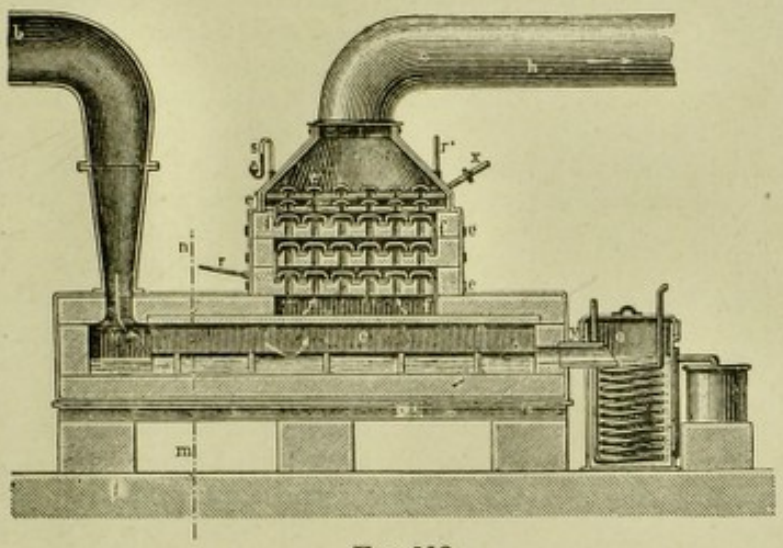


Fig. 112.

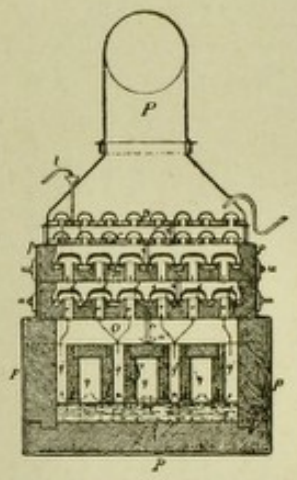


Fig. 113.

and small quantities of acid vapour are collected in a tube at the top and condensed. During the last few years the porcelain capsules have been replaced by capsules of inert iron or quartz. The latter, however, forms very small cracks after some time, through which acid escapes below. 15 kilos of coke are used as fuel for every 100 kilos of 93 per cent. acid which is produced. In 30 vessels 90 cm. high and 40 cm. wide 2 tons of acid may be concentrated in twenty-four hours. If an acid of 97 per cent. H_2SO_4 is produced, the consumption of fuel is doubled.

A double or treble Negrier plant for the production of ten tons of 93 per cent. acid per twenty-four hours costs about £880.

During the last few years the Kessler process (1894) has also been extensively employed in practice and enables commercial acid of 66° Bé. to be obtained by hot-air concentration. Hot gases from a coke producer pass in through a cast-iron pipe, *b*, Fig. 112, and these are drawn along several flues, *q*, made of pumice (Fig. 113), which are hydraulically sealed by the surface of the acid, by means of an air injector, and after having traversed the surface slowly they pass, charged with water vapour and a small amount of acid vapours, through canals, *q'*, at a temperature of 150° into a kind of rectifying apparatus formed of three perforated stoneware plates on which numerous inverted porcelain capsules are placed, the rims of which dip into the acid liquid which is condensed on the surface of the plates. Above these three plates there are two others of perforated lead, and these also support similar inverted capsules.

The acid from the lead chamber passes in through the tube *x* above, and descends in an opposite direction to the stream of gas and vapours coming from below. The almost cold gases are then drawn off into the tube *h*, and contain much water vapour and a little

acid vapour. They are then passed through a coke tower where the vapours are completely condensed. The flues, *q*, are now often advantageously constructed of simple transversal walls of volvic stone, against which the waves on the acid caused by the movement of the current of hot gases impinge, and thus the concentration is more rapid. The corrosion of the air aspirator may be avoided by injecting the air from outside into the apparatus from the front.

By means of this apparatus 100 kilos of acid of 66° Bé. may be obtained with a consumption of 8 kilos of coke in the producer, and 2 to 3 kilos of coal to work the pump.

The power required is about half a horse-power per ton of acid produced. During the last few years the process has been still further improved, and a plant for the production of 10 tons of 93 per cent. acid per day costs about £1120. 98 per cent. acid may now also be produced by this process, but the production is then halved and the consumption of fuel doubled.

Concentrated sulphuric acid is generally clear when produced, but any dark colour may be lessened by passing it through a coke filter.

An industrial concentrating plant for the production of 10 tons of sulphuric acid of 66° Bé. (93 per cent. H_2SO_4) per twenty-four hours costs from £800 to £1600 complete, and should pay for itself in twelve to fifteen years. Since 1908 the system of Gaillard of Barcelona (Eng. Pat. 23,841) has been extensively used in Europe for the concentration of sulphuric acid, and in 1909 there were already 100 plants working. Sulphuric acid of 50° to 60° Bé., previously filtered through silicious sand, is made to fall in the form of a very fine spray from the top of a tower of volvic lava about 16 metres high and about 2 metres in diameter, and a current of hot gases from a coke generator is passed in the contrary direction from below. Water from the dilute acid evaporates and escapes at the top together with the gases at a temperature of 120° to 140°, whilst an acid collects at the base of the tower which has a strength of 92 to 97 per cent. of H_2SO_4 according to the fineness of the spray which was produced. A production up to 10 tons per twenty-four hours is thus obtained. The gases which escape from the top of the tower descend again through a large lead pipe to enter the bottom of a small leaden tower 8 metres high and about 1·35 metres in diameter, filled with coke in order to recover the acid carried over by the current of gas which amounts to 2 tons of 40° Bé. Before being allowed to escape into the air the gases still pass through a leaden box full of coke where half a ton of acid of 14° Bé. is condensed. The gases are drawn through the whole apparatus by means of a fan. Fig. 114 illustrates diagrammatically the arrangement of the apparatus. *k* is the coke gas-producer and costs about £48 ; *T* is the concentrating tower and costs about £1040, including the patent rights ; the tower, *R*, and the chamber containing coke, *kk*, together cost about £280. The fan, *V*, acid elevators, pipes, &c., cost £160, and thus the complete plant costs £1520. The consumption of fuel for the concentration of the acid from 52° to 66° Bé. (93 per cent. H_2SO_4) is 11 to 12 kilos of coke per 100 kilos of concentrated acid which is formed. The consumption of power for raising the acid is estimated at three-quarters of a horse-power per hour per ton of concentrated acid produced. The blocks of volvic lava forming the tower are cemented together with a mixture of pulverised volvic lava and sodium silicate. The tower is covered outside with sheet lead, but a little acid always percolates through the stone, so that it is now proposed to replace the lava with technical

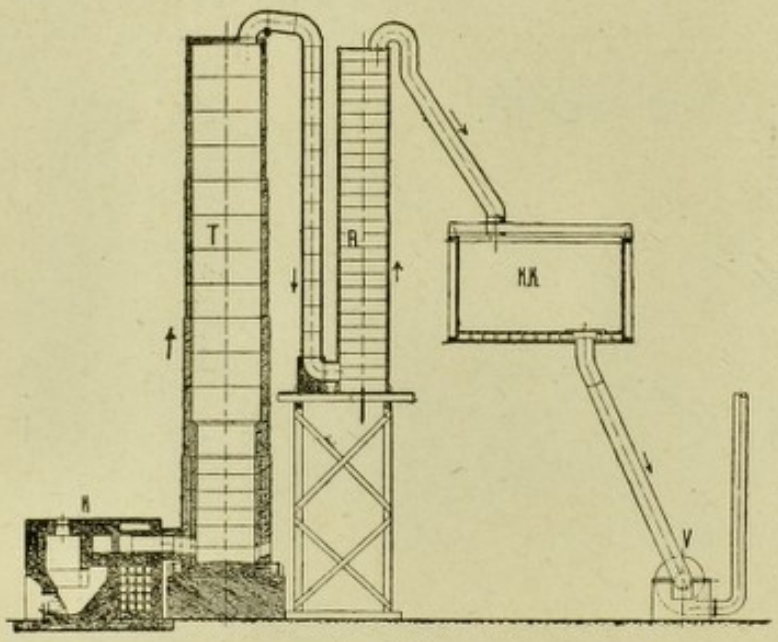


Fig. 114.

and economical advantage by a material called *obsidianite*, which is a vitreous silicate. In U.S. Pat. 909,578, Gaillard perfected the production of acid spray by collecting the acid which is not converted into spray on a conical disc placed at a definite height in the tower which removes it.

Krell, in 1907, managed to concentrate acid to 63° Bé. in special leaden pans without the lead being attacked even at such high temperatures. The final concentration is carried out in inert iron or silicious cast-iron pans which resist boiling concentrated acid very well. When an acid of 66° Bé. is required the purity of which is not of great importance, it can be economically concentrated by passing the dilute acid of 50° to 60° Bé. in a fine stream into a closed pan of cast iron in which a large amount of boiling acid at 66° Bé. is already present ; water evaporates and acid of 66° Bé. is continuously removed below. The pan lasts for one year.

The preparation of *sulphuric acid monohydrate* has already been described on p. 247, although it is to-day prepared by mixing concentrated acid of 66° Bé. with the necessary quantity of fuming sulphuric acid of known strength.

Strong sulphuric acid may be stored and despatched in wrought-iron vessels.[1]

PURIFICATION OF H_2SO_4. Purification is necessary when concentrated sulphuric acid is to be prepared. The sulphuric acid of the Glover tower is more impure than that from the chambers, and contains considerable quantities of arsenic. The more common impurities in chamber sulphuric acid are nitrosylsulphuric acid, lead, copper, iron, lime, alumina, arsenic, N_2O_3, HNO_3, ammonium sulphate, SO_2, organic substances, and sometimes selenium, tellurium, and HF. The greater part of the impurities are deposited spontaneously, and special methods are only required for the separation of arsenic and of N_2O_3. The arsenic is separated by means of hydrogen sulphide obtained from iron sulphide and H_2SO_4; for the purification of 10 tons of chamber acid about 0·2 ton of iron sulphide is required.

The crude sulphuric acid must be diluted to 46° to 50° Bé., as otherwise the H_2S is decomposed : ($H_2SO_4 + 3H_2S = 4H_2O + 4S$) ; moreover the arsenic must be present as arsenious acid and not as arsenic acid. For this purpose SO_2 must be passed through the liquid.

The operation is conducted in a Schwarzenberg tower, into the base of which a current of H_2S is passed, and down which the acid to be purified descends over acid-proof material. The acid is then passed into leaden vessels where the arsenic sulphide is deposited together with other metallic sulphides and selenium. The clear liquid is then decanted from the residue and filtered through asbestos fabrics or through porous earthenware plates under pressure.

According to the United Alkali Company (Eng. Pat. 16,929) arsenic may be separated by adding the necessary quantity of HCl and then passing a current of air through the liquid, by which means it is separated as arsenious chloride. Morange in 1908 proposed to separate arsenic by freezing acid of 63·5° Bé., as the arsenic then remains in the part which is not solidified.

In order to obtain sulphuric acid absolutely free from As, it is necessary to prepare it directly from sulphur.[2]

The nitrous compounds are separated on heating, according to Pelouze, by means of 0·1 to 0·5 per cent. of powdered ammonium sulphate, nitrogen being immediately evolved : ($N_2O_3 + 2NH_3 = 3H_2O + 4N$).

Chemically pure acid is obtained by repeatedly distilling the pure concentrated acid and adding a little chromic acid in order to transform any traces of arsenious acid into arsenic acid, which latter does not distil.

ANALYTICAL CONTROL OF SULPHURIC ACID MANUFACTURE. The quantity of sulphur in pyrites is determined by dissolving, for instance, 0·5 grm. in 10 c.c. of a mixture of 3 parts of concentrated HNO_3 and 1 part of HCl, and evaporating to dryness several times with HCl in order to remove any excess of HNO_3. The residue is

[1] Even acid of 60° Bé. from the Glover tower may be stored in large tanks of wrought iron, and the larger they are the more convenient. Some are made of cylinders 3 metres in diameter and 5 metres high, but better results are obtained with cylinders 8 to 10 metres in diameter and 10 or more metres high.

[2] Sulphuric acid which is to be used for the preparation of foodstuffs, such as compressed ferments, for fermentation of molasses, the revivification of carbon for sugar refineries, for pharmaceutical products, &c., should always be free from arsenic. Such acid is easily obtained to-day by diluting fuming sulphuric acid (oleum) which is free from impurities.

finally dissolved in dilute HCl. The iron is precipitated with ammonia in the heat, filtered and well washed, and the sulphuric acid in the filtrate (proceeding from the sulphur) is precipitated with barium chloride. The weight of barium sulphate after washing, drying, and igniting gives the weight of sulphur in the sample on multiplying by 0·1373.

Copper in pyrites is determined electrolytically in a solution of the pyrites in nitric acid.

The sulphur dioxide in the gas from the pyrites burners is determined by passing a given volume of the gas through a titrated solution of iodine: ($SO_2 + 2I + 2H_2O = H_2SO_4 + 2HI$).

The quantity of oxygen in the gases escaping from the last lead chamber is determined by the usual volumetric methods, that is, by absorbing the oxygen with an alkaline pyrogallate in the Bunte or Orsat burette (*see* section on Combustibles).

The quantity of nitrous acid in the nitrous sulphuric acid and also in chamber acid is determined by adding the acid under examination from a burette to a given volume of a titrated solution of potassium permanganate until this is decolorised; 16 parts of oxygen correspond to 47 parts of HNO_2 (*see* preceding equations: nitrous acid). The total nitrogen (that is, HNO_3 and HNO_2) is determined with Lunge's nitrometer (*see* section on Sodium Nitrate). The strength of sulphuric acid is ordinarily determined by means of its density (*see* Table, p. 251); but in the case of very concentrated acid it is necessary to determine it by titration, after previous dilution, with titrated sodium hydroxide and methyl orange, which latter is coloured red by strong acids.

YIELDS. Theoretically 100 kilos of sulphur should give 200 kilos of SO_2; 250 kilos of SO_3; 306·5 kilos of H_2SO_4 monohydrate, 319 kilos of sulphuric acid of 66° Bé. (96 per cent. H_2SO_4); or 490 kilos of chamber sulphuric acid of 50° Bé. (62·5 per cent. H_2SO_4).

With pyrites burners 10 to 12 per cent. of the sulphur was at one time lost, part of which remained in the burnt pyrites, and the consumption of nitrate was also very great. To-day the total loss of sulphur has been reduced to from 4 to 5 per cent., and the consumption of nitrate is 2 to 3 per cent. of the sulphur which is burnt.[1]

Yields of acid per volume of chamber space have already been mentioned in connection with tangential chambers on p. 261.

COST OF PLANT AND PRODUCTION. Lunge gives the following estimate of the cost of a Niedenführ plant with a production of 20 tons of H_2SO_4 per twenty-four hours, that is, a corresponding production of chamber and Glover acid.

The gases from 12 burners burning lump pyrites pass through the dust flues and then into the base of the Glover tower and pass out at the top through two large pipes into the neighbouring lead chamber at the top. The escaping gases from this chamber pass through three openings at its base in the opposite wall, and then pass through three openings into the top of the second lead chamber, which is close to and parallel to the preceding one. They pass through this chamber in the same way and the issuing gases escape at the base of the opposite wall through three openings and arrive at the third chamber, passing from the opposite wall of this chamber into two Gay-Lussac towers which are placed close to the Glover tower. The remaining gases escape directly into the air. Each of the three chambers is 8 metres high and 32 metres long and together they have a volume of 8800 cu. metres.[2]

[1] The loss of nitrate is shown by the quantity which it is necessary to add to the nitre pots each day to make up for losses. In the case of lead chambers of small capacity, that is, those in which the working is very intense compared to the amount of sulphur or pyrites burnt (2 kilos of Spanish pyrites per cubic metre of chamber space per twenty-four hours), more nitrate is consumed (up to 4 kilos per 100 of sulphur); whilst in chambers of ample dimensions and less intense production 2 per cent. of nitrate is used on the sulphur burnt; the nitrate which circulates in the whole system of chambers and towers is about 12 to 15 per cent. of the sulphur burnt.

[2] The prices of materials in this estimate refer to the year 1902:

	£
I. Freehold, 2500 sq. metres at £1	2500
II. Walls, pavements, foundations, wooden framework and sheds for the furnaces, chambers, boilers, towers, &c.	3800
III. Boilers (40 sq. metres heating surface), pumps, pipes, acid elevators	750
IV. Twelve burners for lump pyrites, dust flues, nitre pots, and connection with Glover tower	1124
V. Chambers and towers: 240 tons of lead, material for filling towers and cost of complete erection (estimated at £1320)	6326
Total	£14,500

Later (*see* Sulphur Trioxide), comparisons will be made between the cost of the acid produced by a similar plant and a more rational plant with five rotary furnaces, two lead chambers, five plate-towers, one Gay-Lussac tower, and one Glover tower for the production of 20 tons calculated as monohydrate. It would, however, appear that in the above estimate Lunge has taken an extremely exaggerated price for land.

SULPHUR TRIOXIDE AND FUMING SULPHURIC ACID

I. SULPHUR TRIOXIDE : SO_3

Until about 1875 the sulphur trioxide of commerce was only prepared by Starck, of Prague, who obtained it by distilling fuming Nordhausen acid. In 1875 Cl. Winkler, who was followed by Squire and Messel, showed that sulphur trioxide is easily formed by the interaction of SO_2 and O in presence of very finely divided platinum, which acts catalytically without taking any direct part in the reaction.[1]

In this process 20,600 cals. are developed, and the maximum yield is obtained between fixed temperature limits, as otherwise the SO_3 is dissociated, regenerating $SO_2 + O$.

This method of Winkler has only attained important industrial application during the last few years, and by means of SO_3 pure sulphuric acid of any concentration is now industrially prepared.

SO_3 was formerly also obtained by decomposing strong sulphuric acid in contact with retorts heated to redness (Debray and Deville's process, *see* p. 179). The mixture of $SO_2 + O + H_2O$ (steam) so obtained was dried in a coke-tower with strong sulphuric acid and the mixture of $SO_2 + O$ passed over platinised clay spheres when the reaction $SO_2 + O = SO_3$ occurred.

Sulphur trioxide may also be prepared by heating sodium pyrosulphate, $Na_2S_2O_7$, which is prepared by heating sodium sulphate with strong sulphuric acid : $SO_4Na_2 + H_2SO_4 = H_2O + S_2O_7Na_2$; acid sodium sulphate, $NaHSO_4$, is formed as an intermediate product, and when heated is then transformed into the pyrosulphate. By adding a further quantity of sulphuric acid and distilling *in vacuo* sulphur trioxide is obtained : $S_2O_7Na_2 + H_2SO_4 = 2SO_4HNa + SO_3$. The two molecules of disulphate which are formed are reconverted into pyrosulphate. Sulphur trioxide is also obtained on heating sodium pyrosulphate directly to 600° : $Na_2S_2O_7 = Na_2SO_4 + SO_3$.

Prud'homme (1909) decomposes various sulphates in the electric furnace and thus obtains SO_3 and metallic oxides : thus from calcium sulphate $CaO + SO_3$ are obtained. R. Frank (1906, Ger. Pat. 194,879) says that SO_3 is formed quantitatively without the presence of a catalyst by heating $SO_2 + O$ at a pressure of 100 atmospheres.

In the laboratory SO_3 is obtained by heating fuming sulphuric acid, which is nothing else than a solution of SO_3 in strong sulphuric acid, and condensing the vapours of SO_3 in a cooled receiver.

It may also be prepared by distilling concentrated sulphuric acid with phosphorus pentoxide in a retort : $P_2O_5 + H_2SO_4 = SO_3 + 2PO_3H$ (metaphosphoric acid).

White fumes are thus formed which condense to a white crystalline silky mass in a receiver surrounded by ice.

PROPERTIES. The needle-shaped crystals of SO_3 melt at 16·8° (Liethig, 1909), yielding an oily liquid of sp. gr. 1·96 (at 20°), which distils at 44·8° without dissociation.

If pure it can be preserved unaltered, but it absorbs moisture with avidity from the atmosphere forming H_2SO_4, traces of which slowly transform it into a white solid mass like asbestos which melts at 50° and appears to be polymerised SO_3. On re-distilling this mass pure SO_3 is again obtained.

It combines violently with water to form sulphuric acid, producing a strong hissing sound, and sometimes even an explosion if a comparatively small quantity of water is present. Its avidity for water is such that it decomposes almost all hydrogenated organic substances, acquiring a brown colour. On heating in red-hot tubes it decomposes into $SO_2 + O$. The quality found in commerce (*see below*, Fuming Sulphuric Acid) contains

[1] It was found afterwards that the oxides of iron, calcium, manganese, copper, and cobalt also react less completely, and that metallic gold, palladium, iridium, glass powder, pumice-stone, burnt clay, bricks, &c., all act as catalysers in the heat and when finely subdivided.

98 to 99 per cent. of SO_3 and 1 to 2 per cent. of H_2O ; but it is to-day preferred dissolved as a liquid in a small amount of sulphuric acid, namely, with 87 to 92 per cent. of total SO_3 = 30 to 60 per cent. of free SO_3. It is then called *oleum* or *fuming sulphuric acid*, and is stored and despatched in wrought-iron vessels.[1]

On pouring a little sulphur into phosphorus pentoxide it dissolves, forming a bluish-green substance which is actually sulphur sesquioxide, S_2O_3.

The heat of formation of SO_3 from $SO_2 + O$ is equal to 86 Kj. (20,600 cals.), and since SO_2 obtained from sulphur and oxygen has a heat of formation of 297 Kj. (= 70,977 cals.) we may deduce a total heat of formation of sulphur trioxide from its elements $S + O_3$ of 383 Kj. (= 91,577 cals.). From these thermochemical data we see that the law of Berthelot, according to which the reacting substances form by preference new substances with a maximum development of heat, is untrue in this case, because on burning sulphur in oxygen

[1] When the anhydride contains 1 per cent. of water this latter is not free but combined in the form of H_2SO_4, with which it forms 5·44 per cent., so that 94·56 per cent. of free SO_3 is really present in the mixture. In the same way, when 5 per cent. of water is present this is in the form of 27·2 per cent. of H_2SO_4, and 72·8 per cent. of free SO_3 is present. The strength or percentage of commercial oleum is indicated by the percentage of free SO_3. The qualities ordinarily used contain from 25 to 45 per cent., that is, 25° to 45° of free SO_3 or 95 per cent. of total SO_3. The strength of these liquids is also often given in terms of monohydrate (22 per cent. of free SO_3, corresponding to 105 per cent. of monohydrate). The following table of strengths is useful :

DENSITIES AND CONCENTRATIONS OF OLEUMS

Density at 35° C.	100 parts by weight correspond to				Density at 35° C.	100 parts by weight correspond to			
	SO_3		H_2SO_4 (monohydrate)	Sulphuric acid of 50° Bé		SO_3		H_2SO_4 (monohydrate)	Sulphuric acid of 50° Bé.
	Total	Free				Total	Free		
1·8186	81·63	0	100·00	160·00	1·9749	91·18	52	111·70	178·72
1·8270	81·99	2	100·45	160·72	1·9760	91·55	54	112·15	179·44
1·8360	82·36	4	100·90	161·44	1·9772	91·91	56	112·60	180·16
1·8425	82·73	6	101·35	162·16	1·9754	92·28	58	113·05	180·88
1·8498	83·09	8	101.80	162·88	1·9738	92·65	60	113·50	181·60
1·8565	83·46	10	102·25	163·60	1·9709	93·02	62	113·95	182·32
1·8627	83·82	12	102·70	164·32	1·9672	93·38	64	114·40	183·04
1·8692	84·20	14	103·45	165·04	1·9636	93·75	66	114·85	183·76
1·8756	84·56	16	103·60	165·76	1·9600	94·11	68	115·30	184·48
1·8830	84·92	18	104·05	166·58	1·9564	94·48	70	115·75	185·20
1·8919	85·30	20	104·50	167·20	1·9502	94·85	72	116·20	185·92
1·9020	85·66	22	104·95	167·92	1·9442	95·21	74	116·65	186·64
1·9092	86·03	24	105·40	168·64	1·9379	95·58	76	117·10	187·36
1·9158	84·40	26	105·85	169·36	1·9315	95·95	78	117·55	188·08
1·9220	86·76	28	106·30	170·08	1·9251	96·32	80	118·00	188·80
1·9280	87·14	30	106·75	170·80	1·9183	96·69	82	118·45	189·52
1·9338	87·50	32	107·20	171·52	1·9115	97·05	84	118·90	190·24
1·9405	87·87	34	107·65	172·24	1·9046	97·42	86	119·35	190·96
1·9474	88·24	36	108·10	172·96	1·8980	97·78	88	119·80	191·68
1·9534	88·60	38	108·55	173·68	1·8888	98·16	90	120·25	192·40
1·9584	88·97	40	109·00	174·40	1·8800	98·53	92	120·70	193·12
1·9612	89·33	42	109·45	175·12	1·8712	98·90	94	121·15	193·84
1·9643	89·70	44	109·90	175·84	1·8605	99·26	96	121·60	194·56
1·9672	90·08	46	110·35	176·56	1·8488	99·63	98	122·05	195·28
1·9702	90·44	48	110·80	177·28	1·8370	100·00	100	122·50	196·00
1·9733	90·81	50	111·25	178·00					

I. Prats (1910) gives the following formula for the dilution of oleum to any percentage of SO_3 by the addition of sulphuric acid of 66° Bé. (95·6 per cent. H_2SO_4) ; if we indicate the quantity in grammes of more dilute oleum which is to be prepared by a, the strength of SO_3 which has to be obtained by h, and the quantity of more concentrated oleum which is used by x, its strength in SO_3 by k, and the amount of sulphuric acid of 66° Bé. to be added by y, then :

$$x = a.\frac{h+20}{k+20};\quad y = a.\frac{k-h}{k+20}.$$

If, for example, we wish to prepare 400 grms. of oleum of 20 per cent. SO_3 from oleum containing 30 per cent. SO_3 and sulphuric acid of 66° Bé., we have the equations : $x = 400\,\frac{20+20}{30+20} = 400\,\frac{4}{5} = 320$, and as $y = a - x$ we have : $y = 400 - 320 = 80$, that is, we must mix 320 grms. of oleum of 30 per cent. SO_3 with 80 grms. of sulphuric acid of 66° Bé. to obtain 400 grms. of oleum of 20 per cent. SO_3. This formula is just as exact as the more complex one of Gnehm.

or air sulphur dioxide is formed almost exclusively (to the extent of 95 per cent.). But this fact is very clearly explained by the law of mass action (*see below* and pp. 64 and 68).

Sulphur trioxide is used in coal-tar colour works, but more especially for the preparation of fuming sulphuric acid.

II. FUMING SULPHURIC ACID

This substance is also called oleum, Nordhausen acid, pyrosulphuric acid, or disulphuric acid, $HO\text{-}SO_2\text{-}O\text{-}SO_2\text{-}OH$.

It is the product of the addition of 1 mol. of sulphuric acid to 1 mol. of sulphur trioxide.

Until a few years ago it was obtained by distilling dry ferrous sulphate, which decomposes in common with all sulphates, except those of the alkali and alkaline earth metals, at a red heat according to the following equation: $2FeSO_4 = Fe_2O_3 + SO_2 + SO_3$. In order to avoid the formation of SO_2 the iron sulphate is oxidised in the air by roasting it. Basic ferric sulphate is thus formed which on heating directly forms 1 mol. of sulphuric acid and a molecule of sulphur trioxide: $4FeSO_4 + O_2 + 2H_2O = 4FeSO_4(OH)$, and from this: $2FeSO_4(OH) = Fe_2O_3 + H_2SO_4 + SO_3$. The iron oxide is then employed as a red mineral pigment under the name of colcothar.

This process was already known to Arab alchemists and was applied on a large scale at Nordhausen (Prussia) during the seventeenth and eighteenth centuries. After 1792 it was prepared on an industrial scale almost exclusively by the firm of Starck in Bohemia by weathering iron pyrites in the air. Ferrous and ferric sulphates were then formed which were extracted with water and the solution evaporated. The residue was then roasted in reverberatory furnaces, in order to obtain a product containing ferric sulphate only, and this was dry-distilled in clay retorts at a red heat: $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$.

Since the industrial preparation of sulphur trioxide by the catalytic process, fuming sulphuric acid is to-day prepared profitably and exclusively by saturating sulphuric acid with sulphur trioxide and comes on to the market in the name of "oleum" of various concentrations. The SO_3 is absorbed by 98·5 per cent. sulphuric acid by passing it over the surface of the acid in closed vessels until an oleum containing 30 per cent. of SO_3 is obtained. In order to obtain a greater concentration this oleum is distilled in ordinary iron pans over direct flame, and the sulphur trioxide is then absorbed by other oleum of 30 per cent. which is kept cool. Oleums containing 60 per cent. and even 80 per cent. of free SO_3 are thus obtained. They form heavy liquids which fume in the air and are slightly brown in colour on account of dissolved traces of organic matter. The specific heat of oleum containing 24 per cent. of free SO_3 is 0·340, with 56 per cent. is 0·400, with 90 per cent. is 0·652. It has a specific gravity of 1·86 to 1·95. The specific gravity is irregular, and is not always proportional to the contents of free SO_3; thus, oleums containing 10 per cent. to 56 per cent. of free SO_3 have gradually increasing densities from 1·856 to 1·977, and then from 57 per cent. to 98 per cent. of SO_3 the specific gravity decreases from 1·976 to 1·840 at a temperature of 35° (*see* preceding Table).

The strength of oleum is determined by weighing a given quantity in a thin glass tube, sealed in the blow-pipe, and then breaking this under cold water. The solution is then titrated with normal NaOH in presence of methyl orange. If any SO_2 is present this is titrated with iodine solution.

Oleum solidifies the more easily at ordinary temperatures the more SO_3 there is present, and this constitutes a practical difficulty, because it is always necessary to heat it to 25° to 30° in order to liquefy it, so that liquid oleum of a strength which is not too high (30 per cent.) is preferred.

The price of oleum of about 30 per cent. of free SO_3 is £3 4*s*. to £4 per ton in large quantities and it is stored and despatched in wrought-iron vessels.

Fuming sulphuric acid is used in very large quantities in the manufacture of aniline colours and explosives, in the refining of mineral oils, paraffin, &c., and in many cases when the strength of dilute sulphuric acid is to be increased.

In 1888 the Badische Anilin und Sodafabrik of Ludwigshafen produced 18,000 tons of sulphur trioxide catalytically, and in 1900 160,000 tons. In Germany 93,000 tons of fuming sulphuric acid were produced catalytically in 1904, and about 100,000 tons in 1905.

INDUSTRIAL MANUFACTURE OF SO_3 AND FUMING SULPHURIC ACID

This is closely connected with the manufacture of sulphuric acid, and will in all probability replace the old system of lead chambers.

It is therefore useful to explain this new and very important process in some detail. Until a few years ago the process of Hänisch and Schröder was used, which was based on the reaction proposed by Winkler in 1875, and was a serious competitor with the only fuming sulphuric acid works of Starck at Prague, who obtained it by distilling iron sulphate. Hänisch and Schröder at first worked with pure concentrated SO_2; they then used dilute SO_2 as obtained from the pyrites burners, bringing it into contact with catalytic masses of platinised asbestos in the heat at a pressure of about three atmospheres in order to obtain a more intimate contact. They thus hoped to obtain an easier reaction and a better yield. The process of Hänisch and Schröder has to-day been completely replaced by more rational catalytic processes, which are used without pressure and by which almost theoretical yields are obtained. Until 1898 the greatest secrecy was maintained on the industrial preparation of SO_3 by catalytic means.[1]

Through the indiscretion of a workman of the Ludwigshafen works, who communicated the secret to competing works, three patents were taken out almost simultaneously by the Badische Anilin und Sodafabrik of Ludwigshafen, the Farbwerke vorm. Meister Lucius und Brüning of Höchst, and the Verein chemischer Fabriken of Mannheim.

In 1901 Knietsch, who had studied the problem at the Badische Anilin und Sodafabrik for years, and who had succeeded after many attempts in discovering the industrial solution of the problem, read a paper before the German Chemical Society at Berlin which threw a little light on this new industry.

An epoch fruitful in practical results in connection with the catalytic manufacture of SO_3 was started in 1875 by the discoveries of Clemens Winkler and of Squire and Messel. They employed platinised asbestos, containing less than 5 per cent. of platinum, and

[1] In 1823 Döbereiner discovered that finely divided platinum becomes hot in presence of O and H by causing them to combine. Dulong, Thénard, Dumas, and Mitscherlich also discovered various substances which cause reactions without being altered themselves. These substances were called *catalytic* substances by Berzelius in 1836. In 1821 a vinegar manufacturer of Bristol named P. Phillips obtained an English patent, 6096, in which he stated that on passing sulphur dioxide mixed with air through a hot tube filled with platinum wire sulphuric acid was formed, on dissolving the product in water, without the necessity for using nitrate or a lead chamber. The same thing happened to Phillips' discovery as has happened to the ammonia-soda process discovered by Dyar and Hemming at that time in England, and the process of mercerising cotton discovered by Lowe, also in England, in 1894; it found no application in that country, but was then studied, and the industrial results were obtained elsewhere, although Phillips' results were confirmed in 1832 in Germany by Magnus and also by Döbereiner. In 1838 it appears that Kuhlmann had taken a French patent of similar trend to that of Phillips. In 1847 a Belgian chemist, Schneider, prepared a small quantity of sulphuric acid by a catalytic process in a small apparatus, employing pumice prepared in a special manner (perhaps with platinum) as a catalytic substance. In 1846 Jullion (Eng. Pat. 245) proposed the use of platinised asbestos in order to obtain oxidised compounds of nitrogen or chlorine from HCl and hot air.

In 1848 Laming prepared H_2SO_4, using pumice impregnated with manganese dioxide and a trace of ammonia as a catalytic substance at about 300°. In 1852 Wöhler and Mohla found that H_2SO_4 is obtained by employing as a catalytic substance copper, iron, or chromium oxides at a red heat, and explained this fact by supposing that these oxides are transformed into lower oxides yielding oxygen; and the reaction also occurred in absence of water. In 1853, Nobb in two English patents proposed as a catalytic substance iron oxide (burnt pyrites), which acted still better in the presence of some manganese oxide.

In 1852 Petrie proposed the use of platinised asbestos for the manufacture of sulphuric acid, and afterwards Thornthwaite (Eng. Pat. 188 of 1854) also proposed platinised asbestos in the heat for the production of H_2SO_4 by contact, or even sesquioxides of iron, chromium, and other metals. In 1855 Piria prepared sulphur trioxide from $SO_2 + O$ in presence of platinised pumice. In 1856 Petrie proposed powdered quartz as a catalytic substance, and this was tried by Hunt, Plattner and Reich, but without much success. In 1871 Deacon and Hurter used as catalytic agents copper salts, which had already been used for obtaining chlorine from HCl and air, but the results were not encouraging. All attempts made up to this time endeavoured to obtain sulphuric acid, as the consumption of pure sulphur trioxide and of fuming sulphuric acid was very small, and thus in all these experiments moisture and dust were not excluded. It is now known that these two substances rapidly paralyse the catalytic action of platinum. In 1862 Graebe and Liebermann prepared synthetic alizarine, and after that time the coal-tar colour works needed large quantities of sulphur trioxide and fuming sulphuric acid in order to prepare the organic sulpho-acids.

succeeded after many attempts in establishing the necessary practical conditions for obtaining an industrial yield of SO_3. They found that this catalytic substance transformed 78 per cent. of SO_2 into SO_3 when SO_2 and O were present in the stoichiometric proportions necessary to obtain SO_3. If, on the other hand, other gases, or even an excess of SO_2 or O, were present, they found that the yield was diminished even to 12 per cent. (but this was shown to be erroneous later).

At that time Winkler, Squire and Messel decomposed concentrated sulphuric acid by Deville's process (*see* p. 179) in order to obtain $SO_2 + O$ in the right proportions [1]; they dried the mixture of $SO_2 + O + H_2O$, in order to separate the water, and then brought $SO_2 + O$ into contact with the hot platinised asbestos. The industrial preparation of SO_3 for the manufacture of fuming sulphuric acid was thus started. Up to that time this acid was a monopoly of the firm of Starck; and before 1877 the price rose very greatly to 2*s.* 7*d.* per kilo of SO_3 on account of the large consumption in the aniline dyestuff works. In 1879 E. Jacob, in Kreuznach, placed fuming sulphuric acid (oleum) on the market, prepared by Winkler's process, obtaining a yield of 70 per cent. by using sulphuric acid of 66° Bé., which was then transformed into oleum containing 43 per cent. of free SO_3.

In 1866 the Farbwerke Höchst acquired the Jacob-Winkler process, but immediately afterwards, instead of decomposing H_2SO_4, they worked with SO_2 from pyrites burners. In 1887 they found it more advantageous to burn Sicilian sulphur, which gave pure SO_2 directly.

Up till 1881 the Badische Anilin und Sodafabrik at Ludwigshafen also worked by Winkler's process, and afterwards by the process of Schröder and Hänisch by which reaction between the pure SO_2 and O was caused in the heat under a pressure of three atmospheres. They only employed the dilute SO_2 gases from pyrites burners later, and this allowed them to give a great impetus to this industry as they were able to produce cheap sulphuric acid in competition with that obtained by the ordinary process in the lead chambers.[2]

The theoretical explanation of the catalytic formation of SO_3 is given by the law of masses: SO_2 and O cannot be completely transformed into SO_3 because the reaction is reversible: $2SO_2 + O_2 \rightleftarrows 2SO_3$, and we must therefore apply the general formula of mass action (p. 66), $\frac{C_1^{n_1} . C_2^{n_2}}{C_1'^{n_2'}} = K$, where $C_1 = SO_2$, $C_2 = O_2$, $C_1' = SO_3$, and where n indicates the number of molecules; we then have $\frac{(SO_2)^2(O_2)}{(SO_3)^2} = K$, whence $\frac{SO_3}{SO_2} = \sqrt{\frac{O_2}{K}}$; if we therefore wish to form larger quantities of SO_3 we must increase the concentration of the oxygen. Theoretically this greater concentration should be produced by means of pure oxygen. Practically, however, the same yield is also obtained by simply employing larger quantities of air so that the oxygen is present in excess compared with the SO_2. The yield is not appreciably influenced by the excess of nitrogen.

With a stoichiometric mixture of $2SO_2 + O_2$ at 450°, Knietsch obtained a yield of 94 per cent., and on maintaining the same relation between SO_2 and O in the form of air he obtained almost the same yield, namely, 91 per cent.

[1] In England the Squire process, which was patented, whilst Winkler did not patent his process in Germany, was gradually perfected in the large works of Thann of London, and, starting with the decomposition of H_2SO_4, they finally used Sicilian sulphur for the preparation of SO_2. They thus obtained 90 per cent. of the theoretical yield of SO_3. The decomposition of the strong sulphuric acid required very high temperatures and the plant was rapidly destroyed, so that the entire resulting process was somewhat dear. Even when burning sulphur they always maintained the stoichiometric ratio between SO_2 and O for many years.

They believed it to be advantageous, in order to obtain a maximum yield, to have at least one of the two gases in a very pure state, and then (after 1880) they used the process of Schröder and Hänisch, which gave pure SO_2, and also used pure electrolytic oxygen. It was only later, by applying the law of mass, that the process was facilitated and completed by increasing the amount of one of the reacting gases.

[2] The attempts to obtain cheap SO_2 directly from pyrites burners date from 1878 and were always kept secret both in the works of Muldener, of Freiberg, who worked by Winkler's process, and in that of Thann, of London, where Squire's process was employed. In 1900 Winkler published the history of all these experiments and mentioned the great difficulty encountered in purifying the gas from the pyrites burners, which easily paralysed the catalytic action of the platinum, and said that it was Jacob (*see above*) who solved the difficulties by burning sulphur instead of pyrites. In 1883 Rath purified the gases from the pyrites burners by first cooling them and then drying them in a tower with a spray of strong sulphuric acid. The gaseous mixture was then suitable for the catalytic action.

The best results have been obtained in practice when the oxygen is present in three times the quantity which is required by theory. The gases from the pyrites burners correspond closely to this composition, namely : $2SO_2 + 3O_2$, because they contain 7 per cent. of SO_2, 10 per cent. of O_2, and 83 per cent. of N_2 by volume.

According to the law of masses the yields should be improved by increasing the pressure, but in practice no advantage is so obtained.

Knietsch found experimentally that the most favourable temperature for the catalytic reaction is from 400° to 450° ; a yield of 99 per cent. of SO_3 compared with the SO_2 present is thus obtained. At higher temperatures the SO_3 decomposes rapidly and at 1200° decomposition is complete if the heating occurs out of contact with the catalytic material ; in presence of the catalytic material the decomposition occurs at even lower temperatures, so that even at 1000° no SO_3 is formed in presence of platinum.

The decomposition of the SO_3 depends on the temperature alone, and thus proceeds equally rapidly whatever may be the catalytic substance. And therefore those catalytic substances only should be suitable which exercise their maximum catalytic effect at a temperature below 450°, that is, between 200° and 450°, whilst other catalysers, which act at higher temperatures, should give a lower yield. Platinum satisfies these conditions, whilst iron oxide, which is also used industrially, is a catalyst, but as it acts at higher temperatures it does not give a yield greater than 60 to 66 per cent. *under these conditions.*

Knietsch also found that by increasing the period of contact or the quantities of catalytic material the equilibrium was not altered, that is, the yield was not improved. There is, on the other hand, an advantage in removing the SO_3 as quickly as it is formed, as may be foreseen by the law of masses.

The greatest difficulty encountered by Knietsch, in passing from laboratory experiments to industrial manufacture, was due to the extraordinary and surprising difficulty in eliminating the last traces of arsenic from the burner gases ; this arsenic acted as a poison on the platinum, rendering it inactive. It was only possible to obtain the burner gases completely pure by cooling them slowly in iron tubes and washing them thoroughly with water and with sulphuric acid. In order to ascertain whether the purification was complete the gases were observed optically through a glass tube some metres long. When they were quite pure they then appeared transparent, without any mist. The chemical test was made with Marsh's apparatus (*see* Arsenic) in water through which the gas was passed for twenty-four hours. In certain cases great difficulty was found in eliminating a very fine mist formed of finely divided sulphur which could not be separated even by washing the gas repeatedly, and thus the catalytic platinum finally became inactive. It was found that these minimal quantities of sulphur were only harmful on account of small traces of arsenic which they contained. This sulphur mist was also successfully separated by mixing the burner gases with a little steam.

A difficulty of another kind consisted in the avoidance of excessive heating of the catalytic substance due to the heat of reaction :

$$SO_2 + O = SO_3 + 86 \text{ Kj. } (20{,}600 \text{ cals.}).$$

Knietsch showed that, contrary to the general opinion up to that time, the yield and the velocity of reaction increase if the tubes containing the platinised asbestos are regularly and continuously cooled.

If the temperature is always maintained by suitable means at about 380° to 450° a yield of 98 per cent. of SO_3 is obtained, and the apparatus works at its maximum capacity. The process is practically controlled by simply watching the temperature of the gases entering and leaving the apparatus. It was also shown that no advantage was obtained by working under pressure.

It was later found that platinum could be economised by replacing the asbestos by other substances which were more porous, for example, the oxides of iron, copper, and chromium, by which means the catalytic action of these substances was utilised together with that of the platinum.[1]

[1] 145 parts of burnt pyrites free from arsenic, in well-sifted pieces of the size of peas, may be taken. These are soaked in 30 parts of a solution of platinum chloride containing 17 grms. of platinum per litre and are then dried at 70°. The platinum is thus finely subdivided and ready for use as a catalyst. This mass does not get crushed together in the apparatus as happens with platinised asbestos, and is more economical. Platinised asbestos is prepared by soaking finely divided asbestos in an aqueous solution of platinum chloride and then

The section shown in Fig. 115 gives an idea of the way in which this process has been applied. The well-washed gases from the pyrites burners enter the peripheral part of the apparatus through many openings, *a*, and by passing through the horizontal tubes, *B*, are homogeneously distributed in the flues, *S*, which are interrupted by walls, *C*, in order to oblige the gas to pass round the tubes containing the catalytic mass. In this way previously cooled gas is used as a cooler for the catalytic mass which is present inside the tubes, *R*, and which is heated by the heat which is developed by the reaction. In order to regulate the temperature of the gases a certain portion of them are passed through the preheater, *G*, before passing through the openings, *a*, whilst another part of the cold gases enters the apparatus directly through the tube, *J*. If much gas is passed through *G* the temperature which is established is higher than when a smaller portion passes through it, if the heating surface remains constant, and thus the mean temperature of the mixture may be varied at pleasure, and the tubes containing the catalytic mass may be cooled to a greater or less extent. The gases from the various tubes reunite at the top of the apparatus in the tube, *F*, and mix homogeneously on entering the chamber, *N*, by pursuing a zigzag path before arriving at the tubes, *R*, containing the catalytic mass.

In the compartments, *D* and *D'*, thermometers are placed. The apparatus works well when there is a temperature of 380° in *D* and 450° in *D'*. Under these conditions 96 to 98 per cent. of the SO_2 is transformed into SO_3 with a production of 40 to 50 kilos of SO_3 per tube in twenty-four hours. 1 kilo of platinum yields one ton of H_2SO_4 per twenty-four hours.

By decreasing the rate of production slightly the yield may be increased to 99 per cent and may be controlled by analysing the gases in *D'*. At the beginning of the operation the lower compartment of the apparatus is heated by the tube, *h*, by means of water gas, and the hot gases escape at the top through the side tube, *L*. When the temperature has reached 300° the process continues alone without further heating.

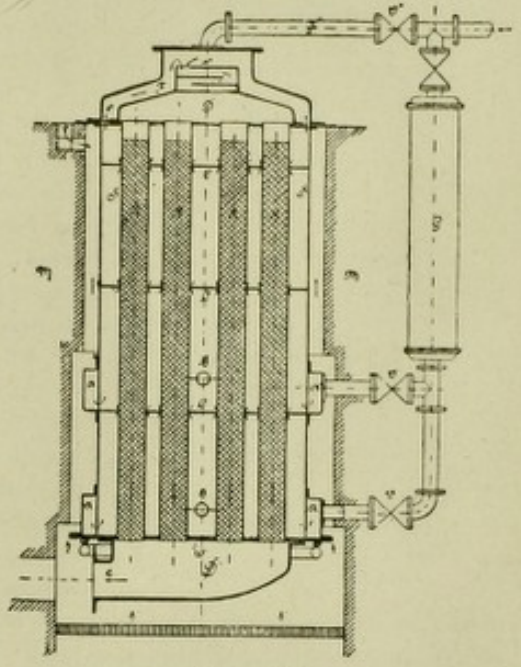


FIG. 115.

The complete absorption of the SO_3 also presented unforeseen difficulties. It had been noted that on dissolving 1 kilo of SO_3 in much water the heat development was 2090 Kj. ; on dissolving in much concentrated sulphuric acid at 66° Bé. 1250 Kj. were developed, from which it appeared easy to absorb all the SO_3 with dilute sulphuric acid from the lead chamber. But in actual practice complete absorption was not obtained either with dilute acid or with water. A fog of SO_3 always remained, causing loss and annoyance to the workmen. After many experiments Knietsch found that the absorption is only complete when concentrated sulphuric acid of 97 to 99 per cent. is employed.

This acid has special properties which were already noted some pages back. Thus its density is at a maximum, more concentrated acid being less dense, and it has also a minimal vapour tension. With more dilute acid a greater vapour tension is obtained due to vapours of H_2SO_4 ; with more concentrated acid there is also a larger vapour tension due to vapour of SO_3, and since the vapours of H_2SO_4 are dissociated into H_2O and SO_3 the minimal *partial pressure* of SO_3 is only obtained with H_2SO_4 of 97 to 99 per cent., and this acid alone is capable of completely absorbing the SO_3. The concentration of the acid is constantly maintained at about 98 per cent. even during absorption, by constantly replacing the more concentrated acid which is formed and passing in more dilute acid (*see below* with reference to vessels for storing fuming sulphuric acid).

By means of the Badische Anilin und Sodafabrik's process one ton of sulphuric acid

in a solution of ammonium chloride ; on then heating the mass to redness the precipitated ammonium platinum chloride separates platinum in a spongy form. This, however, does not adhere very well to the asbestos and it is now considered better to soak the asbestos or other substance directly in an alcoholic solution of platinum chloride. On burning the alcohol the finely divided platinum, which is very active, alone remains ; this catalytic mass only contains 2 per cent. of platinum (Mayert, Ger. Pat. 134,928 of 1901).

was obtained per twenty-four hours per kilo of finely divided platinum ; to-day even less platinum is employed.

The first German patent of the Badische Anilin und Sodafabrik is dated June 3, 1898 (Ger. Pat. 113,933), and one of the last is dated March 24, 1901 (Ger. Pat. 140,353).

The Farbwerke Meister Lucius und Brüning of Höchst also achieved the catalytic preparation of SO_3 through the discovery of Krauss and Dr. Müller von Berneck. The first German patent is that of January 6, 1898 (Ger. Pat. 105,876), and the last one that of February 6, 1902 (No. 135,887). They encountered the same difficulties as the Badische Company and gradually overcame them. The heat of reaction between the SO_2 and O was utilised to heat the gaseous mixture of SO_2 and air proceeding from the pyrites burners, which was cooled by washing with water and with concentrated sulphuric acid.

The arrangement of the apparatus is illustrated in Fig. 116. The cold gaseous mixture enters at *E*, is heated to the desired temperature by passing over the battery of very hot tubes, *R*, and then escapes laterally in order to descend again through *C* over the catalytic mass where it is heated by the reaction which occurs. It then escapes through the tubes, *R*, and gives up a portion of its heat in order to pre-heat gases which arrive through *E*, finally passing out at *A*.[1]

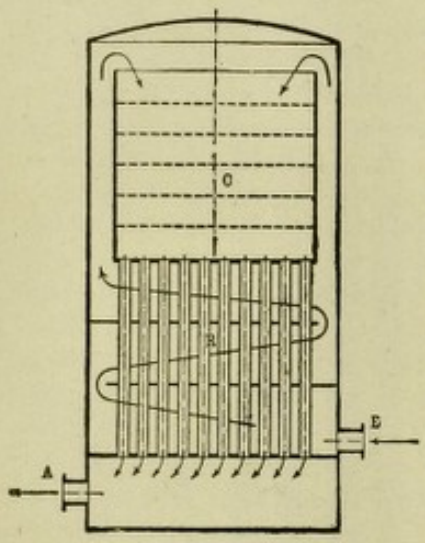


Fig. 116.

The Farbwerke found that they were not tied to the most favourable temperature, but that they could also work at higher temperatures by modifying the equilibrium in a sense favourable to the separation of SO_3 as fast as it was formed, and then passing the gases which had not reacted over the mass for a second time. In this way they obtained a yield of 95 per cent. of SO_3 in practice.

The following substances were found to be dangerous to the platinum, as they acted as catalytic poisons : As, Se, Tl, and Sb. But when arsenic is deposited on the contact platinum it can be completely eliminated, and the activity of the platinum revived, without removing it entirely from the apparatus, by adding a small amount of steam to the gases which pass over the contact mass, whilst this is heated. The Farbwerke, on employing iron oxide, Fe_2O_3, as a catalytic substance, made the following surprising discovery : if a current of SO_2 obtained from the ordinary pyrites burners is passed through a tube containing burnt pyrites at 300° to 400°, less SO_2 is found at the far end of this tube, but the corresponding quantity of SO_3 is *not* present. A part of the SO_2 is thus absorbed by the burnt pyrites, or, more precisely, by the various compounds which this contains. In fact, on adding ferrous sulphate to the burnt pyrites the absorption of SO_2 increases and becomes complete and quantitative if the gases contain a small amount of moisture. On then heating the burnt pyrites to 550° in presence of SO_2 all SO_2 which has been previously absorbed is liberated in the form of SO_3 and H_2SO_4.[2]

The catalytic reaction of the burnt pyrites becomes greater when ferrous sulphate is present, because this is first oxidised and then decomposed, forming finely divided iron oxide, Fe_2O_3, which is then much more active. The residual sulphur, which is ordinarily contained in burnt pyrites, is then also utilised and transformed into SO_3, the burnt pyrites becoming redder in colour. A new process of preparation of SO_3 and of H_2SO_4 has been

[1] The steam necessary for driving the pump which keeps these large masses of gas in circulation was obtained from the hot gases from the pyrites burners, which, at a temperature of 500° to 600°, pass over iron tubes in which water from special boilers circulates.

[2] The Farbwerke found that the following substances also acted as catalysts : vanadic acid, tungstic acid, molybdic acid, and their mutual combinations ; also the more highly oxidised oxides and sulphates of Fe, Co, Ni, Cu, Ag, Mn, Cr, and U, &c., and also the oxides of Ce, Dy, La, Zn, Th, Ti, Si, and those of certain other rare elements. Finely divided platinum is the most energetic of all these substances, and under certain conditions produces a very energetic catalytic reaction even at 200°, instead of 450°.

Russel and Smith showed in 1901 that the following oxides and hydroxides : MnO_2, PbO_2, Fe_2O_3, and Cr_2O_3, also act catalytically on $SO_2 + O$ in the cold, in proportion to the contact surface ; but all action ceases if these substances are completely dry. Even with hot platinum the reaction is minimal or zero if the substances are absolutely dry, whilst it is greatly accelerated by a mere trace of steam. On the other hand, an excess of steam acts as a poison on the platinum and the catalytic action is reduced to a minimum. The mixture of dry gases as it is now prepared industrially, even after drying with strong sulphuric acid, always contains traces of moisture which are very favourable to the catalytic action.

evolved from these experiments and is illustrated schematically in Fig. 117. The burnt pyrites soaked in ferrous sulphate solution, which is obtained during the treatment of burnt pyrites containing copper (*see* Copper Sulphate), is raised by means of an elevator, *L*, and then continuously passed into a tube, *C*, by means of a helical transmitter, *E*. The rotating tube, *C*, is made of wrought iron, and the contents are well distributed by means of fixed longitudinal plates throughout its length (*see* section to left of figure). The tube is rotated on the carrier, *H*, by means of the cog-wheel, *F*; the burnt pyrites descend the tube in the opposite direction to the current of hot gases which passes in from the pyrites burners, *A*. In the upper and colder part of the tube the SO_2 is absorbed by the burnt pyrites and this gradually descends into the lower hotter part of the tube where all the S and SO_2 are completely liberated in the form of vapours of SO_3 and H_2SO_4. These vapours travel up the tube and enter the chamber, K_2, together with the indifferent gases of the atmosphere. In this chamber the dust which is carried over with the gases is deposited, and they pass through the tube, *S*, into the absorbing or condensing apparatus. The burnt pyrites, free from sulphur, is collected in the chamber, K_1, and may then be continually re-employed in order to utilise all the sulphur which it contains (1 to 2 per cent.) in the state of sulphide.

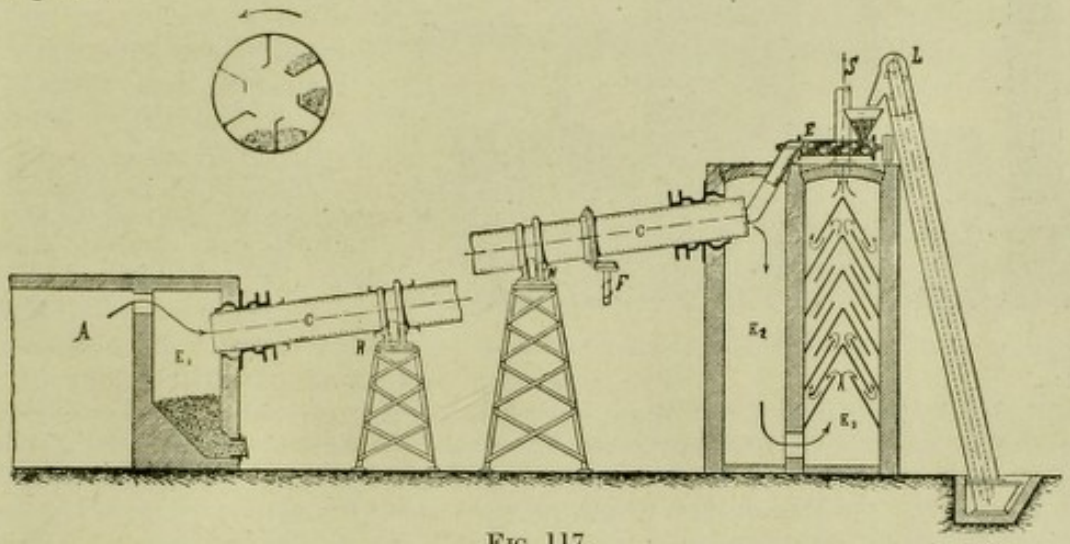


FIG. 117.

This process is used at Höchst, at Hruschau, and at Hamburg. In order to obtain fuming sulphuric acid the SO_3, cooled to 50° to 60°, is dissolved by sulphuric acid of about 95 per cent. To obtain ordinary sulphuric acid the gases are dissolved in water or dilute sulphuric acid. If a concentration of more than 95 per cent. of H_2SO_4 is reached, the acid, which was at first clear, becomes opalescent, because a little ferrous sulphate which is formed in the apparatus and which is only soluble in acid of less strength than 95 per cent. is separated. If the acid is turbid it is readily and completely cleared by adding a little water.

In the Schröder-Grillo process a very active catalytic substance is used which is obtained by subdividing platinum in a magnesium salt; magnesium sulphate is soaked in a solution of a platinum salt and then heated in presence of SO_2, when finely divided platinum separates.

This catalytic mass is very economical because it is very dilute, and contains only one one-hundredth part of the platinum contained in platinised asbestos;[1] with 500 mgrms. of finely divided platinum one ton of oleum is produced per day with a consumption or loss of only 20 mgrms. of platinum per ton of acid. The brown coloration which is often found in acid obtained by this process is removed by the addition of lead peroxide and by then filtering through sand.

About thirty works employ this process to-day and the yields are from 96 to 98 per cent. The first patent obtained was that of Schröder-Grillo of Hamborn of May 17, 1898 (Ger. Pat. 102,244), and the last that of May 20, 1901, which is an English patent. The process of the Verein chemischer Fabriken in Mannheim was discovered by Drs. A. Clemm and

[1] *See also* notes on pp. 278, 279, 280. Schröder found that the catalytic mass is damaged by silicon fluoride, which is often present in burner gases; it is therefore advisable to separate this before the gases pass over the platinum. Arsenic deposited on the platinum is removed by aqua regia or chlorine.

Hasenbach. The first patent obtained was that of July 31, 1898 (Ger. Pat. 107,995), and the last that of December 31, 1901, which is an American patent. The process is based on the observation made by Lunge in 1878 that when gases from the pyrites burners are passed over red-hot burnt pyrites, Fe_2O_3, 18 per cent. of the SO_2 contained in the gases is converted into SO_3.[1]

By the new process the pyrites are burned in previously dried air in such a manner that gases containing 2 to 3 per cent. of SO_2 are obtained. The burners are completely encased in sheet iron and thus hermetically closed in order to prevent the entrance of moist air. The purified gases enter the first chamber which contains a layer of 2 to 3 metres of burnt pyrites (ferric oxide, Fe_2O_3) which at a temperature of about 600° transforms 60 per cent. of the SO_2 into SO_3. The SO_3 is then all absorbed by means of sulphuric acid, and the remaining SO_2 which is dry and pure enters another compartment where it comes into contact with finely divided platinum and is then completely transformed into SO_3.

Fig. 118 illustrates diagrammatically two compartments of the pyrites burner where the combustion of the ore, a^1, a^2, a^3, a^4, takes place.

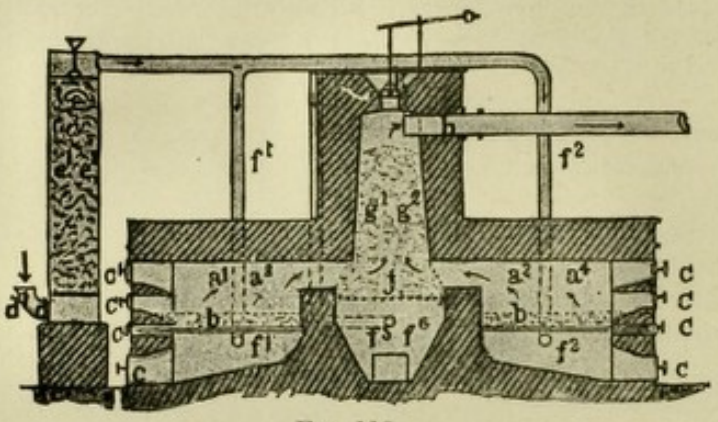


Fig. 118.

The air needed for the combustion passes in through the tube, d, through a drying tower, e^1, e^2, and then through the tubes, f^1, f^2, to below the grate of the furnace.

The mixture of SO_2 and air enters a tall chamber, g^1 and g^2, containing the catalytic mass of burnt pyrites which transforms the SO_2 into SO_3 at a definite temperature. If necessary a larger quantity of air may be passed in directly through the tube, f^5. The SO_3 which is so formed passes out through the tube, b, to the condensing apparatus ; the unaltered SO_2 is passed over the platinum contact mass. In order to renew the iron oxide this is discharged through the revolving grate, j, and the chamber is then recharged with new burnt pyrites through the upper opening, K.

In his theoretical explanation of catalytic phenomena Lunge maintains that the increase of the velocity of reaction which is considered by Ostwald as a simple manifestation of catalytic action may be explained in these cases by the formation of intermediate products ; and in the case of platinum we may suppose these to consist of easily decomposable intermediate oxides. As a matter of actual fact Wöhler discovered oxides of platinum in 1909. The supposed catalytic action of iron oxide may be explained experimentally by the intermediate formation of ferric sulphate which has a temperature of decomposition very close to that of its formation, and we can then understand how under certain conditions SO_3 continues to be formed by decomposition of the sulphate, so that apparently unaltered iron oxide finally results :

$$Fe_2O_3 + 3SO_2 + 3O = Fe_2(SO_4)_3 :$$

and this then decomposes as follows : $Fe_2(SO_4)_3 = Fe_2O_3 + 3SO_3$.

In 1902 Keppeler actually observed that iron oxide first forms ferric sulphate which, at a temperature of 400°, commences to liberate molecules of SO_3, until the partial pressure of this gas (*see* p. 63) is equal to the decomposition tension of the ferric sulphate. The decomposition tension of the sulphate varies with the temperature and depends upon the vapour tension of SO_3. Towards 600° complete dissociation of the sulphate takes place at the ordinary pressure (1 atmosphere), that is, that at that temperature the dissociation

[1] It was also found that chromium and iron oxides and the corresponding sulphates increase the activity of iron oxide. In 1902 Lunge and Pollitt found that copper and arsenic oxides also have a beneficial action on the catalytic activity of iron oxide.

tension of the sulphate has overcome the partial tension of the SO_3. But decomposition may also occur at lower temperatures, because at these temperatures the partial tension of the SO_3 vapours may be lower than the dissociation tension of the sulphate. Thus, for example, if the gases from the pyrites burners are diluted to such an extent that a gas containing 8 per cent. of SO_3 is finally obtained, then the partial vapour pressure of the SO_3 will be $\frac{8}{100}$ of an atmosphere. Thus the dissociation of the ferric sulphate will occur at a much lower temperature, namely, that which corresponds to a dissociation tension of the sulphate of $\frac{8}{100}$ of an atmosphere.

Keppeler has observed that the dissociation tension of the sulphate always commences at about 500°, whilst its temperature of formation is a little lower. Thus, on working with an excess of oxygen, that is, with very dilute burner gases (2 to 3 per cent. of SO_2), this temperature suffices for the continuous formation and dissociation of the sulphate. If the oxygen is not present in excess, then, according to the law of masses, the temperature of formation of the sulphate will be higher. If abundant quantities of this gas are present, that is, if there is great dilution with air, the heat of reaction will raise the temperature of the entire catalytic mass only slightly, and thus the disadvantageous dissociation of SO_3 in contact with the very hot catalytic mass will be diminished (*see above*).

Since burnt pyrites produce their maximum catalytic effect at 625° and since at that temperature a portion of the SO_3 is already dissociated, we can understand why the highest yield which can be obtained by this method is only 70 per cent. and why the remaining SO_2 has therefore to be transformed by means of a platinum contact.

The process of Rabe (1901) deserves to be recorded; it is distinguished by various improvements in the details of certain operations.

In this process there is a special arrangement for purifying and drying the gases from the pyrites burners, by means of which even traces of HCl are removed with sodium disulphite crystals. By cooling the concentrated sulphuric acid which absorbs the SO_3, by suitable means, a very concentrated oleum may be obtained. Several works used Rabe's process; in one of these the complete cost of one ton of SO_3, which includes all expenses, amortisation, &c., is about £2.

We will finally record the process of Hölbling and Ditz (Ger. Pat. 149,677 of 1903) in which a mixture of the sulphates of thorium and cerium together with a little praseodymium sulphate is used as a catalyst, by which means the yield rises to 92 per cent. Küster obtains good results by employing vanadium pentoxide at 450° as a catalyst, and suitably regulating the amount of moisture.

L. Heinz (U.S. Pat. 875,909 of 1908) has recently proposed the purification of the gases which are to be brought into contact with the catalytic mass by first transforming about 20 per cent. of the SO_2 into sulphuric acid in a system similar to that of the lead chambers and then passing the remaining gases, freed from arsenic and from fog, over the catalytic mass.

Vessels for preparing and storing fuming sulphuric acid must not be made of cast iron, although this resists ordinary sulphuric acid monohydrate so well, as these are easily broken and even exploded by oleum, which penetrates into the pores of the metal, producing H_2S, SO_2, and CO (this latter gas being formed from the carbon in the cast iron). Wrought-iron receivers are slightly corroded by weakly fuming acid (up to 27 per cent. of free SO_3), perhaps because such oleum has a greater electric conductivity than acid of other concentrations. If the oleum contains more than 27 per cent. of free SO_3 wrought-iron vessels resist its action very well, and remain unaltered for years. Acid thus stored is free from iron (less than 0·008 per cent.), and such acid is in request for use in accumulators and in the manufacture of pure aluminium sulphate.

The cost of production in Germany, according to Luty and Niedenführ, is as follows: one ton of sulphuric acid calculated as monohydrate obtained in lead chambers at 50° Bé or by catalytic methods from sulphur trioxide, and with reference to a plant for the daily production of twenty tons of monohydrate, will cost as follows:

—	Old plant with lead chambers and furnaces worked by hand	New plant with lead chambers, plate towers, and mechanical furnaces	Catalytic process under the best modern conditions
	Shillings	Shillings	Shillings
Pyrites	12·80	12·80	12·80
Nitrate	2·08	2·08	—
Fuel for heating and power	1·92	1·92	1·60
Labour	2·24	1·68	1·92
Repairs	1·36	1·20	1·20
Amortisation and interest :			
(*a*) Plant and land	6·63	3·68	6·72
(*b*) For patent expenses (£4000)	—	—	1·04
Cost of dilution of the catalytic sulphuric acid about	—	—	1·6
Cost of one ton monohydrate without general expenses	27·03 = (£1 7*s*. 0½*d*.)	23·36 = (£1 3*s*. 4½*d*.)	26·88 = (£1 6*s*. 10½*d*.)

Under these conditions, and it is useless to overlook it, we must consider that the last hour of the lead chambers is not very remote, and although these may continue to be used for some time, this is due to the fact that during the last few years, under the stimulus of the new competing process, numerous and important improvements in the lead chamber process have been introduced as we have recorded above ; but the catalytic process is also being continually improved. The patent licences continually cost less and less and in a few years will be public property. Certain technical specialists have testified that the supervision and regulation of the catalytic process is easier than that of the lead chambers.

To-day already the advantage of the catalytic process is very great when sulphuric acid monohydrate or even concentrated acid of 66° Bé. is to be prepared, because on distilling in platinum apparatus this acid costs at least £1 12*s*. per ton, whilst catalytically it costs about £1 7*s*. 2½*d*.

For large plants the Badische process appears to be the most convenient and for small plants the processes of Rabe or of Schröder-Grillo. In Italy there are three catalytic sulphuric acid plants. In the United States there are five plants, mainly on Schröder-Grillo's system, producing 50,000 tons of oleum. In England there were two plants in continuous work in 1909.

DERIVATIVES OF SULPHURIC ACID

CHLORO-ANHYDRIDES OF SULPHURIC ACID. These may be considered as sulphuric acid in which one or both of the OH groups are replaced by chlorine. They are obtained by treating sulphuric acid with phosphorus pentachloride (PCl_5) ; these anhydrides regenerate sulphuric acid with water.

The **monochloro-anhydride** of sulphuric acid $SO_2\langle^{Cl}_{OH}$ is also called **chloro-sulphonic acid**, and is formed by the following reactions: $SO_2\langle^{OH}_{OH} + PCl_5 = HCl + POCl_3 + SO_2\langle^{Cl}_{OH}$. The phosphorus oxychloride $POCl_3$, which is thus formed, reacts further with sulphuric acid, generating more chloro-anhydride and metaphosphoric

acid. It is also obtained from SO_3 or pyrosulphuric acid ($H_2S_2O_7$) with HCl vapours. It is prepared still more conveniently by passing chlorine through cooled sulphuric acid, or by slowly dropping phosphorus trichloride into it.

It is a colourless, fuming liquid of sp. gr. 1·716, and boils without change at 152°. Its potassium salt $SO_2\langle^{Cl}_{OK}$ is obtained by the action of SO_3 on KCl.

The **dichloro-anhydride** of sulphuric acid $SO_2\langle^{Cl}_{Cl}$ is also called **sulphuryl chloride**, sulphuryl being the name of the SO_2 group in sulphuric acid. It is easily formed by direct interaction of Cl and SO_2 in presence of a little camphor.

It is a colourless liquid of pungent odour which fumes less in the air than the mono-chloro-anhydride ; it has a specific gravity of 1·667 and boils unchanged at 69°.

A **chloro-anhydride of pyrosulphuric acid**, $S_2O_5Cl_2$, is known, and boils at 142°. The chloro-anhydride of sulphurous acid, $SOCl_2$, which is also called **thionyl chloride**, is also known.

AMINO DERIVATES OF H_2SO_4. These compounds have a constitution analogous to that of the chloro-anhydrides, the OH groups of sulphuric acid being replaced by the ammoniacal residue NH_2 (amino) : thus we have

$SO_2\langle^{OH}_{NH_2}$; $SO_2\langle^{NH_2}_{NH_2}$.

Aminosulphonic acid or sulphaminic acid — Sulphamide or amide of sulphuric acid

SULPHAMIDE is obtained, mixed with sulphimide, from NH_3 and SO_2Cl_2, and forms large colourless crystals which melt at 81°. It is soluble in water and has a neutral reaction. The hydrogen united to nitrogen is replaceable by metals. When heated to 200° it forms sulphimide SO_2NH in which two atoms of hydrogen of the NH_3 are replaced by the sulphuryl residue and the residue NH is called *imide*. The hydrogen atom of the imido-group is also replaceable by metals, and salts are thus formed which are better crystallised and more stable than sulphimide itself.

SULPHAMINIC ACID is obtained from SO_3 and NH_3.

An iminosulphonic acid $NH(SO_3H)_2$ (= disulphaminic acid) is also known, and so is nitrilesulphuric acid $N(SO_3H)_3$ (trisulphaminic acid) in which the monovalent SO_3H group, called the *sulphonic* group, is contained three times.

THIOSULPHURIC ACID, $SO_2\langle^{OH}_{SH}$ is not known in the free state, and when it is liberated from its salts (thiosulphates) by means of strong acids it at once decomposes into $SO_2 + S + H_2O$. The salts are obtained by heating sulphites with sulphur : $SO_3Na_2 + S = S_2O_3Na_2$, or by heating sodium sulphide and sodium sulphite with iodine.

POLYTHIONIC ACIDS : these all contain six atoms of oxygen and two of hydrogen with varying numbers of atoms of sulphur. They may also be considered as condensation products of two sulphonic acid groups by means of sulphur atoms.

DITHIONIC ACID : $\dot{S}O_3H\atop\dot{S}O_3H = S_2O_6H_2$. This is only known in a solution obtained from manganous dithionate MnS_2O_6. On heating, it forms $SO_2 + H_2SO_4$.

TRITHIONIC ACID : $S\langle^{SO_3H}_{SO_3H} = S_3O_6H_2$, is not known in the free state ; the potassium salt is obtained by heating acid potassium sulphite in aqueous solution with flowers of sulphur, or from sulphites with hyposulphites and iodine. With strong acids it separates S and SO_2.

TETRATHIONIC ACID : $\dot{S}.SO_3H\atop\dot{S}.SO_3H = S_4O_6H_2$. The salts of this acid are obtained from thiosulphates with iodine : $2S_2O_3K_2 + I_2 = S_4O_6K_2 + 2KI$.

PENTATHIONIC ACID: $S\begin{cases} S—SO_3H \\ S—SO_3H \end{cases} = S_5O_6H_2$, is obtained together with tetrathionic acid by passing H_2S into an aqueous solution of SO_2 at 0°: $5SO_2 + 5H_2S = H_2S_5O_6 + 4\,H_2O + 5S$, by which means *Wackenröder's liquid* is formed.

In contradistinction to sulphuric acid all the polythionic acids yield very soluble barium salts.

PERSULPHURIC ACID, $H_2S_2O_8$ or HSO_4. This acid is not known in the free state, but is formed when sulphur heptoxide, S_2O_7, is dissolved in water. This latter compound is obtained in a crystalline, easily fusible, and easily alterable condition by passing an electric discharge through a mixture of oxygen and SO_2. It is also formed in electric accumulators. A solution of persulphuric acid is easily obtained with the apparatus of Elles and Schönher (Fig. 119). Sulphuric acid of sp. gr. 1·4 is placed in the test-tube, *A*, and a current of 2 amps. and a density of 100 amps. per square decimetre of surface of the electrodes is passed by means of the arrangement indicated in the figure between the platinum anodes and cathodes. Ice and water are placed in the vessel, *F*, in order to cool the apparatus, and the gases formed at the anode during electrolysis escape through the tube, *E*. The solution is decomposed on heating, forming H_2SO_4, nascent oxygen and ozone. The solutions decolorise indigo, but not permanganate solutions, nor do they produce a blue coloration with solutions of bichromates, by which means this acid is distinguished from hydrogen peroxide.

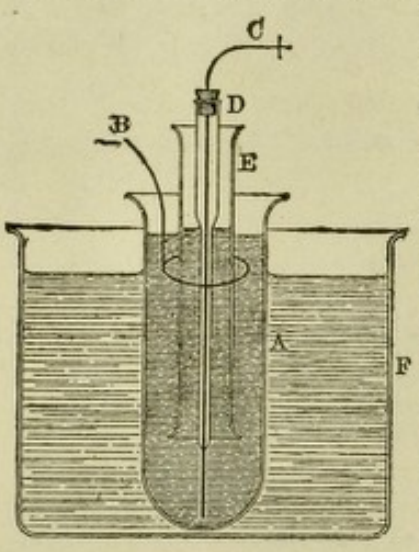


FIG. 119.

The persulphates and their applications are dealt with in Part III.

CARO'S ACID (Oxypersulphuric acid), $S_2O_9H_2$. The formula HSO_5 was first attributed to this acid, but after a series of investigations ranging from 1898 to 1903, its exact constitution was determined; it is obtained by dissolving potassium or ammonium persulphate in strong sulphuric acid with stirring, whilst cooling by means of ice. A pasty mass results, which then solidifies and has very great oxidising power; it is called Caro's reagent and is used in researches on alkaloids.

OXYGEN COMPOUNDS OF Se and Te

SELENIUM DIOXIDE, SeO_2, or SELENIOUS ANHYDRIDE. This compound is formed on burning selenium in oxygen or air. With potassium iodide dissolved in hydrochloric acid, selenium and iodine are separated:

$$SeO_2 + 4KI + 4HCl = 4KCl + 2H_2O + Se + 2I_2.$$

It is a white substance, forming needles which sublime at about 320° without melting. It is easily soluble in water, being transformed into selenious acid, SeO_3H_2. This acid is also obtained by dissolving selenium in concentrated nitric acid and forms large colourless crystals which decompose on heating into $SeO_2 + H_2O$. Selenious acid is reduced by sulphur dioxide with separation of selenium and formation of sulphuric acid:

$$SeO_3H_2 + 2SO_2 + H_2O = Se + 2SO_4H_2.$$

With H_2S its solutions give a yellow colloidal solution of selenium sulphide, which becomes red under the influence of time, heat, light, or pressure. Its salts are called *selenites*.

SELENIC ACID, SeO_4H_2. This acid is obtained by oxidising selenious acid with chlorine: $SeO_3H_2 + H_2O + Cl_2 = 2HCl + SeO_4H_2$. When pure it forms crystals which melt at 58°; at a concentration of 95 per cent. (sp. gr. 2·6) it forms a dense oily liquid. A hydrate, $SeO_4H_2 \,.\, H_2O$, is known, but selenic anhydride is not known. Its salts are called *selenates*.

TELLURIUM DIOXIDE, TeO_2. This substance is obtained as a white crystalline mass by burning tellurium; it melts at a red heat, and then sublimes. It is almost insoluble

in water. *Tellurious acid*, H_2TeO_3, is formed on dissolving tellurium in nitric acid, and separates from the solution as a white powder on diluting with water. This powder is decomposed on heating, forming TeO_2 and H_2O.

TELLURIC ACID, H_2TeO_4. This compound is obtained by oxidising tellurious acid with chromic acid. It is separated from the solution as a white powder by means of concentrated nitric acid. It is only slightly soluble in water and has a feebly acid reaction. On heating carefully it decomposes into water and telluric anhydride (TeO_3), which forms a yellow powder insoluble in water.

NITROGEN GROUP

This group is composed of the elements : *nitrogen*, *phosphorus*, *arsenic*, and *antimony*.

Together with nitrogen we will also study the new gases which have recently been discovered in the atmosphere, namely, argon, helium, krypton, xenon, and neon, which are elements which fit well into the periodic system of the elements, but which have been little studied so far, as no compounds of them are known. The elements of the nitrogen group follow the same rule as those of the other groups, that is, their melting- and boiling-points increase with increase of the atomic weight, and the matter of which they are composed becomes condensed so that they acquire a more or less metallic aspect at the same time. However, in this group also, the resemblance is more pronounced between arsenic and antimony, whilst there are notable differences between the solid much more active phosphorus, and gaseous nitrogen, which is more inert. All these elements form hydrogen compounds containing three atoms of H, and whilst ammonia, NH_3, has an alkaline reaction, this disappears in the case of SbH_3.

The oxygen compounds of nitrogen are strongly acid, whilst, on the other hand, those of antimony are basic.

NITROGEN : N, 14.05

[IN FRENCH AZOTE, OFTEN WRITTEN Az]

Rutherdorf in 1772 in his studies on respiration, and Priestley simultaneously on burning substances in a closed bell-jar, showed that when the oxygen of the air is exhausted a constant volume of inert gas remains, mixed with the carbon dioxide formed by combustion and respiration. They called this gas *mephitic* or *phlogisticated air*.

In 1777 Scheele showed that air is composed of two gases, oxygen and nitrogen.

Nitrogen is found free in nature, in the atmosphere, of which it forms about four-fifths. It is also found in abundance combined in the form of ammonium salts and nitrates, and is an essential and characteristic constituent of the organic substances of the animal kingdom, such as albuminoids, blood, muscles, and nerves. It is found less abundantly in the vegetable kingdom, in seeds, &c., in the form of albuminoids, amino-acids, &c.

PROPERTIES. Nitrogen is a colourless, odourless gas : 1 litre weighs 1·2507 grms., and it has a specific gravity compared with air of 0·97. Its critical temperature is −146° and its critical pressure is 35 atmospheres. In the liquid state it is colourless, boils at −194° at a pressure of 1 atmosphere, has a specific gravity of 0·804 (water = 1), and solidifies at −214°. At −252° it has a specific gravity of 1·0265, whilst that of solid oxygen at the same temperature is 1·4256 (Dewar, 1904). One litre of water at 10° dissolves 16·1 c.c. of gaseous nitrogen.

Nitrogen was believed to be a chemically very indifferent gas, incapable of combining directly with any other substance. To-day, however, the

conditions for obtaining direct compounds of nitrogen have been found, and they are very numerous and important. Lithium, for example, burns in an atmosphere of nitrogen at high temperatures, and so do magnesium, boron, and silicon forming *nitrides*: $3Mg + N_2 = Mg_3N_2$. It combines directly with many metallic carbides (*see below*) and with various other substances under the action of electricity or of organic or inorganic catalysts. If an electric spark is passed through a mixture of nitrogen and oxygen, or of nitrogen and hydrogen, a chemical reaction occurs, and in the first case nitrogen trioxide, N_2O_3, and in the second case ammonia is formed. In the atmosphere, in which nitrogen, oxygen, and water are present, electric discharges produce ammonium nitrite and nitrate.

Nitrogen does not maintain combustion, still less the vitality of an organism, because it plays no part in respiration, although it is not poisonous. In an atmosphere of nitrogen animals die slowly, because the oxygen in their lungs which is necessary in order to transform the blue venous blood into red arterial blood is gradually diminished.

PREPARATION. On passing a current of air over compounds which absorb oxygen, such as red-hot copper, a solution of cuprous chloride, or an alkaline solution of pyrogallol, or on burning yellow phosphorus in a bell-jar containing moist air, all the oxygen is absorbed in the form of solid or liquid compounds, and free nitrogen remains. Until the year 1894 it was believed that the nitrogen obtained in this way was pure, but the numerous experiments of Ramsay and Rayleigh showed that it was a mixture of nitrogen with about one per cent. of argon. Other new elementary gases which had been until that time unknown were later found in the atmosphere. In practice nitrogen is conveniently prepared from a mixture of 1 part of sodium nitrite, 1 to 2 parts of ammonium sulphate, and 1 part of neutral potassium chromate or a few drops of ammonia, in order to fix the acids which may be formed, together with 5 parts of water. The whole is heated in a glass retort and the nitrogen which is developed is purified by passing it through dilute sulphuric acid, which retains the ammonia, whilst traces of oxygen are absorbed by passing it over red-hot copper:

(*a*) $2NO_2Na + SO_4(NH_4)_2 = Na_2SO_4 + 2NO_2NH_4$ (ammonium nitrite).
(*b*) $NO_2NH_4 = 2H_2O + N_2$.

Pure nitrogen is obtained by heating ammonium bichromate or a mixture of potassium bichromate and ammonium chloride in a retort. Another method of obtaining nitrogen consists in passing chlorine into a concentrated solution of ammonia, avoiding an excess of chlorine, which would form a highly explosive substance (nitrogen chloride).

$$2NH_3 + 3Cl_2 = N_2 + 6HCl \text{ (which forms } NH_4Cl \text{ with HCl)}.$$

Pure nitrogen is also obtained by acting on urea with nitrous acid:

$$CO(NH_2)_2 \text{ (urea)} + 2HNO_2 = CO_2 + 2N_2 + 3H_2O.$$

The carbon dioxide so formed is easily separated from nitrogen by passing the gas through a solution of sodium hydroxide. Many organic nitrogen compounds (diazo-compounds) also yield nitrogen on simply heating, for example, by heating diazonaphthalene sulphonic acid with alcohol and sulphuric acid. Certain micro-organisms (*bacteri denitrificanti* studied by Wagner, Burri, Stutzer, and Calmette) have the property of transforming organic nitrogen and nitric acid into free nitrogen, and this is of great importance for agriculture, because these bacteria are more especially nourished by the pentosans contained in straw and destroy the nitrogenous material of stable manure. Calcium nitrate resists this action better than sodium nitrate. Cingolani in 1909 found two bacteria in calves' excrement called *Bact. porticensis denitrificans* (α and β); β reduces nitrates to nitrites and α, on the other hand, does not attack the nitrates, but reduces the nitrites to free nitrogen, and sometimes to ammonia. Similar bacteria were found by Calmette in 1904 in the bacterial beds

used in the purification of sewage (*see* pp. 223–224). The denitrifying bacteria almost always form large amounts of nitrous oxide N_2O from the nitrates (Bijerinck and Minkmann, 1909). In 1897 Sewerin also described a *bacterium pyrocyaneus* and in 1909 a *Vibrio denitrificans* which were still more active, and which reduce nitrates into nitrites in the same manner as the preceding bacteria. Their harmful action, and also the strong heating of dung, are prevented by sprinkling it after removal from the stable with very dilute solutions of sulphuric acid or with a 1 per cent. solution of fluosilicic acid, which is obtained from superphosphate works. Some days before the manure is spread over the fields it is again sprinkled with a dilute 1 per cent. solution of potassium carbonate in order to neutralise the sulphuric acid. A few litres of fresh stable drainings and of urine are then added and the fermentation is thus immediately re-started, so facilitating the decomposition of the grosser organic matter. The admixture of the manure with acid superphosphates or with gypsum containing superphosphates, or the use of beds of peat, had previously been proposed.

Nitrogen is prepared industrially, for example, for the manufacture of calcium cyanamide (*see below*), by the various processes which serve to prepare oxygen from liquid air, or also by passing air through red-hot retorts filled with copper turnings, which retain the oxygen and leave the free nitrogen. Finely divided copper is obtained by soaking porous cylinders or asbestos with copper salts, heating them, and then reducing the oxide at a red heat.

ATMOSPHERIC AIR

Air consists of about four-fifths by volume of nitrogen and one-fifth of oxygen and contains small quantities of water vapour and carbon dioxide, traces of ozone, hydrogen peroxide, and ammonium nitrite, and a very small quantity of the new gases discovered during the last few years, argon, helium, neon, &c. In the lower strata of the atmosphere the most varied micro-organisms abound and cause putrefaction, fermentation, and many other pathological phenomena of great hygienic importance. And in the same way as the hygiene of water is looked after, attention to the hygiene of the air would not be less important; the same reasons which oblige us to maintain water free from impurity also apply to the respiration of infected air, or of close atmospheres in which many people are present. Carbon dioxide and many other poisonous substances should be eliminated or diluted with pure air. The sterilisation of air with ozone (10 mgrms. per cubic metre) has recently been proposed in special cases (Labbé, 1906), by passing the air through an ozonising ventilator.

The atmospheric pressure, measured at sea level, is balanced by a column of mercury 760 mm. high (barometer), and since 1 c.c. of mercury weighs 13·6 grms. the pressure of the atmosphere on each square centimetre of surface is 1033·5 grms.; in Eastern Siberia an atmospheric pressure of more than 800 mm. of mercury is frequently observed. At 0° and 760 mm. pressure 1 litre of air weighs 1·2976 grms., that is, 773 times less than water. The specific heat of air at constant volume is 0·1684 and is 0·2375 at constant pressure.

The quantitative composition of air was first exactly determined by Gay-Lussac and Humboldt in 1801.[1]

They added to a given volume of air, contained in a eudiometer, an excess

[1] In 1650 Boyle, or rather his pupils Hooke and Mayow, commenced to show experimentally that air is composed of at least two gases, one of which maintains combustion and life whilst the other does not. In ancient times, on the other hand, it was believed that air was a simple substance. These fundamental conceptions of Hooke and Mayow, due to their lucid experiments, were afterwards forgotten by chemists, and for a century later the greatest confusion reigned with regard to the composition of air and the cause of the phenomena of combustion. It was at this time that the phlogiston theory arose (*see* p. 15).

Priestley, Cavendish, Scheele, Bayen, and, above all, Lavoisier, by means o careful investigation and numerous experiments on respiration, combustion, the oxidation of metals, &c., succeeded in fighting and definitely burying the phlogiston theory by determining the true composition of air and by showing that air was actually composed of two constituent gases, oxygen and nitrogen, which are present in a well-defined and constant proportion (Cavendish). During the last few years English chemists have again studied the composition of air by means of very delicate experiments, and have discovered that it contains new gases which had formerly been considered as nitrogen (*see below*).

of hydrogen, and then passed an electric spark through the mixture. All the oxygen combined with hydrogen in the proportion of 1 vol. of O to 2 vols. of H, and knowing that the diminution in volume was due to two parts of hydrogen and one part representing all the oxygen present, and knowing also the initial volume of the air, they deduced the exact volume of nitrogen which remained with the excess of hydrogen. This method of fixing oxygen by an excess of hydrogen had already been proposed by Volta for other purposes.

Still more vigorous experiments, based on another method of absorbing oxygen, were carried out by Boussingault and Dumas in 1811. They evacuated a large flask of 20 litres capacity, and after having weighed it, they allowed air which had been dried and freed from carbon dioxide to enter through a red-hot porcelain tube filled with weighed copper turnings, which combined with the oxygen. The increase in weight of the flask gave the amount of atmospheric nitrogen, and the increase in weight of the copper gave the weight of oxygen which had combined with it to form oxide. In this way they found the composition by weight of air per 100 grms. to be 23·095 grms. of oxygen and 76·905 grms. of nitrogen. Since 1 litre of oxygen weighs 1·4291 grms. and 1 litre of atmospheric nitrogen weighs 1·2572 grms., it follows that 100 litres of air are composed of 20·8 litres of oxygen and 79·2 litres of nitrogen.

The volumetric examination may also be made by measuring a definite quantity of air in a graduated glass tube and then introducing a piece of phosphorus or alkaline pyrogallate solution, which absorb the oxygen, leaving free nitrogen behind.

Rigorous analyses were also conducted later by Regnault and Bunsen, who used the method of Gay-Lussac and Humboldt, and obtained the following still more exact results : 20·95 per cent. by volume of oxygen, and 79·05 per cent. by volume of atmospheric nitrogen.

The chemical composition of air is found to be almost the same at all points of the earth (according to the experiments of Kreusler, Hempel, Morley, Leduc (1896), &c.), and is as follows, taking the argon into account :

Nitrogen	78·06 % by volume, or	75·5 % by weight.
Oxygen	21·00 % „	„	23·2 % „
Argon	0·94 % „	„	1·3 % „

Air also contains fifteen parts per million of neon, five parts per million of helium, and one part per million of hydrogen (Claude, 1909).

It appears, however, that originally the atmosphere must have had another composition : Phipson and Koene (1894) believe that when the terrestrial nebula solidified the gaseous atmosphere which remained at that time only contained nitrogen, steam, and carbon dioxide (volcanic), and that oxygen was completely lacking, otherwise the graphite and sulphides which were then present in the primary rocks would have been oxidised. Under these conditions the origin and gradual development of vegetable organisms, both simple and complex, were perhaps possible, because it is known that plants are anaerobic, that is, they can develop perfectly in an atmosphere which contains only nitrogen, CO_2, and water vapour. By means of plant life the amount of oxygen in the atmosphere was gradually increased and the amount of CO_2 gradually diminished, because vegetable organisms absorb CO_2 and evolve oxygen. With the extension of this vegetative process, and in the course of tens of thousands of centuries, the oxygen gradually increased until the beginning of animal life and its development, which is essentially aerobic, was rendered possible. This form of symbiosis gradually developed until a state of equilibrium was gradually attained between the oxygen emitted by plants but absorbed by animals and the carbon dioxide emitted by the latter and absorbed by the former. The continuity of this equilibrium explains the constant composition of the atmosphere ; chemical and physiological processes which fix atmospheric nitrogen are not able to influence it, because these are in turn compensated by other phenomena which liberate nitrogen from various nitrogenous substances (denitrifying bacteria, &c.).

Remembering the enormous mass of oxygen and nitrogen in the atmosphere, it is clear that thousands of years would be required in order to cause any observable modification in its composition, whilst the first exact analyses of the atmosphere were made less than a century ago. We need not therefore fear the near extinction of humanity on account of lack of oxygen, especially as mankind can still live in an atmosphere containing 15 per cent. of oxygen only.

The temperature of the atmosphere at great altitudes is very low, and at the summit of Mont Blanc (4800 metres) it has been calculated by Woikoff and Angot to be $-42°$, whilst direct experiments made during the last few years by means of experimental balloons [1] have shown that it is ordinarily $-5°$ at a height of 3 km., $-16°$ at 5 km., $-39°$ at 8 km., and about $-53°$ at 14 km. The temperature of space in which our earth moves, outside the atmosphere, is certainly lower than $-100°$. Meteorological changes are more common in the lower than in the upper layers of the atmosphere.

The height of the atmosphere was first calculated by Laplace, who stated that at an altitude 6·6 times that of the terrestrial radius the kinetic energy of the particles of air would overcome the power of gravitation, and that thus at this point the atmosphere would cease, and that above it the particles would escape from the earth's attraction. The real limit of the atmosphere appears to be much lower, because on rarefaction and diminution of the temperature of the air, the expansive force of the gas much more easily overcomes the action of gravity. I. C. Schmidt, by supposing that the temperature diminishes regularly with increase of height, finds that the limit of the atmosphere is 58 km. at the equator and 43 km. at the poles. In 1901 Ekholm found by very exact calculations that the atmosphere should be 70 km. high and that its weight should be about 521×10^{13} tons, that is, 0·000,000,856 of the weight of the earth.

The atmospheric pressure on Mont Blanc and also on Monte Rosa at 4560 metres is about 440 mm., and it is found that at a height of 14 km. the atmospheric pressure is not more than 110 mm. The maximum height to which men have attained in balloons is 10,000 metres, and at such altitudes respiration has to be aided with the help of pure oxygen or preferably of oxygen mixed with carbon dioxide (Mosso).

That atmospheric air is not a chemical combination in spite of its constant composition, but a simple mechanical mixture, is proved by the following facts: (1) The air which is contained in solution in water has a different composition (35 per cent. by volume of oxygen and 65 per cent. of nitrogen). (2) On mixing nitrogen and oxygen in the proportion in which they are present in air, there is no evolution or absorption of heat. (3) From liquid air the nitrogen evaporates before the oxygen.

The *relative humidity* of air is determined by the hygrometer, and the *absolute humidity* by passing a given volume of air through a weighed tube containing calcium chloride or strong sulphuric acid which absorbs the water.

In air saturated with water vapour at 25° 22·8 grms. of water vapour (absolute humidity) are contained per cubic metre, and on cooling to 0° 18 grms. of this are deposited as rain. Air ordinarily contains only 50 to 70 per cent. of the amount which it would contain if saturated (degrees of relative humidity).[2]

[1] An *experimental balloon* consists of a small balloon of a few cubic metres capacity filled with hydrogen, and with a lifting power of 15 to 18 kilos. The load consists merely of a light cane cage in which automatically registering instruments are placed, namely, a barometer, a thermometer, and a hygrometer made of aluminium. This balloon dilates when it reaches high altitudes and bursts at a certain height. The cage then commences to fall from a great height which may exceed 15,000 metres. This fall would be dangerous for the instruments if it were not suitably provided for. A small balloon called the pilot balloon is fixed to the main balloon by means of a cord about 20 metres long and precedes it during the ascent; but, not having sufficient lifting force to sustain the car, it serves to retard the fall, and when the whole arrangement reaches the earth it signals the position of the valuable records by remaining suspended a few metres above the ground. Whoever finds the balloon and the cage finds sufficient indications in the latter to enable him to consign the whole to the owner, together with a promise of a generous reward. The instruments are almost always returned.

[2] The hygrometer would always indicate 100° for air *saturated* with water vapour, although the temperature might be different.

In order to regulate the quantity of moisture in living rooms, and especially in workshops, where cotton-spinning, weaving, dyeing, &c., is carried on, and in hospitals in which invalids are exposed to special respiratory cures, it is necessary to take into account not only the relative and absolute humidity, but also the temperature and the humidity which is expelled by the organism during respiration. A healthy man expires 540 litres of air per hour at 37°, producing by means of the oxidisation which occurs in the lungs 12·5 grms. of water vapour

The carbon dioxide (CO_2) in the air is detected by shaking it with a clear solution of barium or calcium hydroxide, which is rendered turbid by the formation of insoluble carbonate. The CO_2 is quantitatively determined in the same manner as the moisture by substituting potassium hydroxide for the calcium chloride or H_2SO_4.

Ordinarily 10,000 vols. of air contain 3·4 vols. of CO_2 gas, or a larger quantity if the air is impure.

LIQUID AIR

PROPERTIES. Liquid air is a milky liquid, because it contains solid carbon dioxide, but if it is filtered a perfectly transparent, very mobile liquid is obtained of a slightly bluish colour. On standing, nitrogen is first lost and it then becomes blue on account of the excess of oxygen. In this liquid not only is mercury frozen, but also ether and alcohol, although they are very difficult to solidify.

Combustible substances, for instance, a piece of charcoal or a wooden match, when first lit and then immersed in liquid air burn with very great intensity.

Dewar has found that wood charcoal at the temperature of liquid air has an extraordinary and surprising capacity for absorbing and fixing gases. Thus, if a vacuum is made in a Crookes tube which communicates with a receiver containing charcoal, then if a vacuum is made of 2 to 3 cm. the electric discharge first has the usual violet colour. If the charcoal is now cooled from outside by means of liquid air the air remaining in the tube is gradually absorbed by it, and we see that the electric discharge assumes all the colours which are seen in a Geissler tube until the vacuum increases and we obtain the beautiful greenish-yellow fluorescence, which is due to the impacts of the electrons: when all the central portion of the cathodic bundle is fluorescent we have a true Crookes tube as used for radiography; but the vacuum still increases up to ten-millionths of an atmosphere, and then the tube becomes dark because the current is unable to traverse it.

Under the action of liquid air india-rubber becomes as brittle as glass; meat, eggs, and flowers become hard and can be reduced to powder; nickel steel at these low temperatures becomes magnetic; the electric resistance of metals diminishes rapidly and becomes almost zero in liquid air, so that we may obtain ideal electric conductors without resistance if the wires are immersed in liquid air, especially as it is also a perfect insulator. The heat of evaporation of a kilo of liquid air is 125 cals. Attempts have been made to destroy the germs of infectious diseases by means of liquid air, for instance, the bacilli of typhus

that is, 1 cu. metre of the expired air contains 23 grms. of water vapour. Air at 37° is saturated by 43·51 grms. of vapour (*see* Table), and thus the air which is inspired from the surrounding atmosphere should contain less than 20·51 grms., that is, 43·51–23 grms. of vapour per cubic metre, in order to avoid the saturation of the air in the lungs themselves during respiration. This is the extreme limit of tolerance, but in order to be able to breathe well there should not be more than 15 grms. of water vapour per cubic metre in the atmosphere, which means that if in an atmosphere we have a temperature of 20° the hygrometer should not indicate more than 87°, because 15 grms. of vapour are 87 per cent. of the vapour of saturation at 20°, which is 17·148 grms.; if the temperature of the atmosphere is 30° the hygrometer should not indicate more than 50 per cent. of saturation, because the 15° of vapour utilised in good respiration are 50 per cent. of the vapour of saturation at 30°, which is 30·079 grms. (*see* Table).

We give a Table of the absolute humidity which indicates the number of grammes of water vapour which saturate 1 cu. metre of air at various temperatures. This is of service in various practical cases, as may be seen from the foregoing examples.

at 0° grm. 4·869	at 10° grms. 9·357	at 20° grms. 17·148	at 30° grms. 30·079
„ 1° „ 5·209	„ 11° „ 9·962	„ 21° „ 18·174	„ 31° „ 31·744
„ 2° „ 5·571	„ 12° „ 10·601	„ 22° „ 19·253	„ 32° „ 33·490
„ 3° „ 5·593	„ 13° „ 11·276	„ 23° „ 20·387	„ 33° „ 35·317
„ 4° „ 6·360	„ 14° „ 11·988	„ 24° „ 21·579	„ 34° „ 37·230
„ 5° „ 6·791	„ 15° „ 12·739	„ 25° „ 22·831	„ 35° „ 39·231
„ 6° „ 7·247	„ 16° „ 13·532	„ 26° „ 24·144	„ 36° „ 41·323
„ 7° „ 7·731	„ 17° „ 14·367	„ 27° „ 25·524	„ 37° „ 43·510
„ 8° „ 8·234	„ 18° „ 15·247	„ 28° „ 26·971	„ 38° „ 45·795
„ 9° „ 8·785	„ 19° „ 16·173	„ 29° „ 28·489	„ 39° „ 48·182
			„ 40° „ 50·674

and of diphtheria, but with negative results, because the spores of these microbes regained their activity, even after being in contact with liquid air for several months, as soon as they regained the ordinary temperature.

On pouring liquid air directly on to the dry skin no burns are produced, because it assumes the spheroidal state, and that part which evaporates prevents contact with the skin, and one merely has a sensation of a light electric discharge ; if, however, the skin is wet burning occurs, but this is only superficial, because the layer of ice which is immediately formed insulates the surrounding parts. On then rubbing the skin with a little wadding soaked in liquid air a white spot is first formed, but it soon acquires a bright colour, and the blood which was first driven from the spot flows back to it. On prolonging the refrigeration the points exposed to it become as hard as ice. Surgical operations performed after such treatment have given brilliant results ; healing was very rapid, and there was a complete absence of pus.

By means of the cold produced by the evaporation of liquid air, petroleum, alcohol, and turpentine are easily frozen ; alcohol no longer burns under such conditions, but becomes

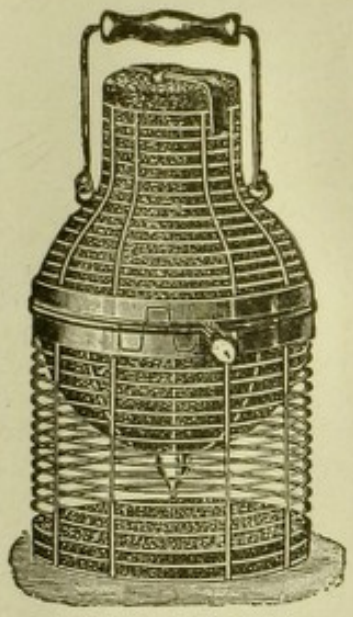


Fig. 120.

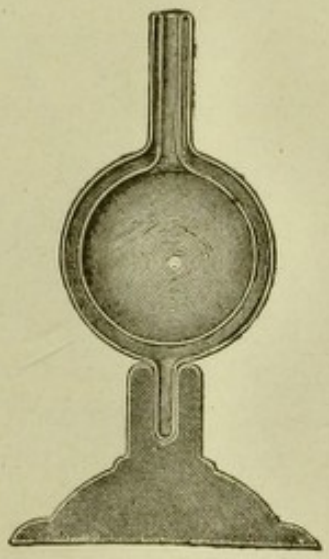


Fig. 121.

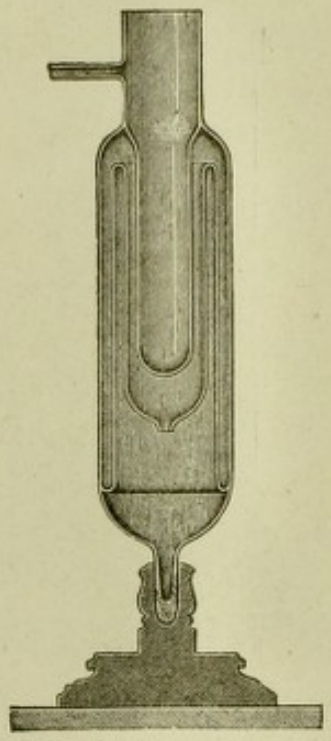


Fig. 122.

a dense and finally amorphous solid ; ether crystallises ; yellow phosphorus acquires a crystalline structure and loses its property of becoming luminous in the dark. On mixing liquid air with red phosphorus an explosive mixture is obtained.

In the air liquid air produces fumes through the condensation of atmospheric moisture. Various reactions in organic and inorganic chemistry are caused or prevented by liquid air.

Liquid air cannot be preserved in closed steel cylinders under pressure in the same way as liquid carbon dioxide, because its critical temperature is at − 140°, and above this point it cannot exist in any other state than as a gas, whatever the pressure may be, so that above this temperature no closed receptacle would be able to resist the pressure.

Liquid air is therefore used on the spot or for the production of oxygen, or it may be kept or despatched in small quantities in open double-walled bottles in which there is a vacuum between the two walls, the inner sides of which are coated with silver. With these bottles, which were devised by Dewar (Fig. 121), the heat rays from outside are refracted and the liquid air in such open bottles, containing two to three litres, slowly evaporates at the rate of 15 to 20 c.c. per hour and lasts for three to four days. For experimental purposes liquid air is placed in Weinhold tubes of glass with triple walls (Fig. 122). In order to transport liquid air for long distances without danger of breaking the flasks (flasks to hold 2 litres cost from 24*s.* to 28*s.*) metallic cages are used (Fig. 120) in which the flask which has been

previously wrapped in wool or felt is placed. When liquid air is poured from such a bottle the neck should be enveloped in a piece of cardboard, which is a bad conductor of heat, and sharp fluctuations of temperature which might break the flask are thus avoided.

PREPARATION. (*See also* Liquefaction of Permanent Gases, p. 29; *and* of Oxygen, p. 181). The first Linde apparatus for the liquefaction of air was introduced into Italy in 1900 by the Society for the Encouragement of Arts and Manufactures of Milan, and was able to produce one litre of liquid air per hour (Fig. 123).

This apparatus is provided with two pumps, *e* and *d*; the former aspirates the outer air and forces it into the latter at a pressure of twenty atmospheres, and the latter then compresses it to 200 atmospheres in a cylinder, *f*, which separates the water used for the lubrication of the pistons in the pump cylinders. The air is heated by the compression and is then passed through a coil arranged in a refrigerating box, *g*, containing ice and salt; it then passes when compressed through a triple concentric coil of stout copper (*see* Figure at side). In the lower portion of the central coil there is a valve, *a*, which permits the compressed air to expand rapidly to twenty atmospheres; it then rises through the second coil which surrounds the first one and reaches the pump, *d*, through the tube, *p'*, in order to be again compressed and allowed to expand. Each expansion lowers the temperature considerably and the cool expanded air which passes through the coil in a contrary direction to the air which arrives acts as a refrigerator for the latter. The temperature finally reaches −189°, and then in expanding a large part is liquefied and is discharged through the valve, *b*, into a double-walled glass flask, *c*. The space between the two walls is evacuated because liquid air can be so kept for a long time, and it may then be poured into other Dewar bottles described above.

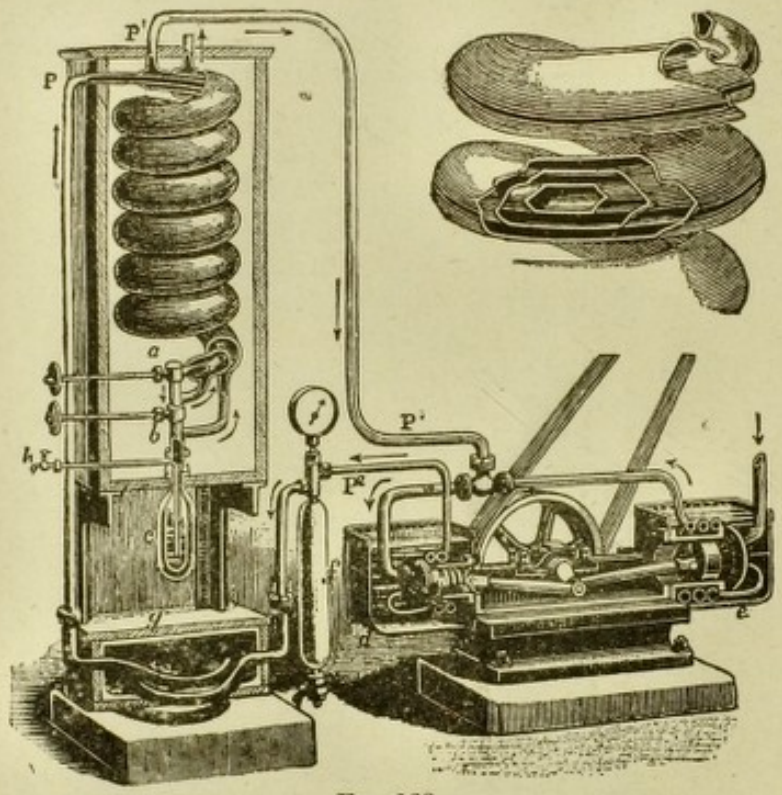


FIG. 123.

Linde calculated the efficiency of his liquid air machines from the formula of Joule and Thompson on the cooling of expanding gases; this cooling is equal to $0{\cdot}276\ (P_1-P_2)\left(\frac{273}{T}\right)$, where P_1-P_2 indicates the difference of pressure in atmospheres before and after expansion and T indicates the absolute initial temperature. According to this formula, by starting at 0° with gas compressed to 250 atmospheres, a cooling of −69° should be produced on expanding to the ordinary pressure; if the air is originally at −141° and at 250 atmospheres, a temperature of −294° should be obtained on expansion, whilst by starting at −194°, −423° should be obtained on expansion.

Mewes in 1901, Pictet in 1903, and Mix in 1901 and 1908, showed that these results are erroneous, and that the formula of Joule and Thompson cannot be applied, because this formula presupposes that the expansion occurs exclusively at the cost of the so-called internal energy, whilst in this case, on the contrary, the work performed is entirely external, as it is exercised by the gas in expanding against the atmospheric pressure, in changing, that

is, to a greater volume, and the lowering of the temperature produced in performing this work may be calculated from simple physical laws (*see also* pp. 25 and 40); the results so obtained coincide with practical experience, for a gas which expands from 250 atmospheres up to 1 atmosphere would be cooled as follows: Starting from 0° the temperature would descend to −61°, starting from −141° we would reach −170·5°, and starting from −194·5° we would reach −212°. The argument lasted for years, and in 1907 Kozic confirmed Linde's hypothesis on the internal work, admitting, however, that the Joule–Thompson formula is not applicable to all gases, especially not to air, and must be modified. Claude still insists that the cooling is also due to external work, more especially in the cases of gases which are not perfect, and that air under these circumstances is not a perfect gas.

The *industrial uses of liquid air* are at present only three in number, namely, the economic preparation of oxygen, of nitrogen, and of explosive materials. The industrial manufacture of oxygen and nitrogen is to-day almost exclusively carried out with liquid air, using various processes, of which we will illustrate the most important, those of Linde, Pictet, and Claude, because these three are at present competing for predominance in this industry, which is continually acquiring greater importance in Italy and other countries.

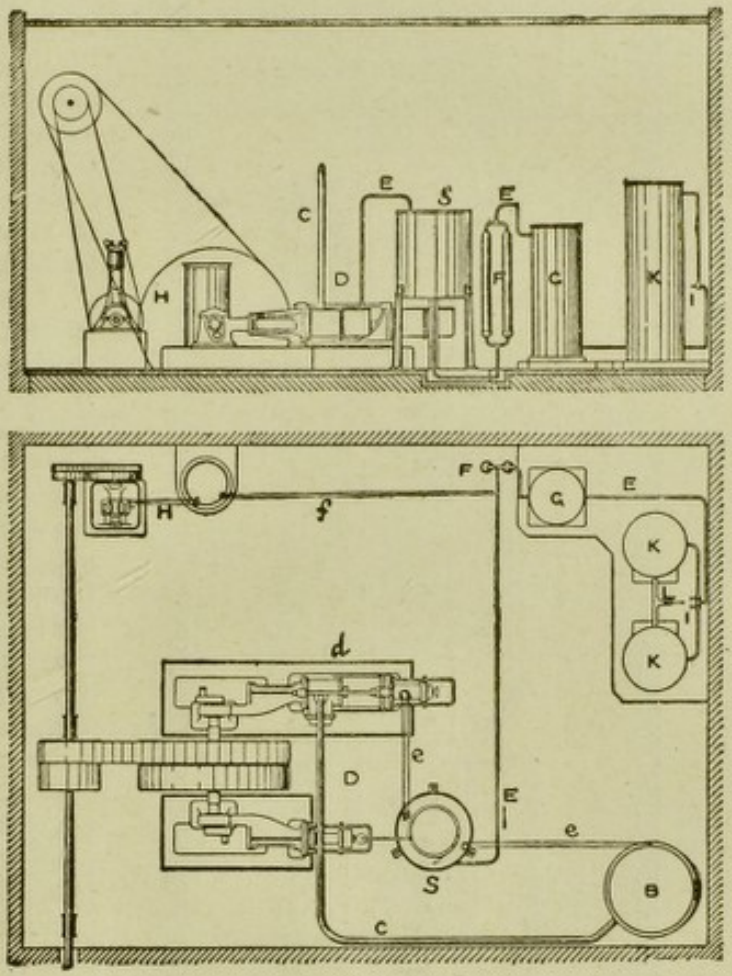


FIG. 124.

H. Siemens in 1857 and E. Solvay in 1884 were the first to attempt to liquefy air by means of compression and expansion together with the production of external work. But when very low temperatures were reached (in the case of Solvay −92°) the machine which was used to produce work by expansion of the gas no longer worked at these temperatures, as no lubricant was then known which was able to prevent excessive friction. During recent years Claude has found that petroleum ether serves very well as a lubricant because it does not solidify until nearly −200°, and when the production of liquid air is once started this forms a suitable lubricant, although it is not completely satisfactory.

I. MANUFACTURE OF OXYGEN AND NITROGEN BY THE LINDE PROCESS.

The Linde patent of 1889, which referred to the liquefaction of air only, was followed by the patent of 1895 (Ger. Pat. 12,528) for the fractional evaporation of air with the object of separating oxygen and nitrogen. In 1902 Linde took out a new patent for a rectifying apparatus with which oxygen was obtained under still more favourable conditions. On account of a series of objections by Pictet, Levy, Mix, and others, the German patent was only conceded in May 1906. A more perfect type of Linde plant has also been at work in Milan since 1905 and we give a diagrammatic illustration of it in Fig. 124.

The air is aspirated from outside and compressed in *d* to a pressure of about 5

atmospheres, by which means it is heated to 40° to 50°. It then passes through the serpentine coil, *e*, immersed in a refrigerator, *S*. It is then freed from CO_2 by passing through a double purifier, *B*, filled with slaked lime which is moistened with a little sodium hydroxide solution. It passes through a tube, *C*, into the other portion of the compressor, *d*, where it is compressed to 35 atmospheres, still in iron tubes, and since it is thus heated to 50° to 60° it is again cooled with water in the same cooler, *S*. It is now compressed to 180 atmospheres in *D*, and as it is thus heated to 60°–70° it is again cooled by water in the ordinary cooler, *S*; from here it passes through the tube, *E*, and through two desiccators, *F*, containing lumps of fused calcium chloride and is then cooled to −15° in *G*, where there is a double concentric spiral coil in the interior of which the compressed air passes in one direction and ammonia passes during expansion through the outer tube in the opposite direction; this ammonia issues from an ordinary ice machine, *H*, to which it returns through the double tube, *f*, through which it is also fed into *G*.

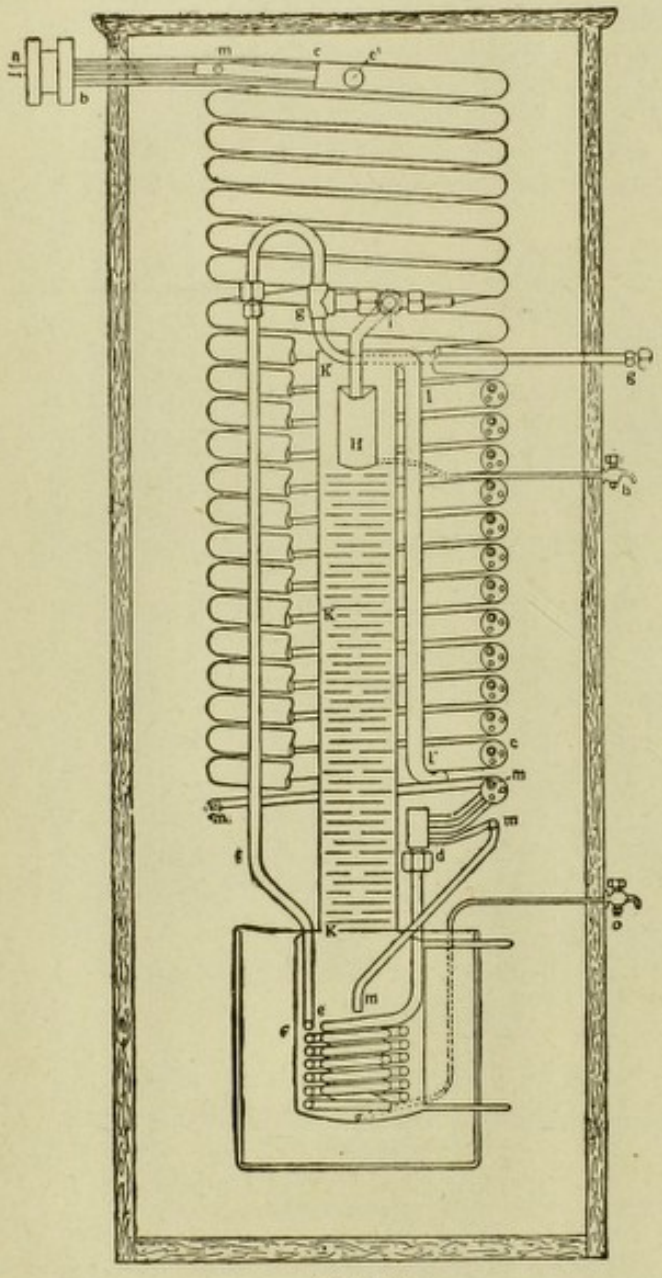


Fig. 125.

The air, compressed to 180 atmospheres and at a temperature of −15°, enters one of the two rectifying columns, *K*, through a distributing cock, the other rectifying column being kept in reserve. The air first enters through the tube, *a* (Fig. 125), which divides into a triple serpentine coil of copper, *b*, enclosed in a large tube, *c*, which surrounds this spiral throughout the rectifying column. At the base of the triple serpentine coil these three tubes reunite to form a single tube, *d*, which is then bent into a spiral coil, *e*, in the interior of the sheet-iron vessel, *F*, and continues its course upwards as the tube, *f*, to the valve, *g*, which regulates the expansion of the air from 180 atmospheres up to a pressure one-fourth of an atmosphere greater than the atmospheric pressure; this valve is regulated by the key, *g*. The expanded air is considerably cooled and passes into the small reservoir, *H*, which is placed at the top of the rectifying column, *K*; from here it then passes through the tube, *l*, which carries it downwards to *l'*, where it enters the large tube, *c*, and rises in a contrary direction to the triple coil which it surrounds and which carries the compressed air. The expanded air escapes above through *c'* at −15°, *i.e.* at the temperature of the compressed air which enters, and serves to cool a part of the coil, *G* (in the preceding Figure), of the ammonia refrigerator; it then escapes into the atmosphere at − 5° to − 6°. The air which expands at the top of the column is thus continually cooled more and more before expanding, and finally it liquefies. This occurs after the apparatus has worked for about an hour, and the liquid air collects in the vessel, *H*, which holds from 3 to 4 litres. When this is full of liquid it overflows, and the liquid falls over the numerous perforated copper plates which form the rectifying column and finally collects in the large vessel, *F*, which holds about 30 litres. It is the nitrogen which mainly evaporates, and this rises through the column, and the shower of liquid air which descends abstracts what little oxygen remains in the ascending nitrogen, which thus escapes almost pure from the tube, *l*.

When 10 or 12 litres of liquid have accumulated in *F*, which is the case after work has continued for 6 or 7 hours, the remaining liquid contains from 96 to 98 per cent. of pure oxygen and the normal working of the apparatus commences. Through the tube, *m*, which dips into the liquid, oxygen rises and is gradually gasified, passing up one of the tubes of the triple spiral ; it escapes above at *m'*, at a temperature of about −5°, and is collected in a gasometer from which it may be passed into suitable compressors, which compress it in steel bombs to about 130 atmospheres pressure. When normal working has set in in the rectifying apparatus, the pressure of the air is no longer kept at 180 atmospheres, but only at 90.

In the Milan works this original plant, which has only half the efficiency of modern plants, produces, during normal working, 6 metres of oxygen per hour ; about 21 h.p. are used for the liquefaction of the air, 3 h.p. for the ammonia ice-machine, and 3 h.p. for the compressors which fill the bombs. The machine works day and night, and there are two workmen, one to fill the bombs and the other to supervise the machinery.

Oxygen of 95 per cent. purity is thus obtained, and by reducing the output by one-fifth the purity may be increased to 99 per cent. Whilst 12 kw., that is, 16 h.p.-hours, are required for the production of 1 cu. metre of oxygen and 2 cu. metres of hydrogen by electrical means, to produce 1 cu. metre of oxygen with a small Linde machine only 5 h.p.-hours are required. In plants which produce 5 cu. metres of oxygen per hour with 20 h.p. the oxygen costs 3·84*d.* per cubic metre, excluding amortisation and patent rights ; in plants producing 50 cu. metres with 100 h.p. it costs 1·35*d.*, and in plants producing 500 cu. metres per hour and using 800 h.p. it costs 0·58*d.* per cubic metre. The consumption of water for cooling is different for the above-mentioned three types of plant, and is respectively 1, 4, and 30 cu. metres per hour. There are to-day several works producing oxygen by the Linde process in Barmen, Berlin, Paris, Birmingham, and Milan. In Paris 600 cu. metres of oxygen are produced per day. There is a new Linde plant in Italy in the calcium cyanamide works at Piano d'Orte which also utilises all the nitrogen obtained by liquefying 3000 cu. metres of air per day. At Naples and Genoa new works for the production of oxygen from liquid air by the Linde and Claude processes have recently been erected.

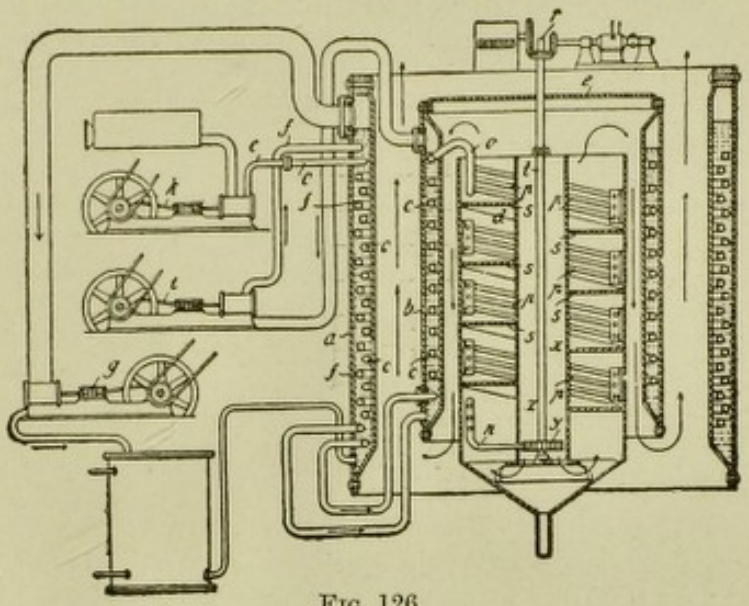


FIG. 126.

II. **PICTET'S PROCESS.** In February 1900 and in July 1901 Pictet took out patents for the liquefaction of air, by employing various cooling liquids and then separating oxygen from nitrogen by heating the liquid air by means of atmospheric air at a pressure below twenty atmospheres and near its liquefying point. Owing to the opposition of Linde and others, the Pictet patent was only conceded in March 1905 (Ger. Pat. 1,652,682 ?). This process differs from Linde's process more especially by the fact that in the Pictet apparatus there is no intimate contact between the heating mass (cold compressed air) and the liquid air, as the two substances flow through distinct channels, one of which surrounds the other, but which do not communicate.

Pictet's apparatus is diagrammatically illustrated in Fig. 126. The air is aspirated and compressed by the compressor, *k*, and passes through the serpentine coil, *c*, arranged in a circular reservoir, *a*, in which Pictet's refrigerating liquid (sulphur dioxide and carbon dioxide) circulates in a contrary direction through another serpentine, *f*. The vapours of the refrigerating liquid are collected again by the compressor, *g*, in order to be again liquefied and repassed through the system. The compressed air is thus cooled to −80°, and passes into the serpentine coil, *c*, which is immersed in the circular vessel, *b*, which is filled with

alcohol, the vapours of which are rapidly collected by the compressor, *t*, in order to be liquefied and again sent into circulation. In this way the compressed air is cooled to − 140° and then enters the spirals, *d*, which are surrounded by the vapours of liquid air which is contained in the base of the central reservoir. The air here liquefies and accumulates at the base together with the already liquefied air. By allowing this air to partially evaporate the vapours evolved, which mainly consist of nitrogen, are made to work a gas turbine, *y*, in order to recover a part of the work by turning the shaft of a dynamo, *r*. The remaining liquid yields oxygen.

III. CLAUDE'S PROCESSES. The question whether nitrogen or oxygen is first liquefied during the liquefaction of air was much discussed by scientists. Linde and Dewar stated that the liquefaction of the two gases occurred simultaneously, and Pictet believed for a long time that the nitrogen was liquefied before the oxygen. Lesueur maintained the contrary opinion, and in 1903 G. Claude produced experimental proof that the oxygen is first liquefied, and then the nitrogen ; and he also showed that evaporation occurs in the reverse sense and that the nitrogen evaporates before the oxygen. Claude also published a curve showing the composition of the vapours given off by liquid air containing various proportions of oxygen. The upper curve starting from *A* shows the composition of liquid air from 20·8 per cent. of oxygen upwards (20·8 per cent. being the amount present in air), and the composition of the vapours formed from such air is given by the lower curve, *D*, which starts with 7 per cent. of oxygen. As the liquid air contains more and more oxygen as indicated by the curve, *A*, which goes up to 100 per cent., the vapours are also correspondingly richer in oxygen as indicated by the curve, *DE*. Vapours containing 20·8 per cent. of oxygen (point *C*) are formed from liquid air containing 47 per cent. of oxygen ; in order to obtain liquid oxygen it is therefore unnecessary to liquefy all the air.

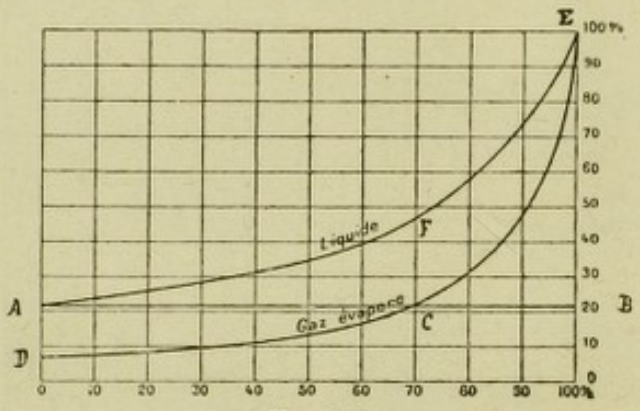


FIG. 127.

In 1903 Claude invented an apparatus for rectifying liquid air based on these results, and analogous to that of Linde, but with this difference, that he condensed the oxygen and the nitrogen apart ; the former, when liquefied, is introduced into the rectifying column at two-thirds of its height where it falls in the form of a spray as in Linde's case, whilst the liquid nitrogen passes to the top of the column and also falls as a spray passing through the vapours which rise and which consist almost entirely of oxygen, so that at the bottom of the column there is pure liquid oxygen and above there is nitrogen vapour which collects in an almost pure state. The nitrogen which escapes in other processes always contains 7 to 8 per cent. of oxygen.

In June 1906 Claude finally invented a new and ingenious modification, namely, that of expansion by means of external work based on the principle that the work performed by the compressed gas is greater the higher its temperature, and therefore smaller the further removed the gas is from the point of condensation or from the state of vapour (in which latter case it no longer follows Boyle's law), and the nearer it is to a perfect gas. By means of his *compound system* Claude obtained a gradual expansion of compressed air, as is seen in the diagram (Fig. 128), cooling it down to −190° as in the other processes, but then allowing the temperature of one part of the partially expanded air to oscillate between −160° and −140° (critical temperature of air), and liquefying further air compressed to 40 atmospheres (critical pressure) by means of this. The compressed air which enters at *M* expands in *A* until it reaches a temperature below the critical point, for example, −160°, producing work which is utilised in *P* by means of a turbine or other machine. Air which is thus partially expanded then passes round the liquefier, *L*, which is fed with compressed air at 40 atmospheres ; this liquefies at a temperature of − 140°, and may be discharged through the cock, *R*, whilst the air surrounding the liquefier is heated from −160° to −140° in such a way that it expands completely in *B*, utilising the work in *P*, and producing a further cooling which causes the air in *L'*, compressed to 40

atmospheres, also to liquefy in the same manner as that in *L*. The expanded air is cooled to −140° and cools the air in the generator, *M*, so that this arrives in the expander, *A*, at a temperature of −140°. The cycle thus becomes continuous, and by means of this process Claude claims to have prepared 0·850 litre of liquid air per h.p.-hour. This yield, however, refers to a plant which utilises 60 to 70 h.p. over and above the recovered work, and assumes that the air compressors supply 6 kilos of compressed air at 40 atmospheres per h.p.-hour (that is, an efficiency of 66 per cent.). With other forms of apparatus which produce spontaneous liquefaction of air at the ordinary pressure and therefore at −190°, the yield is 0·2 litre per h.p.-hour, and for those which liquefy air under pressure the yield does not exceed 0·660 litre. By the combined system the possibility is given of lubricating the machine with petroleum ether, which is a much better lubricant than liquid air itself.

At Boulogne-sur-Seine two plants are working, one of which produces 700 cu. metres of oxygen and the other 1000 cu. metres daily of a strength of 96 to 98 per cent.

In 1909 Claude added 0·5 grm. of alcohol per cubic metre to the air to be liquefied in order to enable it to be more easily dried, as the alcohol which condenses on cooling also carries down with it all the remaining moisture.

Mix-Heylandt has proposed a process by which it appears that 2 litres of liquefied air can be produced per h.p.-hour.

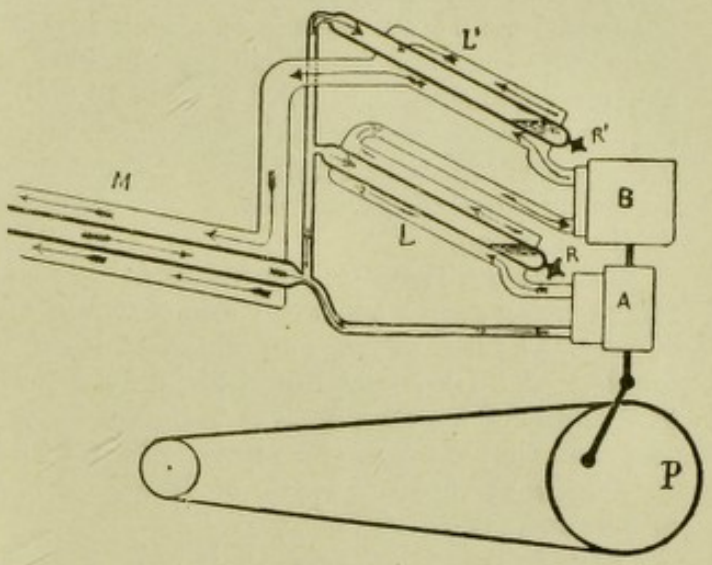


Fig. 128.

Another application of liquid air consists in the preparation of *oxyliquit*, which is a powerful explosive formed by rapidly mixing liquid air, rich in oxygen, with powdered charcoal, petroleum residues, or cotton-wool. The mass is placed in cardboard capsules forming cartridges, and these are exploded by means of an electric fuse and a cap of mercury fulminate. After a quarter of an hour the oxyliquit loses its explosive power because the liquid air partially evaporates. Whilst boring the Simplon tunnel a machine was first used which produced 150 kilos of liquid air daily for the manufacture of oxyliquit, and gave good results, but it was abandoned on account of the great urgency of these boring operations. Oxyliquit has also been used as an explosive in certain work at Powzberg, in Upper Bavaria, and for large mining operations. It costs about 5*d*. per kilo. In an English colliery the explosive effect which is produced by enclosing liquid air in an iron tube which is introduced into the coal seam has been used by allowing the temperature of the whole mass of liquid air to become higher than the critical temperature; the tube then explodes whatever may be the pressure, because the air is gasified and exercises a pressure of 5600 kilos per sq. centimetre, thus dislodging as much as 30 tons of coal by means of the discharge.

The oxygen obtained from liquid air has been applied by the Rhenania Company of Aix-la-Chapelle for the preparation of chlorine by Deacon's process.

Among the future applications of liquid air one may foresee the tempering of steel at low temperatures by immersing it whilst hot in liquid air, by which means it would become very much harder.

The manufacture of liquid air may become of immense importance if the prophecy of Pictet that by this means oxygen will be obtained at a tenth

of a penny per cubic metre is realised. Thus it could then be advantageously applied for lighting purposes by mixing coal-gas with oxygen, and producing an extremely powerful Auer light which, according to Pictet, would achieve an annual economy of £2,000,000 in the city of Paris alone, if applied. At this price it would be possible to use oxygen extensively for metallurgical purposes, perhaps even in blast-furnaces for the direct production of wrought iron without the necessity for Bessemer converters, and in the converters themselves the operation would be rendered more perfect and more rapid. The autogenous welding of large structures of wrought iron, such as bridges, girders, boilers, &c., would then become very common. We will not now speak of all the other industrial applications, as they have already been discussed in the chapter on Oxygen.

The use of liquid air in motors was also prophesied ; but it has now been shown that liquid air as such is not an economical source of motive power because from 14 cu. metres of air by repeated compressions and expansions about 900 grms. of liquid air are obtained, and this only gives 700 litres of gas on expansion, and ($700 \times 20 = 14{,}000$), so that the effect so obtained is twenty times smaller than that which would be obtained by utilising 14 cu. metres of compressed air directly without liquefying it. On the average liquid air is capable of giving up 4 per cent. of the energy employed during its liquefaction.

Neither can there be any industrial importance in the use of liquid air as a refrigerating agent, because 1 kilo of liquid air produces the same refrigerating effect as $1\frac{1}{2}$ kilos of ice, and whilst at least 100 h.p. are required for the production of 50 litres of liquid air, only 3 h.p. are required for the production of 75 kilos of ice (the heat of fusion of ice is 79 cals. per kilo, and 1 kilo of ice costs less than a tenth of a penny, whilst 1 kilo of liquid air costs at least 2*d*.).

During gasification 1 kilo of liquid air is able to cool about 30 cu. metres of air from 20° to 10°.

As a refrigerating agent it is only of importance for laboratory use when temperatures very much lower than 100° below zero are to be obtained.

Liquid air is manufactured in France by the Claude and Linde systems, in Germany by the Linde, Pictet, and P. Heylandt systems, in England by the Hampson and Pictet systems, and in America by the Linde–Tripler process. In America there are two industrial plants using the Linde process, and one using the Claude process, and there are others which are projected.

UTILISATION OF ATMOSPHERIC NITROGEN

One of the problems which occupy the chemical and agricultural world to-day is that of nitrogen. Agriculture alone consumes 75 per cent. of the two most important sources of nitrogen compounds which nature and industry place at the world's disposal, namely, nitrate and ammonium sulphate. The extraordinary progress made by agriculture during the last forty years is closely connected with the growing consumption of artificial manures which were first proposed by Liebig in order to maintain or increase the fertility of the soil.

If agriculture is to tranquilly retain its present extensive domains, then if we consider the source of phosphates and potassium salts necessary for the soil and for the plants we must also speak of the most important problem of the restoration to the soil of all the nitrogen which is abstracted from it by the various crops in order to be transformed into albuminoid vegetable matters used for the feeding of animal organisms, including man.

The plants are not able to obtain their nitrogen directly from that immense and inexhaustible store, the atmosphere, and are not even able to directly absorb nitrogen from the ammoniacal compounds which are present in the soil, as these must first be nitrified before assimilation.

The largest source of combined nitrogen for agricultural purposes was found in the important deposits of nitrate in Chili, which were discovered in 1830 and have been

enormously utilised for agricultural purposes since 1860 ; since that time very large quantities have been imported into Europe.

In 1860 Germany alone imported 6700 tons ; in 1880 the figure rose to 55,000 tons, in 1900 to about 550,000 tons, and in 1909 to more than 665,400 tons. In 1908 the whole of Europe consumed 1,635,000 tons of a value of about £15,000,000 ; and Italy imported 8500 tons in 1890, 40,500 in 1900, 43,780 in 1903, and 60,784 in 1908.

Although the consumption of nitrate was so enormous, it was only recognised a few years ago that there was a serious danger of the exhaustion in a short time of the valuable deposits of Peru and Bolivia. If the consumption continues in its present proportions there will be no more nitrate in Chili after forty or at most fifty years, and this would constitute a veritable calamity not only for agriculture but for the whole of humanity.

Attention was therefore directed to other sources of nitrogen and it was at first thought that the *ammonium sulphate* obtained in the manufacture of lighting gas and metallurgical coke, which had almost the same fertilising power as nitrate, might supply the growing needs of modern agriculture. But, in spite of the increasing world's production of this ammonium salt, which rose from 10,000 tons in 1860 to 570,000 tons in 1903 and 900,000 tons in 1909, no sufficient quantity to satisfy the ever-increasing needs of modern agriculture could be obtained (*see* chapter on Ammonium Sulphate in Part III of this volume).

During the last few years the talents of numerous scientists have been directed to research on some new method of utilising atmospheric nitrogen and these scientific researches have led to three new practical processes for the fixation of this inert gas in the form of fertilising nitrogen compounds.

Fig. 129.

(*a*) **BIOLOGICAL PROCESS.** It is generally known that plants do not directly fix the free nitrogen in the atmosphere, and that even the larger part of the ammoniacal compounds which are found ready formed in the soil are not directly absorbed by them. Before assimilation they have to undergo a process of nitrification underground. This important and beneficent work is carried on by certain bacteria which are always present in the soil. In 1891 Winogradsky discovered and studied two species of bacteria, one of which oxidises ammonia and ammonium salts, transforming them into nitrites, while the other oxidises the nitrites, transforming them into nitrates which are directly assimilable by the plant. Only the potato and certain plants which live in acid soils assimilate ammoniacal salts directly. In 1853 G. Ville had already observed and maintained, against the general opinion, that in the case of certain plants, especially the leguminosæ, more nitrogen was present at the end of growth than had been present in combination in the soil, and that therefore a portion of this must have been provided by the atmospheric nitrogen. On account of the hostility of Boussingault and Dumas the work of Ville was not seriously considered until 1886 when Hellriegel showed experimentally that the papilionaceous leguminosæ were able to fix considerable quantities of atmospheric nitrogen and that this process was especially active when their roots showed numerous small nodules formed of accumulations of bacteria (*bacterium radicicula*, Fig. 129), which were always found more or less abundantly in the soil. These nodules were not formed in sterilised soil and the growing plant was then stunted and remained dwarfed.

This is thus a case of true symbiosis : the vegetable lives and prospers through the vitality of these bacteria. Hellriegel and Wilfart in 1891 and also Breal, Schlösing, Laurent, &c., confirmed this important function of these bacteria which fix atmospheric nitrogen. This nitrogen is elaborated by these organisms and is formed into other compounds which are easily assimilated by the roots of the plants.

For more than two thousand years it had been noticed that the fertility of the soil could be increased by the repeated cultivation of leguminosæ on the same portion of ground, but the cause of this phenomenon has only now been explained. The two most closely studied species of the *azotophagic bacteria* or *azoto bacteria* are *Clostridium Pasteurianum* of Winogradsky and the *azobacterium* of Beyerink ; during the last few years several other species have been described, and it appears from these that they are not true bacteria, but parallel and more or less colourless forms of *cyanoficia*.[1]

In 1894 the firm of Meister Lucius und Brüning of Höchst near Frankfort, after work and experiments expressly conducted by Professor Nobbe, placed on the market *nitragine*, which is a pure culture of these useful bacteria, and when spread over the soil renders the ordinary fixation of nitrogen more active. It was calculated that in a million hectares of good soil the bacteria naturally present annually assimilated as much nitrogen from the atmosphere as would be worth £3,200,000 and that by the addition of pure cultures of nitrifying bacteria these soils should be able to fix at least a quarter more nitrogen, showing a gain of more than £800,000.

Favourable results were, however, not obtained on all soils by the use of nitragine, and the bacteria often succumbed in the struggle for existence compared with the numerous other harmful bacteria which were already present in the soil. Sometimes, therefore, nitragine was employed with bad effects by the farmers themselves, and then its failure was complete.

For these reasons Moore, in America, prepared more powerful cultures of these bacteria by cultivating them on slices of potato instead of in broth, and then drying the cultures on cotton-wool. Professor Remy, in 1907, has shown, however, that this dried American nitragine loses its activity, whilst that preserved in agar or in dry gelatine according to Hiltner's method has been shown to be more effective for the formation of leguminous nodules in the plants.[2]

Of 98 experiments made with nitragine in Bavaria in 1903, 81 gave markedly favourable results, 9 were uncertain, and 8 were negative. In Italy Moore's cultures did not give very favourable results, although in the case of French bean cultivation they produced a marked improvement. Experiments made by Stoklasa in 1908–1909 by inoculating azobacteri in cultivated soil planted with oats, beetroot, and potatoes gave good results in regard to quantity and quality produced. If much calcium carbonate is present in the soil the azobacteri give advantageous results even with non-leguminous plants.

Other bacteria, called *nitrifying bacteria*, have also been discovered in the soil ; these have the property of first transforming nitrogenous organic compounds (albuminoids) into ammoniacal compounds, and these are then nitrified by various other bacteria. In the soil the process of bacterial nitration does not commence before all the ammonia and carbonate of ammonia have been transformed into nitrites ; the other ammoniacal salts, on the other hand, do not harm the bacteria which are sometimes able to transform these directly into nitrates (*see* Biological Purification of Sewage on p. 224).

The nitrifying bacteria need plenty of air and abundant oxygen in the soil and it appears therefore advantageous to add oxidising substances to the soil such as manganese dioxide ; this has been recently tried in the Agricultural School of the University of Tokio, and as is shown by the experiments of Professor Giglioli, the results were generally favourable although not yet decisive. He proposes the addition of 300 to 400 kilos of manganese dioxide per

[1] Lohnis and Westermann in 1908 proposed that these bacteria should be divided into four groups : (1) *Azotobacter chroococcum*, characterised by the blackish-brown colour of its agglomerates when in thick layers. (2) *Azotobacter Beijerinckii*, which when present in the form of sarceni has a yellow colour. (3) *Azotobacter agile*, which is very mobile and fluorescent. (4) *Azotobacter vitreum*, which is immobile, of globular form, and accumulates in transparent mucilaginous layers.

[2] Professor Bottomley, of London, gives the following instructions for the inoculation of soil or seeds with nitragine, which comes on to the market in small boxes containing two or three packets : the packets containing the nutrient salts are dissolved in a tub in 4 to 5 litres of cold but previously boiled water. The packet containing the nitragine culture is then added ; the tub is covered with a cloth and allowed to stand in a tepid place at 24° to 27° for twenty-four to thirty-six hours. When the liquid has become milky this is a sign that the bacteria have developed and multiplied well. The seeds are then moistened with this liquid and are allowed to dry in the shade for some weeks before they are sown ; the liquid which remains after forty-eight hours is no longer serviceable, while the seeds may be sown even after eight or ten days. In Ireland surprising effects were obtained on many sterile soils. In general, however, the best results have been obtained in soils which are not acid or in which the acidity has been corrected with lime, and also in soils which contain plenty of phosphates and of potash.

Hutchinson (International Chemical Congress in London, 1909) obtained good results with cultures of azotobacteri even with non-leguminous plants such as tomatoes

hectare, this being added in such a manner that it penetrates somewhat deeply into the soil. Experiments made in France in 1907 with from 10 to 50 kilos of manganous sulphate per hectare planted with beetroot and potatoes showed hardly any advantage.

(*b*) ELECTRIC PROCESS. The nitrogen problem is to-day rapidly approaching a practical solution, because the valuable work already contributed in this direction by well-known scientists during the last few years has encouraged many others to also endeavour to solve the question.

Once again the happy union of chemistry and electricity has brought forth valuable fruit. The solution of certain great problems requires the contribution of several factors and one of the most important of these, historically speaking, is the time factor ; a problem once propounded rarely finds a rational solution without passing through stages.

In 1781 Cavendish showed experimentally that on burning hydrogen in the air, the water which resulted contained nitric acid, and in 1786 he showed that on rapidly passing electric sparks through a vessel containing air and an excess of oxygen all the nitrogen of the air combines with the oxygen. In 1798 Odier obtained nitric acid by strongly heating oxygen and then mixing it with air.

Nothing was done during this epoch in connection with combined nitrogen. It was necessary for Liebig in 1840 to show that one of the principal factors of the fertility of the soil was the presence of nitrates before this question acquired any importance. But it was so easy to procure nitrates from the important Peruvian deposits that the synthetic production of them from atmospheric nitrogen was not thought of, and also it was necessary that electrotechnology should progress much further before any industrial application of Cavendish's discovery could be considered. It was only when, towards the year 1900, it was proved with certainty that the nitrate deposits were rapidly becoming exhausted, thus threatening a fatal blow at all our flourishing agriculture, that methods of utilising a portion of the 400 trillion tons of nitrogen contained in the atmosphere were seriously studied. Electrotechnology has to-day made enormous strides. The natural forces of waterfalls furnish a large quantity of cheap energy, and thus the factors came together after more than a century which caused attempts to be made to translate the forgotten experiments of Cavendish into practice. In these attempts nitrogen oxides and nitric acid were obtained by burning the nitrogen of the air at very high temperatures obtained by means of the hydrogen flame or by the electric discharge.

In 1892 W. Crookes had already shown that nitrogen burns in the electric arc in presence of oxygen, and he foresaw the industrial manufacture of nitric acid from atmospheric nitrogen.

The first important attempts to bring this new industry into being were made in 1896 by the electrotechnical firm of Siemens and Halske of Berlin (Ger. Pat. 85,103) by submitting a mixture of 100 vols. of dry air and 1 vol. of dry ammonia to the dark electric discharge ; solid ammonium nitrate was thus obtained and deposited on the walls of the containing vessel, but the process did not acquire any industrial importance.

The work of Nernst and the careful experiments of Muthman Hofer and Lepel caused further progress to be made in the solution of this difficult problem.

In 1902 the Atmospheric Products Company, with a capital of £200,000, erected a fairly important plant for the utilisation of one portion of the power from the famous Niagara Falls, by applying a patent of Bradley and Lovejoy. In 1903, however, the works were suspended because the yields were too low, and the plant was still too costly, delicate, and imperfect.[1]

Negative results were also obtained by the process of Kowalski, which was tried in 1904 in a large works.

It is necessary to remember the temperatures of formation and decomposition of nitric oxide because it is an endothermic product which is only formed at very high temperatures, but is also decomposed at high temperatures ; in fact the equilibrium $N_2 + O_2 \rightleftarrows 2NO$, only gives 1 per cent. of NO at 2200° ; 2 per cent. at 2570° ; 3 per cent. at 2854° ; and at 3327° 5 per cent. is not dissociated. It is only at temperatures below 1200° that NO no longer dissociates ; for this reason Helbig at Rome in 1903 passed

[1] The apparatus used at Niagara consisted of an iron cylinder 1½ metres high and 1·25 metres in diameter. A vertical steel shaft revolved in this and carried 23 superposed groups each of six arms, each of which formed as many electrodes, to each of which again an electrode fixed on the internal wall of the cylinder corresponded. Thus 4146 small electric arcs were made and broken every minute. This delicate and costly apparatus, however gave a very small yield, not more than 430 kilos of nitric acid per kilowatt-year.

the electric discharge through liquid air at a temperature of −190°, and obtained considerable quantities of unaltered nitrogen oxides (solid N_2O_3).

But the real and reliable industrial application was started by Dr. Birkeland of Christiania, aided in his experiments by the young engineer Eyde (1903). When the electric arc from an alternating current of high tension (5000 volts) is suitably influenced by strong magnets it assumes the form of a large disc which in suitable furnaces may acquire a diameter of 2 metres. This discovery of Birkeland was immediately applied practically, and after numerous experiments on an enormous scale a works commenced operations in May 1905 at Notodden in the Hitterer region of Norway, which produced a quantity of nitrates corresponding to 1500 kilos of pure nitric acid daily by the Birkeland-Eyde process. The mean yield during five months of uninterrupted work was 550 to 600 kilos of pure nitric acid per kilowatt-year. The theoretical yield of the electric furnaces would be 135 grms. of HNO_3 per kilowatt-hour or 950 kilos per kilowatt-year. There is every indication that the yield may be still further increased and that further improvements may be introduced into the process, as a considerable portion of the energy employed is still lost in the formation of heat, of which 30 per cent. is used for the concentration of the calcium nitrate solutions, 40 per cent. for heating the steam boilers, 10 per cent. for pre-heating the air which enters the furnaces, and 17 per cent. is lost through radiation. Both horizontal and vertical furnaces were tried (*see* Fig. 130). It has now been shown that the vertical are better than the horizontal furnaces. The electrodes are made of copper and are hollow so that they may be kept cold by means of a current of water, thus avoiding the extensive breakages which easily occur with ordinary electrodes.

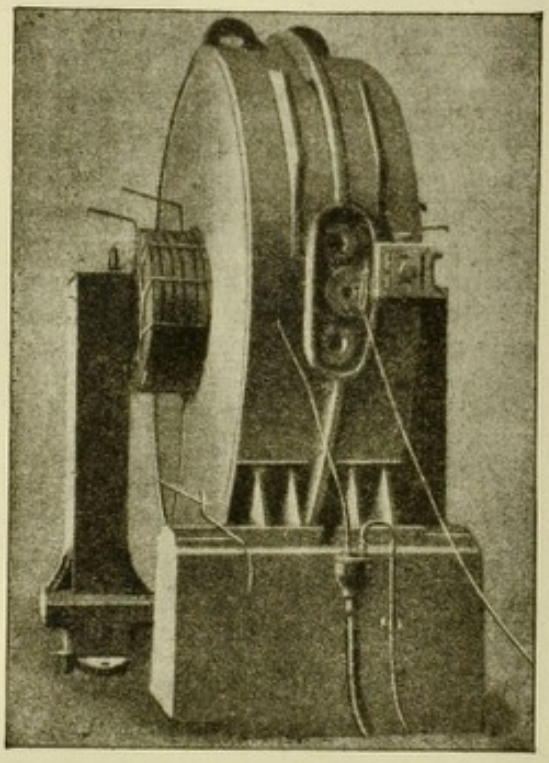


Fig. 130.

The gases which pass out from these electric furnaces are very hot and contain 1 to 1½ per cent. of nitric oxide (NO). In order that the oxide may not be decomposed it is necessary to cool the gas rapidly; and therefore these gases are used to heat the steam boilers and to concentrate the nitrate solutions which are produced in the works. During this phase the nitric oxide below 600° and in contact with excess of atmospheric oxygen is transformed into the dioxide NO_2, and then the current of gas passes through granite towers from the top of which a spray of water falls which transforms the nitrogen dioxide partly into soluble nitric acid and partly into nitric oxide which in turn combines with the oxygen of the air forming dioxide which is then absorbed in other towers and so on. The dilute aqueous solution of nitric acid is repeatedly pumped to the top of the towers until 50 per cent. of nitric acid is obtained which is transformed by means of lime and marble into calcium nitrate and is then evaporated.

Ordinary calcium nitrate is not suitable for agricultural purposes because it is deliquescent, but it has been found that *basic calcium nitrate* remains dry and may be converted into a powder suitable for spreading over the ground. In soils which are somewhat acid through the presence of carbon dioxide it forms calcium carbonate and normal calcium nitrate which is deliquescent, thus soon reaching the roots of the plants. The calcium nitrate so prepared always contains a little calcium nitrite, which is by some considered harmful to germination, whilst, on the other hand, it appears not to be harmful if distributed over the seed when this is already somewhat developed.

Calcium nitrate has the advantage over Chili saltpetre that it does not contain perchlorates, that sodium salts do not accumulate to any extent in the soil, and that it has an advantageous effect on soils which show a deficiency of lime. On the other hand, it is less well assimilated by plants than sodium nitrate.

Calcium nitrate containing 13 per cent. of nitrogen now costs £4 8*s.* per ton, whilst sodium nitrate containing 15·5 per cent. of nitrogen costs from £8 16*s.* to £10 8*s.* per ton.

In 1905 the Franco-Norwegian Company was formed at Christiania with a capital of £280,000, in order to immediately utilise a waterfall of 40,000 h.p. in Telemarken, Norway, by the Birkeland-Eyde process, for the manufacture of *nitric acid*, *nitrates*, and *alkali nitrites*. These latter can be obtained in abundance if the gas from the electric furnaces is absorbed by much cold water, whilst they are scarcely formed at all if the water is warmer. At Notodden in 1909 36 electric furnaces were working. These are constructed of cast steel and iron, lined with refractory bricks in such a manner that a chamber of circular section is formed into which the electrodes are introduced (Fig. 131).

The electrodes have to be changed every three or four weeks and the fireproof lining of the furnace every four or six months. The temperature of the flame of the arc is about 3500°. The products of reaction escape from the furnace at a temperature of 800° to 1000°,

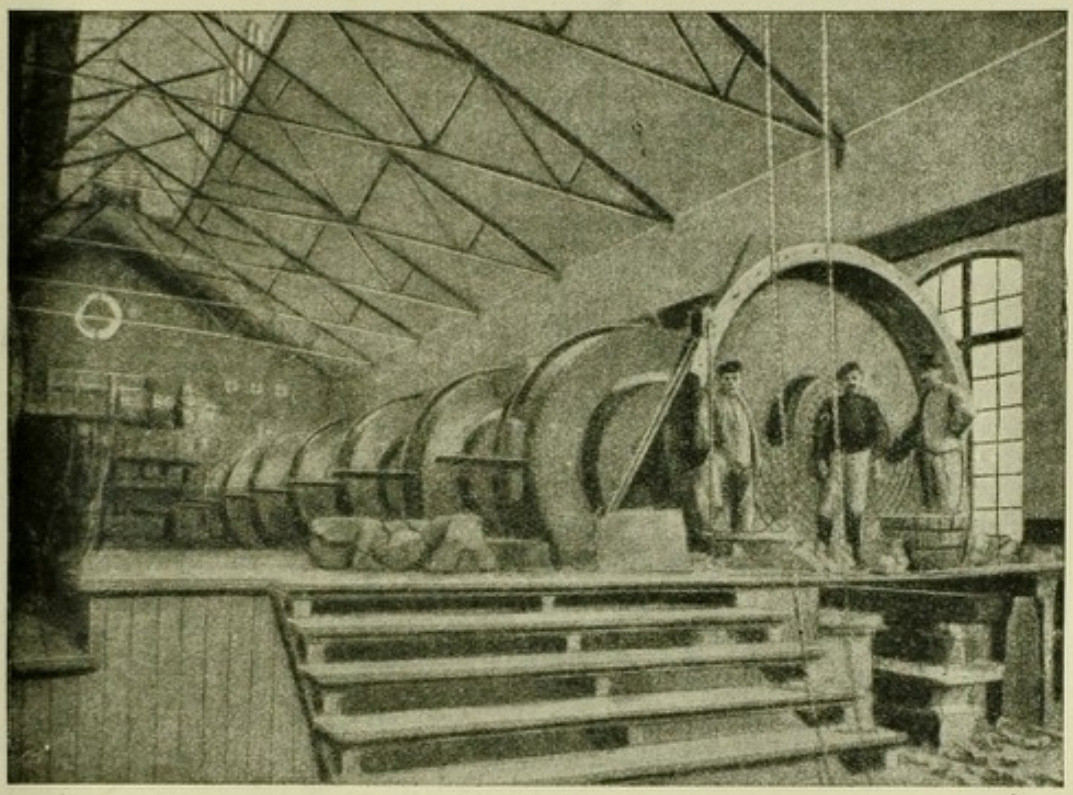


Fig. 131.

and they pass through two conduits of 2 metres diameter to the four boilers where their high temperature is utilised for the production of steam which is used to concentrate the liquids which are finally obtained.

The gases then pass through a large number of *aluminium tubes* which are cooled by a current of water into cylinders of wrought iron lined with acid-proof bricks, where the oxidisation of the nitric acid is completed. They then pass to the absorption towers.

The first series of towers is built of granite and they are supplied with water ; the other towers are of wood and supplied with a solution of soda. The gas passes from the furnaces to the towers through the action of an aluminium fan ; the absorbing liquid circulates in the granite towers until it finally contains 35 per cent. of nitric acid by volume. It is then run into granite cisterns and finally into granite channels containing limestone. The solution of calcium nitrate which is thus obtained is concentrated *in vacuo* and then poured into iron drums or into shallow iron pans ; the solution of sodium nitrate which is formed in the wooden towers is concentrated in a similar manner and allowed to crystallise.

In 1909 about 40,000 h.p. were used at Notodden and 16,000 tons of calcium nitrate were produced.

The Birkeland process is already able to compete with Chili saltpetre to-day because the hydraulic power utilised in Norway enables an electric horse-power-year to be obtained at a price of 12*s.* only. It would not, therefore, be applicable in any other

country with the actual yield which is obtained, because elsewhere electrical energy is much dearer.

With the yield which is obtained to-day all the waterfalls in Europe would not suffice to completely replace Chili saltpetre by artificial calcium nitrate, and, however much the Birkeland process may be improved, it would with difficulty suffice by itself if no other nitrate were obtainable to satisfy the needs of agriculture. A proposal has recently been made to utilise the dilute nitric acid which is first obtained by treating phosphorite directly with it in order to avoid the expense of concentration. In this way a superphosphate containing a large percentage of nitrates would be obtained.

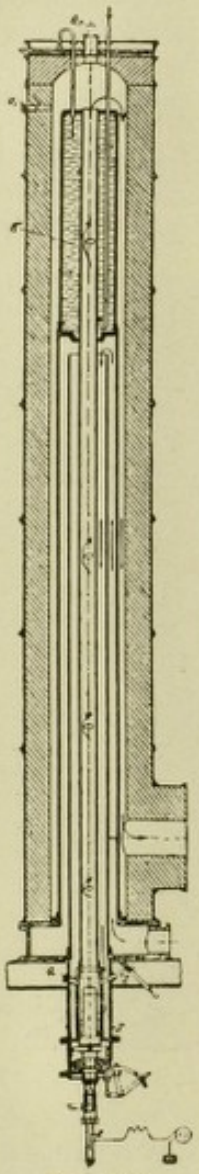


Fig. 132.

Meanwhile, however, the bold initiative caused further progress, and new processes arose which allow one to foresee a great development of this marvellous industry of the combustion of atmospheric nitrogen in the near future. Haber and König found that on using rarefied air and an excess of oxygen the action of the electric arc leads to a concentration of 14 per cent. of nitric oxide and therefore it would appear easy to apply this process practically on an industrial scale. A large works is already in construction at Christiansand in southern Norway to apply the new electrical process of the Badische Anilin und Sodafabrik of Ludwigshafen, patented in 1905 (Ger. Pats. 201,279; 204,997; and 212,051); these patents are based on the work carried out by Brunck since 1890 and completed in the works at Ludwigshafen by Schönbein and Hessberger, who obtained industrial yields equal, and perhaps superior, to those of Birkeland and Eyde. In a long vertical iron tube open above, which acts as an electrode, an electric arc is made to pass by approaching another insulated electrode to within a few millimetres of the base. If a current of air is now passed into the lower part of the tube in a tangential direction (Fig. 132) in such a manner that a spiral air current is produced, the flame of the arc increases in length, following the air current, and finally fills the whole of the tube and becomes strongly luminous especially along the axis (Fig. 133); at the top of the tube a collecting tube carries off the air which contains up to 2 per cent. of nitric acid. The tube may also be constructed of non-conducting material, and then the continuous arc is started by placing a metallic spiral inside it.

Fig. 133.

Nitric oxide is formed in the arc especially along the axis and is gradually repelled from the centre to the circumference where the colder air prevents its decomposition; the upper part of the tube is cooled outside by means of water.

A small industrial trial plant with these tube-furnaces was constructed at Christiansand in 1907 with furnaces of 600 h.p. and also of 1000 h.p. and a current of 4200 volts. Long luminous arcs up to 7 metres in length were obtained with an air current of 1100 cu. metres per hour. The air entered below through adjustable openings by means of which the length of the arcs could be controlled. The lower electrode is hollow and made of iron and can be cooled internally with a current of water. The hot gases which escape from the furnaces pass into an annular tube in the interior of which a current of cold air passes in the opposite direction and is thus preheated before passing into the furnace, whilst the hot gases are cooled by it. The nitric oxide mixed with air, when cooled below 600°, commences to react with the oxygen, being slowly transformed into the dioxide NO_2, and the gaseous mass then assumes a brown colour. The nitrogen dioxide is in turn transformed in contact with cold water into nitric acid to the extent of two-thirds of its weight, whilst the other third regenerates nitric oxide according to the following equation:

$$3NO_2 + H_2O = 2NO_3H + NO;$$

this latter is again transformed into dioxide by the excess of air and so on. By repeatedly utilising the same water a solution of nitric acid of 40 per cent. strength is obtained.

The transformation of the NO into NO_2 occurs in large lead chambers, and the nitric acid is formed in granite towers filled with lumps of quartz in order to subdivide and intimately mix the water which falls from above and the gas which enters below ; the gases which escape from the first towers are washed with milk of lime in other towers.

The solution of nitric acid is then treated with lime and concentrated *in vacuo* in multiple effect evaporators ; it is finally heated in furnaces, and basic calcium nitrate containing 13 per cent. of nitrogen is thus obtained.

In 1909 Schlösing proposed to avoid the intermediate preparation of nitric acid by passing the gases whilst still hot at 350°, and containing nitrogen dioxide, directly over solid slaked lime arranged in the form of bricks inside iron tubes. In this way calcium nitrate is at once obtained together with free lime and a little calcium nitrite.

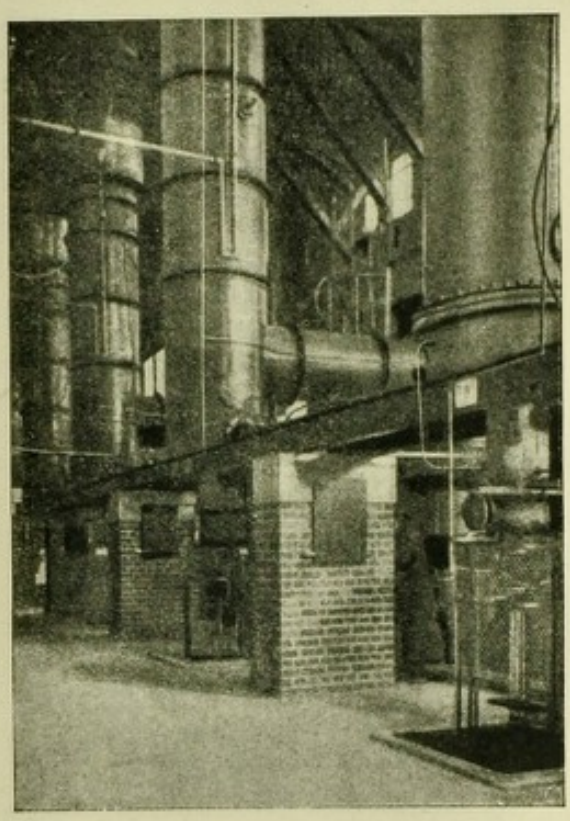


Fig. 134.

But almost pure sodium nitrite or calcium nitrite may also be obtained from nitrogen dioxide if it is treated with hot solutions of soda or of milk of lime in granite towers. The calcium nitrite contains 21 per cent. of nitrogen.

In 1907 the Franco-Norwegian Company of Notodden combined with an industrial group which was headed by the Badische Anilin und Sodafabrik, and this combination formed two distinct companies ; one with a capital of £880,000 was constructed for the utilisation of the large hydraulic powers of Norway and the transformation of these into electrical energy ; and the other with a capital of £1,000,000 was formed for the erection of works to manufacture calcium nitrate, nitrite, and synthetic nitric acid. Works for obtaining 140,000 h.p. from 10 turbines of 14,000 h.p. each are already well advanced. This power is all to be obtained from a single fall of 50 cu. metres of water and a further 100,000 h.p. are to be produced from a second fall at Telemarken-Rjukan. When these works are completed a few years hence they will be able to produce 100,000 tons of calcium nitrate annually.

We may thus readily comprehend how much hydraulic energy will be necessary one day in order to replace all the nitrate which is to-day supplied from Chili, namely, 1,800,000 tons, and it is evident that this day is still a long way off, so that a rapid change in the commercial prospects of natural nitrate is not to be feared.

Simultaneously with the large works in Norway a large works was erected at Patsch near Innsbruck, Tyrol, where the electric arc was diverted by the process of the brothers Pauling by blowing in air between two electrodes impinging at an angle (Fig. 135). In this way a blow-pipe flame about 1 metre long was obtained (Fig. 136). At Patsch there are 24 very simple electric furnaces utilising 15,000 h.p., and up till now the gases which are obtained contain 1½ per cent. of nitric oxide with a yield of more than 500 kilos of nitric acid per kilowatt-year. Sodium nitrite and nitric acid of a concentration of about 35 per cent. are manufactured. Attempts to concentrate this acid by electrolytic means have not yielded practical results. Although the unit of nitrogen in nitric acid is three times as valuable as in calcium nitrate, the economical concentration, sale, and transport of this acid are not an easy problem. These and other reasons explain the want of success of the first Italian works erected at Legnano on Pauling's system, by the Electro-Chemical Company of Dr. Rossi, which were to utilise 10,000 h.p. of electric energy during 10 hours at night when it was not required by other industries. The power so

obtained costs less than £1 per kilowatt-year. Attempts made in 1907 and 1908 by the Electro-Chemical Company of Caffaro at Brescia, utilising patents of Dr. Helbig of Rome, could also not be applied industrially on a large scale because the yields were still too low, and more especially on account of the cost of electric power in the vicinity being too high.

Helbig's furnace is very simple and is easy to work and regulate (U.S. Pat. 926,413). It contains three electrodes and is worked with a high-tension three-phase current. The flame of the arc is widened to a disc by means of a current of compressed air which is passed between the electrodes from two capillary tubes which are placed in front of and perpendicular to them.

In any case it is necessary to remember that it is not possible to manufacture nitrate from atmospheric nitrogen profitably without the use of a large source of hydraulic power which does not cost more than £1 4*s*. per h.p.-year in the form of electrical energy, and unless it is possible to give the holders of the patents an interest in the concern, instead of paying them the usual fabulous sums in advance, because in this form of industry improvements and modifications are possible from one day to another, and a new patent may cause the value and advantage of those preceding it to be lost. In order to avoid unfortunate disappointments, it is also necessary to be very prudent

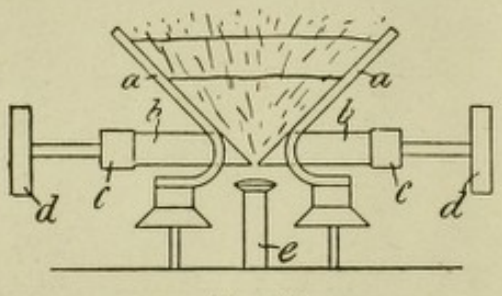


FIG. 135.

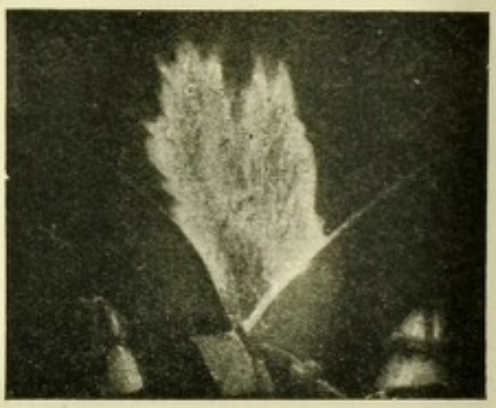


FIG. 136.

because these new processes are very attractive, but, on the other hand, are full of surprises.

(*c*) **CHEMICAL PROCESSES.** The latest discoveries in this field appear to have led to a definite and satisfactory solution of the nitrogen problem. On a small scale in the laboratory it has been observed at various times that certain metallic oxides, for example, those of calcium, magnesium, &c., form minimal traces of nitrites and of potassium nitrate in presence of potassium carbonate solution and air when heated. A little nitrogen is also oxidised during the combustion of hydrogen in air (Kolbe).

Metallic magnesium, lithium, &c., also absorb much nitrogen when heated, forming nitrides which yield ammonia with water. Ilosvay (1890) and Loew used the catalytic action of heated platinum to oxidise atmospheric nitrogen, and Ostwald, in 1902, patented a process for the preparation of nitric acid by passing a mixture of ammonia and air over platinum black heated to redness ; this reaction, however, appears to have been noted a long time before, and carried out by Kulmann. The yields in the laboratory were 100 per cent., but in industrial practice they were at first only 75 per cent., but were further improved, and to-day nitric acid and ammonium nitrate are produced in this manner on a large scale ; the latter contains 37 per cent. of available nitrogen for agricultural purposes and for explosives, at less cost for transport compared with ammonium sulphate which contains 22 per cent. of nitrogen only. The practical solution of the problem appears to await in the near future another chemical reaction which for the present has not been clearly interpreted.

In 1895 Frank and Caro (Ger. Pat. 88,363) took out patents for the preparation of cyanides by absorbing atmospheric nitrogen, mixed with steam, by barium carbide heated to 700° to 800°. The process was then simplified by two other patents (Ger. Pats. 92,587 and 95,660), but in 1898 (Ger. Pats. 108,971, 116,087, and 116,088 ; and Eng.

Pat. 25,475) it was found that during the reaction only traces of cyanide are formed and that the product is almost exclusively barium cyanamide : $BaC_2 + N_2 = NC \cdot NBa + C$. The process became more economical when Pfleger, Rothe (1898), and Freundenberg showed that calcium carbide may be employed instead of barium carbide and absorbs 85 to 95 per cent. of the theoretical amount of nitrogen at 1000° to 1100°. It was then found that it is not necessary to first prepare calcium carbide, but that a single operation suffices in which the ingredients which serve for the preparation of the carbide itself are heated in the electric furnace in presence of nitrogen : $CaO + C_2 + N_2 = CO + NC - NCa$ (calcium cyanamide). The atmospheric nitrogen is first freed from oxygen by passing air over red-hot copper ; by means of this direct reaction a blackish product of crude cyanamide is obtained containing 12 to 14 per cent. of nitrogen ; but when the carbide is used the crude product containing 20 to 22 per cent. of nitrogen is obtained. This substance, which is very well adapted for the preparation of pure potassium or sodium cyanide by fusing it with the corresponding alkali, was first manufactured by the Cyanid Gesellschaft of Berlin under the direction of Dr. Caro, Dr. Frank, and Dr. Erlwein, of the firm of Siemens and Halske. But the excellent results which have been obtained with these substances as a nitrogenous manure are more interesting. The agricultural experiments independently conducted by Prof. Wagner and Prof. Gerlach have shown that the nitrogen in crude cyanamide has the same fertilising value as that in ammonium sulphate and is equal to 90 per cent. of that contained in sodium nitrate. Naturally the effects of this new fertiliser vary with the nature of the soil ; thus in peaty, sandy, or marshy soils or soils rich in humic acid satisfactory results have not been obtained so far. On the other hand, it gives good results on calcareous or clay soils. Since it is harmful to the germination of seeds and to any vegetation, especially during the dry and hot weather, it is advisable to spread it over the soil ten to fifteen days before sowing, and to then immediately start ploughing and harrowing. It is rather harmful to meadows because it cannot be mixed with the soil. An excessive amount of moisture is also prejudicial to the action of this manure, although in Italy good results have been obtained with it by application to rice fields.

Calcium cyanamide is decomposed by various bacteria in the soil into ammonia and calcium carbonate. Recent experiments of Immendorf (1905), Pozzoli, Ulpiani, and Fascetti (1906) show that calcium cyanamide reacts with carbon dioxide in the cold to finally form calcium carbonate and *dicyandiamide* ($C_2N_4H_4$) which is not injurious to seeds or vegetation and is fermentable. If, on the other hand, it is acted on by carbon dioxide and water at temperatures higher than the ordinary temperature the final products are calcium carbonate and cyanamide ($NC \cdot NH_2$), which is poisonous, unfermentable, and capable of forming ammonia in the more harmful nascent state. Soils containing much lime facilitate the former reaction. In opposition to the general opinion Perotti in 1907 maintained that cyanamide is not injurious to vegetation.

In 1910 C. Ulpdani showed that underground calcium cyanamide is first transformed into urea by the action of certain colloidal substances in the soil which act as catalysts and that then, perhaps through the action of microbes, it is transformed into ammonium carbonate. Dicyandiamide may be formed before urea, but is immediately decomposed by the earth, forming urea.

Calcium cyanamide may be mixed with potassium salts, or with basic slag, but not with superphosphates, because it then causes a portion of the phosphoric acid to become insoluble ; but it does no harm when employed for the manuring of rice fields. When mixed with sodium disulphate calcium cyanamide gives a good nitrogenous manure. Calcium cyanamide has the disadvantage that it develops acetylene when moistened, but this fault may be remedied by grinding the fresh product with a little water, which immediately decomposes the small amount of calcium carbide which is still present. Birkeland in 1908 proposed the absorption of nitrogen dioxide (NO_2) prepared in the electric furnaces by calcium carbide, which is thus transformed into calcium nitrate and ammonium nitrate, containing about 25 per cent. of nitrogen.

The process of Frank and Caro was directly applied in 1903 by Siemens and Halske of Berlin in a small industrial plant at Martinikenfeld. The nitrogen which was required was obtained by passing air over red-hot copper which removed the oxygen. The process, however, did not prove to be sufficiently economical in Germany, because the electrical power required for the production of the calcium carbide was too dear and the separation of the atmospheric nitrogen was too costly.

Italy was the country which produced calcium carbide at the lowest price, and in Italy, therefore, through the initiative of the Electro-Chemical Company of Rome, the Società Italiana per la fabbricazione dei prodotti azotati was formed in 1904 with a capital of £280,000 in order to prepare calcium cyanamide on a vast scale by utilising electrical energy at Piano d'Orte where it costs only £2 per h.p.-year. This large establishment commenced work in 1905 and in 1906 the production was 1200 tons, whilst in 1908 with new retorts it rose to 4000 tons of the value of £30,000.

In these works retorts were first used which were similar to those used in the manufacture of lighting gas (*see* vol. ii, "Organic Chemistry"), but constructed of steel. The nitrogen was produced from liquid air. The retorts proved to be unserviceable after a short time and were renewed, but the results obtained were not much better. The form of the retorts was completely changed in 1908 and 150 vertical retorts were constructed 1·4 metres high and 1 metre wide, each of which held 400 kilos of calcium carbide whilst the old horizontal retorts only contained 100 kilos; and the mass was heated by producer-gas with frequent stirring. These new retorts were heated by electric resistance, starting from the centre by means of an arm of graphite, and thus the heat was gradually propagated from the centre towards the circumference, the heat produced by the exothermic reaction being also used. In twenty-four hours a compact homogeneous mass containing 20 to 21 per cent. of nitrogen is obtained; this is then powdered and granulated by means of a spray of a weak aqueous solution of glue or of tar-oil; in this way the small amount of unchanged carbide is decomposed and the mass does not become powdery when spread over the soil, and does not develop acetylene. Calcium carbide is to-day manufactured by the same company at Bussi with Tofan furnaces, and costs about £4 per ton. By means of all these improvements the cost of the resulting calcium cyanamide is about 8*d.* per unit of nitrogen, and it is sold at 11*d.* to 1*s.*, whilst the unit of nitrogen in ammonium sulphate is sold at 1*s.* 3*d.* and that in sodium nitrate at 1*s.* 4*d.*[1]

In spite of all these improvements this industry does not prosper because agriculturists still have doubts, and further endeavours are now being made to decompose calcium cyanamide with steam, so liberating the ammonia and manufacturing ammonium sulphate.

In Europe in 1908 there were eleven large works of the total capacity of output of 170,000 tons, but the actual production was less than 40,000 tons.[2]

As they have assisted the cyanamide process we must also mention certain improvements, especially those of F. Polzenius, which form the subject of a patent (Ger. Pat. 163,320, November 1, 1901) in which it is shown that on adding about 10 per cent. of calcium chloride to the powdered calcium carbide the fixation of nitrogen already occurs at temperatures of 700° and more rapidly. The chloride acts as a flux and accelerator of the reaction. This product has been manufactured since 1905 by the Nitrogenous Fertiliser Company of Westeregel in Germany—Stickstoffdünger Gesellschaft– which has a production of 5000 tons annually and is already erecting further works for a larger production. The new product is almost identical with calcium cyanamide; it is commercially called Stickstoffkalk or nitro-lime.

Carlson has used 10 per cent. of calcium fluoride as a catalyst since 1906; the resulting calcium cyanamide is not as hygroscopic as that prepared with calcium chloride.

In 1907 E. and G. Pollacci proposed the preparation of calcium cyanamide with greater ease and of greater manurial value by employing 4 per cent. of potassium carbonate as a catalyst. They also proposed to treat this calcium cyanamide with sulphuric acid in

[1] The cost price of one ton of calcium cyanamide containing 20 per cent. of nitrogen and formed from 800 kilos of carbide in this Italian works, of which the patent alone is valued at £80,000, may be calculated approximately for an annual production of 10,000 tons from the following figures: 800 kilos of calcium carbide are required at £4 16*s.* per ton = £3 16*s.* 8*d.*; 200 kilos of nitrogen at 1·15*d.* = 19*s.* 2*d.*; amortisation of capital invested in plant, patents, &c., £1 4*s.*; interest at 5 per cent. on the capital, £1 4*s.*; cost of labour, technical supervision and administration, about 6*s.* 5*d.*; cost of power, including water, coal, light, lubricants, &c., 4*s.* 10½*d.*; general expenses, repairs, packages, unforeseen circumstances, losses, &c., 4*s.* 10½*d.*; total cost per ton, £8. No account is taken of the possible utilisation of oxygen nor of the practical yield compared with the theoretical, as we have taken the theoretical yields.

[2] We here give the possible output (not the actual production) of the various works using Frank and Caro's process: At Odde in Norway, 13,750 tons; at Mühlthal (Prussia), 3300 tons; at Martigny (Switzerland), 4400 tons; at Notre Dame de Briançon (France), 13,200 tons; at Trostberg (Bavaria), 16,500 tons; at Callestatti, St. Marcel, and Piano d'Orte (Italy), 33,500 tons; at Sebenico and Almisso Fiume (Dalmatia), 60,000 tons. Working by the Polzenius process we have: At Westeregel-Brühl, 10,000 tons; at Bromberg, 2500 tons. Apart from these works, some of which have suspended work, we must add a Canadian works which utilises the Falls of Niagara and has a capacity of 40,000 tons yearly, and another at Muscle Shoals, in Tennessee (U.S.A.), of a capacity of 40,000 tons.

order to obtain a fertiliser containing ammonium sulphate which no longer has the same caustic action as ordinary calcium cyanamide (Ger. Pat. 210,808).

This process has to-day entered the ranks of large-scale industrial operations, and we may tranquilly await the more or less near exhaustion of the Chili nitrate deposits.

NEW GASES DISCOVERED IN THE ATMOSPHERE

In 1892 Lord Rayleigh, whilst studying and controlling the density of the elementary gases by exact methods, constantly found a difference of density between nitrogen separated from the air (1·2572) and nitrogen prepared from ammonia or from nitric acid (1·2507). Rayleigh, although one of the best experimental physicists, considered it advisable to continue these studies together with a chemist, Ramsay. In August 1894 these workers communicated to the British Association at Oxford that the increased density of atmospheric nitrogen was due to the presence in air of another gas, *argon*. In March 1895 Ramsay, whilst seeking for other sources of argon and heating uranium minerals, discovered another elementary gas, *helium*, the existence of which had been foreseen for some time on account of its characteristic lines, which were always found in the solar spectrum. More recently Kayser has found small quantities of helium in air.

These two new gases are characterised by their indifference towards all other substances ; in fact they have not yet been combined with any other element. It was shown that their molecules were monatomic even at the ordinary temperature, whilst before that time free atoms were only known at high temperatures ; this fact was deduced by determinations of the relations between their specific heats at constant pressure and at constant volume. This ratio, $\frac{Cp}{Cv}$, was found to be 1·67, as is the case for all monatomic gases, whilst for molecules of di- or polyatomic gases the relation varies between 1 and $\frac{5}{3}$ (*see* p. 51).

Recently Ramsay, whilst searching for a new element which should occur in the periodic system between helium and argon, found four other new gaseous elements contained in air, and succeeded in separating them in an impure state by evaporating 750 c.c. of liquid air to a volume of 70 c.c. He thus discovered krypton, of atomic weight 45, with a characteristic spectrum containing a green, a red, and a yellow line similar to the spectrum of the aurora borealis ; and at the same time he found xenon, and finally also neon, with a density of 20 compared with hydrogen, which perhaps constitutes the intermediate member sought for between argon and helium.

ARGON : A, 39.9

Air contains 0·935 per cent. of this gas by volume and atmospheric nitrogen about 1·183 per cent., so that we inspire about 20 litres of it daily.

It is found in certain mineral waters and in the gas of certain springs, and in small quantities together with helium on heating certain uranium minerals. Certain gases occluded in rock salt contain argon, and it has also been found in a meteorite ; it is prepared from air in two ways :

(1) Atmospheric nitrogen freed from oxygen and from water vapour is passed over a red-hot magnesium spiral ; magnesium nitride is thus formed : $N_2 + Mg_3 = N_2Mg_3$, whilst the argon does not react. This process is repeated many times until the gas no longer diminishes in volume. The nitrogen may be still more rapidly absorbed by means of lithium or with a red-hot mixture of magnesium and calcium oxide, that is, with finely divided free calcium : Mg + CaO + Ca (the method followed by Ramsay).

In 1908 Fr. Fischer and Ringe prepared argon very easily by passing a current of air (purified and dried with KOH, H_2SO_4, and P_2O_5) over calcium carbide mixed with 10 per cent. of calcium chloride and previously heated *in vacuo* to 800° ; in this manner both the nitrogen and the oxygen are absorbed, as the latter transforms the calcium cyanamide into CaO, carbon and cyanamide. In order to free it from the last traces of nitrogen, Fischer and Hähnel (1910) passed this argon several times over red-hot calcium.

(2) Lord Rayleigh mixes atmospheric nitrogen with oxygen in presence of sodium hydroxide solution, and then subjects the mixture to an electric spark for a long time ; sodium nitrite is formed and a mixture of argon and oxygen remains, which is passed over red-hot copper in order to remove the oxygen.

In 1785 Cavendish already observed that on treating air in this way all the atmospheric nitrogen is not transformed into sodium nitrite, but that a small quantity of gas remains, which he did not examine, but which he found to have a constant volume, namely, about $\frac{1}{120}$th of the volume of the air.

Argon thus prepared still contains *helium* and *neon*, which are lighter, and krypton and xenon, which are heavier, and therefore it is liquefied by means of liquid air and subjected to fractional distillation.

One litre of argon weighs 1·780 grms., and its density compared with air is 1·376. It is solid at −190° and boils at −185°. Its critical temperature is −121° and its critical pressure 50·6 atmospheres. It is more soluble in water than oxygen (two and a half times more, 100 vols. of water dissolving about 4 vols. of argon at 12°). It therefore accumulates in the gases of rain water and also in the oxygen prepared by Mallet's process (p. 180). By means of its spectrum Crookes was able to distinguish argon clearly from other gases because, apart from various lines in the red and orange and five lines in the green, there is a blue line more intense than that of nitrogen and five other intense and characteristic lines in the violet.

Up till now no chemical combinations of argon are known, in spite of the yellow solid compound obtained by Berthelot by means of the electric discharge in benzene vapours and argon.

Even the new attempts of Fr. Fischer and Iliovici and Schröter (1909 and 1910), by passing the electric arc through pure liquid argon from electrodes of various metals at − 189°, led to negative results, as they merely obtained metallic powders of various colours, often in the pyrophoric condition.

HELIUM: He, 4

This is an absolutely inactive gas like argon, and is one of the rarest elements on the earth's surface. It is, however, present in abundance in the luminous solar atmosphere and in other stars, together with hydrogen. It was discovered spectroscopically in the solar photosphere by N. Lockyer in 1867, and he studied it in 1869 together with Frankland, and called it helium.

Palmieri observed it on the earth for the first time in 1882 on studying spectroscopically a stone from Vesuvius.

It was only isolated in March 1895 and defined by means of a complete spectrum by W. Ramsay; before that only the line D_3 nad been known. Ramsay found it while searching for sources and methods of preparation of argon.

On heating certain rare minerals composed of salts of uranium, yttrium and thorium—for example, cleveite, uraninite, and monazite—helium is evolved, together with hydrogen, nitrogen, argon, and carbon dioxide. It is also obtained by treating them with dilute sulphuric acid (1 : 8) or with sodium disulphate. Kaiser found it in minimal quantities in the air, and this fact was also confirmed by Ramsay and Travers.

This gas is also found, like argon, in the gases of various springs at Wildbad, at Abano near Padua, and also in the Soffioni of Lardarello in the Tuscan marshes.

The molecule of helium is monatomic. Dewar believed that he had succeeded in liquefying it by means of rapid evaporation of liquid hydrogen, but Olszewski showed in 1906 that he had been mistaken. It was certainly liquefied for the first time by Kamerlingh Ommes on July 10, 1908. It boils at − 268·5° and its critical temperature is perhaps −268°.

Helium is the least soluble in water of all known gases. When subjected to powerful electric discharges in a Plücker tube it is absorbed by the platinum electrode, and may be separated from nitrogen in this way; on heating the electrode it is again liberated. The emission spectrum contains five well-marked lines. At a temperature of 900° it diffuses through quartz. The formation of helium from radium and from radio-active substances has already been mentioned on pp. 122 *et seq.* G. Claude (1909) found that in a million litres of air there are 16 litres of neon, 5 litres of helium, and less than 1 litre of hydrogen.

NEON: Ne, 20. This gas is liquid at a temperature of −243° and is solid at −252°. Its critical temperature has been calculated to be −220°. Its spectrum consists of green lines and several orange lines. Collie noticed in 1909 that on passing a bubble of pure dry neon into the evacuated chamber of the Töpler pump this acquires a red luminosity.

KRYPTON: Kr, 83. This element is liquid at −152° and solid at −169°. The green

lines of its spectrum are especially characteristic and are also found in the aurora borealis. It is contained in air to the extent of about one part per million.

XENON : X, 130.7. This gas liquefies at $-109°$ and solidifies at $-140°$. Its spectrum contains various characteristic blue lines. It is present in air to the amount of about one part in forty millions.

PHOSPHORUS : P, 31

This element is not found free in nature on account of its great affinity for oxygen ; it abounds, however, in the form of calcium phosphate as *phosphorite*, *sombrerite*, *apatite* $Ca_4(PO_4)_3.CaF$, and *coprolite* ; it is also found as iron phosphate in *vivianite*, $Fe_3(PO_4)_2.8H_2O$, and as aluminium phosphate in *wavellite* $[Al_2(PO_4)_2]_2.Al_2(OH)_6.9H_2O$; it is present to a small extent in all rocks, and therefore in all soils, of which it constitutes one of the principal fertilising factors, as it enters into the composition of the seeds of all plants.

It is of great importance for the life of vertebrate animals because it is the principal constituent of the skeleton and the bones in the form of calcium phosphate, and enters into the composition of muscle, albuminoids, brain substance, and the nervous system in the form of lecithin.

PREPARATION. Phosphorus was prepared for the first time by Brand in Hamburg, and immediately afterwards by Kunkel in Wittenberg about the year 1670, by calcining the residue of evaporation of large quantities of urine in which they were seeking for the philosopher's stone (*see* p. 14).

Scheele in Sweden in 1755 prepared it from bones, and until a few years ago the same process was still used with slight modifications. Fresh bones contain 25 to 27 per cent. of phosphoric acid as tricalcium phosphate $(PO_4)_2Ca_3$, together with considerable quantities of fat, which are extracted with benzine or carbon disulphide, and also contain a fair portion of connective tissue which may be extracted with steam and then forms the glue or gelatine of commerce.

In certain cases the bones are directly decomposed by dry distillation in iron retorts in absence of air, " Dippel's animal oil " being thus obtained. *Bone charcoal* or *bone black* remains in the retort, and after pulverisation serves as a decoloriser in many industries and especially in sugar refineries, its specific properties not being shared by wood charcoal.

In the past the bones were calcined directly in open kilns such as are used for burning lime, and were then powdered in order to obtain the so-called *bone ash*, which contains more than 50 per cent. of phosphoric acid. In order to obtain bone ash to-day, bone charcoal which has already been used for decolorising purposes is burnt in the air. 150 kilos of this ash are washed at one time in lead-lined wooden boxes with hot water and then with 150 kilos of 60 per cent. sulphuric acid. In 48 hours the whole of the tricalcium phosphate is transformed into monocalcium phosphate, which is soluble in water :

$$\text{(I)} \qquad (PO_4)_2Ca_3 + 2H_2SO_4 = 2SO_4Ca + (PO_4)_2H_4Ca.$$

It is diluted with water so that a liquid of sp. gr. 1·05 to 1·07 is obtained and the insoluble gypsum (SO_4Ca) is allowed to settle. The clear solution of monocalcium phosphate is then decanted off. The water which is obtained on washing the gypsum serves for succeeding operations. The solution of the phosphate is concentrated to a sp. gr. 1·45 in large shallow leaden pans, the hot fumes from the furnace in which the bones are calcined being used for this purpose. The solution is then passed into iron pans and heated over a direct flame, a quarter of its weight of coarsely powdered wood charcoal being added. When the mass is solid and contains no more than 6 per cent. of moisture, it is placed in terracotta retorts 1 metre long, in batches of 10 kilos ; these retorts are placed horizontally back to back in several rows in a suitable furnace (Fig. 137). The temperature is raised in twenty-four hours to a red heat, and the monocalcium phosphate is thus all transformed into calcium metaphosphate :

$$\text{(II)} \qquad (PO_4)_2H_4Ca = 2H_2O + (PO_3)_2Ca.$$

On finally heating (in 46 hours) to a white heat, tricalcium phosphate is formed

together with carbon monoxide, which is evolved, and free phosphorus, which distils, and is condensed in water in receivers, *b* :

$$\text{(III)} \qquad 3(PO_3)_2Ca + 10C = 10CO + (PO_4)_2Ca_3 + P_4.$$

The end of the reaction is indicated by the disappearance of the blue flame of CO. From 100 kilos of bone ash about 15 kilos of crude phosphorus are obtained.

As the product melts at 44° it was formerly purified under hot water at 50° to 60° on carbon filters, after which it was pressed through the pores of a piece of chamois leather. To-day, however, it is usually refined by a further distillation with 15 per cent. of moist sand. In the works of Violet at Paris it is obtained pure and almost colourless by melting it and stirring it in water with 4 per cent. of potassium dichromate together with sulphuric acid. It is formed into small cylinders by means of Seubert moulds placed under water.

A long time ago Wöhler proposed the preparation of phosphorus from phosphatic minerals by mixing them with quartz sand (30 per cent.) and coke (10 per cent.), and then heating to a very high temperature :

$$Ca_3(PO_4)_2 + 5C + 3SiO_2 = 5CO + 3SiO_3Ca + 2P.$$

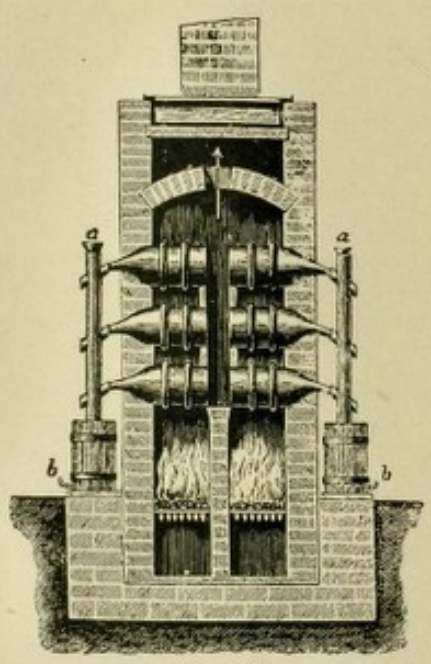


Fig. 137.

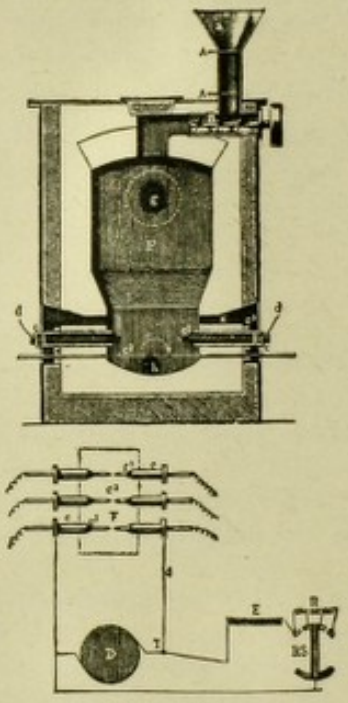


Fig. 138.

This method has been industrially employed with the help of electric furnaces proposed by Readman, Robinson, and Parker (1898). The factory of Albright and Wilson at Aldburg alone, and its branch at Niagara Falls, prepare about 13 tons of phosphorus per month.

The process is continuous as the fused slag is separated continuously at the base of the furnace at *h* (Fig. 138), and the phosphatic mixture is introduced through a hopper *A* and a helical screw from above ; phosphorus fumes escape above through a large tube *g*, and are condensed under water in copper receivers.

During the reaction a current of inert gas such as coal gas may also be passed through the apparatus in order to prevent the oxidation of the phosphorus.

In 1897 Hilbert and Frank, and more recently Bradley and Jacobs, prepared phosphorus by starting from calcium phosphate and carbon only, simultaneously obtaining calcium carbide. This carbide cannot be used for the manufacture of acetylene as it contains phosphorus, but it may be used for the preparation of calcium cyanamide (*see* p. 309).

PROPERTIES. Distilled phosphorus, which is called *yellow* or *white phosphorus*, has the appearance of somewhat transparent white wax, and unless it is very pure has a yellowish colour ; it has a specific gravity of 1·83 ; it is soft, but becomes brittle at 0° ; it melts at 44·4° and boils at 287°. When exposed to light it becomes brownish yellow ; it is insoluble in water, but

dissolves in carbon disulphide from which it crystallises in rhombododecahedra. It is slightly soluble in alcohol and ether. It is luminous and phosphorescent in the dark probably on account of the formation of hydrogen phosphide which burns in the air. The phenomenon of phosphorescence is very complex and depends considerably on the pressure of the oxygen. It increases with rarefaction until the substance catches fire.

Moist phosphorus oxidises rapidly in the air giving white fumes of phosphorous and phosphoric acids and phosphorus pentoxide, together with hydrogen peroxide and ozone. It spontaneously catches fire in the air, forming phosphorus pentoxide (P_2O_5), especially if finely divided, as may be shown by pouring a solution of phosphorus in carbon disulphide on to a sheet of paper. The carbon disulphide quickly evaporates, and the paper catches fire spontaneously.

If melted under water and heated to 50° phosphorus catches fire and burns under the water if brought in contact with a stream of oxygen; it reacts energetically with Cl, Br, and I.

If phosphorus vapours are mixed with hydrogen the gas burns with a flame which is green in the centre and is characteristic and noticeable even when minimal traces of phosphorus are present. In presence of minimal quantities of phosphorus the vapours from boiling water carry off a portion of it, and these vapours become phosphorescent in the dark. Mitscherlich devised an apparatus for the detection of minimal traces of phosphorus in poisoning cases by means of this reaction. The suspected substance is placed in a flask with water and boiled. The water vapour becomes phosphorescent in the dark, whilst passing up the tube of the vertical condenser, if phosphorus is present. The vapours are then condensed in a solution of silver nitrate so that the presence of phosphorus may be confirmed.

Phosphorus dissolved in carbon disulphide is a strong reducing agent, and therefore separates various metals from their salts forming phosphides; thus, for example, it precipitates PAg_3 mixed with Ag from silver nitrate and Cu_3P_2 from copper sulphate. Silver nitrate may be used for healing burns caused by phosphorus.

Phosphorus is a powerful poison, and 0·1 grm. is sufficient to cause death. In cases of phosphorus poisoning it is found absorbed in the liver, which is distended, in the blood, and in the expired air. The antidote consists of 1 grm. of copper sulphate dissolved in half a litre of water. The chronic illnesses caused by phosphorus poisoning are shown amongst operatives in match factories, by necrosis of the bones and especially of the teeth and jaws.

The density of phosphorus vapour between 500° and 1000° leads to a molecular weight corresponding to P_4, and this molecule still exists in the cold, as may be shown cryoscopically in its solutions. Two *allotropic forms* of phosphorus other than yellow phosphorus are known, namely *red* and *black* phosphorus, which are denser and have a smaller specific heat. Black phosphorus or metallic phosphorus is also called Hittorf's phosphorus, and is obtained by crystallising it from solution in molten lead; it has a specific gravity of 2·32.

RED PHOSPHORUS OR AMORPHOUS PHOSPHORUS. This substance was discovered by Schrötter in 1845 and was believed to be amorphous, but it has now been shown that it crystallises in the hexagonal system and is a polymer of yellow phosphorus.

It is formed on exposing yellow phosphorus for a long period to light, or on heating it *in vacuo* or out of contact with the air to 300°. The transformation already occurs at 200° if a trace of iodine is added.

It is prepared industrially in Albright's apparatus (Fig. 139), which consists of a glass or porcelain vessel, *P*, immersed in a second receiver containing sand, S_1, which is in turn heated in another sand-bath, *S*, placed directly over a furnace, *F*; the internal vessel is almost

completely filled with yellow phosphorus and is then closed with a screw top, which carries a curved tube, *R*, dipping into water or mercury, *W*, and thus forms a hydraulic seal. As the whole is gradually heated the internal air escapes through the tube, which is closed after a certain time by the cock, *K*, whilst the heating is continued for 8 to 10 days at 230° to 250°. A mass of red phosphorus results, which is poured into water and boiled with sodium hydroxide to dissolve the last traces of yellow phosphorus which remain, PH_3 and sodium hypophosphite being thus formed. It is then further washed with water and the mass of red phosphorus is dried in stoves. Yellow phosphorus can also be easily separated with carbon disulphide, but the operation is more dangerous.

Red phosphorus consists of an apparently amorphous, bright reddish-brown powder without odour, of sp. gr. 2·19; it is not phosphorescent in the dark, does not alter in the air, and is not set on fire by friction; it is not poisonous, is insoluble in carbon disulphide, and only catches fire at a temperature above 200°; when heated rapidly to 260° in an atmosphere of carbon dioxide it is transformed into vapours of ordinary yellow phosphorus. It does not melt, even at a red heat, but at 100° it already slowly gives off vapours. When heated for a long time to 360° in sealed tubes, red phosphorus is transformed into black phosphorus, formed of rhombohedral crystals of sp. gr. 2·34.

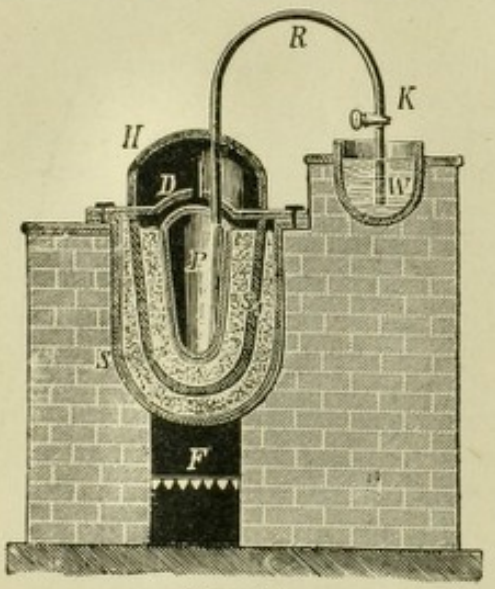


FIG. 139.

When yellow phosphorus is transformed into red phosphorus 114 Kj. are evolved, so that the latter contains less energy and is therefore more stable and indifferent.

Yellow phosphorus is kept under water or, better still, under alcohol or glycerine. It is sold in hermetically sealed tin-plate boxes.

USES OF PHOSPHORUS. *The Match Industry.* This is an essentially chemical industry, a product of the nineteenth century, but is to-day combined with perfect machinery which renders it one of the most interesting modern industries. The history and the first development of the match industry are so well known by everybody to-day that we need not dwell on it in a special manner. The first matches were manufactured by Chancel in Paris in 1805; they consisted of a splint of wood which was covered at one end with a mixture of sugar and potassium chlorate. On touching this wood with a piece of asbestos soaked in sulphuric acid fire was produced. These matches were used until about 1840. Then, however, a wooden match which lit by friction appeared. These had been discovered about 1832 almost simultaneously by the German chemist Kammerer, the Viennese Preshel, and the French medical man Sauria, to whom a marble monument was erected a few years ago at Saint-Lothaire, a small community in the Jura, his native country. The wooden matches had a head formed of a mixture of potassium chlorate and antimony trisulphide, held together with some kind of gum; they were lighted by rubbing them on a sheet of paper covered with powdered glass, and were drawn between two fingers. At first they were called by the name of Congreve, an English general of artillery, who since the beginning of the century had prepared the most various and surprising rockets for use in warfare and as fireworks. Towards 1833 the discovery of Sauria and of Kammerer was introduced in a practical and convenient form in various countries simultaneously by means of wooden matches made with yellow phosphorus. In 1816, already, Derosne had attempted to prepare matches with yellow phosphorus but had not succeeded practically, and it was only much later that they were met with in the form of thin splints of wood covered at one end with sulphur, which served to transmit to the wood the flame formed at the head by a mixture of yellow phosphorus and potassium chlorate. These sulphur matches were very soon in common use in all countries, reaching even to the smallest villages, so that they were used both in the palace and the cottage.

The mixture forming the head of these sulphur matches had, however, two serious objections, which were very soon also noticed by the public, namely, that they were dangerously explosive and poisonous.

In 1837 Preshel commenced to replace the potassium chlorate by brown lead peroxide, and then by minim mixed with manganese dioxide, which was still less dangerous ; one of the disadvantages was thus eliminated. But there still remained the danger due to the phosphorus, which had already claimed many victims through the poisoning of children who were unconscious of danger, and through the necrosis of the bones, which inexorably attacked the workmen using yellow phosphorus. It was only in 1848 that Professor Böttger of Frankfort-on-Maine prepared the so-called safety matches, free from phosphorus, for the first time. In these the head contained no phosphorus, but only a mixture of substances containing much oxygen, *e.g.* a mixture of 16 per cent. of gum, 50 per cent. of potassium chlorate, 5 per cent. of potassium chromate or calcium plumbate, 5 per cent. of sulphur, and 25 per cent. of a filling made of zinc oxide or chalk, and various colouring matters. Safety matches only ignite when they are struck on a specially prepared surface containing 50 per cent. of red phosphorus, which is not poisonous, 20 per cent. of gum, 10 per cent. of antimony sulphide, water, and inert filling material. In various countries the yellow phosphorus in matches was replaced by phosphorus sesquisulphide, which is less dangerous.

These matches are also called Swedish matches, because it was in Sweden that they were first manufactured on a large scale, as their substitution for matches containing yellow phosphorus was enforced by law. From Sweden safety matches were imported to all the other countries, and in some of these—North America, France, England, Switzerland—and now also in Germany, laws were passed absolutely forbidding the manufacture of matches containing yellow phosphorus. Until a few years ago safety matches had the disadvantage that they could only be ignited by striking them on a specially prepared surface. Now, however, matches are prepared in France and in Switzerland which are made with completely harmless phosphorus sulphide, and which light on striking them on any roughened surface. By heating white phosphorus with phosphorus tribromide Schenck recently obtained *scarlet phosphorus*, which is nothing more than a mixture of 70 parts of phosphorus and 30 parts of phosphorus tribromide PBr_3 ; this substance is not poisonous and is more active than ordinary amorphous phosphorus, so that it is adapted for the preparation of non-poisonous matches which may be struck on any surface.

It is difficult to understand why the manufacture of non-safety matches has not been forbidden even in Italy, because to the many processes of manufacturing safety matches another was added in 1903 by an Italian chemist, Purgotti, who advantageously uses ammonium sulphocyanide mixed with potassium chromate instead of yellow phosphorus. But in Italy the health of thousands of workmen continues to be injured, and that of the consumers themselves constantly menaced, perhaps in order not to harm the interests of a few manufacturers.

The greatest advance in the match industry has occurred since 1860, when, with the help of engineers, machines were produced which enable matches to be manufactured on a large scale with a minimum amount of hand labour. From the first machine by Sebold the marvellous machines of Sévène and Cahen were gradually evolved. These perform all the necessary operations in an absolutely automatic manner. The sawing of the wood into sheets is followed by cross-cutting, which forms thousands of sticks at a single stroke, and these are arranged separately from one another in suitable frames, which then pass on to be coated with paraffin, immersed in molten sulphur, the heads covered with the inflammable mixture, dried, and finally filled automatically into the boxes, labelled and packed into cases. This is one of the examples, so frequent to-day, in which machinery is more perfect and rapid than manual labour. By means of these machines three workmen produce 500 boxes of matches, ready for sale, in ten hours.

The large match industry gradually extended from Sweden to Russia, Austria, Germany, and later also to France and Italy. For some time competition has also arisen from new factories in America and Japan. In the whole world there are to-day more than 700 important match factories. The large factory of Jönköping, in Sweden, produces about 60 million matches daily. In 1907 Sweden produced matches to the value of £720,000 and exported 21,800 tons. Germany produces matches to the value of about £4,600,000 annually, and it is calculated that the mean daily consumption is twelve

matches for each inhabitant. In 1906 1385 tons were exported of the value of £38,000. The Argentine has 10 large match factories, which employ 3500 workpeople and consume 700 tons of stearine annually, producing matches to the value of £400,000, of which, however, £80,000 represents the value of the boxes. In France the production in 1877 was 25,179 millions, in 1897 33,349 millions, and in 1907 41,369 millions, for which 12·140 tons of red phosphorus, 31·427 tons of phosphorus sulphide, 224·127 tons of potassium chlorate, and 844·871 tons of sulphur were required. The manufacturing profit was about £1,120,000. In Brazil in 1908 425 million boxes of matches were produced. Italy in 1903 exported 1258·4 tons of wooden matches, and in 1908 1541·4 tons of the value of £37,000 and 1610·4 tons of wax matches. In 1908 1879·3 tons of wax matches, of a value of £180,400, were produced. In Italy there are to-day 115 large and small match factories, which in 1908 produced 41,000 million wooden matches and 26,800 million of wax or paraffin matches; the internal consumption was 36,700 million of the former and 11,400 million of the latter. The exports were 5300 million of the former and 14,300 million of the latter. The Government receives £400,000 a year from the match tax. Exports go more especially to Turkey, Egypt, and Australia. In 1901 Japan exported 41,407,000 gross of matches of the value of £1,200,000, and in 1908 it exported 34,000,000 gross; 25,000 workpeople are employed in 150 works; the export forms two-thirds of the production, and 50 per cent. of it goes to China.

The *production of phosphorus* in 1864 in France and England was altogether 175 tons, in 1874 it was 1200 tons; in 1800 1500 tons were produced in France and 1750 tons in England.

The world now consumes 3000 tons of phosphorus yearly in the match industry, in the preparation of aniline colours, and still more in the manufacture of very important metallic alloys, mainly prepared by new electric processes.

The most important phosphorus works are found in America (Oldburg Electron-Chemical Co. at Niagara), England, France (Lyons), and Germany (Griesheim and Frankfort); a little is produced in Sweden and in Russia. A factory using wavellite (aluminium phosphate) has recently been started at Harrisburg. In 1905 Italy imported 199 tons of red and yellow phosphorus of the value of £29,850, that is, at a mean price of 3*s.* per kilo. In 1907 the imports were only 79·5 tons and in 1908 105·1 tons, valued at £14,714.

Germany imported 313 tons of phosphorus in 1901 and exported 150 tons; in 1909 it imported 178·6 tons and exported 168·5 tons.

The price of yellow phosphorus is about 3*s.* 2½*d.* per kilo, that of red phosphorus of first quality about 5*s.* 2½*d.* per kilo, and of second quality about 3*s.*

ARSENIC: As, 74.96

Arsenic is contained in various minerals which have been known since ancient times, and Gebir described arsenic oxide clearly, and obtained it by burning arsenic sulphide. Brandt in 1773 knew metallic arsenic.

Arsenic is found in nature in the free state as a mineral, but more abundantly combined in the form of sulphides (realgar, As_2S_2, orpiment, As_2S_3) or arsenical pyrites, FeSAs, and smalt or mispickel, CoSAS.

It is found in small quantities in many mineral waters, for instance, in the waters of Roncegno, where it was found for the first time by Will and then by Fresenius.

It is obtained by heating AsFeS out of contact with the air; the arsenic sublimes and iron sulphide remains, or, as in the case of the metals, it is obtained by heating arsenious oxide, formed by roasting the sulphide in the air, in presence of carbon:

$$As_2O_3 + 3C = 3CO + As_2.$$

Attempts have been made to prepare it electrolytically in the same manner as antimony (*see below*) by using its solutions in alkali sulphides and hydrosulphides (Siemens and Halske process); a greater practical success appears, however, to have been obtained by Westmann's process (1900) according to which the arsenical mineral is heated in an electric furnace with iron sulphide in an atmosphere of nitrogen.

Arsenic crystallises in the hexagonal system and has a specific gravity of 5·73.

It is known in various crystalline forms and also in the amorphous state, but in reality this latter variety is an agglomerate of microscopic crystals of the regular system. But truly *amorphous arsenic* is also known and is obtained by distilling arsenic in a current of hydrogen ; this product has a blackish and but slightly lustrous aspect and a specific gravity of 4·7, and on heating to 360° it is transformed into crystalline arsenic with evolution of heat. When heated with a solution of sodium hypochlorite it acquires a lustrous metallic aspect ; thus, also, if heated with a trace of iodine it forms arsenic iodide, which evaporates immediately, leaving lustrous crystalline arsenic behind.

A new form has recently been prepared, namely, *yellow arsenic*, by distilling black arsenic *in vacuo* at 450° in a dark chamber with a red light. The vapours which distil are condensed in a vessel surrounded with liquid air. Under the action of light or heat it is immediately transformed into black arsenic.

On heating arsenic in an indifferent gas such as CO_2 at 450° it sublimes without melting, but when exposed to strong pressure and heated in closed tubes it melts. The vapours of arsenic are yellowish ; the vapour density indicates a tetratomic molecule, As_4. At 1700° it dissociates into diatomic molecules, As_2. On heating in the air it catches fire at 180°, burning with a weakly bluish flame and giving off an odour of garlic with formation of arsenious oxide, As_2O_3. When gently heated under the influence of light, yellow arsenic, As_4, is first transformed into brown arsenic As_2, and then into metallic arsenic As, which is monatomic and a conductor of electricity. A form of arsenic, As_8, also appears to exist, and is insoluble in various solvents. It catches fire in an atmosphere of chlorine, and combines with various metals in a similar manner to sulphur, but in all its other properties is more closely related to nitrogen ; at the same time it has certain metallic characteristics.

The metallic arsenides and sulphides are isomorphous and replace one another reciprocally atom for atom—for example, FeS_2, FeAsS, $FeAs_2$, although sulphur is divalent and arsenic trivalent.

Metallic arsenic is only used to-day in the manufacture of small shot, and costs £6 16*s.* per 100 kilos when pure and crystalline ; the impure commercial product (80 per cent.) costs £5 12*s.* per 100 kilos.

In 1905 Germany produced 4913 tons of arsenical minerals and Italy 451 tons, valued at £1010 (in 1908).

ANTIMONY (STIBIUM) : Sb, 120.2

This element is found in nature more especially as the sulphide Sb_2S_3, called *antimonite*, and accompanies arsenic in various minerals.

Its appearance is more metallic than that of arsenic, and although it has many metallic qualities it is closely connected with arsenic and phosphorus in its chemical behaviour.

It is prepared by heating the sulphide in presence of iron :

$$3Fe + Sb_2S_3 = 3FeS + Sb_2,$$

and is purified by melting it with saltpetre. It may also be prepared by first heating the mineral without iron in presence of air ; the sulphide then burns and antimony trioxide remains, $Sb_2S + 9O = Sb_2O_3 + 3SO_2$. The trioxide is then reduced by heating with carbon, and free antimony is obtained which is the purer the better the trioxide has been purified.

Antimony has a lustrous silvery appearance, and forms crystalline aggregates of the same character as those of arsenic. It has a specific gravity of 6·7 and is friable ; it melts at 140° and evaporates between 1500° and 1700°. It does not oxidise in the air at ordinary temperatures, but when heated it burns with a greenish-blue flame forming white fumes of antimony trioxide. It burns in a current of chlorine, is insoluble in HCl, gives antimonious acid with dilute nitric acid, and antimonic acid with concentrated nitric acid.

INDUSTRIAL PREPARATION OF ANTIMONY. The antimony sulphide is first separated from the gangue in the ore by heating in a furnace over a direct flame, on a sloping

floor along which the fused sulphide passes into a channel, which then carries it into a vessel placed outside. The sulphide thus purified is broken into pieces and placed in a reverberatory furnace where it is continuously stirred until completely transformed into antimony oxide, Sb_2O_3. After this roasting process the mass is mixed with soda and carbon, placed in crucibles and heated in suitable furnaces. The fused antimony separates and forms a single mass which, when allowed to solidify slowly, is transformed into a characteristic striated crystalline mass which may be purified from the last traces of arsenic by melting it repeatedly, first with a little antimony sulphide and soda and then with soda alone, until the slag has a light yellow colour.

Antimony may be also obtained from the sulphide by heating it with iron, the following mixture being used : 65 per cent. of antimony sulphide, 27 per cent. of spongy iron, 6 per cent. of calcined sodium sulphate, and 2 per cent. of charcoal. The most economical is the English process, in which the mineral containing the antimony is charged, whilst already hot, into a furnace containing iron sulphide and molten iron. The antimony separates rapidly and may then be refined.

The industrial preparation of antimony by the electrolytic process of Siemens and Halske (1893) has been attempted, by electrolysing the double salts obtained by dissolving antimony sulphide in alkali sulphides or hydrosulphides. 30 per cent. of antimony sulphide, Sb_2S_3, is mixed with 66 per cent. of sodium sulphide crystals (of the formula $Na_2S.9H_2O$) and 3 per cent. of sodium chloride. The process was improved in 1902 by Izart and Thomas.

APPLICATIONS AND PRODUCTION. This element has now acquired importance because it is an essential component of many metallic alloys which are largely used, for example, hard lead, and *type metal*, which contains about 25 per cent. of Sb, 10 to 20 per cent. of tin, a little copper, nickel, bismuth, and the remainder of lead.

Hard lead is used in many chemical industries, and consists of lead containing 10 to 15 per cent. of antimony.

When mixed with tin it forms *Britannia metal*. When alloyed with zinc, copper, &c., it forms *white metal* (*anti-friction metal*), which is much used for bearings in place of the harder alloys containing much tin. It is used for mineral pigments which are not poisonous and which resist light better than zinc oxide.

The product which is known commercially as "antimonium crudum" is not really crude antimony but the sulphide (Sb_2S_3), and is used more especially for fireworks.

Germany produced 2794 tons of antimony in 1905 ; the price has varied during the last few years from £48 to £100 per ton. The chemically pure metal costs 5*s*. 7*d*. per kilo. Italy produced 7892 tons of antimony ores in 1907 and 2841 tons in 1908, valued at £11,224, and 345 tons of metallic antimony in 1908 valued at £9058 ; the imports of antimony metal were 49·7 tons in 1906 and 152·7 tons in 1908, valued at £10,384. In Asia Minor about 1000 tons of antimony were produced in 1907, but when the price is higher more is produced. Ores containing 50 to 55 per cent. of antimony cost £14 per ton.

EXPLOSIVE ANTIMONY. If a solution of antimony trichloride, containing at least 10 per cent., is electrolysed with one antimony and one platinum electrode, a lucent metallic coating is formed on the latter which explodes violently when rubbed with another substance. Gore, who first studied it in 1858, found that it was formed of 93·5 per cent. of antimony, 0·5 per cent. of HCl, and 6 per cent. of $SbCl_3$, and the latter substance could not be extracted with ordinary solvents ; therefore Cohen (1903) has pointed out that electrolytic antimony cannot be used for atomic weight determinations. The cause of this special property of antimony is not at present known.

HYDROGEN COMPOUNDS OF N, P, As, Sb

These elements combine with three atoms of hydrogen, but other less important hydrogen compounds are known.

The basic character of these hydrides diminishes with increase of the molecular weight and finally disappears. Ammonia, NH_3, has an alkaline reaction and is a strong base which easily forms ammoniacal salts with acids. Hydrogen phosphide, PH_3, is already less basic and combines with HBr and HI only at ordinary temperatures. Arsenic hydride, AsH_3, and antimony hydride, SbH_3, no longer have any basic characters.

AMMONIA: NH_3, 17

This compound is found combined with certain acids, in the air, in natural waters, and in the soil, but always in small quantities. It is present abundantly as ammonium sulphate in the *soffioni* of Tuscany and is found as ammonium carbonate in the large guano deposits of Peru.

Ammonia was studied by Priestley, who called it alkaline air; its composition was determined by Berthollet in 1785.

FORMATION. It is formed from hydrogen and nitrogen in small quantities (2 per cent.) by means of the electric discharge, but in the presence of moisture, as in the atmosphere, ammonium nitrate is directly obtained: $N_2 + O + 2H_2O = NO_3NH_4$. On the other hand, ammonium nitrite, NO_2NH_4, is obtained whenever combustion occurs in the air and in the electrolysis of aerated water: $N_2 + 2H_2O = NO_2NH_4$. A mixture of NO and H in presence of Pt or of Fe_2O_3 also gives NH_3 on heating.

On dissolving certain metals, such as zinc, in dilute nitric acid, the nascent hydrogen reduces the nitric acid: $NO_3H + 4H_2 = 3H_2O + NH_3$, and thus ammonium nitrate is obtained together with the zinc nitrate. Salts of nitric acid are also reduced by nascent hydrogen in alkaline solution with production of ammonia.

Its formation from magnesium nitride, N_2Mg_3, is interesting; this substance is obtained by passing N over red-hot Mg, and reacts vigorously with water to form ammonia: $Mg_3N_2 + 3H_2O = 3MgO + 2NH_3$.

A large source of ammoniacal salts, and the only one until some time ago, is the putrefaction and decomposition of nitrogenous organic matter or, better still, its dry distillation. It was obtained in this way from urine, camel's dung, &c.

To-day ammonia is obtained almost exclusively by distilling the gas liquor obtained in the manufacture of illuminating gas, which is prepared by the distillation of coal, although during the last few years certain other industrial processes have been tried (*see below*).

It is prepared in the laboratory by heating a mixture of solid ammonium chloride and slaked lime mixed to a paste in a glass or iron flask on a sand-bath:

$$2NH_4Cl + Ca(OH)_2 = CaCl_2 + 2H_2O + 2NH_3.$$

It is collected over mercury because it is very soluble in water. It is dried by passing it over quicklime (CaO), and not over calcium chloride, with which it combines. It may also be collected by displacement of air in an inverted cylinder, as it is lighter than air.

PHYSICAL PROPERTIES. Ammonia is a colourless gas with an intense, suffocating odour; it has a density of 0·56 (air = 1) at 10°, and at a pressure of 6·5 atmospheres or at −40° at the ordinary pressure it is converted into a colourless mobile liquid of sp. gr. 0·623 (water = 1) which boils at −33·5° and solidifies at −85°.

One volume of water at 0° dissolves 1146 vols. of ammonia, and at 20° about 739 vols., so that one part by weight of water dissolves 0·526 part by weight of NH_3. A saturated aqueous solution at 15° contains 35 per cent. by weight of NH_3 and has a specific gravity of 0·880. In its aqueous solutions the specific gravity becomes less as the quantity of dissolved ammonia becomes greater, as is seen from the Table on the following page.

On heating, all the NH_3 is evolved from aqueous solutions and pure water remains. When ammonia dissolves in water much heat is evolved, and much is absorbed when it is evaporated or liberated, and these properties were practically utilised for the first time by Carré for the preparation

of artificial ice from water. When a solution of NH_3 which is kept saturated is cooled to $-79°$, thin crystals of $NH_3.H_2O$, containing 48·6 per cent. of NH_3, separate, together with thick crystals of $(NH_3)_2H_2O$ containing 65·4 per cent. of NH_3. A solution containing 33 per cent. of NH_3 becomes very dense and viscous at $-100°$.

CHEMICAL PROPERTIES. On passing electric sparks through ammonia for a long time, or on heating it to above 500°, it decomposes to the extent of 98 per cent.

Ammonia does not burn in the air, but burns in oxygen with a yellowish flame, yielding free nitrogen, nitric oxide, and ammonium nitrite. When magnesium is heated in a current of NH_3 it catches fire, forming hydrogen and magnesium nitride: $3Mg + 2NH_3 = Mg_3N_2 + 3H_2$; potassium acts similarly: $3K + NH_3 = NK_3 + 3H$.

If a current of chlorine is passed into a flask full of ammonia the chlorine catches fire and continues to burn, forming white vapours of ammonium chloride together with nitrogen: $NH_3 + 3Cl = 3HCl + N$, and $3NH_3 + 3HCl = 3NH_4Cl$.

In aqueous solution or in the state of gas it has always a strongly basic action (*see* explanation in Part III in chapter on Ammonium) and saturates acids forming salts analogous to those of the alkali elements, potassium and sodium:

$2NH_3 + SO_4H_2 = SO_4(NH_4)_2$ analogous to SO_4K_2 and SO_4Na_2.
$NH_3 + HCl_3 = NH_4Cl$,, ,, KCl ,, NaCl, &c.

Thus the group NH_4, which is called *ammonium*, may be considered almost as an element, and in its behaviour it is similar to the alkali metals and even forms an amalgam with mercury in the same way as these do (*see* Part III). Its salts are called ammonium salts and their ammonia may be eliminated by the action of more energetic bases such as lime, sodium hydroxide, &c.:

$$2NH_4Cl + CaO = 2NH_3 + CaCl_2 + H_2O.$$

Traces of ammonia are detected by means of Nessler's reagent (*see* Analysis of Water, p. 214, *and* Mercury Iodides).

The heat of formation of NH_3 from its elements is 50·2 Kj. (12,000 cals.) and it develops a further 31·1 Kj. on dissolving in water.

Sp. gr. at 15°	Degrees Bé.	Per cent. by weight of NH_3	1 litre of the solution contains grms. of NH_3	Sp. gr. at 15°	Degrees Bé.	Per cent. by weight of NH_3	1 litre of the solution contains grms. of NH_3
0·998	10·5	0·45	4·5	0·938	19·5	16·22	152·1
0·994	10·9	1·37	13·6	0·934	20·3	17·42	162·7
0·990	11·5	2·31	22·9	0·930	21·1	18·64	173·4
0·986	12·0	3·30	32·5	0·926	21·8	19·87	184·2
0·982	12·5	4·30	42·2	0·922	22·4	21·12	194·7
0·978	13·0	5·30	51·8	0·918	23·0	22·39	205·6
0·974	13·9	6·30	61·4	0·914	23·6	23·68	216·3
0·970	14·5	7·31	70·9	0·910	24·4	24·99	217·4
0·966	15·0	8·33	80·5	0·906	25·0	26·31	238·3
0·962	15·7	9·35	89·9	0·902	25·7	27·65	249·4
0·958	16·3	10·47	100·3	0·898	26·5	29·01	260·5
0·954	17·0	11·60	110·7	0·894	27·4	30·37	271·5
0·950	17·7	12·74	121·0	0·890	28·0	31·75	282·6
0·946	18·3	13·88	131·3	0·886	28·7	33·25	294·6
0·942	19·0	15·04	141·7	0·882	29·5	34·95	308·3

The constitution of ammonia may be determined from its analysis, that is to say, from its percentage composition, and the density of the gas, and directly by the electrolytic decomposition of aqueous solution of ammonia in a Hofmann voltameter, the ammonia solution being saturated with sodium chloride, which renders it more conductive ; at the negative pole 3 vols. of hydrogen are separated, and 1 vol. of nitrogen at the positive pole, so that the ammonia decomposes forming 3 vols. of H and 1 of N. On passing the electric spark through a definite volume of ammonia for some time, it is completely decomposed into N and H, forming a volume double that of the NH_3 : 2 vols. NH_3 = 1 vol. N_2 + 3 vols. H_2.

INDUSTRIAL PREPARATION OF AMMONIA

The only natural salts which are utilised for this purpose are the ammonium sulphides of the soffioni of Tuscany. From four soffioni 1500 kilos of ammonium sulphate have been extracted in twenty-four hours together with 150 kilos of boric acid, 1750 kilos of magnesium sulphate, and 750 kilos of iron and magnesium sulphates.

A small quantity of ammonia is also prepared from beet-sugar residues (molasses), which contain nitrogenous organic substances (*betaine* and *aspartic acid*), which yield ammonia and trimethylamine on dry distillation. This latter compound is in turn decomposed by HCl forming ammonium chloride and methyl chloride, CH_3Cl. Ammonia is also obtained from putrefied urine by Figuera's process (at Chicago, for example, the putrefied urine from the large slaughter-houses for the pigs is utilised).[1]

We must also mention the industrial preparation of NH_3 from atmospheric nitrogen by means of calcium cyanamide and steam or hot water under pressure (*see* p. 310) and also by the catalytic process from its elements (Ostwald and also the Badische Anilin und Sodafabrik ; Fr. Pat. 406,943 of 1909).

Almost the whole of the ammonia which is prepared to-day is derived from the gas water of gasworks, and from the distillation of coal during the preparation of metallurgical coke (*see* vol. ii, " Organic Chemistry ").[2]

In order to liberate the ammonia, these ammoniacal liquors are distilled with lime (not more than 5 per cent. of the weight of the NH_3 gas) and the ammonia is absorbed by strong sulphuric acid. Crystallised ammonium sulphate is thus directly obtained and is easy to handle and transport.

A very simple apparatus used in many works is that of Lunge (Fig. 140). The cold ammoniacal liquor passes into the reservoir, *d*, and there cools the coil which carries the ammoniacal vapours from the pan, *a*, into which the ammoniacal liquor passes through the tube, *e*, from the vessel, *d* ; *b* is a stirrer for preventing the lime from settling on the bottom ; *g* is a valve from which the exhausted liquor is discharged through the tube, *f*. When the gas liquor in *d* is sufficiently heated it evolves vapours which escape through the tube, *i*, and join those proceeding from the boiler ; *k* is a washing vessel for the ammoniacal vapours, which are then absorbed by strong sulphuric acid in the vessel, *l*, which is lined with lead. The sulphuric acid passes into this saturator from the reservoir, *O*, through the syphon, *P* ; the crystals of ammonium sulphate are collected with a ladle into a perforated bucket, *S*, which is lifted by means of a counterpoise. The evil-smelling gases which are not absorbed by the strong sulphuric acid contain hydrogen sulphide and cyanogen compounds. These gases cannot be led directly up the chimney because they would cause annoyance in the

[1] During the fermentation of urine the urea which it contains is transformed into ammonium carbonate, $CO(NH_2)_2 + 2H_2O = CO_3(NH_4)_2$, and this is readily decomposed on heating, forming $CO_2 + 2NH_3 + H_2O$. Every adult person produces 30 grms. of urea daily, corresponding to an annual production of more than 20 kilos of ammonium sulphate, so that the urine of the inhabitants of Milan would suffice for the annual production of more than 10,000 tons of ammonium sulphate.

[2] Of the nitrogen contained in coal (up to 1½ per cent.) only 15 per cent. is transformed into NH_3 and 35 per cent. is evolved as free nitrogen, because in the retort in which the coal is distilled a temperature of 1200° is reached whilst ammonia already commences to dissociate into H and N at 500° ; 48 per cent. of the nitrogen of the coal remains in the coke. If NH_3 had a higher value it would be possible to increase the yield during gas manufacture by distilling the carbon in presence of steam, which carries off the NH_3 and lowers the temperature.

According to the quality of the coal the ammoniacal liquor from gasworks contains from 12 to 35 grms. of NH_3 per litre, largely in the form of ammonium carbonate and sulphide and in smaller quantities as chloride cyanide, and sulphocyanide.

neighbourhood ; it is therefore preferable to burn them by passing them into the hearth of a furnace containing red-hot coal, or the cyanogen compounds which they contain may be utilised by passing them through suitable solutions, afterwards utilising the hydrogen sulphide in a Claus kiln for the recovery of the sulphur, or they may be absorbed by iron oxide (*see* Part III, Leblanc Soda).

The most widely spread forms of apparatus in practice are those based on the principle of Savalle's rectifying column, such as is used in spirit distilleries. Among the many forms which are used (Beckton, Mallet, Garcis, Solvay, Feldmann, &c.) one of the most perfect, which yields very good results, is the new apparatus of Grüneberg and Blum, which completely exhausts the ammoniacal liquor until only one part of NH_3 remains per 10,000 parts of water, and is capable of treating 30 to 50 cu. metres of liquor per twenty-four hours.

The ammoniacal liquor passes through the tube, *a*, into the pre-heater, *B* (Fig. 141), and from there through the tube, *b*, into the rectifying column, *A*, where it descends and encounters the hot vapours which pass up from below. At the bottom of the column the liquid passes through the tube, *e*, into the vessel, *F*, containing milk of lime, which decomposes the ammoniacal salts and liberates ammonia. When the liquid in *F* rises to the level

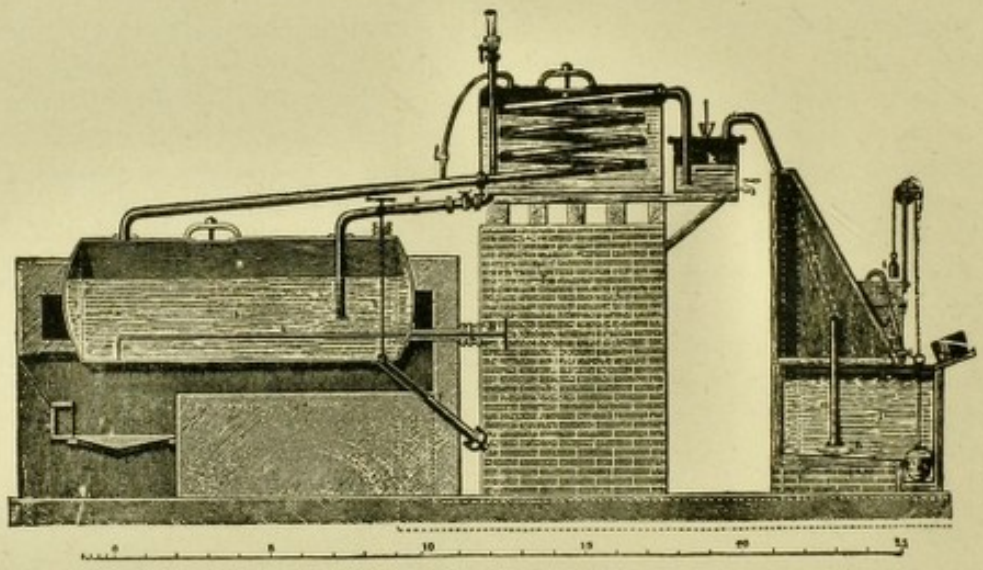


Fig. 140.

of the tube, *f*, it passes into the vessel, *g*, and when this is full it overflows into *h*, and over the circular plates which are arranged in steps. In this way the quantity of liquor which covers the first step gradually expands over wider and wider surfaces as it descends because the circumference of the circular steps increases, and thus the layer of liquid gradually becomes thinner. In the chamber surrounding the steps there is a series of concentric vertical diaphragms, *i*, which pass down almost to the level of the steps, forcing a current of steam proceeding from the boiler, *G*, and the tube, *d*, to traverse the liquid surface as it passes down the steps in such a way that even the last traces of ammonia are completely removed. The exhausted water is discharged by the hydraulic syphon, *k* ; the steam and ammonia ascend through the tubes, *m*, and are forced by the tubes, *n*, to pass through the milk of lime in *F*, being thus further enriched with ammonia, and then pass up the rectifying column where the water is separated. The ammonia, on the other hand, issues from the top of the column from the tube, *p*, and passes into the saturator, *D*, containing H_2SO_4. The moist ammonia passes into sulphuric acid of 60° Bé. During normal working the acid in the saturator is maintained between 32° and 35° Bé., the acid which is removed in the form of crystallised ammonium sulphate being replaced by fresh quantities of acid of 60° Bé. The acid in which the crystals of ammonium sulphate float passes along a tube provided with a steam injector into a leaden box with an inclined bottom, where the crystals are deposited ; these are then centrifugated whilst the decanted acid is returned to the saturator. The evil-smelling gases containing H_2S which are collected in *q* pass through the tubes, *r* and *s*, and into a furnace, where they are burnt, or the cyanogen and sulphur compounds are utilised as described above or are absorbed by natural ferric hydroxide. The pump, *G*, is used for passing the milk of lime into *F*.

The whole of the apparatus, the pipes and utensils, used in the manufacture of ammonia must be made of cast or wrought iron. There must be no copper or brass parts because these are strongly attacked by NH_3.

If the preparation of aqueous ammonia is desired instead of ammonium sulphate, the sulphuric acid in the separator must be replaced by water which is kept very cold. In order, however, to obtain ammonia free from gaseous impurities such as H_2S, CO_2, &c., it is desirable to add milk of lime to the ammoniacal liquor from the beginning. The gaseous ammonia which escapes at the top of the rectifying column is passed through a washer containing a paste of milk of lime and ferric hydroxide or through sodium hydroxide solution before being absorbed.

Crude commercial ammonia has a yellow colour due to sulphides, pyridine compounds, and tarry matter, and must be purified by distilling it in presence of a little potassium permanganate.

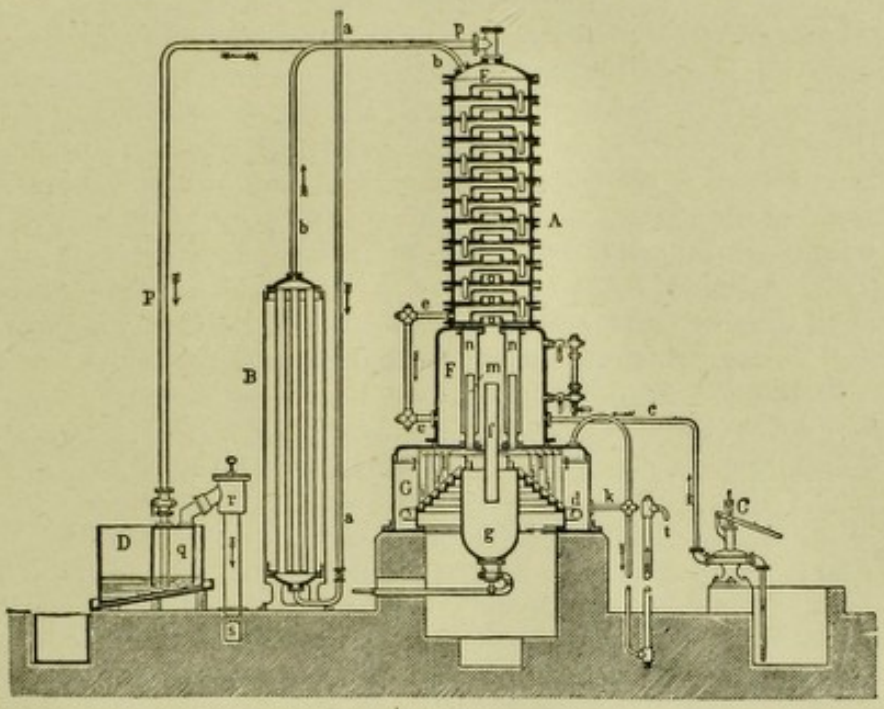


FIG. 141.

In certain cases NH_3 is also obtained from animal refuse, such as solid excrement, horns, hides, nails, tendons, cuttings from hides, woollen waste, corpses of animals, &c. These substances contain 12 to 18 per cent. of nitrogen and on dry distillation yield an *animal oil* rich in organic bases, such as pyridine, picoline, lutidine and collidine, together with cyanides, ammonium sulphide, and more particularly ammonium carbonate. Such substances are treated in iron retorts similar to those used in the manufacture of lighting gas.

Pure ammonia is obtained according to Frerichs (U.S. Pat. 905,415 of December 1908) by first heating commercial ammonium sulphate to 200° to decompose organic impurities and then to 350° to 400°, at which temperature NH_3 and $(NH_4)_2S_2O_7$ are formed.

According to a patent of Ireland and Suyden of London (Ger. Pats. 175,401 of 1903 and 176,606 and 180,141 of 1905), ammonia is formed from the atmospheric nitrogen by passing into a cylinder filled with peat and heated to 400° a current of hot air and of atomised water in such a manner as to maintain a temperature of 400°, as the reaction is exothermic. The quantity of air is regulated in such a manner as to burn the peat in four to six hours. The gases then pass into a tower filled with pebbles or charcoal in order to retain dust and tar, and then into a second tower similar to the preceding one, but through which a hot solution of soda or of lime passes in order to absorb the acetic acid; they are finally passed through two other towers down which

hot sulphuric acid is passed to absorb the ammonia. 12·5 kilos of crystallised ammonium sulphate are obtained from 300 kilos of peat. Coke, coal, wood, lignite, &c., may be used instead of peat. In an almost identical patent (Eng. Pat. 8358 of 1906) Woltereck starts from the fact that on passing H and N over almost red-hot reduced iron ammonia is formed, and he replaces the necessary hydrogen by moist peat containing 65 to 75 per cent. of water, whilst by other processes dry peat is used. At Carnlong, in England, a similar plant gives a yield of 5 to 7 per cent. of ammonium sulphate calculated on the dry peat, 1 per cent. of acetic acid, and 3½ to 6½ per cent. of tar and paraffin. The cost of production of the ammonium sulphate is £4 16*s*. to £6 per ton. It appears, however, that the ammonia is formed from the nitrogen in the peat of which about 60 to 85 per cent. is transformed into ammonia (dry peat contains 2 to 2½ per cent. of nitrogen). In this process combustible power gas is not obtained as is the case in the processes of Mond and of Frank and Caro, although it appears that in practice this cannot be very remunerative.[1]

Effront beats up the peat with 6 to 7 per cent. of water and 2 to 3 kilos of sulphuric acid per 100 kilos of peat, and heats the mass under pressure at three atmospheres; he then renders it alkaline with lime, and at 43° adds 40 grms. of aluminium sulphate, 20 grms. of superphosphate and considerable quantities of alcoholic ferments cultivated in extracts of molasses or of cereals (Ger. Pat. 215,531 of 1908). When the fermentation is completed the alcohol is distilled and collected separately from the ammonium salts. In a similar manner Effront obtains ammonia and organic acids from the residues of distilleries which contain amino-acids.

ANALYTICAL TESTS. The strength is usually determined by means of the density (*see* Table, p. 322); when the product is pure it should not leave any residue on evaporation in a capsule; on adding HNO_3 and $AgNO_3$ no opalescence due to chlorides should appear, nor should there be any turbidity on saturating with HCl and adding barium chloride (sulphates); no turbidity should be caused with excess of lime-water (carbonates); 10 c.c. to which 20 c.c. of dilute sulphuric acid (1 : 3) have been added should remain coloured with one drop of decinormal permanganate (tarry matter). The ammonia in ammoniacal compounds is determined by treating them with excess of sodium hydroxide and distilling in a current of steam. All the ammonia distils and is condensed in a titrated solution of normal acid coloured with methyl orange; the excess of acid is then titrated back with normal soda; 1 c.c. of normal acid corresponds to 0·017 grm. of NH_3.

PURE LIQUID AMMONIA, free from water, is prepared by distilling the

[1] By the Mond process the nitrogen contained in coal of poor quality, lignite, and peat is utilised by being transformed into ammonia. These fuels are burnt in gas-producers in presence of a little air and an excess of superheated steam. A gas is thus distilled which yields its ammonia to the condensed water, or in towers moistened with a spray of sulphuric acid, and the gas is then used to drive gas-motors producing considerable quantities of mechanical energy.

Dr. Caro applied this process to the waste coal from the mines, containing up to 60 per cent. of ash, and obtained in the crushing and washing of the coal. Frank and Caro applied the same process to moist peat containing 40 to 65 per cent. of moisture, and in an industrial test made in 1908 on 350 tons of peat containing 1 to 0·5 per cent. of nitrogen and 3 per cent. of ash (referred to the dry peat) they obtained from each ton of dry fuel 2800 cu. metres of gas, which when freed from tar contained 18 per cent. of CO_2, 10 per cent. of CO, 24 per cent. of H, 3 per cent. of methane, 44 per cent. of nitrogen, and traces of oxygen, and had a calorific power of 1400 Cals. per cu. metre. On distilling peat containing 65 to 70 per cent. of moisture the volume of gas was increased, but its calorific power was diminished, although it could still be utilised in internal-combustion engines in the same way as blast-furnace gases, which are still poorer, and also for heating purposes. The first gas produces one effective h.p.-hour of energy per 2·4 cu. metres of gas, and therefore 1160 h.p.-hours per ton of dry peat per hour; that is, from 2 tons of peat containing 50 per cent. of moisture. The gases which escape from the gas-engine have a temperature of 500°, and may be used for the production of steam in boilers which is used in the producers and to work the pumps, &c. In this way one may calculate a net yield of 1000 h.p. utilisable in other ways. Furthermore, 40 kilos of ammonium sulphate are obtained, so that 77 per cent. of the nitrogen contained in the peat is utilised. Peat containing 2·8 per cent. of nitrogen (on the dried matter) gave up to 110 kilos of ammonium sulphate per 1000 kilos of dry matter.

In the important peat beds of Tuscany (Orentano) in 1909 a plant was erected for utilisation of dry peat containing 1·5 per cent. of nitrogen; about 20 tons of the peat gave 210 tons of ammonium sulphate, 45,000,000 cu. metres of gas, and about 2000 continuous h.p.-hours, that is, about 3½ cu. metres of gas per h.p.-hour; 70 tons of peat are worked per day, costing about 3*s*. 2*d*. per ton at the works, by a plant which costs about £12,000 and is very remunerative. The peat from Codigoro ferrarese contains about 2·5 per cent. of nitrogen on the dried substance. Woltereck's patent (*see above*) differs but little from the Mond and Frank and Caro methods of working. Dr. Ekenberg carbonises peat in autoclaves under pressure.

concentrated aqueous solution or by using gas directly from the first condensing tower. In either case it is dried in towers containing quicklime and then liquefied in steel cylinders by means of a pump, 6·5 atmospheres being required at + 10°. The compressor and cylinders are similar to those used for the liquefaction of sulphur dioxide (pp. 245–246). The product may be employed in the manufacture of ice. At 0° it has a specific gravity of 0·6233. It boils at −32·5° and forms a mobile colourless liquid which solidifies at −88·3° and then melts at −78·3°; its critical temperature is + 131°. Liquid ammonia is one of the few substances which have a higher specific heat than water, this being 1·02 between 0° and 20°. Its heat of evaporation is about 300 Cals. per kilo, but varies somewhat with the temperature, being 333 Cals. at −40° and 278 Cals. at + 40°. The vapour pressure of liquid ammonia at −40° is 270 grms. per square centimetre; at 0° it is 4350 grms., at 20° 8790 grms., and at 40° 16,000 grms. The requirements demanded of commercial liquid ammonia are: 100 c.c. should leave a residue of less than 0·5 c.c.; 1 grm. of liquid ammonia should not contain more than 0·12 c.c. of foreign gases in solution; the vapours of NH_3 above the liquid ammonia should not contain more than 0·6 c.c. of other gases per gramme.

APPLICATIONS AND PRICES OF NH_3. Aqueous commercial ammonia containing about 25 per cent. of NH_3 is used in laundries, dyeworks, textile print works, colour factories, &c. (after dilution), and costs about £20 per ton or £8 if it contains 10 per cent. of NH_3. The purest aqueous solution costs 20 per cent. more. Liquid ammonia free from water is used in ice factories and costs up to 1*s.* 7*d.* per kilo at the works, which does not include the hire of the steel cylinders (*see* p. 177); delivered at Milan it costs about 2*s.* 4*d.* per kilo.[1]

In 1909 about 60 tons of liquid ammonia were used in Italy, almost the whole of which was imported from Germany and Belgium, a small quantity only being produced in a works at Turin (4 tons in 1908 of the value of £320).

In 1902 Italy imported 79·8 tons of ammonia in solution of the value of £1468; in 1904 only 66·2 tons were imported of the value of £1218; in 1906 129·6 tons; in 1907 121·4 tons; and in 1908 146 tons valued at £2470. In Italy 16,373 tons of ammoniacal liquor from gas-works of the value of £3863 and 150 tons of commercial aqueous ammonia were produced valued at £1950.

DIAMINE OR HYDRAZINE: N_2H_4, or $H_2:N.N:H_2$

This compound, which appears to be derived from the condensation of 2 mols. of NH_3, was known in the form of many of its organic derivatives, but had not been obtained in the free state; many inorganic derivatives were also prepared by Curtius after 1889, and in 1895 Lobry de Bruyn prepared pure diamine. It is obtained to-day in various ways by decomposing its hydrochloride with alcoholates or by distilling its hydrate with barium oxide. It is a colourless liquid which boils at 113·5° and fumes strongly in the air; it has a specific gravity of 1·003 at 23° and solidifies at 0°. It is not explosive and is distinguished from ammonia by its reducing power.

HYDRAZINE HYDRATE: $N_2H_4 . H_2O$, forms an energetic base similar to ammonia but of great reducing power, and readily decomposes silver and copper salts.

AZOIMIDE OR HYDRAZOIC ACID: N_3H, that is: $\begin{matrix} N \\ \| \\ N \end{matrix}\!\!>\!NH$. It was first prepared by Curtius in 1890 from the corresponding organic derivatives. He then obtained it from inorganic substances by pouring nitrous acid (liquefied red vapours obtained by the action of arsenious acid on nitric acid) into hydrazine hydrate:

$$H_2N . NH_2 + NO_2H = 2H_2O + N_3H.$$

It is also obtained in aqueous solution by distilling metallic hydrazides with dilute sulphuric acid.

[1] The cost of a small plant for the manufacture of 10 cu. metres of aqueous ammonia in twenty-four hours would be about £200 for the distilling apparatus, including the pump for the milk of lime and the pipes. The apparatus for obtaining concentrated aqueous ammonia with 15 per cent. of NH_3 comprises a reflux condenser, two condensing vessels, piping and cocks, and, with erection, costs £200. In order to obtain more concentrated solutions of pure aqueous ammonia, containing 30 per cent. of NH_3, 3 lime-washers, 6 coke filters, and two absorption vessels are required at a cost of about £200.

When pure it forms a mobile colourless liquid of very pungent odour, which boils at 37° and explodes with extraordinary violence. It is an endothermic compound and the heat absorbed in its formation and solution is −260 Kj. The alkali salts are not explosive, but its alkaline earth and other salts explode.

NITROGEN CHLORIDE : NCl_3. When ammonia reacts with an excess of chlorine then instead of free nitrogen (*see* p. 288) ammonium chloride is first formed which immediately produces nitrogen chloride : $NH_4Cl + 3Cl_2 = 4HCl + NCl_3$. This chloride is a yellow, oily liquid of disagreeable odour and of sp. gr. 1·65. It is extremely dangerous to handle, and the slightest shock, even rubbing with a feather, suffices to cause a violent explosion due to the extreme facility with which it decomposes into its elements. It is decomposed by means of concentrated HCl into the substances from which it is formed, $NCl_3 + 4HCl = 3Cl_2 + NH_4Cl$ (inverse reaction to the reaction of formation).

Aqueous NH_3 also decomposes it slowly, forming $N + NH_4Cl$.

NITROGEN IODIDE : NI_3. If ammonia is added to a solution of iodine in potassium iodide a black powder of NI_2H is first formed and then $N_2I_3H_3$ ($= NI_3 + NH_3$) ; this separates NI_3 with much water. These compounds are extraordinarily explosive when dry, being exploded even by the slightest friction. HCl, SO_2, and H_2S easily decompose these nitrogen iodides.

IODIDE OF AZOIMIDE (or TRIAZOIODIDE) : $\begin{matrix} N \\ \| \\ N \end{matrix}\!\!>\!\!NI$. This compound, which was prepared in 1900, appears to be a derivative of hydrazoic acid and is, in fact, obtained by the action of silver azide on iodine in ethereal solution in the cold : $N_3Ag + I_2 = AgI + N_3I$.

It forms a bright yellow solid substance which already decomposes with water and is also very explosive.

The great instability and explosibility of the halogen compounds of nitrogen are explained by the fact that they are strongly *endothermic.*

HYDROGEN PHOSPHIDE (PHOSPHINE, PHOSPHURETTED HYDROGEN) : PH_3

This substance is formed as a gas by the action of nascent hydrogen on phosphorus. It is also obtained by treating phosphonium iodide with potassium hydroxide :

$$PH_4I + KOH = H_2O + KI + PH_3.$$

It is obtained easily in a less pure condition mixed with liquid hydrogen phosphide, P_2H_4, from potassium hydroxide and phosphorus :

$$P_4 + 3KOH + 3H_2O = PH_3 + 3PH_2O.OK \text{ (potassium hypophosphite).}$$

The reaction is carried out in a flask completely filled up to the stopper with a concentrated solution of potassium hydroxide (Fig. 142) ; two or three pieces of white phosphorus are then added, and the flask is well closed with a cork stopper provided with a delivery tube, filled with water, dipping into tepid water in such a way that no air remains in the flask, in order to avoid the formation of the explosive mixture : $O + PH_3$. The flask is then heated with a small flame and bubbles of PH_3 gas are evolved ; these ignite in contact with the air as they are produced, forming rings of white smoke which enlarge as they rise in the air ; the ignition in the air is due to the presence of liquid hydrogen phosphide, P_2H_4, which is present in small quantities. If the gas is first passed through a cooled glass tube or is washed with alcohol, ether, or HCl, which absorb the P_2H_4, it no longer catches fire in the air.

PH_3, mixed with P_2H_4, is also obtained from calcium phosphide, Ca_3P_2, and HCl : $P_2Ca_3 + 6HCl = 2PH_3 + 3CaCl_2$. It is also obtained by heating phosphorous acid : $4PO_3H_3 = PH_3 + 3PO_4H_3$ (phosphoric acid). Calcium phosphide may now also be prepared by the Goldschmidt process (1910) by heating the phosphate with aluminium powder (*see* Thermite).

Hydrogen phosphide is a colourless gas with a disagreeable odour of garlic ; it is very

poisonous even when diluted with much air (1 to 10,000). It is liquid at −85°, solid at − 133·5°, and only catches fire at 100°, although oxidising agents such as HNO_3 render it spontaneously inflammable by forming P_2H_4; when mixed with oxygen it does not catch fire when pure, but catches fire spontaneously with explosive violence if the pressure is diminished (*see also* p. 315). On heating or by means of the electric discharge it is decomposed into $P + H_3$. It burns with a luminous flame, forming P_2O_5. When mixed with chlorine it explodes violently: $PH_3 + 3Cl_2 = PCl_3 + 3HCl$.

It is an energetic reducing agent and precipitates a black mixture of metal and metallic phosphide from solutions of copper sulphate or silver nitrate; by means of this reaction it may also be separated from other gases. Its composition may be determined by passing a given volume of PH_3 over red-hot copper, which has been previously weighed and which combines with the phosphorus. The hydrogen which remains may then be collected and measured. It has basic properties, but these are much less marked than those of NH_3, although with dry HI or HBr it easily forms phosphonium iodide and bromide, $PH_3 + HI = PH_4I$. The group PH_4, which behaves like a metallic radical, is called *phosponium* analogously to ammonium.

PHOSPHONIUM IODIDE forms colourless crystals, and is most easily obtained from P_2I_4 with a little water, or more precisely, by adding iodine to a solution of phosphorus in carbon disulphide, evaporating the mixture and treating it with water.

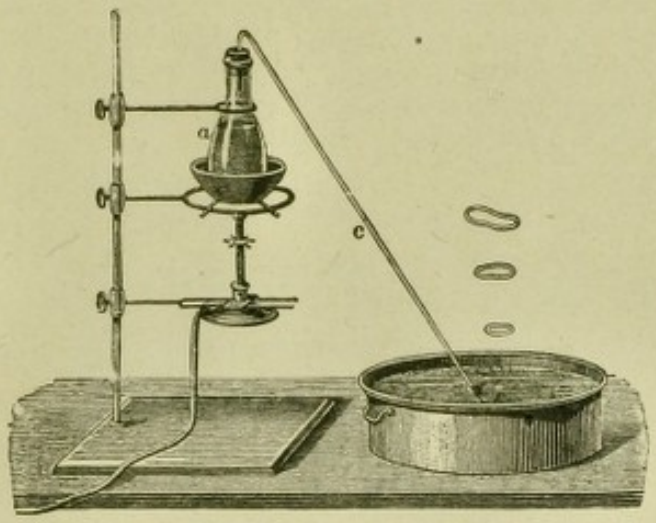


Fig. 142.

PHOSPHONIUM CHLORIDE: PH_4Cl, is only formed at − 30° and under pressure, and dissociates already at 15°. **PHOSPHONIUM BROMIDE** is solid and less stable than the iodide, but more so than the chloride: it dissociates at 30°.

LIQUID HYDROGEN PHOSPHIDE: P_2H_4. This compound is separated from PH_3 by passing the mixture obtained from calcium phosphide (*see above*) through a very cold tube. It is a colourless liquid which boils at 58° and decomposes easily into PH_3 and solid P_4H_2. It easily catches fire in the air.

SOLID HYDROGEN PHOSPHIDE: $P_{12}H_6$. This compound forms a yellow powder insoluble in water, which catches fire at 160°. Various forms of solid hydrogen phosphide are known, one of which perhaps has the formula, P_4H_2.

PHOSPHORUS TRICHLORIDE: PCl_3. This compound is obtained by passing a current of dry chlorine over a gently heated phosphorus in a small glass flask. The phosphorus catches fire, and PCl_3 distils together with a little PCl_5, which is transformed into PCl_3 on adding a little phosphorus and redistilling. It forms a colourless liquid of pungent odour, of sp. gr. 1·6, which boils at 76°, and is solid at −119°. It fumes in the air because it has a great attraction for water, giving HCl and phosphorous acid: $PCl_3 + 3H_2O = PO_3H_3 + 3HCl$. It is a good solvent for phosphorus, and mixes with ether, benzene, chloroform, and carbon disulphide; it is much used in laboratories, and costs about 3*s.* 7*d.* per k·lo.

PHOSPHORUS PENTACHLORIDE: PCl_5. This compound is obtained by the action of an excess of chlorine on phosphorus or by reacting on PCl_3 with still more chlorine, or by passing a current of Cl into a solution of phosphorus in carbon disulphide.

It is a slightly yellow crystalline mass of irritating odour, which attacks the eyes. It sublimes without melting and on heating decomposes partially into PCl_3 and Cl_2. It melts under pressure at 148°; it fumes in moist air because it reacts energetically with water forming three different derivatives according to the quantity of water:

$PCl_5 + H_2O = 2HCl + POCl_3$ Phosphorus oxychloride.
$PCl_5 + 3H_2O = 5HCl + PO_3H$ Metaphosphoric acid.
$PCl_5 + 4H_2O = 5HCl + PO_4H_3$ Phosphoric acid.

Its vapour density in an atmosphere of PCl_3 corresponds to the formula PCl_5; at higher temperatures, however, it commences to dissociate into $PCl_3 + Cl_2$. At 300° dissociation is complete and the gaseous mass has a greenish colour due to the free chlorine.

PCl_5 is often used in the laboratory, especially for many reactions in organic chemistry, when the OH group is to be replaced by chlorine. It costs about 4*s.* 5*d.* per kilo.

PHOSPHORUS BROMIDES and **IODIDES** are analogous to the chlorides, and are obtained by dissolving white phosphorus in carbon disulphide and then adding the calculated quantity of bromine or iodine a little at a time; carbon disulphide is then separated by distillation. The pentaiodide, PI_5, is not known.

Pure **PHOSPHORUS PENTAFLUORIDE: PF_5**, has been prepared by heating PCl_5 with arsenic trifluoride, $3PCl_5 + 5AsF_3 = 3PF_5 + 5AsCl_3$, and **PHOSPHORUS TRIFLUORIDE** is also known. These are more stable gases than PCl_5 and PI_3, and are extremely sensitive even to minute traces of water, which decompose them. Moissan was able to liquefy and solidify them in 1904. PF_3 melts at −160° and boils at −95°, whilst PF_5 melts at −83° and boils at −75°. Phosphorus oxyfluoride boils at −40°.

THERMOCHEMICAL BEHAVIOUR OF HALOGEN DERIVATIVES OF P. Whilst such derivatives of nitrogen are pre-eminently endothermic and explosive, the phosphorus halides are exothermic, that is to say, formed with evolution of heat, and are therefore more stable. In this respect they approach more nearly to the halogen compounds of the metals. Their heat of formation diminishes with increase of the atomic weight of the halogen, and this explains how it is that PI_5 is not known and why PF_5 is a more stable compound:

$$P + Cl_5 = PCl_5 + 439 \text{ Kj. } (= 105{,}000 \text{ cals.}).$$

Also on dissolving these compounds in water much heat is developed:

$$PCl_3 + 3H_2O + \text{aq.} = PO_3H_3 \text{ aq.} + 3HCl \text{ aq.} + 272 \text{ Kj.}$$

ARSENIC HYDRIDE (ARSENIURETTED HYDROGEN, ARSINE): AsH_3

This gas was discovered by Scheele in 1755 and is always obtained when a mineral acid such as HCl or H_2SO_4 acts on metallic zinc mixed with arsenic compounds. The nascent hydrogen which is formed unites with the arsenic: $As_2O_3 + 6H_2 = 3H_2O + 2AsH_3$.

It is also obtained from the alloy of Zn and As or of Na and As on treating it with HCl or H_2SO_4, thus: $As_2Zn_3 + 6HCl = 3ZnCl_2 + 2AsH_3$.

It is a powerful poison and the chemists, Gehlen in 1815, Bullacke, and recently Schulze at St. Jago, who worked with it without proper precautions, died after prolonged agonies through having breathed it in small quantities. Bunsen recommended fresh ferric hydroxide, prepared by precipitating a soluble ferric salt with magnesia, as an antidote. It has a repugnant odour of garlic; it is liquid at −55°. When lit it burns in the air with a pale bluish flame forming arsenic trioxide, As_2O_3. At a red heat or under the action of the electric discharge it decomposes into As and H; thus, by passing a current of AsH_3 through a glass tube which is heated at a certain point with a flame a black shining deposit of arsenic (mirror) is formed, and thus also, if a cold body such as a porcelain dish is placed in the flame of H and AsH_3, shining spots of arsenic are deposited on the dish. Arsenic hydride has less basic chemical properties than phosphorus hydride, so that it no longer combines with the halogen hydracids, whilst it has a tendency to combine with metallic salts, forming metallic arsenides. Thus, for example, with a concentrated solution of silver nitrate it gives a yellow precipitate, $AsAg_3 \cdot 3AgNO_3$, from which on dilution with water black metallic silver separates, arsenious acid and nitric acid being also formed (Gutzeit's reaction):

(*a*) $AsH_3 + 3AgNO_3 = 3HNO_3 + AsAg_3$ (Reckleben, 1909).

(*b*) $AsAg_3 + 3AgNO_3 + 3H_2O = 3HNO_3 + AsO_3H_3 + 6\,Ag$.

This reaction of Gutzeit is extremely delicate and is used for the detection of arsenic, as 0·001 grm. of As_2O_3 can still be detected; it is carried out practically as follows: A portion of the substance to be tested is placed in a test-tube and zinc and sulphuric acid are added; the test-tube is then loosely closed with a little cotton-wool in order

to retain any spray, and its mouth is covered with a strip of filter paper on to which a drop of a 50 per cent. solution of silver nitrate is poured. In the presence of even minimal traces of arsenic the filter paper acquires a yellow colour which turns to black on washing with water.

Since the same reaction is given by H_2S and by PH_3 it is necessary to first oxidise the substance by heating with HCl and potassium chlorate if there is any chance of these substances being formed.

By means of these reactions it is easy to detect even the smallest traces, even down to 0·01 mgrm. of arsenic, especially in poisoning cases, by introducing the substances into Marsh's apparatus (Fig. 143). This is formed of a flask, *a*, which contains pure zinc and pure dilute H_2SO_4 free from arsenic. The nascent hydrogen which is developed forms volatile AsH_3 with arsenic compounds, and is dried in a calcium chloride tube, *c*, and passed through the tube, *d*, which is drawn out at more than one point. This tube is then heated in front of the constriction, by which means AsH_3 is decomposed and deposits metallic arsenic in the drawn-out portions, in the form of black shining mirrors.

It is necessary to drive out all the air from the apparatus before heating and then the hydrogen at the end of the tube may be kindled (*see* p. 129).

The black mirror which is formed in the capillary tube, *d*, or on the porcelain capsule introduced into the hydrogen flame, is distinguished from similar spots formed of antimony, because the spots due to arsenic are soluble in sodium hypochlorite whilst those due to antimony are not.

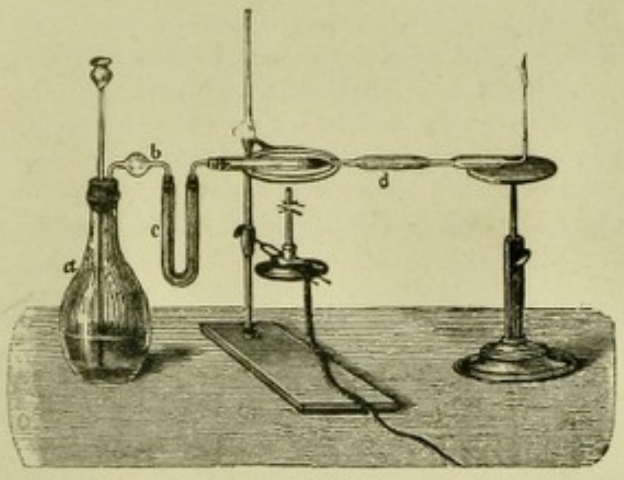


Fig. 143.

The compound, As_2H_4, analogous to P_2H_4, is not itself known, but its organic derivatives are known, for example, the organic derivatives of *cacodyl*: $(CH_3)_2 : As . As : (CH_3)_2$, which have an extremely repugnant odour and are obtained on heating potassium acetate to redness with arsenious oxide; cacodyl oxide is formed and serves for the recognition of small quantities of arsenic by means of its characteristic odour.

SOLID ARSENIC HYDRIDE: As_4H_2, is known as a brown powder, which is formed from AsH_3 in the absence of nitric acid.

ANTIMONY HYDRIDE: SbH_3

This compound is completely analogous to arsenic hydride in all its physical and chemical properties, and also produces black spots of antimony in Marsh's apparatus, at lower temperatures; these spots are less lustrous than those of arsenic and are insoluble in a solution of sodium hypochlorite.

With silver nitrate, SbH_3 gives a black compound of antimony and silver, $SbAg_3$, mixed with metallic silver.

The composition of the hydrogen compounds of As and Sb is determined as in the case of PH_3, by passing them over red-hot copper.

HALOGEN DERIVATIVES OF As AND Sb

These are analogous to those of phosphorus, and are formed by the direct interaction of their component elements. In the case of arsenic, however, the derivatives with five atoms of halogen are not known, but only in the case of antimony.

ARSENIC TRICHLORIDE: $AsCl_3$, is obtained by the action of hydrochloric acid on arsenious oxide in an analogous manner to the chlorides of the metals: $As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O$.

It forms an oily colourless liquid which fumes in the air. It has a specific gravity of

2·2, boils at 13°, and solidifies at −18°. It dissolves in a little water, remaining unaltered; with much water, on the other hand, it decomposes, forming As_2O_3 and HCl, the reverse reaction to that shown above.

ARSENIC TRIBROMIDE : $AsBr_3$, is a white crystalline mass; **Arsenic Tri-iodide**, AsI_3, is a red crystalline mass; and **Arsenic Trifluoride**, AsF_3, which is a liquid, is also known.

ANTIMONY TRICHLORIDE : $SbCl_3$. This compound is easily formed by dissolving antimonious oxide or sulphide in strong hydrochloric acid:

$$Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3.$$

The solution is evaporated and the $SbCl_3$ is then distilled.

When pure it forms a scaly crystalline mass which has about the consistency of butter (butter of antimony), and is deliquescent in the air.

It dissolves in water acidified with HCl, whilst in presence of much water it is decomposed, giving a white powder (powder of Algaroth) which is formed of a mixture of SbOCl, antimony oxychloride, and Sb_2O_3, and is used in medicine.

The instability of the halogen compounds of antimony and arsenic in presence of water is also characteristic of other non-metals, whilst the metallic chlorides are stable.

ANTIMONY PENTACHLORIDE : $SbCl_5$. This compound is obtained by the action of Cl on $SbCl_3$, and forms a yellowish, very hygroscopic liquid, which solidifies at −6° and decomposes on heating into $SbCl_3 + Cl_2$. At 21° and at reduced pressure it distils unaltered, and with much water it decomposes forming pyroantimonic acid ($Sb_2O_7H_4$) and HCl. With water it forms crystalline hydrates: $SbCl_5$, H_2O, and $SbCl_5 . 4H_2O$.

Derivatives of bromine, iodine, and fluorine are also known, and are analogous to the chlorides in their chemical behaviour.

ANTIMONIOUS FLUORIDE : SbF_3, is obtained by dissolving Sb_2O_3 in HF, and is of industrial importance because when mixed with sodium fluoride, NaF, it forms so-called *antimony salt*, which is advantageously used as a mordant in cotton-dyeing instead of tartar emetic, which costs more than double the amount with the same contents o antimony. Antimony salt, containing 47 per cent. of Sb_2O_3, costs about £4 per 100 kilos.

HYDROXYLAMINE : NH_2OH

This compound is a product of the partial reduction of oxy-compounds of nitrogen. It was prepared in 1865 by reducing the organic esters of nitric acid, but was only obtained pure and free from water in 1891. It is also formed by treating nitric acid with tin, or nitrogen oxides with HCl and tin.

Nascent hydrogen reduces nitric acid, nitrates, and nitrogen oxides:

$$NO_3H + 3H_2 = 2H_2O + NH_2OH.$$

Hydroxylamine hydrochloride is easily obtained by treating mercury fulminate ($C_2N_2O_2Hg$) with hydrochloric acid. It forms colourless, odourless crystals, melts at 43° and boils at 58° at reduced pressure (22 mm.).

It is a liquid which is stable below 15°; at higher temperatures it commences to decompose into N, N_2O_3, NH_3, and at about 130° it explodes.

It is hygroscopic; has basic characters and forms salts with acids, like ammonia, by direct addition: $NH_3O + HCl = NH_3O.HCl$, hydroxylamine hydrochloride, which is distinguished from ammonium chloride by being soluble in alcohol. The aqueous solution of hydroxylamine acts as a strong reducing agent, and thus separates silver from silver nitrate.

OXYGEN DERIVATIVES OF N, P, As, AND Sb

The acid compounds of the halogens, whether oxidised or otherwise, contain one atom of hydrogen; thus we have HCl, $HClO_3$, $HClO_4$; the compounds of the sulphur group contain two atoms of hydrogen, thus: SH_2, SO_3H_2, SO_4H_2, &c. (the same for selenium and tellurium); the compounds of the nitrogen group generally contain three atoms of hydrogen: NH_3, PH_3, AsH_3, SbH_3, PO_3H_3, PO_4H_3, AsO_4H_3, AsO_3H_3, &c.

These acids, containing three atoms of hydrogen, are called *ortho* or *normal* acids ; and by abstracting one molecule of water from these they are transformed into acids containing a single atom of hydrogen only, which are called meta-acids. Thus we have metaphosphoric, PO_3H (from $PO_4H_3 - H_2O = PO_3H$), and sodium metaarsenite which is formed from sodium orthoarsenite as follows : $AsO_3Na_3 - Na_2O = AsO_2Na$, Na_2O being separated instead of H_2O.

In the case of nitrogen the ortho-acids are not known but only the corresponding meta-acids. Thus, to the hypothetical orthonitric acid, H_3NO_4, ordinary nitric acid, HNO_3, corresponds. To the hypothetical orthonitrous acid, H_3NO_3, ordinary nitrous HNO_2 corresponds.

OXYGEN COMPOUNDS OF NITROGEN

Nitrous Oxide, N_2O, to which by the addition of 1 mol. of water, 2 mols. of hyponitrous acid NO.H correspond.

Nitric Oxide, NO, which has no known corresponding acid.

Nitrogen Trioxide or **Nitrous Anhydride**, N_2O_3 or O : N.O.N : O, which yields 2 mols. of nitrous acid, HNO_2, with H_2O.

Nitrogen Dioxide (or peroxide), NO_2.

Nitrogen Tetroxide, N_2O_4, which may be considered as a mixed anhydride of nitrous and nitric acids.

Nitrogen Pentoxide or **Nitric Anhydride**, N_2O_5, which forms nitric acid, NO_3H, with water.

NITROUS OXIDE : N_2O

This compound is easily obtained by heating ammonium nitrate to above 100°, $NO_3NH_4 = 2H_2O + N_2O$; towards 240° the reaction becomes tumultuous and even explosive, therefore it is preferable to heat a mixture of sodium nitrate and ammonium sulphate to 230°. The evolution of gas is regular, and it may be collected over mercury or over hot water, as it is somewhat soluble in cold water.

The formation of N_2O from an isomer of ammonium nitrate, namely, hydroxylamine nitrite, which already gives N_2O in aqueous solution, is of interest, $NO_2H . NH_2OH = 2H_2O + N_2O$.

It is also formed, together with NO, by treating zinc and tin with nitric acid of sp. gr. 1·1 ; also by the action of moistened iron filings on NO, and was thus obtained for the first time by Priestley in 1772, together with iron oxide.

Nitrous oxide is a colourless gas of a sweetish taste ; 1 litre weighs 1·97 grms. and 1 vol. of water at 0° dissolves 1·3 vols. of the gas ; it is still more soluble in alcohol. By pressure and cooling it is transformed into a colourless mobile liquid, which boils at − 89·8°, and when allowed to evaporate rapidly solidifies at −102° to a white crystalline mass.

It maintains and revives the combustion of phosphorus, wood, &c., more easily than nitric oxide, in spite of the fact that it contains less oxygen, because it is less stable, and immediately liberates the oxygen which it contains.

With an equal volume of hydrogen it forms an explosive mixture, and although in many respects it behaves similarly to oxygen it may be distinguished from the latter gas as it does not combine with NO, whilst oxygen and NO together form reddish-brown vapours of NO_2 and N_2O_3 ; it does not combine with oxygen, by which means it is easily distinguished from NO. When inspired in small doses it produces a form of inebriation, so that it has also been called "laughing gas." When inspired pure or mixed with 1 vol. of oxygen it acts as an anæsthetic and is used in surgery.

It is an endothermic compound and absorbs 75 Kj. during its formation.

HYPONITROUS ACID : $H_2N_2O_2$

This compound has been discovered during the last few years and is supposed to be derived from N_2O and H_2O ; this reaction, however, has not yet been effected, but, on the other hand, N_2O has been obtained by abstracting water from hyponitrous acid obtained by other means.

It is prepared in various ways—by reducing nitric or nitrous acid or by oxidisation of

hydroxylamine. Thus, for example, on reducing potassium nitrite with sodium amalgam, potassium hyponitrite is formed ; the sodium hydroxide formed by the amalgam is neutralised with acetic acid and the hyponitrous acid separated by means of silver nitrate as yellow, solid, amorphous, silver hyponitrite, which is decomposed with HCl. The hyponitrous acid so liberated is extracted with ether and the ethereal solution then evaporated *in vacuo*, when a scaly crystalline, unstable mass of free hyponitrous acid remains. It explodes easily and catches fire in contact with solid sodium hydroxide ; it is hygroscopic and soluble in alcohol, ether, and chloroform. It is slowly transformed in aqueous solution into $N_2O + H_2O$.

It separates iodine from potassium iodide and decolorises potassium permanganate, being transformed into nitric acid.

NITRIC OXIDE : NO

This compound was first studied by Priestley in 1772. It is not found free in nature because it readily combines with oxygen, forming nitrogen dioxide. It is formed from its elements at temperatures above 1200°, and industrially by the action of the electric discharge in air (*see* p. 304) ; but the gaseous mixture which results does not contain more than 1·5 per cent. of NO.

It is also formed on dissolving various metals in dilute nitric acid even in the cold, for example, from copper turnings and HNO_3 of sp. gr. 1·2 or from copper with concentrated nitric and sulphuric acids, but the yield is small :

$$3Cu + 8NO_3H = 3(NO_3)_2Cu + 4H_2O + 2NO.$$

A regular evolution of the gas is obtained from mercury with strong sulphuric acid to which 2 per cent. of sodium nitrite has been added.[1]

When all the air in the apparatus has been displaced red vapours of NO_2 are no longer formed, but only colourless NO which may be collected in a cylinder by displacement of water. The gas is obtained pure from a mixture of potassium nitrite, yellow potassium prussiate, and acetic acid. It is produced more conveniently, abundantly, and economically by Schlösing's reaction, by heating 1 part of sodium nitrate with 10 parts of ferrous sulphate and 10 parts of sulphuric acid of 52° Bé.

Nitric oxide is a colourless gas, only slightly soluble in water, but very soluble in solutions of ferrous chloride or sulphate which are coloured reddish brown ; from these solutions it is again evolved in a purified condition on heating. It also dissolves in nitric acid, forming brown, yellow, green, or blue solutions according to the concentration. With pure HNO_3 it forms nitrous anhydride, N_2O_3 ; it is insoluble in sulphuric acid (*see* Gay-Lussac Tower, p. 262). The constitution of nitric oxide is determined from the fact that when a given volume of it is treated with sodium Na_2O and N_2 are formed ; the latter gas occupies half the space which was at first occupied by the NO.

One litre of the gas weighs 1·3426 grms. It is only liquefied at −154°, and is solid at −167°. It is transformed by potassium permanganate into nitric acid. It maintains the combustion of substances which evolve much heat on oxidation, for example, phosphorus, but not sulphur. When mixed with carbon disulphide vapours it burns with an intense blue flame very rich in actinic rays.

It is a strongly endothermic compound (− 90 Kj. = − 21,500 cals.) and this explains the fact that its molecules are more unstable than those of oxygen, so that on burning substances such as P and C in an atmosphere of NO 21,500 cals. more are evolved than on burning the same substances in oxygen. This shows that in order to dissociate the atoms of an oxygen molecule more heat is required than to dissociate the molecule of NO.

By means of sufficient oxygen it is immediately and completely transformed into nitrogen dioxide : 2 vols. NO + 1 vol. O_2 = 2 vols. NO_2.

When a deficiency of oxygen is present nitrous anhydride, N_2O_3, is formed.

[1] This reaction is applied in connection with sulphuric acid manufacture in order to titrate the nitrous sulphuric acid in the nitrometer by liberating NO through the action of mercury and measuring the gas which is so formed (*see* Nitrometer).

With chlorine and bromine it forms nitrosyl chloride, NOCl, and nitrosyl bromide, NOBr.

At a red heat it forms NO_2 and N. It burns with hydrogen on heating, forming a greenish flame: $NO + H_2 = N + H_2O$. In presence of spongy platinum, on the other hand, it forms NH_3.

NITROSYL CHLORIDE : NOCl, is to-day used industrially for bleaching, especially for bleaching wheaten flour, according to Wesener's patent (Ger. Pat. 209,550 of 1908); its preparation has been suggested by passing a current of 2 vols. of NO and 1 vol. of Cl over bone charcoal at 60° (Francesconi and Bresciani, 1904), but it is difficult to obtain a good yield, and moreover combination also occurs in the cold and in absence of the charcoal. Its preparation by treating nitrosylsulphuric acid with sulphuric and nitric acids in presence of sodium chloride is more successful; or it may be obtained from nitric acid and dry sodium chloride with strong sulphuric acid; Cl and NOCl are evolved and the latter is condensed by means of ice and salt. It is a gas of brownish-orange colour which forms an orange-red liquid on cooling. This liquid boils between −8° and −6°, and is solid at −65°, forming crystals of a blood-red colour. It is easily decomposed by water. With sulphuric acid it forms nitrosylsulphuric acid and hydrochloric acid; it colours the skin yellow in the same way as strong nitric acid. With 1 kilo of nitrosyl chloride, diluted with a large quantity of air, 200 tons of flour may be bleached.

NITROGEN TRIOXIDE (NITROUS ANHYDRIDE) : N_2O_3

This gas is obtained from NO with a limited quantity of oxygen at −18°: $2NO + O = N_2O_3$; or by saturating liquid nitrogen tetroxide with NO: $N_2O_4 + 2NO = 2N_2O_3$, and also by passing NO into pure concentrated cold nitric acid. Helbig obtained it in the solid state in bluish-green flocks by passing the electric arc through liquid air. It then melts at −111°, after which it partially decomposes.

It is conveniently prepared by heating nitric acid of sp. gr. 1·25 with starch or arsenious oxide on the water-bath in a flask with a delivery tube, and condensing the vapours which are formed in a U-tube surrounded by ice:

$$As_2O_3 + 2NO_3H + 2H_2O = 2AsO_4H_3 + N_2O_3.$$

It is always formed when nitrates are heated with strong sulphuric acid to high temperatures.

N_2O_3 is fairly stable at −21° and forms a blue liquid of sp. gr. 1·44 at 0°, which boils at −3·5° and gradually decomposes, forming brown vapours: $N_2O_3 = NO_2 + NO$. These two gases re-form N_2O_3 in the cold; at a red heat it forms NO and also N.

With H_2SO_4 it forms nitrosylsulphuric acid which is immediately decomposed by water, forming nitrous vapours and sulphuric acid, as occurs in the lead chamber (*see* p. 253).

With a little cold water and still more readily with much hot water it is decomposed, forming HNO_3 and NO. A fresh aqueous solution of N_2O_3 is stable but *does not show the reactions of nitrous acid*, and it is quantitatively transformed by hydrogen peroxide into nitric acid whilst it is not completely oxidised by permanganate.

NITROUS ACID : HNO_2

This compound is not known free, but only in the form of its salts called *nitrites*, which are obtained by heating nitrates to redness: $NO_3K = NO_2K + O$; the reaction is facilitated by the addition of oxidisable metals such as lead. The nitrites give brown vapours of $NO_2 + NO$ with sulphuric acid.

Nitrous acid is supposed to exist free in aqueous solution. It is a strong oxidising agent and separates iodine from iodides, transforms sulphurous into sulphuric acid, ferrous

sulphate into ferric sulphate, and yellow potassium ferrocyanide into the red ferricyanide. Sometimes, however, it acts as a reducing agent ; thus it decolorises red solutions of potassium permanganate, being transformed into HNO_3. This reaction in dilute solution occurs quantitatively both for nitrous acid and for nitrites in presence of sulphuric acid, and on this reaction a quantitative method of analysing commercial nitrites is based. The end of the reaction is indicated by the disappearance of the red colour :

$$5NO_2H + 2MnO_4K + 3SO_4H_2 = 5NO_3H + SO_4K_2 + 2SO_4Mn + 3H_2O.$$

NITROSYLSULPHURIC ACID, $SO_2{<}^{ONO}_{OH}$ (or NITROSO-SULPHURIC ACID)

This acid has already been described in connection with the preparation of sulphuric acid (*see* p 252), and forms the well-known crystals of the lead chamber ; when dissolved in sulphuric acid it forms the so-called nitrous sulphuric acid. Mercury and also sulphur dioxide liberate NO from this acid and this explains the denitrifying action of the SO_2 in the Glover tower during sulphuric acid manufacture. It is always formed when nitrogen oxides (excepting N_2O) come into contact with sulphuric acid ; it is easily prepared by passing pure sulphur dioxide in the cold into fuming nitric acid until the latter is saturated ; a crystalline mass of nitrosylsulphuric acid then separates. These pure crystals melt at 73°, being transformed into the anhydride $S_2O_5(NO_2)_2$. It is decomposed by water into sulphuric acid and nitrous fumes ; it is soluble in sulphuric acid, its solubility increasing with concentration of the acid. This solution is colourless in the cold and yellow when hot. It is stable at high temperatures when the acid in which it is dissolved has a concentration greater than 60° Bé.

NITROGEN PEROXIDE : $(NO_2)_x$; NITROGEN TETROXIDE : N_2O_4 ; and NITROGEN DIOXIDE : NO_2

On passing the electric arc through a mixture of dry oxygen and nitrogen NO is first formed which with sufficient oxygen from the air is transformed into NO_2 (*see* conditions of its formation, p. 303).

It is conveniently prepared by heating dry lead nitrate :

$$(NO_3)_2Pb = PbO + O + 2NO_2 ;$$

the oxygen is then separated from the reddish-brown vapours of NO_2 by cooling below 0° until the latter are liquefied ; a yellowish liquid formed of N_2O_4 is thus obtained which is transformed at −20° into a colourless crystalline mass.

The tetroxide N_2O_4 is only stable below 0° ; at higher temperatures it gradually dissociates, forming NO_2, and at 150° the transformation into NO_2 is complete, as may be easily deduced from the gradual diminution in the vapour density on increasing the temperature. On again cooling to 0° the gaseous tetroxide, which is only very slightly coloured, is re-formed, whilst the gaseous dioxide has a red-brown colour. At −20° the tetroxide forms a white crystalline mass which melts at from −10° to −12°. Above 0° the liquid acquires a brownish-yellow colour and boils at 26°, forming red-brown vapours which steadily become darker with elevation of the temperature and consequent increase in the amount of NO_2.

With a little very cold water nitrogen tetroxide, N_2O_4, forms nitric acid and nitrous anhydride which colours the liquid blue :

$$2N_2O_4 + H_2O = N_2O_3 + 2NO_3H ;$$

with excess of cold water colourless nitric and nitrous acids are formed : $N_2O_4 + H_2O = NO_3H + NO_2H$, showing that nitrogen tetroxide is simply a mixed anhydride of nitric and nitrous acids, $NO_2{-}O{-}NO$ (analogous to chlorine tetroxide).

If hot water is used instead of cold water the nitrous acid is decomposed and evolves NO, whilst nitric acid remains : $3NO_2H = H_2O + NO_3H + 2NO$.

It is an energetic oxidising agent, maintaining combustion and separating iodine from soluble iodides. It differs from NO in not being very soluble in water, or even in sulphuric acid. Metals which have been recently reduced with hydrogen, for instance, copper, absorb up to 1000 vols. of N_2O_4, forming *nitro-metals* (Cu_2NO_2).

During the formation of NO_2 heat is absorbed (−22 Kj.), whilst during the formation of N_2O_4 from NO_2 heat is developed (54 Kj.).

NITROGEN PENTOXIDE : N_2O_5 (NITRIC ANHYDRIDE)

This is the most highly oxidised compound of nitrogen, and is obtained, together with metaphosphoric acid, by heating a mixture of nitric acid and phosphorus pentoxide to a moderate temperature in a retort : $2NO_3H + P_2O_5 = N_2O_5 + 2PO_3H$.

The distillate condenses as a solid in a flask cooled with ice.

It is obtained pure by the action of perfectly dry chlorine on dry silver nitrate $2NO_2OAg + 2Cl = NO_2ONO_2 + 2AgCl + O$.

Nitrogen pentoxide forms prismatic crystals of the rhombohedric system, melting at 30° and boiling at 47°. It decomposes easily, even with spontaneous explosion, and readily forms nitrogen tetroxide, N_2O_4, and O. It is immediately transformed by water into nitric acid with evolution of heat : $N_2O_5 + H_2O = 2NO_3H$. The heat of formation of gaseous N_2O_5 is zero. On passing into the solid state 55 Kj. are evolved, and on then dissolving in water a further 70 Kj. (16,750 cals.) are formed.

NITRIC ACID : HNO_3

This compound is rarely found free in nature, but is, on the other hand, abundant in the form of salts, as calcium, ammonium, and potassium nitrates, and especially sodium nitrate (Chili Saltpetre, *see* Part III), in regions with very low rainfall, such as Peru, Chili, and Bolivia. It is sometimes formed in minimal quantities by the action of electrical discharges on moist air, but more easily in the presence of NaOH, when sodium nitrate is formed ; it is formed in the soil through the oxidation of ammonia and ammoniacal salts.

HNO_3 is prepared in laboratories by distilling sodium or potassium nitrate with strong sulphuric acid in a retort, and collecting the nitric acid which distils in a glass flask cooled in a stream of cold water. The acid sulphate of sodium or potassium remains in the retort :

$$NaNO_3 + H_2SO_4 = NaHSO_4 + NO_3H.$$

This reaction already occurs at a temperature of about 130°, but if this temperature is much exceeded (above 200°) the acid sulphate can be converted into neutral sodium sulphate, so that a single molecule of H_2SO_4 is then able to decompose 2 mols. of the nitrate ; but the nitric acid which is formed at this temperature is decomposed into $NO_2 + H_2O + O$ and the NO_2 dissolves in the nitric acid which is first formed so that an acid of yellow-brown colour, called *fuming nitric acid*, is produced.

Until 1855 potassium nitrate was used technically for the manufacture of HNO_3 instead of sodium nitrate, in spite of the fact that the former was dearer, because the potassium nitrate crystallises more easily, and is therefore more easily obtained pure, so that a purer acid was obtained.

Since 1855, however, the improvements introduced into the purification of sodium nitrate (Chili saltpetre) have made it possible to obtain this salt in a very pure crystallised condition, and from that time it has been adopted exclusively in the nitric acid industry.

PROPERTIES. Nitric acid completely free from water has not yet been obtained, but concentrations of 99·8 per cent. of HNO_3 have been reached. This acid is colourless and fumes in the air. It has a specific gravity of 1·56, and solidifies at −47° to a crystalline mass ; it decomposes at relatively low temperatures, especially in direct sunlight, then acquiring a brownish-yellow colour through the formation of NO_2. It commences to boil at 86° and is slowly decomposed to a small extent, so that the first portions which distil are yellowish, whilst afterwards the distillate is colourless but contains a little water.

The vapours are decomposed at 260° : $2NO_3H = 2NO_2 + H_2O + O$.

It is extremely soluble in water, and on distilling dilute nitric acid water first passes over ; then at 121° an acid containing 68 per cent. of HNO_3 and of sp. gr. 1·414 distils, and this forms the concentrated nitric acid of commerce. If this acid is distilled with five parts of strong sulphuric acid, pure nitric acid almost free from water is obtained, and on passing a current of air through this acid a little NO_2 is liberated which remains in solution.

We give a Table of the various concentrations of nitric acid, but this does not apply to fuming (yellow) nitric acid, because the dissolved N_2O_4 increases the specific gravity in a very irregular manner :

Sp. gr. at $\frac{15°}{4°}$ (vacuum)	Degrees Baumé	100 parts by weight contain grms. of HNO_3	1 litre contains kilos of HNO_3	Sp. gr. at $\frac{15°}{4°}$ (vacuum)	Degrees Baumé	100 parts by weight contain grms. of HNO_3	1 litre contains kilos of HNO_3
1·005	0·7	1·00	0·010	1·305	33·7	48·26	0·630
1·015	2·1	2·80	0·028	1·315	34·6	49·89	0·656
1·025	3·4	4·60	0·047	1·325	35·4	51·53	0·683
1·035	4·7	6·37	0·066	1·335	36·2	53·22	0·710
1·045	6·0	8·13	0·085	1·345	37·0	54·93	0·739
1·055	7·4	9·84	0·104	1·355	37·8	56·66	0·768
1·065	8·7	11·51	0·123	1·365	38·6	58·48	0·798
1·075	10·0	13·15	0·141	1·375	39·4	60·30	0·826
1·085	11·2	14·74	0·160	1·385	40·1	62·24	0·862
1·095	12·4	16·32	0·179	1·395	40·8	64·25	0·896
1·105	13·6	17·89	0·198	1·405	41·6	66·40	0·833
1·115	14·9	19·45	0·217	1·415	42·3	68·63	0·971
1·125	16·0	21·00	0·236	1·425	43·1	70·98	1·011
1·135	17·1	22·54	0·256	1·435	43·8	73·39	1·053
1·145	18·3	24·08	0·276	1·445	44·4	75·98	1·098
1·155	19·3	25·60	0·296	1·455	45·1	78·60	1·144
1·165	20·3	27·12	0·316	1·465	45·8	81·42	1·193
1·175	21·4	28·63	0·336	1·475	46·4	84·45	1·246
1·185	22·5	30·13	0·357	1·485	47·1	87·70	1·302
1·195	23·5	31·62	0·378	1·495	47·8	91·60	1·369
1·205	24·5	33·09	0·399	1·501	48·2	94·60	1·420
1·215	25·5	34·55	0·420	1·503	48·3	95·55	1·436
1·225	26·4	36·03	0·441	1·505	48·4	96·39	1·451
1·235	27·4	37·53	0·463	1·507	48·5	97·13	1·464
1·245	28·4	39·05	0·486	1·509	48·6	97·84	1·476
1·255	29·3	40·58	0·509	1·511	48·8	98·32	1·486
1·265	30·2	42·10	0·533	1·513	48·9	98·73	1·494
1·275	31·1	43·64	0·556	1·515	49·0	99·07	1·501
1·285	32·0	45·18	0·581	1·517	49·2	99·34	1·507
1·295	32·8	46·72	0·605	1·520	49·4	99·67	1·515

In aqueous solution nitric acid is almost completely decomposed into the monovalent ions NO_3' and H'. It is an energetic acid and oxidises and dissolves almost all metals excepting platinum and gold. Ag, Cu, and Hg are dissolved on heating, but only in presence of NO, though traces of this gas suffice. It transforms almost all non-metals into the corresponding oxy-acids.

It is a strong oxidising agent which attacks organic substances. If turpentine is added to a mixture of nitric acid with a little sulphuric acid, it catches fire ; thus also if resinous coal is ignited it continues to burn if immersed in concentrated nitric acid. It transforms benzene directly into nitrobenzene,

which is an artificial substitute for bitter almond oil. (This only occurs in presence of strong sulphuric acid.—*Translator's note.*) Boiling HNO_3 transforms sulphur into H_2SO_4.

It oxidises wool and skin, colouring them yellow. It decolorises indigo, forming lower nitrogen oxides (NO and NO_2). Many metals, for example, zinc, are dissolved by dilute nitric acid without evolution of hydrogen, because the latter reduces the nitric acid to ammonia when in the nascent state ; and in the solution ammonium nitrate is then found together with the metallic nitrate.

$$2NO_3H + Zn = Zn(NO_3)_2 + H_2.$$
$$2NO_3H + 4H_2 = NO_3.NH_4 + 3H_2O.$$

If, on the other hand, the nitric acid is more concentrated, and contains above 10 per cent. of HNO_3, N_2O, N_2O_3, and N_2O_4 are formed instead of NH_3.

The transformation of nitric acid and of nitrates into NH_3 occurs still more easily in alkaline solution (in presence of NaOH with the nascent hydrogen produced from zinc dust, iron filings, &c.). Tin dissolves in nitric acid with formation of ammonia and also of hydroxylamine.

Nitric acid is monobasic and forms salts called *nitrates*, which are all soluble in water.

FUMING NITRIC ACID. This substance contains much nitrogen dioxide in solution, and has an orange-yellow or brownish-yellow colour.

It is obtained by the reaction between 2 mols. of nitrate and 1 mol. of sulphuric acid at temperatures of over 200°, so that disodium sulphate is obtained together with a portion of the nitric acid in the form of NO_2. It may also be easily prepared by distilling strong commercial nitric acid with strong sulphuric acid. Industrially, however, it is obtained by the direct addition of a little starch (3 to 5 per cent.) to the nitrate in the retort.

It is a more energetic oxidising agent than colourless nitric acid and has a specific gravity of 1·5 to 1·54.

AQUA REGIA. This substance is obtained by mixing 1 vol. of concentrated nitric acid with 3 vols. of concentrated hydrochloric acid. It is a liquid which has the property of easily dissolving gold and platinum, because the mixture contains free nascent chlorine and nitrosyl chloride (*see above*) :

$$3HCl + NO_3H = 2H_2O + Cl_2 + NOCl.$$

Neither of these acids separately dissolves the above metals.

INDUSTRIAL MANUFACTURE OF NITRIC ACID. The following advantages are obtained by employing sodium nitrate instead of potassium nitrate : Sodium nitrate costs less than half as much as the corresponding potassium salt, and the same weight produces about 20 per cent. more nitric acid, because the molecular weight of the potassium nitrate is higher. The sodium disulphate which is formed in the first phase of the reaction is more easily decomposed than potassium disulphate, so that the second phase of the reaction occurs at a lower temperature and there is less decomposition of the nitric acid.

In practice, however, it is not found convenient to force the reaction up to the second phase, and it is found preferable to remain at the stage of disulphate even though this has little or no value.

The glass retorts which were once used have now been completely abandoned and were first replaced by cylindrical, horizontal cast-iron retorts arranged in a furnace with direct flame, which were charged with 75 kilos of sodium nitrate and 80 kilos of sulphuric acid of 60° Bé. The nitric acid which was evolved as vapour was condensed in a series of vessels which have been specially described in an earlier portion of this work.

In France large stoneware pots were used by preference, with an almost vertical delivery tube reaching to the bottom in order to raise the molten disulphate ; they first had a capacity of 250 kilos of nitrate, but it was then found more convenient to increase the capacity until they could take a charge of 600 kilos of nitrate and 660 kilos of sulphuric acid of 66° Bé.

Both in the cylindrical retorts and in these stoneware pots the heat of the furnaces was badly utilised, and as much as 40 kilos of coal were used per 100 kilos of nitrate. The distillation lasted from 15 to 20 hours. Valentiner introduced important improvements in the whole apparatus used in nitric acid factories ; he introduced retorts of the shape indicated in section and plan in Fig. 144, which hold a charge of as much as one ton of nitrate. During heating the retort is evacuated in order to increase the yield with a smaller consumption of fuel. These large retorts are formed of two pieces which are joined with a flange and asbestos packing tightened by screws.

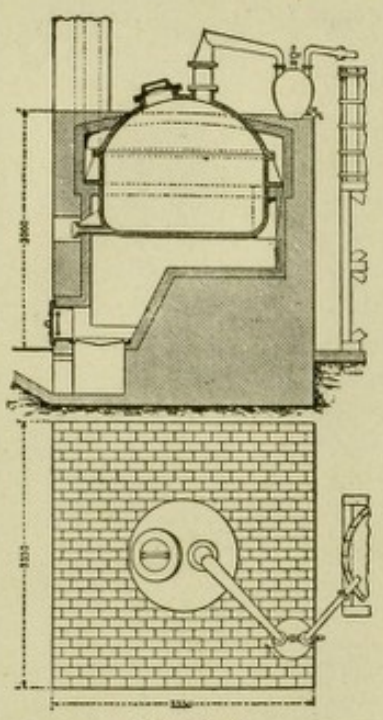


Fig. 144.

The upper tube which leads away the nitric acid vapours is simply screwed on to the still-head, and may thus be easily changed when corroded without having to change the whole pot. The HNO_3 vapours, instead of passing directly into the battery of condensers, first pass through a small condensing vessel where the salts which are carried over and the froth, which is often formed on working with sulphuric acid of 66° Bé., are separated. When working with acid of 60° Bé., less froth is formed. With this apparatus a purer acid is obtained ; the consumption of coal is reduced to 20 kilos per 100 kilos of nitrate and the duration of the process is only 12 hours.

In 1902 Valentiner and Schwarz (Ger. Pat. 144,633) introduced notable improvements which allowed the most concentrated nitric acid of almost 100 per cent., and very pure, to be obtained in a single operation, without the formation of froth, with the use of sulphuric acid of 66° Bé. Instead of adding all the sulphuric acid at once they pass it on to the nitrate a little at a time, dividing it in a suitable vessel before passing it into the retort, and thus the vapours of nitric acid which are gradually evolved are also passed into a vessel where they are washed with concentrated sulphuric acid, which retains the impurities, nitrous fumes, and steam. The vapours which escape from this vessel are pure and very concentrated, and on condensing give an acid of almost 100 per cent. strength.

Prentice devised an apparatus for automatic and continuous charging and discharging of the retort, but this has not given good results in practice, so that when the patent lapsed in 1898 it was not renewed.

In 1905 the Electron Works of Griesheim patented a process for concentrating dilute nitric acid by mixing it with an excess of sodium polysulphate $(SO_4)_2HNa_3$ and then distilling it at 120° to 130°. All the nitric acid was thus obtained pure ; the polysulphate loses all its water of hydration at 230° to 250°, and can then be used again.

The condensing plant is, however, much more important than the distilling plant, and after many changes has to-day reached a remarkable degree of perfection, so that all the gases which are evolved together with the HNO_3 vapours are obtained separately. These gases consist more especially of nitrogen trioxide, N_2O_3, HCl, nitrosyl chloride, chlorine, iodine (if the nitrate contains it), and probably also oxygen. The lower the temperature at which the sulphuric acid reacts with the nitrate the less nitrogen dioxide, NO_2, is formed. The HCl is formed by the action of the sulphuric acid on chlorides contained in the nitrate, and this HCl, in contact with nitric acid, is in turn partly transformed into chlorine and nitrosyl-chloride, $NO_3H + 3HCl = NOCl + Cl_2 + 2H_2O$, and since HCl, Cl, and NOCl are evolved at lower temperatures, these are found in the first products of distillation. If the nitrate contains perchlorates chlorine derivatives are also formed towards the end of the distillation. All these impurities are soluble in nitric acid, so that on simply condensing the vapours from the distillation, which was once the general practice and still is in certain works to-day, a very impure nitric acid is obtained, which

must then be separately purified, whilst in modern plants pure nitric acid is obtained directly.

The old condensing systems were formed of two batteries of seven double-necked receivers which were superposed in series, with a final condensing tower for the vapours which escaped from them. The condensation was caused by the cooling effect of the external atmosphere in which the receivers were placed, and one can thus understand how the working was irregular at various seasons, because the difference in the outside temperature in winter and summer is often one of 40° to 50°. The numerous joints also favoured the escape of gas, and such plants occupied much space. The yield did not exceed 90 per cent. of the theoretical amount of HNO_3.

The first improvement which was introduced was the initial cooling of the vapours in a stoneware coil immersed in cold water, by which means the number of receivers was diminished.

These coils of baked stoneware, which are difficult to construct, were first manufactured in England. For the last fifteen years they have also been manufactured by Rohrmann in Kranschwitz, near Moscow, and by the earthenware works of Bettenhausen, near Cassel. Since these coils are costly they are preceded, in order to preserve them from damage, by a receiver (Fig. 145) which slightly cools the acid vapours and retains the solid and liquid substances which are carried over. After passing through the coil the vapours which are not yet condensed pass through two or three receivers, and the last traces are retained in a plate tower (Lunge-Rohrmann, *see* p. 262), through which a spray of water passes. The remaining gases, before passing up the chimney, deposit their moisture in a final receiver which is provided with a window in order that the colour of the gases passing out of the tower may be noted.

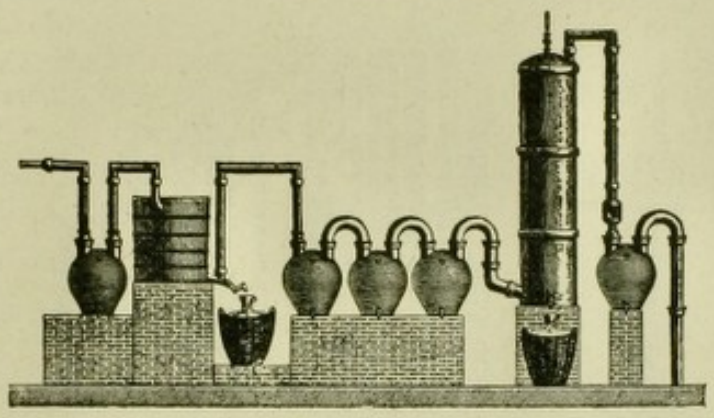


FIG. 145.

Acid thus prepared is of a strength of 36° to 42° Bé., though the last acid which distils is always more dilute because the temperature is higher and the sodium disulphate gives off water. It also contains a considerable quantity of nitrous fumes which colour the acid brownish yellow.

In order to decolorise and refine this acid it is necessary to heat it to a temperature of 60° to 80°, and a current of dry air is then passed through it. The operation is shortened by the direct employment of a current of hot air which simultaneously heats the acid and carries off the nitrous vapours. In 1888 Hirsch improved the method by slowly passing the crude acid through a coil immersed in hot water and passing a current of air up through the coil in a contrary direction. By carefully regulating the outflow, a colourless acid is obtained which is then cooled in a second coil surrounded by cold water, whilst the current of air saturated with nitrous fumes passes into the condensing tower. The addition of urea nitrate to the acid has been proposed in order to free it from nitrogen oxides, as it transforms them into $CO_2 + N + H_2O$.

In this manner such a coil can be used for the production of 100 kilos of colourless nitric acid per hour, which does not contain more than 0·3 per cent. of N_2O_3 and is free from chlorides.

In order to avoid the necessity for specially bleaching the acid Guttmann and Rohrmann bleach it directly during the distillation by employing a series of seven long vertical condensing tubes of stoneware (Fig. 146) communicating with one another below by means of a single tube which collects the colourless condensed acid, whilst a current of hot air is blown into the delivery tube of the distillation apparatus as is seen to the left of the figure, and carries the nitrous vapours which are not condensed through the final absorbing tower. The condensing tubes are immersed in a large vessel of water the temperature of which may be regulated and are preceded by the small receiver. By means of this apparatus

a concentrated acid is obtained with a yield of 98 to 99 per cent. of that required by theory; in some works the condensation is now effected in simple glass tubes.

In 1891 Valentiner introduced with advantage the employment of a vacuum in the whole apparatus by means of a pump stationed at the end of the system. The vapours which are not condensed finally pass through several receivers containing lime in order to absorb all the acid vapours and prevent damage to the suction pump. The lime must be frequently renewed.

In the first plant for working with a vacuum sulphuric acid of 66° Bé. could not be employed to react with the nitrate because too much frothing occurred, and acid of 60° Bé. was used, a more dilute nitric acid of 40° to 43° Bé. being thus obtained. This acid has to be concentrated by distilling it in vacuum with an equal weight of sulphuric acid of 66° Bé., the remaining, more dilute, sulphuric acid being used to decompose the nitrate. By a recent patent of Valentiner and Schwarz, which has already been mentioned, the process was much simplified and a very concentrated acid of 49·5° Bé. was directly obtained.

During the last few years the manufacture of nitric acid by combination of atmospheric nitrogen and oxygen in electric furnaces has become of great importance, especially in Norway (*see* p. 304), but on account of the difficulty and high cost of concentrating the dilute acid so obtained the greater part of it is directly transformed into calcium nitrate; since the process of electrolytic concentration (Ger. Pat. 180,052) proposed and tried by the brothers Paulin in the works at Innsbruck has not yet given satisfactory results, and concentration by distillation with sodium disulphate is also accompanied by certain inconveniences, attempts have been made to increase the yield of nitrogen oxides in the electrical furnace by injecting hydrocarbons (Ger. Pat. 209,966). It has also been shown that on burning carbon monoxide in presence of air in closed apartments under pressure nitrogen oxides and nitric acid are formed on rapidly cooling the CO flame against the cold walls (Fr. Pat. 396,375 of 1908).

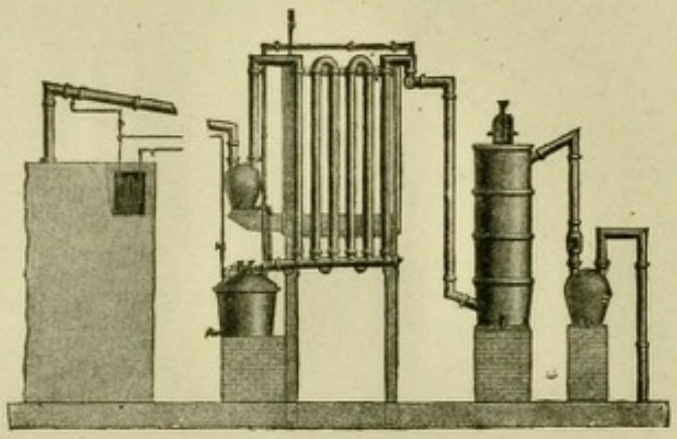


Fig. 146.

The day will come when nitric acid will be profitably prepared from synthetic calcium nitrate. In fact according to Ger. Pat. 208,143 dry calcium nitrate is treated with strong sulphuric acid and the operation started by the addition of a little nitric acid; the reaction then occurs even in the cold, with formation of concentrated nitric acid and insoluble calcium sulphate, which is separated by filtration.

Ostwald and Brauer (1902) continued the preceding experiments of Kuhlmann, who transformed ammonia into nitric acid by passing it, together with air, over platinum sponge heated to 300°. Ostwald observed that the yields were low because the reaction proceeded until free nitrogen was formed, and he therefore studied the conditions for fixing the intermediate product (nitric acid), using as a catalyst platinum plates and a little platinum sponge, and carefully regulating the current of gas: the process has been applied industrially at the Lothringen Hütte, near Bochum, where they start from ammonia from the ammonia liquor of a gas factory. Frank and Caro perfected the catalyst by the addition of a little tellurium oxide and cerium oxide. In this way they succeeded in transforming 85 per cent. of the NH_3 into HNO_3. Until now the manufacture of nitric acid has been almost completely based on the old process of the decomposition of sodium nitrate, which may perhaps one day be replaced by synthetic calcium nitrate. Hence the numerous improvements which are continually introduced in order to obtain a better yield with maximum economy by the ordinary process, by continually increasing the capacity of the retorts in order to work with larger charges of nitrate and by concentrating the nitric acid in plant constructed of inert iron (*see* p. 269). According to Fr. Pat. 406,969 of 1909, a great advantage is gained by using a continuous process of distillation, that is, by arranging five retorts in series at different levels and continuously passing the mixture of nitrate

and sulphuric acid from one retort to the next by means of syphons ; the first retort is heated to 110° to 120° and yields 60 per cent. of the total acid at a concentration of 96 to 97 per cent. of HNO_3 ; the second retort has a temperature of 150° to 170° and yields an acid of 88 to 90 per cent. ; the third is at 220° to 250° and yields an acid of 60 per cent. ; the fourth at 260° to 280° yields an acid of 15 per cent. ; and the fifth at 280° to 300° yields an acid of 3·5 per cent. and continuously discharges pure molten sodium disulphate.[1]

APPLICATIONS. Nitric acid is employed in the manufacture of sulphuric acid and of nitroglycerine, which is used for dynamite. It is also used in the preparation of picric acid, guncotton, organic nitro-compounds such as nitrobenzene, and ferric nitrate for dyeing. (At Lyons alone 10 tons of ferric nitrate are used daily for dyeing silk.) It is also used in the preparation of mercury fulminate, and in large quantities for the manufacture of smokeless powder, aniline dyestuffs, artificial silk, and for refining and treating the precious metals.

The most highly concentrated nitric acid is despatched in iron or leaden vessels, or in glass carboys which are packed in kieselguhr (infusorial earth). It is a strongly corrosive substance and a powerful oxidising agent, and sometimes produces fires when it comes in contact with organic matter.

When large quantities of nitric acid are accidentally spilt, it is not advisable to absorb it with sand or sawdust, but it is better to render it harmless with a powerful stream of water.

QUANTITATIVE EXAMINATION OF HNO_3. The approximate strength may be found from the density (*see* Table, p. 338),but for exact determinations it is necessary to titrate it after dilution with $\frac{N}{2}$ potassium hydroxide solution, and in order that the nitrous acid may not attack the methyl orange used as an indicator it is first poured into an excess of alkali ; the indicator is then added and the excess of alkali titrated back. In the case of fuming nitric acid the strength cannot be deduced from the density by means of the Tables which we have given, because the specific gravity is increased by the dissolved N_2O_4. Thus, the quantity of this oxide dissolved in concentrated acid of 48° Bé. (1·496) may be deduced by knowing that when 1 per cent. of N_2O_4 is dissolved the specific gravity is increased by 0·0030 ; with 4 per cent. by 0·0252 ; with 8 per cent. by 0·0532 ; with 12 per cent. of N_2O_4 the specific gravity of concentrated nitric acid is increased by 0·0785. From the density of fuming nitric acid, by deducting the increase due to N_2O_4 (which may be determined by dropping a given volume of fuming nitric acid into a measured volume of a titrated solution of potassium permanganate) (*see* p. 336), the strength of the true nitric acid may be found from the usual Tables independently of the nitrous acid which it contains.

Pure nitric acid should leave no residue on evaporating 50 c.c. in a capsule ; after dilution it should give no opalescence with $AgNO_3$ (chlorides) ; on concentrating 10 c.c. up to 1 c.c. and diluting with water to 100 c.c. it should not become turbid on adding a few drops of barium nitrate (sulphates or sulphuric acid) ; when diluted with a double volume of water and saturated with ammonia it should be unaltered by the addition of a few drops of ammonium sulphide and oxalate (heavy metals and alkaline earths).

PRICES AND STATISTICS. Nitric acid of 36° Bé. is sold at about £12 per ton, and acid of 43° Bé., pure and free from chlorine, at £18 per ton. Chemically pure acid of 38° Bé. costs £20 per ton, of 47° Bé. £34, of 48·7° Bé. (sp. gr. 1·510) £52 per ton. Pure yellow fuming nitric acid of sp. gr. 1·480 is sold at £34, and red fuming acid of sp. gr. 1·525 (49·5° Bé.) at £42 per ton.

The world's production of nitric acid in 1880 was 50,000 tons, of which 14,000 tons were produced in the United States ; and in 1890 it was 100,000 tons, of which 23,000 were produced in the United States.

[1] The sodium disulphate may then be utilised by the Oehler process (Ger. Pat. 136,923) for the manufacture of strong hydrochloric acid and sodium sulphate ; the disulphate is finely powdered and well mixed with a quantity of sodium chloride less than that required by the theoretical equation : $NaHSO_4 + NaCl = HCl + Na_2SO_4$. This mixture does not interact in the cold, but at 100° it reacts to the extent of 7 per cent., at 200° to 42 per cent., at 250° to 70 per cent., at 300° to 90 per cent., and at 400° to 98 per cent. It is heated in muffle-furnaces the internal temperature of which is 450° to 500°. In this way a pure sulphate and a pure and a very concentrated hydrochloric acid are obtained in the ordinary Cellarius receivers (*see* p. 162).

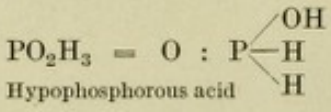
Since 1890 the production has greatly increased on account of the large consumption for the manufacture of smokeless powder. In 1880 Germany consumed 12,585 tons of nitric acid; in 1894 it produced 54,000 tons; in 1901 about 70,000 tons; and in 1909 it exported 2138 tons. Italy produced 2087 tons of nitric acid in 1903, only 1455 tons in 1905, about 2220 tons in 1906, more than 4800 tons in 1907, and 5562 tons in 1908, of the value of £106,600. (The imports were 10 tons in 1903, 15 tons in 1906, 38 tons in 1907, and 350 tons in 1908.) In 1893 the Italian production was 1990 tons. The production of the United States in 1908 was 50,000 tons.

OXYGEN AND HALOGEN COMPOUNDS OF PHOSPHORUS

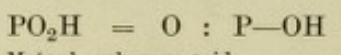
OXIDES

Phosphorus suboxide, P_4O. Phosphorus trioxide or phosphorous anhydride, P_4O_6 (or P_2O_3). Phosphorus tetroxide, P_2O_4. Phosphorus pentoxide or phosphoric anhydride, P_2O_5.

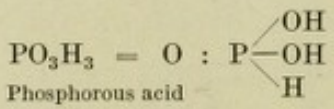
ACIDS



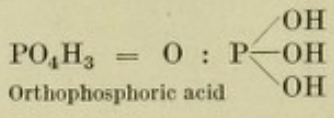
Hypophosphorous acid



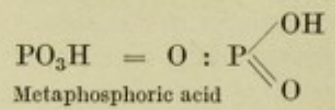
Metaphosphorous acid



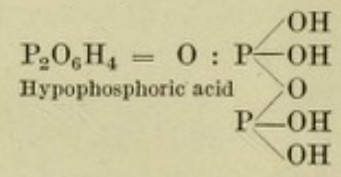
Phosphorous acid



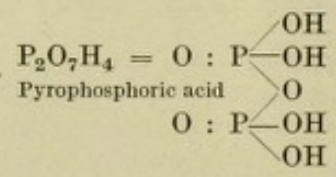
Orthophosphoric acid



Metaphosphoric acid



Hypophosphoric acid



Pyrophosphoric acid

The oxides combine with various quantities of water to form the corresponding acids:

$$P_4O_6 + 2H_2O = 4PO_2H \text{ (metaphosphorous acid)}$$
$$P_4O_6 + 6H_2O = 4PO_3H_3 \text{ (phosphorous acid)}$$
$$P_2O_4 + 3H_2O = PO_3H_3 + PO_4H_3$$
$$P_2O_5 + H_2O = 2PO_3H \text{ (metaphosphoric acid)}$$
$$P_2O_5 + 2H_2O = P_2O_7H_4 \text{ (pyrophosphoric acid)}$$
$$P_2O_5 + 3H_2O = 2PO_4H_3 \text{ (orthophosphoric acid)}$$

Theoretically the orthophosphoric acid should be $P(OH)_5$, but this compound does not exist; the phosphoric acid, PO_4H_3, ordinarily called orthophosphoric acid, is formed from this acid by the elimination of one molecule of water, and by the elimination of a further molecule of water metaphosphoric acid is obtained.

The basicity of these acids is given by the number of hydroxyl (OH) groups which are shown in the constitutional formulæ (*see above and* p. 48), as on acting on these acids with bases only the hydrogen of the hydroxyl groups is replaced by metals with formation of salts, and not that which is directly linked to phosphorus. The salts corresponding to the acids in the order in which they are given at the top of this page are called *hypophosphites, metaphosphites, phosphites, phosphates, metaphospates, hypophosphates,* and *pyrophosphates.*

PHOSPHORUS SUBOXIDE: P_4O (PHOSPHORUS PROTOXIDE)

When white phosphorus is dissolved in potassium hydroxide, previously dissolved in aqueous alcohol, H and PH_3 are evolved, and a bright red liquid remains which on acidification separates a gelatinous mass, mainly composed of P_4O; on filtering and repeatedly freezing, pure P_4O is obtained. It has an orange colour, is hygroscopic, and reacts with water, partially forming PH_3. At rather high temperatures it decomposes with formation of P_2O_5 and P. It is strongly attacked by halogens and by nitric acid.

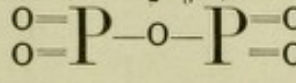
PHOSPHORUS TRIOXIDE : P_4O_6 (or P_2O_3) (PHOSPHOROUS ANHYDRIDE)

This compound is obtained on heating phosphorus gently in a tube in a current of dry air, the phosphoric anhydride which is formed at the same time, and which is less volatile, being retained by a plug of asbestos, whilst the phosphorous anhydride condenses in a cold flask. It may also be obtained by heating phosphorous acid with phosphorus trichloride: $2PO_3H_3 + 2PCl_3 = 6HCl + P_4O_6$.

It forms white crystals united to form a wax-like mass which melts at 22·5°, easily sublimes, and boils out of contact with the air at 173°. Its vapour density leads to the formula P_4O_6 ; the formula P_2O_3, which was used in the past, is therefore not correct.

It dissolves in cold water, forming metaphosphorous and phosphorous acids. It reacts actively with hot water, forming red phosphorus and phosphoric acid. At about 60° it catches fire in the air forming P_2O_5. At 400° it decomposes forming red phosphorus and **phosphorus tetroxide**, P_2O_4, which forms transparent crystals which yield phosphorous and phosphoric acids with water. P_2O_4 may thus be considered as a mixed anhydride of these two acids (analogous to nitrogen tetroxide, p. 336).

PHOSPHORUS PENTOXIDE : P_2O_5 (PHOSPHORIC ANHYDRIDE)



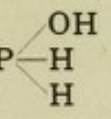
On burning phosphorus in iron cylinders in a current of dry air a soft, white powder, consisting of P_2O_5, is formed.

Since it also contains lower oxides it is purified by sublimation in a current of oxygen in presence of red-hot spongy platinum. It is known in two modifications : one is crystalline, sublimes at 250°, and, when heated to above this temperature, is transformed into the second modification, which is amorphous and only volatilises at a red heat, then condensing in the crystalline form.

It is extremely hygroscopic, so that it is deliquescent in the air, and dissolves very actively in water, producing a hissing sound, evolving heat and being transformed into phosphoric acid.

It is used in many chemical operations as it is the most energetic dehydrating agent known. It forms various acids with water (*see above*). It is placed on the market in hermetically closed vessels at a price of about 4*s*. per kilo.

HYPOPHOSPHOROUS ACID : $H_3PO_2 = O : P(OH)(H)(H)$



It is obtained by heating a concentrated solution of sodium hydroxide or lime or baryta water with white phosphorus ; PH_3 is formed together with sodium, calcium, or barium hypophosphite :

$$8P + 3Ba(OH)_2 + 6H_2O = 3Ba(PO_2H_2)_2 + 2PH_3.$$

Free hypophosphorous acid is obtained from the barium salt with sulphuric acid ; the liquid is filtered and concentrated at reduced pressure ; a syrupy liquid remains which sometimes crystallises in white scales, melting at 17°. In the heat it decomposes thus : $2PO_2H_3 = PH_3 + PO_4H_3$.

It has a great affinity for oxygen which transforms it into phosphoric acid, so that it is a strong reducing agent ; thus it reduces H_2SO_4 to SO_2, and then to sulphur ; it separates the metals gold, silver, and mercury from certain of their salts in solution ; it precipitates copper hydride, Cu_2H_4, on heating with copper sulphate, $CuSO_4$, and by this means is distinguished from phosphorous acid.

It is a monobasic acid, because it has only one hydroxyl hydrogen atom, which can be replaced by metals ; its salts, which are called *hypophosphites*, are soluble in water and are easily transformed into phosphates in the air. It is reduced by nascent hydrogen to PH_3.

METAPHOSPHOROUS ACID: $HPO_2 = O : P—OH$

This compound is formed in very slender crystals by the slow oxidation of phosphine at reduced pressure: $PH_3 + O_2 = H_2 + PO_2H$. It is also obtained from phosphorous anhydride with a little water. It is transformed by steam into phosphorous acid.

PHOSPHOROUS ACID: $H_3PO_3 = O : P(OH)(OH)H$

This compound is obtained by the action of phosphorus trichloride on water: $PCl_3 + 3H_2O = 3HCl + PO_3H_3$; the solution thus obtained is evaporated *in vacuo*, and a colourless crystalline rather hygroscopic mass, readily soluble in water, is thus obtained. It melts at 70°, and is decomposed at higher temperatures into phosphoric acid and phosphine, $4PO_3H_3 = PH_3 + 3PO_4H_3$.

It is also formed, together with phosphoric acid, hypophosphoric acid and ozone, by the slow oxidation of white phosphorus in moist air.

It is a strong reducing agent, as it abstracts oxygen from air and water, in presence of halogens, with formation of phosphoric acid. It precipitates the metals from solutions of silver nitrate, gold chloride, and mercury chloride; it differs from hypophosphorous acid by not reacting with copper sulphate.

Since it contains two hydroxyl groups it is a dibasic acid and forms two classes of salts: *neutral* and *acid phosphites*, two hydrogen atoms being replaced by metals in the former and one only in the latter. The phosphites differ from the hypophosphites by not being oxidised by the air, but are oxidised by strong oxidising agents. They separate metals from certain salts in the same way as phosphorous acid. On heating to redness they form hydrogen, pyrophosphates, and metallic phosphides. The phosphites of calcium and barium are insoluble in water.

With nascent hydrogen phosphorous acid forms PH_3. Certain compounds are known in which phosphorous acid appears to have a symmetrical constitution $P(OH)(OH)(OH)$.

PHOSPHORIC ACID: H_3PO_4 (ORTHOPHOSPHORIC ACID)

$O : P(OH)(OH)(OH)$

This acid is abundant in nature in the form of phosphates. It is obtained in the laboratory by dissolving P_2O_5 in hot water: $P_2O_5 + 3H_2O = 2PO_4H_3$, or by decomposing phosphorus pentachloride with water:

$$PCl_5 + 4H_2O = 5HCl + PO_4H_3.$$

It is also obtained from phosphorus oxychloride and water:

$$POCl_3 + 3H_2O = 3HCl + PO_4H_3.$$

It is prepared industrially by decomposing bone ash (tricalcium phosphate), by heating it with the calculated quantity of dilute sulphuric acid:

$$(PO_4)_2Ca_3 + 3H_2SO_4 = 3CaSO_4 + 2PO_4H_3.$$

It is obtained in a purer form by oxidising white phosphorus, first in the air and then with nitric acid and traces of iodine, and evaporating the solution; the acid then remains in the form of a syrup.

When free from water it forms prismatic colourless crystals deliquescent in the air, which melt at 38·6°; it is very soluble in water and the solution, which is strongly acid, evolves hydrogen with various metals. When heated to 200° to 300° water is evolved and pyrophosphoric acid, $H_4P_2O_7$, is formed, together with a little metaphosphoric acid. When heated to above 400° it is all transformed into metaphosphoric acid in the vitreous form.

Phosphoric acid contains three H cations, and is thus tribasic, forming three series of salts (*see* Part III, Calcium Phosphate, &c.). Thus we have:

NaH_2PO_4, *primary* sodium phosphate, monosodium phosphate, also called acid sodium phosphate ;

Na_2HPO_4, *secondary* sodium phosphate, or di-sodium phosphate, which is the ordinary laboratory preparation, called the neutral phosphate ;

Na_3PO_4, *tertiary* sodium phosphate, or tri-sodium phosphate, also called basic phosphate.

All the alkali phosphates and the primary phosphates in general are soluble in water and give a yellow precipitate of silver phosphate, Ag_3PO_4, with silver nitrate. This precipitate is soluble in ammonia and in nitric acid ; the other phosphates of the alkaline earths are insoluble in water.

Magnesium salts, in presence of ammonia, precipitate phosphoric acid or soluble phosphates in the form of magnesium-ammonium phosphate :

$$MgSO_4 + PO_4HNa_2 + NH_3 = SO_4Na_2 + Mg(NH_4)PO_4$$

(with $6H_2O$ of crystallisation).

The yellow precipitate which is formed by ammonium molybdate with phosphoric acid or phosphates in presence of nitric acid at a temperature of about 60°, is also of analytical importance ; the product has the formula : $PO_4(NH_4)_3.11MoO_3 + 6H_2O$ = *ammonium phosphomolybdate.*

Phosphoric acid is used in the preparation of various phosphates and also of hydrogen peroxide. The crude acid in paste form (48 to 50 per cent.) costs about £20 per ton ; the commercially pure liquid acid of 44° Bé. (40 per cent.) costs £14 ; the chemically pure solution of 34° Bé. costs 1*s.* 1½*d.* per kilo, and of 63° Bé. 2*s.*, and the crystallised solid 3*s.* 3*d.* per kilo.

METAPHOSPHORIC ACID : $HPO_3 = O : P{<}^{OH}_{O}$

This compound is formed by heating phosphoric acid to redness ; it is also easily obtained by treating phosphorus pentoxide with the calculated quantity of water : $P_2O_5 + H_2O = 2PO_3H$, or by heating diammonium phosphate : $(NH_4)_2HPO_4 = 2NH_3 + H_2O + PO_3H$.

It forms a transparent glassy mass which melts on heating, and evaporates without decomposition. It is the most stable and the most energetic at high temperatures of the oxy-acids of phosphorus. It is, however, very soluble in water, and therefore very hygroscopic. It is distinguished from ortho- and pyrophosphoric acids by its property of coagulating an aqueous solution of albumen. The aqueous solution of metaphosphoric acid is transformed at ordinary temperatures into orthophosphoric acid : $HPO_3 + H_2O = PO_4H_3$.

It contains a single atom of hydroxylic hydrogen and is thus a monobasic acid. Its salts are called metaphosphates and are prepared by heating the primary orthophosphates : $PO_4NaH_2 = H_2O + PO_3Na$. The reverse reaction is obtained on heating the metaphosphates with water. It forms a white precipitate with barium or calcium chloride, differing thus from pyrophosphoric acid.

Metaphosphoric acids, and corresponding salts, are known which are formed by the polymerisation of one or more molecules of ordinary metaphosphoric acid ; there appear to be well-defined di-, tri-, tetra-, and hexa-metaphosphoric acids : $[HPO_3]n$.

PYROPHOSPHORIC ACID : $H_4P_2O_7 = \begin{matrix} HO \\ HO \end{matrix}{>}P{=}O\ \ O{=}P{<}\begin{matrix} OH \\ OH \end{matrix}$ (O bridging)

This acid is obtained by heating orthophosphoric acid to over 210°, with separation of water : $2PO_4H_3 - H_2O = P_2O_7H_4$. A little metaphosphoric acid is, however, always formed at the same time, so that it is better to prepare it by heating disodium phosphate : $2PO_4HNa_2 = H_2O + P_2O_7Na_4$; the sodium pyrophosphate is dissolved in water and precipitated with a soluble lead salt ; the lead is then eliminated with H_2S and the solution filtered. On concentrating the solution of the free acid *in vacuo* a white crystalline mass remains, which is very soluble in water ; in course of time the aqueous solution is transformed into orthophosphoric acid.

It is a tetrabasic acid, and its salts are called pyrophosphates. However, only two series of salts are known, the di- and tetra-substituted salts ; these are stable, and only regenerate the normal phosphates under the action of mineral acids.

Pyrophosphoric acid is distinguished from orthophosphoric acid by giving a *white* precipitate of silver pyrophosphate with silver nitrate. It does not coagulate egg albumen, and is not precipitated by barium chloride, differing in these respects from metaphosphoric acid.

HYPOPHOSPHORIC ACID: $H_4P_2O_6 = O : P\begin{matrix}OH\\OH\end{matrix}O—P\begin{matrix}OH\\OH\end{matrix}$

This compound may be considered to be formed by the dehydration of one molecule of phosphoric acid and one molecule of phosphorous acid:

$$\left.\begin{matrix}PO_3H_3\\PO_4H_3\end{matrix}\right\} - H_2O = P_2O_6H_4.$$

It is obtained by the slow oxidation of moist white phosphorus in the air, together with phosphorous and phosphoric acids, from which may be separated by neutralising the mixture with NaOH, because it forms a sodium salt: $P_2O_6Na_2H_2 + 6H_2O$, which crystallises well, and is only slightly soluble in water; with aqueous barium chloride insoluble barium hypophosphate is obtained, which is then decomposed with dilute sulphuric acid; on filtering, a stable solution of free hypophosphoric acid is obtained. At temperatures below 30° it can also be obtained in crystals. At high temperatures it is decomposed into phosphoric and phosphorous acids. It is distinguished from phosphorous acid by not reducing metallic salts. It is a tetrabasic acid as it contains four atoms of hydroxylic hydrogen and four series of salts are known.

The following characteristic reactions suffice to distinguish ortho-, pyro-, and metaphosphoric acids from one another. Of the aluminium and chromium salts only the orthophosphates are soluble in acetic acid. Cobalt meta- and pyrophosphates have a red colour and are soluble in excess of the same phosphates, but insoluble in acetic acid; cobalt orthophosphate, on the other hand, is blue, insoluble in excess of orthophosphates, but soluble in acetic acid; in this way even traces of orthophosphoric acid may be detected in presence of the other two acids. Alkaline solutions of bismuth (and also amminocobaltic solutions) only form a precipitate with metaphosphates, soluble in excess of metaphosphates. The pyrophosphates alone give a precipitate with copper salts, which is soluble in excess of pyrophosphate; the ortho- and metaphosphates are not precipitated by copper salts.

VARIOUS PHOSPHORUS DERIVATIVES

PHOSPHORUS OXYCHLORIDE: $PCCl_3$. This compound may be considered as a chloride of orthophosphoric acid, in which the three hydroxyl groups are replaced by three atoms of chlorine. It is produced by treating phosphorus pentoxide with a little water: $PCl_5 + H_2O = 2HCl + POCl_3$, or preferably by distilling PCl_5 with phosphorus pentoxide: $3PCl_5 + P_2O_5 = 5POCl_3$, or with boric acid:

$$3PCl_5 + 2BO_3H_3 = 3POCl_3 + B_2O_3 + 6HCl.$$

By the action of ozonised air on phosphorus trichloride, the oxychloride is also formed by direct addition of one atom of oxygen:

$$PCl_3 + O_3 = POCl_3 + O_2.$$

Potassium chlorate also reacts energetically with phosphorus trichloride:

$$3PCl_3 + ClO_3K = 3POCl_3 + KCl.$$

It is a colourless liquid which fumes strongly in the air, of sp. gr. 1·68; it boils at 107° and solidifies below 2°.

It is decomposed by water into meta- and orthophosphoric acids:

$$POCl_3 + 2H_2O = PO_3H + 3HCl,$$

and with much water: $POCl_3 + 3H_2O = PO_4H_3 + 3HCl$.

Phosphorus oxychloride is also prepared by distilling 1 part of dry oxalic acid with 2 parts of PCl_5. It costs about 4*s.* 6*d.* per kilo.

The chlorine in $POCl_3$ can be replaced step by step by means of NH_3 with ammoniacal residues, and one thus obtains, for example, $POCl_2 . NH_2$ and $PO(NH_2)_3$; the compound
(Chlorophosphoric amide) (Phosphoric triamide)
$O : P\begin{matrix}(OH)_2\\NH_2\end{matrix}$, aminophosphoric acid, is also known and also $O : P\begin{matrix}OH\\(NH)_2\end{matrix}$ = diaminophosphoric acid; so are also $O : P\begin{matrix}NH_2\\NH\end{matrix}$, phosphamide, and $P_3H_3N_6$, phospham, &c.

PHOSPHORUS SULPHOCHLORIDE : $PSCl_3$. This compound is of analogous composition to the oxychloride, and is obtained by heating phosphorus trichloride with sulphur to 130°, or by the following reaction : $PCl_5 + H_2S = PSCl_3 + 2HCl$.

It forms a colourless liquid, which boils at 124° to 125°, of sp. gr. 1·6. It is decomposed by water, forming phosphoric acid, hydrochloric acid and hydrogen sulphide.

PHOSPHORUS TRISULPHIDE and PENTASULPHIDE : P_2S_3 and P_2S_5. These compounds are obtained by the direct interaction of sulphur and red phosphorus ; with white phosphorus explosions easily occur. They are crystalline yellow compounds ; the former boils at 540°, the latter at 520°, and melts at 275°. With water they form H_2S and phosphorous and phosphoric acids respectively. P_2S_3 is to-day used in large quantities for the manufacture of safety matches which may be struck on any surface.

P_2S_5 is often employed for the preparation of various organic products (thio-esters, &c.) ; with potassium sulphide it forms potassium thiophosphate, K_3PS_4.

PHOSPHATES, SUPERPHOSPHATES, and CHEMICAL FERTILISERS (*see* Part III).

OXYGEN AND HALOGEN COMPOUNDS OF ARSENIC

Arsenic trioxide, arsenious anhydride, $As_4O_6(As_2O_3)$.
Arsenic pentoxide, arsenic anhydride, As_2O_5.
Arsenious acid, H_3AsO_3 (not known in the free state).
Arsenic acid, H_3AsO_4.

ARSENIC TRIOXIDE, ARSENIOUS OXIDE : As_4O_6, or As_2O_3

This compound is commonly called *arsenic*, *white arsenic*, or *arsenious acid*. It is found in small quantities in nature as arsenolite, As_2O_3, in octahedric crystals and in various minerals. It is formed by burning arsenic, or arsenic minerals in general, in presence of air. As_2O_3, which is volatilised, is collected in suitable chambers. It is also formed as a white powder by oxidising arsenic with dilute HNO_3. It is ordinarily manufactured in large quantities from the dust which separates from pyrites gases (*see* p. 257), or from other arsenical minerals when they are roasted in a furnace. From such dust the As_2O_3 is obtained by sublimation.

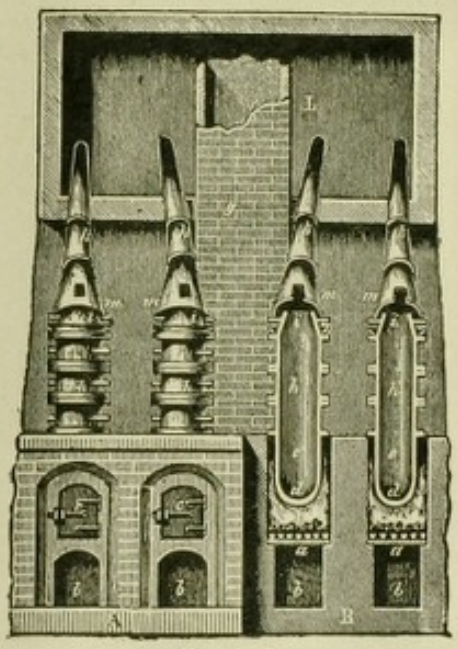


FIG. 147.

In order to purify it, it is sublimed from iron retorts and then on slow cooling forms an amorphous transparent glass-like mass (vitreous arsenic) of sp. gr. 3·74, which gradually becomes opaque like porcelain. If, on the other hand, the vapours are rapidly cooled it is obtained in a crystalline form. The crystals are regular and of sp. gr. 3·69 ; but in nature it is sometimes found in a monoclinic form known as claudetite, As_2O_3.

In some works the sublimation is carried out in vertical, cast-iron, cylindrical retorts, holding 200 kilos of the material (Fig. 147), and surmounted by two or three cast-iron cylinders, *h*, of which the uppermost contains an opening, *m*, in order to aid the removal of any obstructions in the bonnet-shaped tubes by which it is surmounted, and which enter a condensing chamber, *L*. The whole is heated by direct flame, the temperature being gradually raised and finally maintained constant for twelve days, and the chamber, *L*, is kept at such a temperature that the As_2O_3, which condenses as a powder, is softened, and forms a compact mass, which, after being removed from the furnace and cooled, forms compact glassy blocks, suitable for sale. In the Figure the chimney, *g*, which causes the

necessary draught is also shown. Regular blocks of vitreous or marbled white arsenic are obtained by compressing the powder in moulds and then heating the blocks so obtained more or less strongly and continuously. The workmen in arsenic works should wear overalls and a hood to cover the head, and their hands should be encased in gloves. They should also wash themselves with water containing a little ferric hydroxide (Bunsen's antidote).

PROPERTIES. When heated in the air it sublimes at 218° without melting. Amorphous arsenic trioxide dissolves in 25 parts of water; the crystalline form requires 80 parts of water; the solution has an acid reaction. It is easily soluble in HCl, but insoluble in alcohol: it has a sweetish taste, is odourless, and poisonous.[1]

In spite of its highly poisonous properties this compound is used as a stimulant for ill-nourished people and for rapidly fattening beasts for market.[2]

[1] *Investigation of Cases of Arsenic Poisoning.* Arsenic, especially in the form of As_2O_3 (white arsenic), is in common use in the arts and industries, and is sometimes also used for domestic purposes—for example, in paste form as a rat poison. It has no external properties which reveal its poisonous nature; it is a white, odourless, tasteless powder, and may inadvertently cause poisoning.

0·1 to 0·2 grm. of As_2O_3 when *dissolved* may be fatal to a man; whilst in the solid state, on the other hand, people have been known to swallow as much as 7 grms. without dying. It is then found in the body, more especially in the stomach, the spleen, the liver, and the intestines.

The symptoms of arsenic poisoning are nausea, burning in the stomach, continuous vomiting of slimy and even blood-stained matter, violent thirst, extremely painful cramp in the intestines, a hurried but feeble pulse, cold perspiration on the body with great internal heat, distressed and even contorted face. There follow convulsions, fainting fits, delirium, and finally death, which in rare cases occurs in a few hours, more often after one or two or even several days, sometimes even after a week. When poisoning has once commenced death is rarely prevented, and the medical man is only able to attempt to eliminate the still unaltered arsenic from the system by means of emetics. Bunsen's antidote, which is prepared from a solution of ferric sulphate containing 10 grms. of iron per 250 c.c. and 250 c.c. of magnesia suspension prepared with 15 grms. of calcined magnesia, is very effective. After this has settled and been decanted a spoonful may be given every half-hour. Sometimes the poisoned individual may be placed out of danger in twelve hours.

In legal processes the court relies especially on the chemical examination, which should therefore be conducted by an expert, because serious responsibility is implied. The materials which are ordinarily received for the investigation consist of the suspected food, of vomited matter, and the contents of the stomach and intestines preserved in pure spirit. The chemist should take every precaution that the material is not tampered with in his laboratory, and should guarantee this, and prevent the entry of any unauthorised person, by placing seals on the door, metallic netting over the windows, &c. When possible it is desirable to keep about half of the material received until the end of the process, so that it can be used for an eventual appeal. As far as is possible the quantity of arsenic should also be determined, because traces of arsenic are to-day found everywhere, especially in certain wall-paper pigments, in fabrics, and in the air, and as volatile products formed by the action of certain moulds, penicillium brevicaule, on non-volatile arsenic compounds. Thus in such cases the mere presence of traces of arsenic does not always prove poisoning.

Before the investigation is started it is necessary for the chemist to control his reagents in order to be certain that they are free from arsenic by making a blank test, that is, by making a complete test for arsenic in the reagents before the addition of the suspected material.

The material under examination is first minutely examined with a lens in order to search for any granules of arsenious oxide which may remain unaltered; in this case they are washed with water and then placed in a drawn-out glass tube, closed at the lower end, and a piece of charcoal is then placed above them and the whole heated in the flame. If arsenic is present a metallic mirror is formed in the upper portion of the tube. The charcoal is removed, the lower part of the tube is opened with a file, and it is then heated whilst held at an angle, the arsenic being thus transformed into a white coating of oxide, which on dissolving in hot water gives a characteristic yellow precipitate with silver nitrate.

If poisoning with arsenious oxide or arsenites is alone suspected, it is sufficient to distil the suspected matter with fused sodium chloride and a little pure sulphuric acid (an excess of acid produces SO_2). Arsenic trichloride, $AsCl_3$, is thus produced, which is volatile, and on distillation condenses in water and is precipitated carefully with hydrogen sulphide on warming. The As_2S_3 is then separated and examined apart.

When it is not known by what arsenic compounds the poisoning may have been produced the following general procedure is adopted. After the whole of the substance to be analysed has been well subdivided it is moistened with a little water, and as much pure HCl of sp. gr. 1·2 is added as there is solid matter present. It is then heated on the water-bath, adding a small piece of potassium chlorate every five minutes, and this process is continued until all the organic matter is decomposed. The whole is then heated, until finally a clear yellow liquid remains which no longer smells of chlorine. This is then filtered, saturated with H_2S at a temperature of 70°, and allowed to stand for twenty-four hours. Any precipitate which may have formed is collected on a filter and the liquid is tested with H_2S to see if any further precipitate is formed. The mass remaining on the filter may also contain lead, antimony, tin, &c. It is heated with ammonia, filtered, the liquid taken to dryness and evaporated again several times with nitric acid. It is then neutralised with sodium hydroxide and again evaporated to dryness. The residue is melted with a mixture of soda and pure potassium nitrate, free from chlorides, because these would form volatile $AsCl_3$ on heating. The fused matter is then digested with a little water and filtered. If Sb is present it remains undissolved. The arsenic in the filtered liquid is precipitated with H_2S in the manner already described, and the arsenic sulphide so formed may also be weighed in order to have an approximate figure for the quantity of arsenic which was used if poisoning has occurred.

On treating the sulphide with nitric acid and evaporating to dryness As_2O_3 is formed, which is dissolved in hot water and may then be introduced into the Marsh apparatus in order to obtain arsenic mirrors, soluble in sodium hypochlorite. These mirrors may be carried into court as legal evidence.

[2] It is usual to administer white arsenic in gradually increasing doses to cattle and to horses, because they then fatten more quickly and also acquire a glossy coat. The horses, when they sweat, then form a dense white froth, which is esteemed as a sign of a horse of pure breed. The animals may in this way be accustomed to large

It crystallises from hydrochloric acid in fine crystals, and during crystallisation the vitreous oxide becomes phosphorescent, whilst that which is opaque like porcelain does not show this phenomenon. On cooling vapours of As_2O_3 rapidly crystals of the regular system are obtained; but on cooling slowly monoclinic crystals are formed. Acids dissolve arsenious oxide, and on boiling the solution in hydrochloric acid arsenic trichloride, $AsCl_3$, is volatilised; with nascent hydrogen it forms arsenic hydride, AsH_3. When heated with carbon an odour of garlic is produced, and it is reduced to free arsenic which collects as a metallic mirror if the heating took place in a closed tube. With strong oxidising agents, such as Cl and HNO_3, it forms arsenic acid.

The size of the molecule varies with the temperature; vapours at 500° to 700° contain a double molecule, As_4O_6; above 700° dissociation commences, and at 1800° only molecules of As_2O_3 are present.

Its heat of formation is 647 Kj.

As_2O_3 is used in the preparation of numerous arsenical compounds, for the manufacture of certain pigments such as Schweinfurt green and Paris green, for the preservation of hides, for treating felt in hat manufacture, as a mordant in calico printing, in the production of glass, in agriculture for fattening beasts, and for keeping the hair of cattle and horses bright. At one time it was much used in aniline dyestuff factories, for reducing nitrobenzene. (*Translator's note.*—By this is not meant the production of aniline, &c., but the manufacture of magenta—fuchsine—and similar dyestuffs.)

Commercial As_2O_3 in lumps costs about £36 per ton and in powder £32; in 1909 the price fell to about half. Pure As_2O_3, in powder, for pharmaceutical use, is twice as expensive.

The world's production reached 6000 tons in 1903 of the value of £94,000 at a mean price of £16 per ton. Of this quantity 233 tons were produced in Canada, 2770 tons in Germany, 1088 tons in Spain, 917 tons in England, &c. The United States used about half of the world's production for the manufacture of Paris green and colouring matters and for agricultural purposes, importing about 2000 tons.

The production of the individual countries in 1903 was: United States, 600 tons; England, 917 tons; Spain, 1088 tons; Germany, 2768 tons; Canada, 233 tons.

Italy imported 275 tons in 1904; 147 tons in 1906 and 270 tons in 1908, to the value of £7580. In 1908 it produced 16·2 tons of the value of £375 17*s.*

ARSENIOUS ACID: $H_3AsO_3 = As(OH)_3$

This acid is not known in the free state; it perhaps exists in aqueous solution, although it appears to be dissociated into ions corresponding to the formula, H_3AsO_3, and more still into $HAsO_2$. Being a *tribasic* acid it is able to form three series of salts called *arsenites*. It ordinarily forms tertiary salts, for example, Ag_3AsO_3, which is of a yellow colour, and is obtained from the neutral solution of an arsenite with silver nitrate. The alkali arsenites are soluble in water and act as strong reducing agents, being transformed into arsenates, especially in presence of iodine. With silver nitrate in neutral solution yellow silver arsenite is formed which is soluble in acids and in ammonia. With H_2S in acid solution yellow As_2S_3 is precipitated, which is insoluble in acids but soluble in ammonium carbonate or sulphide.

doses without symptoms of poisoning. In the case of sheep as much as 15 grms. may be thus given per day. Before slaughtering such beasts it is, however, necessary to stop the arsenic treatment for at least fifteen days.

Certain men—the "Arsenic Eaters" of Lower Austria and Hungary—accustom themselves to doses of 0·25 grm. of arsenic per day, which they take in order to maintain themselves healthy and robust, and for the prevention of disease. Under the action of arsenic metabolism is rendered much more intense, but when the treatment with arsenic ceases the organism rapidly degenerates.

The alkali salts appear to have an asymmetric constitution derived from the hypothetical dibasic acid, O : As(OH)(OH)H, corresponding to phosphorous acid.

The arsenites of the other metals correspond to the formula, $H_6As_2O_6$, and are only slightly soluble or entirely insoluble in water. In cases of arsenic poisoning ferric hydroxide is administered as an antidote, as it forms an insoluble iron salt (*see* preceding Note).

ARSENIC PENTOXIDE : As_2O_5 (ARSENIC ANHYDRIDE, ARSENIC OXIDE)

This compound is formed by heating arsenic acid, H_3AsO_4, until no further water is formed : $2AsO_4H_3 = 3H_2O + As_2O_5$, and forms a white glassy mass of sp. gr. 3·73, slowly soluble in water with generation of arsenic acid. On heating it strongly to redness it gives off oxygen and forms As_2O_3, and this explains why on burning As in the air As_2O_3 alone is formed, as this is the more stable compound. Its true molecular weight has not yet been directly determined.

ARSENIC ACID : H_3AsO_4

This compound is formed by oxidising arsenic and As_2O_3 with concentrated nitric acid, and crystallises from the solution in rhombic prisms, $AsO_4H_3 + \frac{1}{2}H_2O$. At 100° it loses the water of crystallisation, forming H_3AsO_4, which is transformed at 140° to 180° into *pyroarsenic acid*, which forms white shining crystals : $2AsO_4H_3 = H_2O + As_2O_7H_4$. Pyroarsenic acid in turn loses water at 200°, forming white crystals of *meta-arsenic acid*, $HAsO_3$. These two latter acids regenerate arsenic acid with water. On heating a solution of arsenic acid in HCl, a portion of the former is volatilised as $AsCl_3$.

Ordinary or orthoarsenic acid is tribasic : O : As(OH)(OH)(OH), and forms three series of salts called *arsenates*, which are analogous to the phosphates and isomorphous with these. With silver nitrate in neutral solution it forms a *reddish-brown* tri-silver arsenate which is insoluble and analogous to silver phosphate, which is yellow, whilst arsenites in neutral solution, on the other hand, form a *yellow* precipitate. Hydrogen sulphide acts on acid solutions of arsenates forming a yellow precipitate of arsenic sulphide, insoluble in acid and soluble in ammonium sulphide or carbonate. With a mixture of NH_3, NH_4Cl, and magnesium sulphate (magnesia mixture) arsenates form a white crystalline precipitate of ammonium magnesium arsenate,

$$Mg(NH_4)AsO_4 + 6H_2O.$$

They also form a yellow precipitate, analogous to that produced by phosphates, on boiling with ammonium molybdate in presence of HNO_3.

Arsenic acid was at one time very much used in the manufacture of aniline dyestuffs. It is placed on the market to-day in strong solutions of 75° Bé. for use in calico printing at £36 per ton, or as a solid at £64.

ARSENIC SULPHIDES : As_2S_2, As_2S_3, As_2S_5

These are formed directly from the elements ; the two latter are also obtained from the arsenic oxides with H_2S (in which particular arsenic behaves as a metal) :

$$As_2O_3 + 3H_2S = 3H_2O + As_2S_3 ; \quad As_2O_5 + 5H_2S = 5H_2O + As_2S_5.$$

ARSENIC DISULPHIDE : As_2S_2. This compound is found in nature as a mineral, *realgar*, and forms ruby-red crystals of sp. gr. 5·5. It is prepared by melting together the calculated quantities of As and S.

It was used in painting, but its use has now been abandoned as it is poisonous. It is

used for fireworks, in the manufacture of rubber balloons, in calico printing (as a reducing agent for indigo) and also for removing the hair from hides. It costs about £40 per ton.

ARSENIC TRISULPHIDE : As_2S_3. This compound is also found in nature as the mineral *orpiment*, in yellow, crystalline, scaly lustrous masses of sp. gr. 3·4. Arsenious acid and arsenites in acid solution form with H_2S a bright yellow, amorphous precipitate of As_2S_3, insoluble in water and in acids, but soluble in alkalis or alkali sulphides ; when melted it forms a product similar to orpiment, but of sp. gr. 2·7. It is prepared industrially by melting As_2O_3 with sulphur. When boiled for a prolonged period with HCl it forms volatile $AsCl_3$. It was much used in oil pigments, but less is used to-day. It is used for the reduction of indigo, and is also sometimes used as a depilatory, and costs about £38 per ton.

ARSENIC PENTASULPHIDE : As_2S_5. This compound is formed, together with a little As_2S_3, on passing a copious stream of H_2S through an acid solution of arsenic acid or of an arsenate at 80° : $2AsO_4H_3 + 5H_2S = As_2S_5 + 8H_2O$; under other conditions, however, H_2S reduces arsenic acid to arsenious acid, with separation of sulphur. It is also obtained by melting the disulphide with sulphur ; also, as a yellow powder, by treating sodium sulpharsenate, AsS_4Na_3, with an acid. It is insoluble in water and acids.

SULPHOSALTS OF ARSENIC

These compounds are formed from arsenic sulphides (which may be considered as sulphoanhydrides) by dissolving them in alkali sulphides :

$$As_2S_3 + 3K_2S = 2AsS_3K_3 \; ; \; As_2S_5 + 3K_2S = 2AsS_4K_3.$$

They are also obtained from arsenates with H_2S :

$$AsO_4K_3 + 4H_2S = 4H_2O + AsS_4K_3.$$

The alkali sulphosalts form crystals soluble in water, whilst those of the other metals are insoluble. On attempting to obtain sulpharsenious or sulpharsenic acid by the action of HCl, decomposition occurs with separation of As_2S_5 and H_2S.

CHLORIDES AND IODIDES OF ARSENIC

ARSENIC TRICHLORIDE : $AsCl_3$. This compound is formed on burning arsenic in a current of chlorine, even at low temperatures. It is prepared by adding dry sodium chloride to a hot solution of As_4O_6 and concentrated H_2SO_4 ; the trichloride distils and is then condensed in an efficient refrigerator in the form of an oily, colourless, fuming, and very poisonous liquid of sp. gr. 2·205 at 0°. When pure and free from chlorine it solidifies at −18°, and boils at 134°. The formula As_2Cl_6 has also been attributed to this compound.

In contact with water it is partially decomposed into oxide and HCl until a definite equilibrium is established, which depends upon the concentration of the substances which are present, the reaction being reversible :

$$4AsCl_3 + 6H_2O \rightleftharpoons As_4O_6 + 12HCl.$$

The presence of sulphuric acid is necessary for the formation of arsenic trichloride from sodium chloride and As_4O_6, in order to combine with the water and prevent the reverse reaction. As_4O_6 is also transformed into $AsCl_3$ by an excess of HCl. Since $AsCl_3$ is volatile on heating, whilst the oxide is not, it is not permissible, during chemical analysis, to evaporate solutions of the oxide in presence of HCl or arsenic is lost ; in order to avoid this loss the solution is made alkaline, or it is oxidised with chlorates or nitric acid because arsenic acid is then formed on heating, and cannot form the corresponding pentachloride or any other volatile chloride, even in presence of much HCl. These facts are utilised in the elimination of arsenic from sulphuric acid (*see* p. 271), the arsenic being reduced to the state of arsenious acid with sulphur dioxide and a current of HCl then passed into the hot acid, thus rendering the arsenic volatile in the form of $AsCl_3$. The reverse process is also used in the *purification of hydrochloric acid* by oxidising the arsenic which it contains and then distilling it. Pure hydrochloric acid then passes into the distillate, whilst the arsenic acid remains behind.

The heat of formation of $AsCl_3$ is 299 Kj. ; the commercial product costs 12*s.* per kilo.

ARSENIC TRIBROMIDE, $AsBr_3$, which is colourless, melts at 25°, and boils at 220°, and **ARSENIC TRI-IODIDE, AsI_3,** a red solid, are also known, and are formed from the elements in presence of carbon disulphide ; they are decomposed by water.

ARSENIC PENTACHLORIDE : $AsCl_5$. This compound is formed by the action of chlorine on $AsCl_3$ at $-60°$. It forms yellow crystals which melt at $-40°$ and are soluble in ether ; at the ordinary temperature it is already decomposed into $AsCl_3 + Cl_2$.

OXYGEN AND HALOGEN COMPOUNDS OF ANTIMONY

The lower oxide (Sb_2O_3) possesses no acid characters, even when dissolved in water, but is somewhat basic, and thus forms salts both with acids and with bases, showing that antimony already has a somewhat pronounced metallic character. The pentoxide still possesses acid characters and thus forms antimonic acid which behaves in an analogous manner to phosphoric acid, so that the classification of antimony with the non-metals is justified.

ANTIMONY TRIOXIDE (ANTIMONIOUS OXIDE) : Sb_2O_6 or preferably Sb_4O_6

This compound is found in nature as *senarmontite*, in regular octahedra of sp. gr. 5·3, and as *flowers of antimony* in rhombic prisms of sp. gr. 5·57. It is not isodimorphous with As_2O_3, as was once believed. It is prepared by burning antimony in the air or by oxidising it with dilute HNO_3. It is volatile at very high temperatures, and its vapour density at 1560° corresponds to the formula Sb_4O_6. At still higher temperatures simple molecules of Sb_2O_3 are probably also formed. It forms a yellowish-white crystalline powder, consisting of both regular and rhombic crystals. It is insoluble in water, HNO_3, and H_2SO_4, but is soluble in HCl, tartaric acid, and alkalis.

The **HYDROXIDE**, $Sb(OH)_3$, corresponds to the oxide, Sb_2O_3, but is not analogous to arsenious acid, AsO_3H_3, and is obtained from tartar emetic with dilute sulphuric acid. It easily loses water, forming *antimonyl hydroxide* or *white meta-antimonious acid*, SbO.HO, which forms Sb_2O_3 on heating.

When either the oxide or the hydroxide, $Sb(OH)_3$, is dissolved in sodium hydroxide solution they form unstable salts called meta-antimonites, which are decomposed on simply evaporating their aqueous solutions.

Antimonious oxide, Sb_2O_3, or the corresponding hydroxide, $Sb(OH)_3$, and also the metahydroxide, SbO.OH, which is usually obtained by precipitating $SbCl_3$ with sodium carbonate, also form salts with acids (metallic character) ; for example, $SbO_3(NO_2)_3$ or $Sb(NO_3)_3$, antimony nitrate, and also the sulphate, $Sb_2(SO_4)_3$.

The SbO radical in the metahydroxide SbO.OH, which is called *antimonyl*, may be considered as a stable group, which has much the same function as a monovalent metal, so that the compound is analogous to K.OH, and as such forms salts $SbO.NO_3$, antimonyl nitrate, and $(SbO)_2SO_4$, antimonyl sulphate. A more important salt is *tartar emetic*, the double tartrate of potassium and antimonyl, $K(SbO)C_4H_4O_6 + \frac{1}{2}H_2O$, which is obtained by boiling a solution of cream of tartar (potassium hydrogen tartrate) with Sb_2O_3.

These salts, especially the organic salts, are, however, decomposed on simple dilution with water, which shows that antimonious oxide has only a *weakly* basic character.

Antimonious oxide is used as a substitute for white lead, because it has good covering power, and costs about £50 per ton.

On heating the trioxide in the air, it forms *antimony tetroxide*, Sb_2O_4.

ANTIMONY PENTOXIDE (ANTIMONIC ANHYDRIDE): Sb_2O_5

This compound is formed on oxidising antimony with fuming nitric acid or on heating antimonic acid to 300°. It consists of a bright yellowish powder of sp. gr. 5·6, insoluble in water and in nitric acid. It is soluble, however, in concentrated HCl, and also in aqueous solutions of alkali sulphides. On fusion with alkali carbonates it forms *antimonates*.

Above 300° it commences to decompose, forming oxygen and antimony tetroxide, Sb_2O_4, that is, $SbO_2.O.SbO$ (a mixed antimonious-antimonic anhydride), which forms a white powder becoming yellow on heating, and decomposes at about 950° into oxygen and

antimony trioxide, Sb_2O_3. Thus we see that, as in the case of arsenic, the more stable oxide at high temperatures is Sb_2O_3 (or Sb_4O_6).

ANTIMONIC ACID : H_3SbO_4. This compound may be obtained by heating antimony with concentrated nitric acid or by adding $SbCl_5$ to cold water :

$$SbCl_5 + 4H_2O = SbO_4H_3 + 5HCl.$$

It is obtained more conveniently by precipitating a solution of potassium antimonate with nitric acid ; potassium metantimonate is obtained by melting 1 part of antimony with 4 parts of potassium nitrate, and with water this forms monopotassium antimonate, KH_2SbO_4, which in turn yields antimonic acid with nitric acid.

It forms a white powder ($2H_3SbO_4 + H_2O$), almost insoluble in water and in nitric acid. It has a weakly acid reaction. It is a tribasic acid, but ordinarily behaves as though it were monobasic. At a temperature of 100° it already loses water forming *pyroantimonic acid*, $H_4Sb_2O_7$; at 175° it is transformed into *metantimonic acid*, $HSbO_3$, and at 275° this is then transformed into antimony pentoxide Sb_2O_5.

PYROANTIMONIC ACID : $H_4Sb_2O_7$, is more especially known in the form of its salts, among which dipotassium pyrantimonate, $K_2H_2Sb_2O_7 + 6H_2O$, is used as a reagent for the precipitation and recognition of sodium compounds, because it forms with these a crystalline disodium pyrantimonate, $Na_2H_2Sb_2O_7 + 6H_2O$, which is insoluble in cold water.

ANTIMONY TRISULPHIDE : Sb_2S_3. This is found naturally, crystallised in dark grey, rhombic, radiating and lustrous masses under the name of *stibnite*, the specific gravity of which is 4·7. It melts on heating and then distils (sublimes). When prepared by the precipitation of a salt of antimonious oxide in acid solution with hydrogen sulphide, it forms a red, amorphous mass which is transformed into a blackish crystalline mass on heating with dilute HCl. It is dissolved on heating with concentrated HCl, with formation of H_2S and $SbCl_3$.

CINNABAR OF ANTIMONY : $(Sb_2S_2O)_3$. This is found already formed in nature, and is also prepared artificially by treating $SbCl_3$ with a solution of sodium thiosulphate, or better still by heating Sb_2S_3 in a current of air and steam. It is used as a red colouring matter to replace ordinary cinnabar, and costs from £4 16*s*. to £16 per 100 kilos, according to the quality.

Mineral kermes, used in medicine, is a mixture of antimony trisulphide and antimony trioxide. It is obtained by boiling antimony sulphide with a solution of sodium carbonate.

ANTIMONY PENTASULPHIDE : Sb_2S_5. This substance is also called *golden antimony sulphide*. It is obtained from antimonic acid in weakly acid solution with hydrogen sulphide, or by treating a solution of sodium sulphantimonate, SbS_4Na_3, with dilute HCl or H_2SO_4, H_2S being formed simultaneously. It forms an orange-red powder, insoluble in dilute acids, whilst it dissolves in strong HCl, forming sulphur, H_2S and $SbCl_3$. On heating strongly it decomposes into Sb_2S_4 and sulphur.

The pentasulphide or golden sulphide was formerly much employed in medicine and in veterinary surgery. It is only used to-day to vulcanise rubber and to impart to it a red colour, and also in certain match factories. It costs from £80 to £140 per ton, according to its state of division, degree of colour, and free sulphur content.

SODIUM SULPHANTIMONATE (Schlippe's salt), $Na_3SbS_4 + 9H_2O$, is obtained by boiling Sb_2S_3 with sulphur and sodium hydroxide solution. It crystallises in large yellowish tetrahedra, which, on exposure to air, are rapidly covered with a brown layer of Sb_2S_5, because it is decomposed even by carbon dioxide. It is used in pharmacy for the preparation of golden antimony sulphide.

Free sulphantimonic acid is not known.

GROUP OF VANADIUM, COLUMBIUM, AND TANTALUM

This group is connected with the phosphorus group, especially on account of the analogy which exists between the derivatives of the one and the other group, and also because the more highly oxidised compounds have an acid character. In the free state, however, they are similar to the metals, especially to chromium, iron, and tungsten. The three elements are very rare.

VANADIUM : V, 51.2. This element was discovered by Del Rio in 1801, who confounded it with chromium. In 1830 Sefström characterised it as an element. It is found in nature more especially in *vanadinite*, $Pb_5(VO_4)_3Cl$, a chlorovanadate of lead, and is often accompanied by minerals containing iron, copper, nickel, uranium, &c. For some time the basic slag of the Creusot works in France has been treated for the extraction of vanadic acid.

It is obtained in the metallic state by heating vanadium chloride in a current of hydrogen. A greyish powder is thus obtained of metallic lustre and of sp. gr. 5·5. It is difficult to melt and is only oxidised very slowly in the air. It is obtained in silver-white crystals, which are, however, less pure, containing 4 per cent. of carbon, by heating vanadic acid and carbon in an electric furnace in a current of hydrogen. Its specific gravity is then 5·8. It burns when heated, forming vanadium pentoxide, V_2O_5. It combines easily with nitrogen, forming vanadium nitride, VN.

Derivatives analogous to those of phosphorus are well known, such as *vanadium trichloride*, VCl_3 ; *vanadium trioxide*, V_2O_3, which is obtained by heating V_2O_5 to redness in a current of hydrogen and forms a black powder. The corresponding *sulphate*, $V_2(SO_4)_3$, is also known, and forms alums with alkali sulphates in the same way as iron and chromium.

Vanadium pentoxide, V_2O_5, dissolves in alkalis forming salts of *vanadic acid*, H_3VO_4, and of *metavanadic acid*, HVO_3.

The *vanadates* are isomorphous with the corresponding phosphates. *Ammonium metavanadate*, VO_3NH_4, is insoluble in solutions of ammonium chloride and serves to separate vanadium from its ores. These are first melted with sodium hydroxide and potassium nitrate in order to obtain sodium vanadate, which is soluble in water. On adding ammonium chloride to this solution NH_4VO_3 is precipitated and yields V_2O_5 on heating. *Vanadious oxide* VO, a *dioxide* VO_2, a *dichloride* VCl_2, a *tetrachloride* VCl_4, and an *oxychloride* $VOCl_3$, are also known. *Vanadic salts* of the type VX_3, and *vanadious salts* VX_2, are also known. *Vanadious sulphate*, VSO_4, crystallises with $7H_2O$ and is isomorphous with various metallic sulphates.

Certain vanadium compounds are used industrially, for example, in the dyeing and printing of cotton (aniline black), as vanadic acid readily gives up oxygen to reducing agents, oxidising these, and thus acts as an oxidising catalyst. By the action of hydrogen peroxide on the oxides and acids of vanadium, peroxides and peracids of vanadium are obtained, and are variously coloured. Vanadium salts are sometimes used in the manufacture of glass and porcelain. The principal use of metallic vanadium is in metallurgy, especially in the preparation of special steels of high value. For this purpose vanadium is placed on the market at £4 to £4 8*s*. per kilo. This is obtained in the electric furnace. Pure vanadium costs more than £40 per kilo and vanadic acid costs more than £6 8*s*. per kilo.

COLUMBIUM : Cb, 93.5 (discovered by Rose in 1844) and **TANTALUM : Ta, 181.** These elements are found together in certain rare minerals, in the form of columbates and tantalates, for example, in *columbite*, $[(Fe.Mn)Cb_2O_6]$, and *tantalite*, $(FeTa_2O_6)$. The chlorides $NbCl_5$ and $TaCl_5$ are decomposed by water. This is also the case with the fluorides and the double fluorides, $2KF.CbF_5$ and $2KF.TaF_5$, which are used for the separation of the two elements, because the former is soluble and the latter insoluble in water. The oxides, Cb_2O_5 and Ta_2O_5, form with alkalis the salts of *columbic* and *tantalic* acids, CbO_4H_3 and TaO_4H_3. On heating columbic acid with carbon in the electric furnace free columbium is obtained, which is very resistant to the action of acids, similarly to boron and silicon.

Tantalum nitride, TaN, is also known.

Tantalum has now acquired great importance, especially on account of its application in the manufacture of electric lamps with tantalum filaments, prepared by the firm of Siemens and Halske. These lamps consume less than half the electric energy of the ordinary incandescent lamps with a carbon filament, for the same intensity of light.

Tantalum is now prepared in the pure state by first forming small rods of a paste of tantalum pentoxide and paraffin and then immersing these in charcoal powder at a temperature of 1700° ; brown tantalum tetroxide is thus formed and is a good conductor of the electric current ; this is then placed in a glass vessel which is evacuated and an electric current is then passed through it ; oxygen is evolved and pure tantalum remains. On the large scale the double fluoride of potassium and tantalum, $2KF.TaF_5$, is heated with metallic sodium and the metallic tantalum so obtained is purified by melting it in the electric arc *in vacuo*, after first rendering it a conductor by means of strong pressure.

Pure tantalum melts between 2250° and 2300°, and has a specific gravity of 16·6, a specific heat of 0·0365 from 10° to 100°, and a specific resistance of 0·165 for a length of 1 metre, and a cross-section of 1 sq. mm. On heating tantalum to redness and transforming it into a sheet with a mallet, and then heating it to redness and hammering it repeatedly, it finally acquires a hardness equal to that of the diamond and a greater power of perforation ; it is also remarkable for its high density and its resistance to chemicals, especially acids ; its extraordinary hardness is perhaps due to the presence of traces of oxide.

Since tantalum resists the action of acids, aqua regia and also alkaline solutions, it is now used instead of platinum for the preparation of electrodes and of vessels which are resistant to acids, chlorine, and oxidising agents. For this purpose the manufacturers start from tantalum hydride, which is considered by some as a stable alloy of H and Ta. This is worked to a paste and the objects to be prepared are moulded to the desired shape and heated to 1200°, when the hydrogen escapes and compact and homogeneous tantalum remains without the necessity of heating to the melting-point of 2300°.

Tantalum lamps are produced in a similar manner to incandescent carbon lamps by means of a small glass bulb which is evacuated, and in the interior of which is half a metre of very fine tantalum filament (0·05 mm. in diameter) which is arranged in zigzag form, being supported on small hooks which hold it taut. These lamps are sold at 2*s.* 6*d.*, of 25 or more candle-power.

CARBON GROUP : (C, Si, Ge, Sn)

This group comprises four elements, namely, two non-metals, carbon C = 12 and silicon Si = 28·3, and two metals, germanium Ge = 72·5 and tin Sn = 119.

All these elements are tetravalent and combine with the halogens forming compounds of the general formula, MX_4, in which M is the tetravalent element of this group and X the monovalent halogen. They all combine with oxygen forming compounds of the general formula, MO_2, which possess an acid character. On the other hand, whilst carbon and silicon readily form volatile hydrogen compounds in common with all the other non-metals, germanium and tin are clearly distinguished by not forming such, and generally behave as metals. We will, therefore, study them further in the portion of this volume devoted to metals.

CARBON : C, 12

This is one of the elements which are most widely diffused in nature and is the principal component of all organic compounds. It is also found abundantly in inorganic compounds, such as marble, dolomite, &c. In combination with hydrogen it forms petroleum, paraffin, &c. In combination with oxygen it forms carbon dioxide and carbon monoxide.

It is found naturally in the free state in three allotropic forms, namely, as diamond, which is crystalline and transparent, as graphite, and as amorphous carbon. None of these forms possess much chemical activity under ordinary conditions, although carbon in a state of combination is able to give rise to thousands of compounds.

Carbon does not melt even at 3500°, and in the electric arc it is volatilised directly. The three allotropic forms of carbon all burn in oxygen, yielding carbon dioxide.

These allotropic forms differ from one another by containing varying quantities of internal energy, which may be determined indirectly by measuring the thermal tonality of their conversion into CO_2 on burning 12 grms. of each of these allotropic forms separately in oxygen. Thus the thermal tonality of amorphous carbon is 97,650 calories, of graphite 94,910, and of diamond 94,310 ; from which we may deduce that during the transformation of 12 grms. of amorphous carbon into graphite 2840 cals. are evolved, and that in passing from 12 grms. of graphite to the same quantity of diamond a further 500 cals. will be evolved.

DIAMOND. This substance is more especially found in South Africa, whence diamonds of the total value of £140,000,000 have been extracted during the last forty years (at the Cape six new mines yielded diamonds to the amount of 34,000 carats in 1902 and 1903) ; in Brazil, from which about 2000 kilos of diamonds have been exported from 1727 up to date, and in India and Borneo. These diamonds are found mixed with siliceous sand and sedimentary rocks ; diamond is also found in meteoric iron. In 1906 Brazil exported diamonds to the value of £1,000,000 and black diamonds (carbonado) to the value of £840,000.

Diamond is generally considered as the hardest of all known substances and forms the degree of 10 on Mohr's scale ; however, crystallised boron is equally hard. Diamond is therefore used on account of this quality for cutting glass and for the cutting surfaces of rock-drills ; for this purpose coloured diamonds of small value are used.

It crystallises in the regular system, rarely in octahedra, and more often in rhombododecahedra. The crystalline faces are not perfectly plain, but are slightly convex. Diamond powder is of a dark grey colour and when very fine appears almost black.

If a diamond is colourless its high degree of transparency and refractivity constitute its very high value. When, however, the colorations, which are due to certain impurities, are very beautiful, they may even increase its value rather than decrease it. When it is coloured black it has no great value, is called carbonado, and is employed for rock-drills. When thus crystallised its specific gravity is 3·5, and its index of refraction, n, is 2·42. At very high temperatures, between the two poles of a powerful electric battery, it softens, swells up, and then assumes a graphitic appearance. Unlike graphite it is not a conductor of electricity.

In 1694 Averani and Targioni, of the Accademia del Cimento, succeeded in burning diamond. Lavoisier in 1775 and Davy in 1814 showed that on burning diamond in the air carbon dioxide alone was formed. It already burns in oxygen at 700°, giving CO_2, although it is not attacked by a mixture of nitric acid and potassium chlorate.

Various hypotheses on the origin of diamonds have been put forward, but none of them has any positive basis. It is, however, probable, according to Moissan, that they are formed from carbon, through the decomposition of organic matter at high temperatures and pressures in the interior of the earth. The carbon would thus be liquefied and would then crystallise during very slow cooling. It is also supposed that there may be large deposits of diamonds in the interior of the earth's crust. The other forms of carbon are obtained when diamond is heated to high temperatures without pressure and then evaporate without being liquefied, and are condensed at colder parts of the vessel in the graphitic form. Under the action of cathodic rays diamonds slowly turn brown.

Diamonds acquire a high value on being cut, that is, after facets have been formed, converting them into *brilliants* or into *rosettes*. Diamonds are cut by means of diamond dust. Diamonds of any value are weighed in conventional units.[1] At one time the

[1] The most celebrated diamonds are the following :

The *Regent* or *Pitt* diamond weighs 136½ carats, and weighed 410 carats before being cut. Its value has been estimated at more than £480,000, and it is the purest and finest stone which is known. It belonged to the Treasury of the French Crown and is to-day in the museum of the Louvre in Paris.

grain was used, which was the constant weight of a dried Indian seed, but to-day the *carat* is in use and corresponds to *four grains*, or to 205 milligrammes. The value of a diamond is not proportional to its weight, but the value of each carat increases with the increase of the total weight. However, the principal factor of the value is the purity of the water and the refractive power towards light. Diamonds weighing one carat cost on the average £8 ; if they weigh two carats they cost £16 per carat ; three carats £20 per carat ; five carats £24 per carat ; six carats about £25 per carat, &c.

In 1893 Moissan obtained *artificial diamonds* in very small scales up to 0·5 mm. long, and in 1905 he obtained some of 0·75 mm. diameter by saturating molten iron at a high temperature (1100° to 3000°) in the electric furnace with carbon and then cooling it rapidly. At such temperatures iron dissolves considerable quantities of carbon which remain enclosed in the iron on cooling under very high pressure.

Fused magnesium silicate also dissolves carbon, which then separates on cooling in the form of small scales of diamond.

GRAPHITE, BLACK LEAD, PLUMBAGO. This substance is found in nature, either crystallised, in hexagonal tablets, or in amorphous, lustrous masses. It has a greyish-black colour and is used for the preparation of pencils, for which purpose it was already used at the end of the sixteenth century. It is much used to-day for the construction of crucibles and all other bodies which have to resist very high temperatures, and also, in the form of very fine powder, for coating iron bodies in order to preserve them from rust.

It is distinguished from the diamond by forming *graphitic acid* with strong nitric acid and dry potassium chlorate. This is a yellowish crystalline substance (Brody's reaction) ; amorphous carbon gives carbon dioxide with this reagent. Charpy in 1909 obtained a more evident reaction with a mixture of strong sulphuric acid and potassium permanganate or chromic acid. With potassium permanganate in alkaline solution it forms mellitic acid, but this reaction is also shown by amorphous carbon. Graphite has a specific gravity of 2·1 to 2·25 ; it is a good conductor of heat and electricity, and conducts best when it is purest. Its electric conductivity increases with elevation of the temperature as is the case for conductors of the second class (electrolytes), and in this respect it differs from conductors of the first class (metals), of which, on the contrary, the conductivity increases on lowering the temperature. It

The *Polar Star* weighs 40 carats, is very pure, and belongs to the Crown treasures of Russia.

The *Orlow* weighs 195 carats and for a long time formed one of the eyes of a statue of Brahma. It was acquired in 1794 for £80,000, and was sold for an annuity of £640 yearly and a title of nobility for the vendor. It is to-day placed at the extremity of the sceptre of the Czar of Russia.

Southern Star. When found in Brazil it weighed 250 carats, and after cutting in order to transform it into a brilliant its weight was 125 carats.

The *Florentine* weighed 139½ carats. It has a slight yellowish tint which is not apparent in artificial light, when it appears very brilliant. It belonged to the Grand Duchy of Tuscany and now forms part of the Crown treasures of Austria. Its value is estimated at £100,000.

The *Nassak* is also a very celebrated diamond.

The *Great Mogul* now weighs 280 carats, whilst until the year 1600 it weighed 787 carats. Through the inexperience of some one who ordered it to be cut by an incapable person, it was greatly reduced in weight during cutting ; the artist, a Venetian, was then obliged to partially make good the damage. The Great Mogul originally came from India and now belongs to the English Crown.

The *Koh-i-noor* weighed 280 carats before 1850, and it is said to have been obtained from a fragment obtained in cutting the Great Mogul. It was acquired in 1850 by the English Crown, which had it cut in Amsterdam ; to-day it only weighs 106 carats.

The *Sancy* weighs 53½ carats. It was bought by Antonio of Portugal in 1489. It then passed to the King of France, and was bought in 1835 by Prince Demidoff of Russia for £80,000 and resold in 1836 in Paris for £26,000.

The *Shah* weighs 86 carats and is very pure. It was presented to Alexander II of Russia by a Persian prince, and has been set in a chain to be carried round the neck.

The *Pasha of Egypt* weighs 40 carats. It is a blue diamond, the beautiful and intense colour of which is due to minimal traces of metallic oxides. It was sold in 1908 to the Sultan of Turkey for £80,000 in spite of its comparatively small weight.

The *Great Victoria* is a large diamond which was found at the Cape in 1884 and weighs 457 carats.

The *Excelsior* was found in the Orange Free State at Jagersfontein in June 1893, and was then the largest diamond known, having a weight of 972 carats. It is a very fine diamond of a slightly bluish shade and was valued at £1,000,000. Its first proprietor was Bernheimer, who then deposited it in the Bank of England.

A diamond weighing 3032 carats was discovered on January 26, 1905, at Pretoria in the Transvaal, and had the form of a tablet (10 cm. × 6·25 × 3) at that time ; it had not then been cut and was supposed to have a value of £800,000. After cutting, however, it was found impossible to realise this figure, and the finest piece which was obtained was cut by experts at Antwerp and formed the brilliant Cullinan, weighing 800 carats, which is valued at about £100,000. It was then acquired by the Cape Colony, which presented it to the King of England in 1909.

is not altered, even at the highest temperatures, when out of contact with the air.

On heating in the air it combines with oxygen to form carbon dioxide, but with greater difficulty than diamond, and leaves 2 to 5 per cent. of ash.

Graphite is found abundantly in Cumberland (England), Brazil, Siberia, Ceylon, &c.

The more impure varieties are powdered and treated with potassium chloride and sulphuric acid; they are then washed with water and the residue is dried by heating. It contains silica, which is eliminated by treating it with sodium fluoride and H_2SO_4. Natural graphite is considered to be of good commercial quality if it contains 90 to 96 per cent. of carbon; samples containing 70 to 80 per cent. of carbon are said to be of medium quality, and those containing 40 to 50 per cent. only are considered inferior.

The carbon is determined quantitatively by heating 1 grm. of graphite to a high temperature with 40 to 50 grms. of litharge, in an analogous manner to Berthier's process for the analysis of coal (*see below*).

A certain quality of graphite in very fine powder is commercially called Brody's graphite, and according to the degree of fineness this costs from £4 to £10 per ton, but according to the degree of purity Ceylon graphite may cost from £60 to £140 per ton.

Graphites which swell on moistening them with strong sulphuric acid and then heating them to redness are also called *graphitites*. True graphites are those which do not swell under such conditions.

Graphite is artificially obtained by passing acetylene mixed with CO and CO_2 through red-hot tubes, or over red-hot calcium carbide: (*a*) $C_2H_2 + CO = 3C + H_2O$; (*b*) $2C_2H_2 + CO_2 = 2H_2O + 5C$; (*c*) $CaC_2 + CO = 3C + CaO$.

Artificial graphite is to-day prepared in large quantity, more especially for the manufacture of the electrodes which are employed in electrochemical industries, and which have to be very resistant to the most energetic chemicals. The process which is most used is that of Acheson (U.S. Pat. 568,523). He obtained it as a secondary product in the preparation of silicon carbide (carborundum) using as carbon petroleum coke mixed with pitch and silica or iron oxide. These latter substances act at a temperature above the evaporating point of their carbides as catalysers, and transform large quantities of carbon into graphite. When the graphite is to be used for pigments or for crucibles, anthracite is used as a source of carbon. The International Acheson Graphite Company work with power from the Niagara Falls in furnaces formed by channels of refractory material 9 metres long, lined internally with carborundum. The charge consists of 3 to 3½ tons of coal, and an alternating current of 1500 amps. at 210 volts is passed through from the ends; in the course of a few hours the current is raised to 3600 amps. and the temperature of graphite formation is then reached and is maintained for twenty-four hours. As the temperature gradually rises the conductivity increases and the current passing rises to 9000 whilst the voltage descends to 80, so that a current of about 1000 h.p. is used.

The Acheson Company produced 73 tons of graphite in 1897 and over 390 tons in 1900, 1500 tons in 1904, valued at £44,000, and at a mean price of £28 per ton; in 1907 the production was 3500 tons.

In America a further 2300 tons of natural crystalline graphite were produced in 1904 valued at £35,440, and in 1906 about 2700 tons were produced, together with 2800 tons of amorphous graphite, to which must be added 17,000 tons of imported graphite. In 1906 Ceylon produced more than 35,000 tons of natural graphite.

In 1904 Germany produced 3784 tons of natural graphite, valued at £8400, and imported 2628 tons of crude graphite, valued at £22,400; in 1905 it produced 4921 tons, and in 1909 imported 29,191 tons and exported 2387 tons.

7920 tons of natural graphite were produced in Italy in 1903, valued at £6000. In 1907 the production of the 22 Italian mines in Liguria, Piedmont, &c., was 11,000 tons, valued at £12,800, and in 1908 1600 tons of artificial electrode graphite were also produced, valued at £15,640.

In 1908 Italy produced 8781 tons of ground graphite, valued at £20,668. In 1906, 360 tons of graphite were imported and 4900 tons exported; in 1908 the imports were 383 tons and the exports 7009 tons, valued at £21,028.

COMBUSTIBLES. Wood and coal may be considered as true storehouses of solar energy. Coal especially is but a great accumulation of solar energy of a very far distant epoch, because there is no doubt to-day that coal was formed by the slow decomposition

of enormous quantities of plant residues buried under heavy layers of rock. The imprints which have been discovered in blocks of coal by means of suitable chemical treatment, aided by the microscope, have also shown that at that time certain regions were covered by dense forests of gigantic conifers. Through the enormous pressure, terrestrial heat, water vapour, and in all probability through the successive interventions of special micro-organisms, these buried vegetables—which are mainly composed of cellulose, that is, of hydrogen, oxygen, and carbon—gradually lost hydrogen and oxygen during a period of several hundred thousand years, thus becoming enriched in carbon. And according to the more or less advanced state of decomposition, we find in the various geological strata of the earth's crust peat and lignite which were formed after the cretaceous epoch, and contain 60 to 70 per cent. of carbon. In the older strata, before the cretaceous epoch, we find enormous deposits of common coal containing 90 per cent. of carbon, and, the most ancient of all, deposits of anthracite containing 96 to 98 per cent. of carbon. And now we are to-day consuming solar energy which was stored thousands of centuries ago, because a great portion of this was utilised in the growth of vegetable organisms. It has been calculated that every hectare (2·47 acres) of pine and fir woods grows 3½ tons of fresh wood each year, and we know that there are 4,500,000 hectares of forest land in Italy, 20,000,000 hectares in Sweden, 200,000,000 in the United States of America, and 323,000,000 in Canada. We may thus form a vague idea of the enormous annual accumulation of solar energy stored up by plants. We may also estimate this directly in calories by remembering that 1 kilo of wood furnishes, on burning, about 2800 cals. We may also note that only about 5 per cent. of the total solar heat is utilised by plants, whilst all the rest is utilised in heating the atmosphere, the soil, water, and all the various terrestrial bodies. 34,000,000 cubic metres of wood are consumed annually in Sweden, of which 17,000,000 are used for domestic purposes, 7,000,000 for wooden structures, 5,500,000 as fuel, 4,500,000 for wood-pulp, &c.

The treasure in the form of fuel which was formed in the bowels of the earth, and which we profit by daily, is truly enormous, because coal has been used by man for centuries, and in the nineteenth century, through the marvellous development of industry, the consumption gradually increased in a truly surprising proportion, increasing together with the progress of the enormous and various works of which it is a condition of life. We give a very significant Table[1] which requires no further explanation, because it explains in itself the philosophy of the marvellous progress of the nineteenth century:

[1] PRODUCTION AND CONSUMPTION OF COAL, EXCLUDING LIGNITE AND PEAT

Country	Production in millions of tons					Exports	Imports	Consumption
	1850	1880	1895	1904	Present			
Russia	—	3	8	16	18 (1907)	—	—	23 (1905) 25 (1907)
Austria-Hungary	1	6	10	12 ?	40 ? (1907)	—	—	19½ (1905) 24 (1907)
Belgium	6	17	19	24	24 (1907)	6½ (1904)	—	19 (1905) 23 (1907)
France	4	19	28	35	37 (1907)	—	13½ (1904)	50 (1908)
Germany	5	47	80	121	136½ (1906) 148½ (1908)	21½ (1904) 23½ (1909)	7½ (1905) 12 (1909)	107 (1905) 128 (1907)
England	46	149	192	260	272 (1907) 265·7 (1908)	65 (1907)	—	169 (1905) 182 (1907)
United States of America	6	60	172	352	480 (1907) 416 (1908)	8½ (1904)	—	343 (1905) 417 (1907)
Japan	—	—	—	11	13 (1907)	—	—	1 (1905)
Italy	—	—	—	—	0·5 (1908)	—	—	8½ (1908)
Spain	—	—	—	3	3·3 (1907)	—	—	5½ (1905)
Turkey (Anatolia Heraclea)	—	—	—	—	0·7 (1906)	—	—	—
Canada	—	—	—	7¾	10·5 (1907)	—	—	13 (1905)
Australia	—	—	—	7½	11 (1907)	—	—	¼ (1904)
British India	—	—	—	8½	11 (1907)	—	—	1 (1905)
China	—	—	—	—	11 (1907)	—	—	—
Sweden	—	—	—	0·2	—	—	—	—
Transvaal and Cape Colony	—	—	—	4	3·3 (1909)	—	—	—
Other Countries	1	1½	2	2½	5 (1907)	—	—	—
World's Production	69	302½	511	862	990 (1905) 1018 (1907)	—	—	—

In Germany in 1905, 427,000 men were employed in the coal mines, which produced 121,300,000 tons of coal.

Italy possesses no coal deposits, and Italian industry has therefore to depend entirely upon coal which is imported, especially from England. Though during the last few years very rapid progress has been made in the rational and large-scale utilisation of hydraulic energy, the importation of coal is constantly increasing and indicates the very considerable progress of Italian industry. We will now give some instructive figures on the importation of coal into Italy :

			£
In 1880	1,737,746	tons of coal and coke, valued at	1,920,000
1885	2,957,436	,, ,,	
1895	4,304,787	,, ,,	
1900	4,917,180	,, ,,	
1904	5,904,578	,, ,, valued at	6,040,000
1906	7,673,435	,, ,, ,,	8,600,000
1907	8,300,500	,, ,, ,,	9,280,000
1908	8,452,300	,, ,, ,,	10,480,000

The Italian Royal Navy consumes 30,000 tons of coal per year in the arsenals and harbour services, and 100,000 tons in warships. The railway consumes about 1,000,000 tons of coal, whilst the French railways consume about 6,000,000.[1] Italian gasworks distilled 1,059,000 tons of coal in 1908.

Considering the growing world-consumption of coal, which is not arrested even by the imposing hydro-electric installations which have been erected of late years, the question continually arises whether if the demand continues at the present rate we are not quickly and unconsciously approaching the exhaustion of the coal-seams and therefore the future ruin of industry and a terrible unknown future for the whole of humanity.

Capable technologists and competent commissions have studied the problem, and from investigations seriously carried out in various countries, it is found that a prosperous future may be tranquilly awaited, because in Belgium alone the coal still contained in the seams is estimated at 23,000,000,000 tons, and in England and Ireland the deposits still buried underground are at least 190,000,000,000 tons. In Germany there are still about 300,000,000,000 tons and in North America about 2,000,000,000,000 tons under ground. In France there are 19,000,000,000, in Austria 13,000,000,000, and in Russia 40,000,000,000 tons. From this it may be easily foreseen that the lead in European coal production, which to-day belongs to England, will pass to Germany before many years have passed, and that later Europe will derive its supplies from America, which has already commenced to sell coal to France and Russia. It is not possible for us to discuss here the great progress which has been made in coal-mining in connection with methods of extraction of the black and precious mineral, and the method of constructing the shafts and the galleries in order to easily arrive at the thinner coal-seams. We are not able to pause to consider all the progress made during the last century in the construction of coal-mines in order to render the work less difficult to the hundreds of thousands of meritorious workers who pass half their lives in the dark and disagreeable depths of the earth, often losing limbs and even life in the still all too frequent explosions of the terrible firedamp which is released from the carboniferous seams and which on mixing with air or with dust catches fire and explodes in a terrible manner through a spark struck from the rock by the pick of a miner or from a badly closed lamp. In a moment the exit gallery is obstructed by heaps of corpses and holds the dead, the living, and the wounded in one tragic whole. The survivors and wounded are often drowned by water which invades the mine on account of the destruction of the pumps by the force of the explosion. And thus of this army of humble but heroic workers who extract the coal to serve for heating purposes, and as the lifeblood of all our industries, entire regiments of the best men are sacrificed every year in order to benefit the community ; but the frequency of these cruel disasters, which is still terribly great, is sometimes only to be explained to-day (now that science has made

[1] In Italy English coal is mainly consumed, and the types which are most commonly placed on the market are the following, to which we add the price per ton on board at Genoa and Venice, prices which frequently vary and which are only given in order to compare the qualities : Cardiff 1*a*, £1 4*s*. 9½*d*. ; New Pelton, £1 ; Cowdenbeath, £1 4*s*. ; Newcastle, £1 1*s*. 8*d*. ; Best Hamilton, £1 ; Scotch, 19*s*. 2*d*. ; Cardiff briquettes, £1 5*s*. 7*d*. ; Anthracite smalls, 16*s*. ; Anthracite (according to size from peas to nuts, &c., also for power gas), £1 10*s*. 5*d*. to £1 16*s*.

so much progress and done so much to prevent them) by the culpable carelessness of the masters, or by the ignorance and carelessness of the men.[1]

A less dangerous process of mining coal has now been proposed, and has been applied in certain cases, namely, by means of water pressure up to 500 atmospheres instead of explosives, and there are also special safety explosives which are manufactured for use in mines (*see* vol. ii, " Organic Chemistry ").

FOSSIL CARBON (peat, lignite, common coal, and anthracite) is formed by the decomposition of enormous masses of vegetable residues of periods which are earlier than our own (*see above*). Peat and lignite were formed after the cretaceous period, for the greater part of the tertiary period and to a certain extent in the diluvial period. Common coal and anthracite, on the other hand, were formed before the cretaceous period. The cellulose of the wood has gradually lost oxygen and hydrogen under the influence of heat, great pressure, water vapour, and the action of micro-organisms, and become richer in carbon, first forming peat which contains about 60 per cent. of carbon (+ 6 per cent. of hydrogen and nitrogen), then lignite containing 65 to 75 per cent. of carbon, and finally common coal containing about 90 per cent. of carbon, 3 per cent. of hydrogen, 2 per cent. of oxygen, nitrogen, and 5 per cent. of ash. Anthracite is the oldest form of fossil carbon and the richest in carbon, of which it contains 95 to 97 per cent., and has completely lost its fibrous vegetable structure. One phase of this decomposition of wood cellulose was certainly due to anaerobic bacteria, namely, of micrococcus carbo, bacillus carbo, micrococcus petrolei, &c. (Renault). According to Omelianski (1906), two anaerobic bacilli, forming spores which are extremely resistant at 90°, more especially participate in the fermentation and decomposition of cellulose, and the more active of these produces methane and CO_2 while the other produces H and CO_2.

All these forms of carbon contain variable quantities of mineral matter (ash) which may be extracted with hydrochloric acid, and may be separated by burning the carbon.

The fossil carbons constitute the most important source of heat and mechanical and electrical energy for industrial purposes. The world's annual consumption of coal amounts to about 500,000,000 tons. The consumption has hitherto been proportional to the industrial development of the various nations and serves as an index of progress and of civilisation. But to-day much hydraulic energy is used, so this index has partly lost its value.[2]

PEAT. In the natural formation of coal peat may be considered as the most recent decomposition product of immense layers of marsh plants, which still clearly show their structure and external appearance and are mixed with earth. When formed in deeper layers it has lost its structure and has a lustrous appearance.

It is found in large deposits in marshy countries, and when extracted is very damp, containing more than 70 per cent. of water. After drying in the air, especially if it has first been frozen, it still contains 30 to 40 per cent. of water and gives from 5 to 15 per cent. of ash. When it contains very much ash (sand, earth, &c.) it is not suitable for use as a fuel.[3] One cubic metre of peat weighs from 150 to 200 kilos. In certain countries peat is

[1] In 1900 the number of miners in the world, who were mainly employed in coal mines, was 4,355,000, of whom there were 875,000 in England, 500,000 in Germany, 445,000 in the United States of America, 320,000 in India, 310,000 in Ceylon, 293,000 in France, 240,000 in Russia, 219,000 in Austria-Hungary, 160,000 in Belgium, 119,000 in Japan, and 60,000 in Italy, of whom half are employed in the Sicilian sulphur mines and a considerable portion in the Sardinian mines and in the marble quarries of Carrara. Of the 972,000 miners in England in 1907, more than 940,000 were employed in the 3227 collieries.

[2] About 25 years ago the coal produced in England was consumed by various industries and for various other uses in the following proportions:

For the production of iron and steel	30 per cent.
For heating and domestic use	17 ,,
For steam-engines	12 ,,
In ships	3 ,,
On the railways	2 ,,
In the mining industry	7 ,,
For gas manufacture	6 ,,
For the manufacture of glass and porcelain	4 ,,
In chemical works, breweries, distilleries, metallurgical works, excluding iron and steel, &c.	9 ,,
Export	10 ,,

Naturally these relations are not absolute and do not apply to all periods. They change together with the evolution of industry, and do not apply to all countries. These proportions have been notably altered to-day by the use of hydroelectric energy.

[3] There are large deposits of peat in Ireland, Scotland, Norway, Sweden, Germany, Russia, and the North of France. In Italy the various peat deposits have a total area of about 3000 hectares, and yielded

used with advantage for the preparation of peat charcoal. The price of peat in Switzerland and Germany is from 4*s*. 10*d*. to 5*s*. 7*d*. per ton, contains 20 to 25 per cent. of moisture, and has a calorific power of 3000 to 3500 cals. The yield of charcoal is 30 to 40 per cent. and the price of this varies from £1 4*s*. to £1 12*s*. per ton.

On pp. 325-326 we have recorded the various processes of obtaining ammonia and gas for power or for illuminating purposes from peat. Attempts to obtain alcohol from peat have not yielded satisfactory results up to the present (*see* vol. ii, "Organic Chemistry").

LIGNITE. This product is also formed by a process of moist putrefaction of wood which has been carried much further than in the case of peat. It is much more closely akin to ordinary coal, but is distinguished from this by still having the fibrous structure of wood, whilst in ordinary coal this structure is almost completely destroyed. It also contains less nitrogen, and when heated in a test-tube it evolves vapours of acid reaction (acetic acid), whilst coal gives vapours of alkaline reaction (ammonia or ammoniacal bases). Also on heating powdered lignite with a solution of sodium hydroxide, the latter is coloured brown, whilst with ordinary coal it is not coloured (though certain Russian coals form exceptions). There are, however, some lignites which resemble ordinary coal in this particular.

Donath in 1906 maintained that lignite was produced from plants richer in lignin than those forming ordinary coal, and does not, therefore, admit that lignite would in time be converted into ordinary coal.

Air-dried lignite contains on the average 20 per cent. of water and from 5 to 10 per cent. of ash. The most certain method of distinguishing these products is Donath's reaction with dilute (1 : 10) HNO_3 ; on heating lignite with this reagent, the liquid acquires a red colour which it does not with ordinary coal.

Lignite is used as a fuel and also in certain districts for dry distillation, by means of which paraffin, tar, light and heavy mineral oils, illuminating gas, and a coke which is used in metallurgy are obtained.[1] For the production of lignite in Italy *see footnote*.

A special quality of lignite called *pyropissite*, which is found in certain deposits in Saxony and Thuringia, deserves mention. It is perhaps formed from oil-containing plants, and on distillation it yields very abundant oily products, especially paraffin. To-day, however, these deposits are almost exhausted and it has been found, on the other hand, that instead of distilling certain lignites, it is much more convenient to extract them with a solvent, because larger quantities of paraffin of better quality are so obtained (*see* vol. ii, "Organic Chemistry"). In Germany 600,000 tons of various lignites are distilled each year.

COMMON COAL. This product is abundant in England, Germany, Belgium, and America, and is also found in France and Russia. In Italy, on the contrary, it is almost completely absent. The following more important qualities of coal are distinguished for industrial purposes :

(1) *Fat coal*, which when powdered and heated in a crucible fuses together and forms a homogeneous mass of compact, fused coke. It is very rich in hydrogen and is easily lighted, giving a long flame. It is largely used for gas manufacture as it yields 25 to 30 per cent. of gas.

(2) *Caking coal* is that which is more commonly used for boilers. On powdering and heating in a crucible, it gives a solid agglutinated mass which is, however, not fused, but

about 20,922 tons in 1903, 59,440 tons in 1907, and 33,325 tons in 1908, valued at £13,432 ; about half of this is produced at Codigoro, in Ferrara, in the form of strongly compressed briquettes, and large quantities will be utilised in future in Orentano, in Tuscany, for the production of ammonia, power gas, &c., by the Mond process (*see* p. 326) especially from the peat-beds of Angera, Varese, Casale-Litta, Iseo, Vicenza, Udine, Viareggio, Livorno, &c. Peat is employed in various industries near the locality of production, so that there may be no high freight charges.

In Germany there are about 2 million hectares of peat land in which about 9000 million tons of peat are present. In Russia 944,640 tons of peat were produced in 1908, employing 17,000 workmen.

[1] STATISTICS. It has been estimated that the various deposits in Italy still contain 100,000,000 tons of lignite. 342,219 tons were obtained in 1903 ; 453,000 tons in 1907 valued at £160,000, and 477,000 tons in 1908 ; this was partly sold, partly distilled, and partly burned as such. The best qualities are the black lignites of Sarzana and Casteani, with a calorific power of 5500 cals. ; there are very abundant woody lignites in Valdarno which when dried give 400 cals., though after extraction they contain 40 per cent. of water. Lignite is obtained in the provinces of Vicenza, Bergamo, Cagliari, Cuneo, Savona, Pisa, Siena, &c. The consumption increases together with the price of ordinary coal. Germany produced 48,000,000 tons of lignite in 1904, more than 52,000,000 tons in 1905, and about 66,000,000 tons in 1908, valued at £9,000,000, apart from 14,000,000 tons of briquettes of compressed lignite ; in 1909 Germany imported 8,000,000 tons of lignite and 90,000 tons of briquettes, but exported 475,000 tons of briquettes valued at £169,200. In Austria-Hungary 32,000,000 tons of lignite were produced in 1907 ; in France 762,000 tons were produced in the same year.

forms a light and porous coke. Some of it gives little gas and some a good deal. It often contains a little iron pyrites.

(3) *Lean or dry coal* is the poorest quality. It contains much oxygen and little hydrogen. It costs less, and is used for lime and brick kilns, &c. One cubic metre of good coal weighs from 700 to 900 kilos.

In the mechanical sorting which takes place at the mine, in order to separate the various sizes, and in the washing to which the better part of the coal is subjected, enormous quantities of fine rubbish are obtained which sometimes contain up to 60 per cent. of ash, and are thrown into heaps because only the better part is utilised to form briquettes (*see below*). Recently, however, Dr. Caro (Ger. Pat. 198,295) has proposed to utilise these residues by the Mond process (p. 326) for the production of ammonia and power gas.

ANTHRACITE. This product may be considered as natural coke containing very minute quantities of bituminous matter and hydrogen. It no longer has any vegetable structure nor is it crystallised, but its structure is conchoidal and irregular. It is brittle, does not fuse in the furnace, and burns with a very short and non-luminous flame. The composition of British anthracite varies between the following limits: 1 to 2 per cent. of ash, 1 to 3 per cent. of volatile matter, 0·6 to 1·2 per cent. of sulphur, 92 to 95 per cent. of carbon, and it has a calorific power of 7600 to 8200 calories.

Cannel coal and *boghead coal* are found in large quantities near Edinburgh, and are distinguished by the large amounts of hydrogen which they contain. They, therefore, yield very much gas, together with paraffin and mineral oils for lighting purposes (petroleum), &c. (*see* vol. ii, " Organic Chemistry ").

LAMPBLACK (AMORPHOUS CARBON). This substance is obtained by carbonising various organic substances out of contact with the air. The purest form of amorphous carbon is that which is called *lampblack*, and is obtained by the incomplete combustion of resins containing much carbon, such as oil of turpentine, colophonium, camphor, tar, oil, &c., which are burnt in presence of a limited amount of air, whilst an iron cylinder which is kept cool is rotated in the flame. The carbon is then deposited in a very finely divided state on this cylinder. According to its purity, this product costs from £50 to £400 per ton.

In 1907 Italy imported 198·6 tons of lampblack and in 1908 about 170 tons.

RETORT CARBON (GAS CARBON or METALLIC CARBON) also belongs to the amorphous forms of carbon. It is formed by the decomposition of the hydrocarbons which are evolved during the dry distillation of coal in gasworks and is found as a deposit on the internal walls of the retorts. It is very hard, has a metallic appearance and is a good conductor of electricity and heat. It is used in certain galvanic cells for the carbons, for arc lamps and for carbon electrodes in general. It is sold in pieces or lumps at from £14 to £50 per ton.

COKE is mainly obtained as an abundant by-product (60 to 70 per cent.) in the distillation of the coal used for the manufacture of lighting gas and also as metallurgical coke. During this distillation the ammonia and tar which serve for the preparation of various organic compounds, such as benzene, anthracene, naphthalene, pitch, &c., are also utilised.

To-day coke is also prepared especially in suitable ovens for various industrial and domestic purposes. It contains much carbon, gives no tarry fumes on burning and may be used for obtaining high temperatures in presence of sufficient quantities of air. From coke and steam one obtains water gas, which is used as a power and illuminating gas (*see below*) and is formed of a mixture of H, CO, and CO_2.

Coke is a hard spongy form of amorphous carbon, which is a good conductor of heat and electricity. It is used as a fuel, but more especially in very large quantities for metallurgical purposes in blast furnaces, on account of its great hardness, in iron foundries, &c., and costs from £1 to £1 8*s*. per ton (1 cu. metre of coke weighs about 400 kilos). (These prices do not, of course, apply to English conditions.—*Translator.*)

The coke produced in gasworks cannot be used as metallurgical coke as this must be free from volatile products and consist as far as possible of pure carbon. It should be compact and hard, and therefore can only be obtained when the gases which are developed on heating (hydrocarbons) remain in contact with the porous mass of coke which is formed, for a prolonged period. In this way the pores are partly filled by a graphitic mass. This is what occurs during the manufacture of metallurgical coke, but not during that of illuminating gas, so that the coke obtained during the latter process is not used metallurgically, in the

same manner that the carbon obtained by the distillation of wood in retorts cannot be used instead of wood charcoal obtained in kilns for various metallurgical operations.

It would appear that in the preparation of metallurgical coke it would not be possible to recover volatile products of great value as these would be consumed by the coke production itself. If one remembers, however, that of the products of distillation of coal those of greater value only form a small fraction of the whole mass, it appears possible to save the more valuable volatile products, whilst burning those of minor value for the production of coke. In order to obtain compact, hard coke without consumption of the more valuable volatile products, *coke-ovens* have been invented which are very narrow and very high and long, and are so constructed that the weight of the upper layers of coke, pressing on those below, hinders the swelling of the coal during heating, and a coke results which is less porous and harder. From the vapours produced on distillation tar and ammonia are extracted, and the remaining gas is burnt in the regenerative furnaces, or, as is the case in many works, the benzene is first separated from these gases before burning them. This is done by cooling them strongly in order to condense the benzene, or by passing them through tar oils of high boiling-point by which the benzene is dissolved (Franz Brunck's process). The benzene is then recovered from these solvents by simply heating them. By this process but little toluene is obtained, whilst more is obtained by

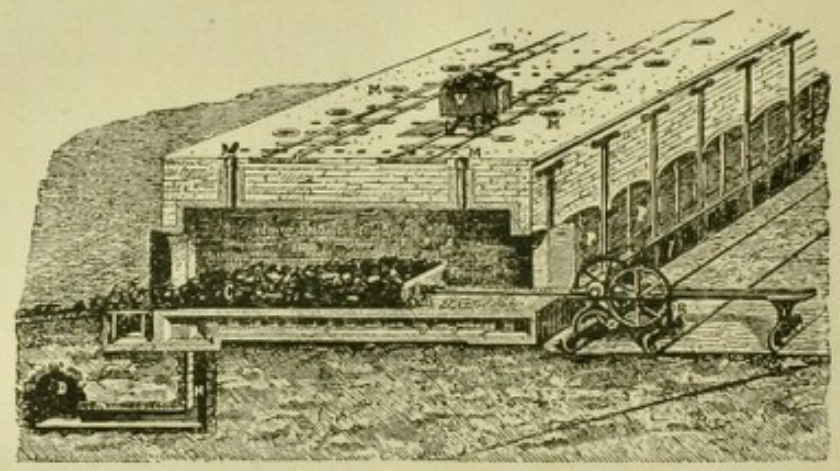


Fig. 148.

distilling gas tar. At one time only 5 per cent. of the benzene thus formed was condensed, but to-day by means of this system of washing the vapours, the quantity of benzene has been trebled. Thus in Germany, where 15,000 to 20,000 tons of benzene were at first obtained, 80,000 tons and more are obtained to-day.

In Fig. 148 we give the general aspect of an old coke-oven which is charged from above and heated below by flues below the sole, in which the gases escaping from the distillation are burnt. Before being charged into the oven the coal is crushed, and then, after some days of heating, is discharged as indicated in the Figure by means of a mechanical ram which enters at one door and forces the coke out at the other end, while still red hot ; it is then quenched with water. In Fig. 149 a battery of modern coke-ovens is shown in section, and in this we see that the charge is heated by means of a series of flues, S, S_1, in which the gas proceeding from the regenerator, h, is burnt. Above we see the tubes, i, k, l, in which the gases and vapours obtained by the distillation of the coal are led away. As we see from the section, the chambers of these furnaces are 0·5 to 0·6 metre wide, 1·6 to 1·7 metres high, and 9 to 10 metres long. They take a charge of 5½ to 6 tons. In large works for the production of metallurgical coke, powdered coal is used to-day, together with small pieces. These are slightly moistened and are compressed in long large blocks which have almost the dimensions of the furnace mouth. These blocks are carried, by means of a suitable car, up to the furnace, into which they are made to enter by means of a suitable arrangement, in such a way that the new block of coal is forced into the furnace and forces out the red-hot block of coke, which has just been finished, at the other end. The heating of the coal for the production of coke lasts from 36 to 48 hours, and the yield of coke varies from 68 to 75 per cent., with simultaneous production of about 2 per cent. of tar and of about 1 per cent. of ammonium sulphate. The most modern types

of oven, which have lately become widely adopted for the recovery and utilisation of the vapours, gases, and tar, are the Semet-Solvay and Otto-Hoffmann ovens. In 1898 1800 Semet-Solvay ovens were already at work in various countries, and there were also 5000 Otto-Hoffmann ovens at work in Europe, whilst in the United States alone 4000 Otto-Hoffmann ovens were constructed between 1902 and 1906. From 1906 to 1908, however, other ovens were more frequently constructed without the recovery of secondary products, because these could no longer be remuneratively placed on the market.

Figs. 150 and 151 give an idea of modern coke-ovens heated by means of Siemens' regenerating furnaces, h and h_1, of which we give a description in Part III in the chapter on Glass. h and h_1 are alternately used for heating the air which is required for the combustion of the purified gases proceeding at one period from n and at the other period from o. In the middle of the vaulted roof of each oven (Fig. 151) there are two large pipes, c, which carry away the gases, vapours, and tar which are formed on heating coal out of contact with air ; these are cooled in suitable condensers, such as are used in the manufacture of lighting gas. Each chamber is charged through three manholes above,

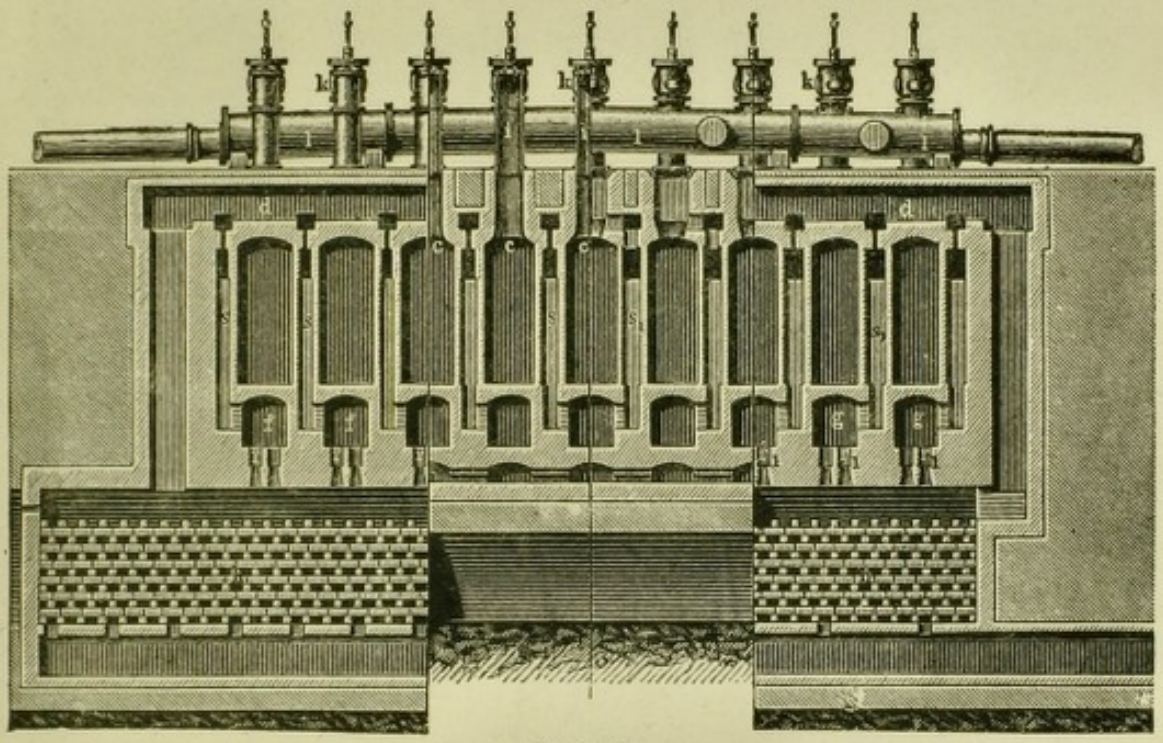


Fig. 149.

the coal being carried on trucks. Between each oven and its neighbours there is a series of vertical flues, S and S_1, which lead upwards into a horizontal canal G, and below into a canal divided into two halves, f and g. If during the first phase of the operations the air is heated in the generator, h, combustion commences already in the neighbourhood of the openings, r and p, and the hot combustion gases pass from f through the vertical canals, S, and through G, then descend the flues, S_1, and thus arrive in g, in order to then heat the regenerator, h_1, before passing out into the air.

During the second phase the gas current is reversed. The regenerator, h_1, now heats the air, and gas passes from g and through the flues, S_1 and S, into the regenerator, h. With this scheme of working there is no chance of any possible admixture of air and gas as there is when these are able to pass through neighbouring regenerators, when they sometimes cause fusion of the material and explosions. Until now, preheating of the combustible gases has not been applied. The regenerators are used alternately for heating the air of which a volume six times that of the combustible gases is required. This air arrives cold alternately through the tubes, n and o, and is introduced alternately into the flues S or S_1. Since the air acquires a temperature of 1000° in the regenerators, it is not necessary to burn all the gas in order to work the ovens, and a part may be economised by using it as a source of power. Air being completely excluded from the coke-ovens, the coke yields are 7 per cent. greater than those obtained in the old type of oven. In

each chamber, charged with from 5·8 to 6 tons of coal, apart from gas used in heating, 100 cu. metres of gas are now produced per day of the following composition: Benzene, 0·6 per cent.; ethylene, 1·61 per cent.; H_2S, 0·42 per cent.; CO_2, 1·39 per cent.; CO, 6·41 per cent.; H, 52·69 per cent.; methane, 35·67 per cent.; water vapour, 1·21 per cent.; this gas may be used for lighting purposes or as power gas. For the yields of tar, illuminating gas, coke, &c., obtained on distilling both coal and wood, *see* vol. ii, "Organic Chemistry."

The world's production of coke (both metallurgical and gas coke) is valued at about £6,800,000, and is about 60,000,000 tons. The United States of America alone produced 22,500,000 tons in 1902 in 69,000 coke-ovens, of which 1663 recovered the by-products, whilst in 1880 the production was only 6,500,000 tons.

In 1880 England produced 15,500,000 tons of coke. In 1904 Germany produced 12,000,000 tons of metallurgical coke and in 1906 more than 20,000,000 tons. In 1909 Germany imported 673,000 tons of coke and exported 3,448,000 tons.

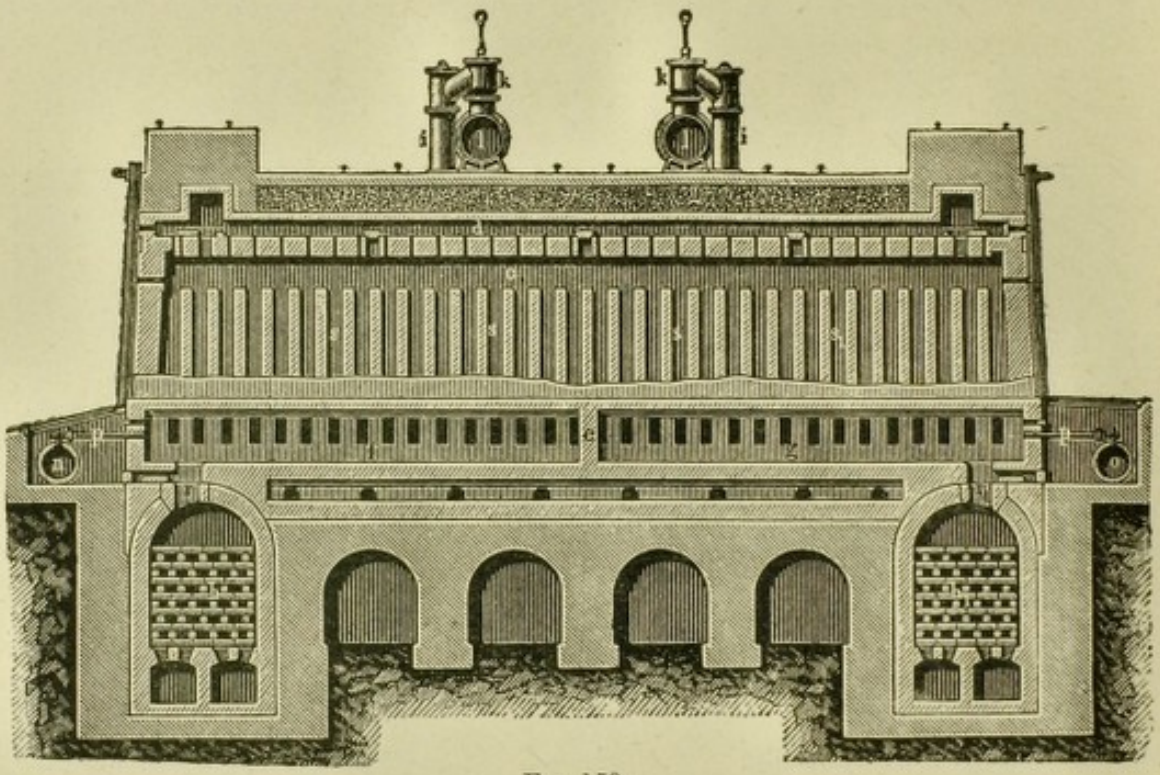


Fig. 150.

In Italy about 100,000 tons of metallurgical coke were used in 1903, of which 40,000 tons were supplied by the Savona works; another portion by the company working the blast furnaces on the Island of Elba, and the remainder was imported from England and Germany. The gasworks produced about 709,000 tons of coke in 1908, which was used as an ordinary fuel.

WOOD CHARCOAL. This is produced by heating wood out of contact with the air in pieces and in logs in large heaps covered with earth. A few openings are left for the escape of the gases which are formed during the combustion. This is started by lighting the wood at the bottom and the process lasts several weeks. The end of the process is recognised by the colour of the smoke.

In this way all the volatile products, which are of great value, are lost, and to-day carbonisation is often conducted in suitable furnaces or retorts, which allow the volatile products, consisting of lighting gas, methyl alcohol, acetic acid, and tar, to be utilised. (*Translator's note.*—Acetone should also be mentioned as one of the most important by-products.)

On account of its high degree of porosity wood charcoal, apart from its use as a fuel, is used for the absorption of gases, for the decolorisation of syrups and purification of liquids such as alcohol. It is also used as a reducing agent for obtaining metals from various ores, more especially from their oxides. According to the fineness of the ground

powder and its purity wood charcoal costs from £8 to £14 per ton. If it is purified with HF it may cost as much as 2*s.* 5*d.* per kilo.

In Russia, Sweden, and North America wood charcoal is still used for the production of iron. In the United States alone 400,000 tons are produced annually for this purpose, and in Sweden in 1903 456,000 tons were produced, corresponding to 6,000,000 cu. metres of wood.

In 1908 Italy exported 24,603 tons of wood charcoal.

ANIMAL CHARCOAL (BONE CHARCOAL) is another form of amorphous carbon and is obtained by heating various animal substances, such as blood or freshly defatted bones in closed retorts (p. 313). That produced from bones contains 10 per cent. of carbon and 90 per cent. of mineral matter. It should not colour a solution of sodium hydroxide. It has the power of decolorising various solutions to a high degree and is therefore employed industrially, especially in sugar refineries, in order to decolorise the sugar solutions, and also forms the best means of removing fusel oil from spirits. The decolorising power of animal

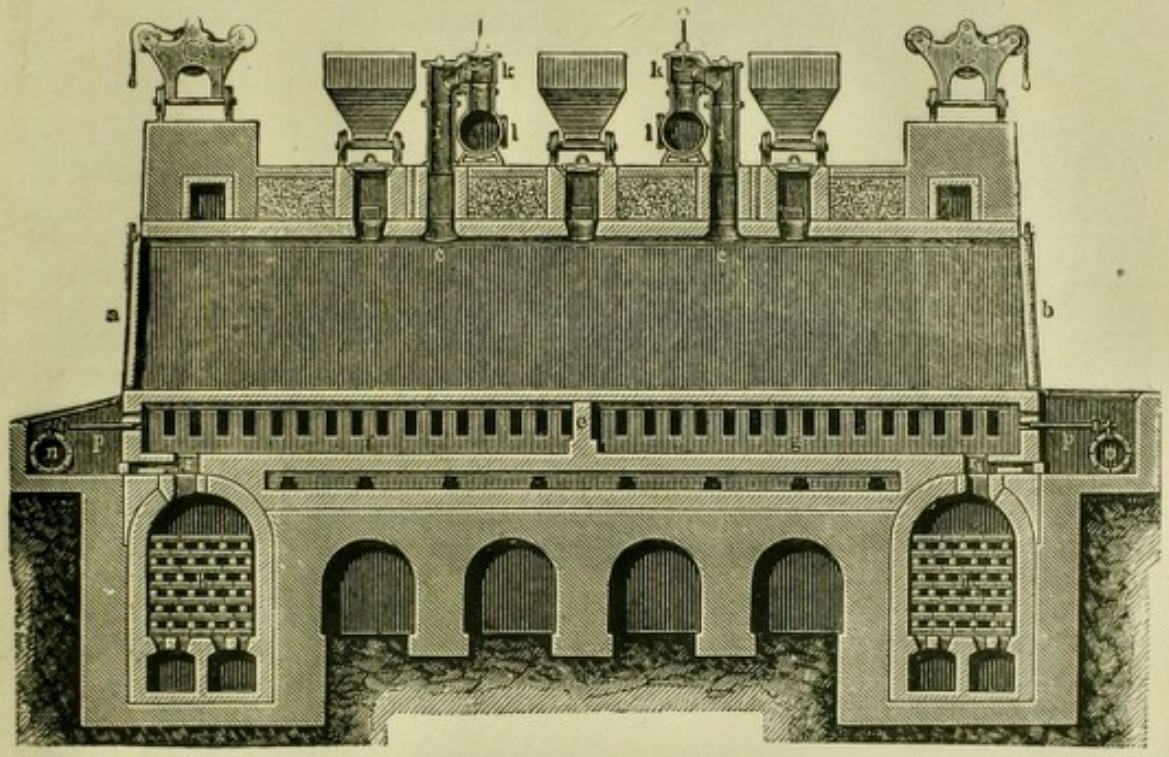


FIG. 151.

charcoal is much higher than that of wood charcoal on account of its special composition and structure.

It becomes inactive during use, and is revivified by washing with HCl, then boiling with a solution of sodium hydroxide, washing well, treating with steam, drying and heating to bright redness (*see* vol. ii, "Organic Chemistry," chapter on Sugar). When impure, in powder or in lumps, it costs from £12 to £14 per ton; when partially refined it costs £40, and when pure and moist, up to £70. When chemically pure (washed with acids, &c.) it is sold at £200 per ton.

AGGLOMERATED COAL (BRIQUETTES). These are prepared from coal or lignite dust by mixing with a small amount of binding material and exposing the mass to very high pressure in suitable moulds by means of special presses (Fig. 152).

Ordinarily dust or the smaller portions of lean coal (though not as lean as anthracite) are used, which are not suitable for the preparation of coke; 6 to 8 per cent. of coal-tar pitch is mixed with the already pulverised mass, which is then raised by means of elevators into a cylinder provided with a stirrer and heating arrangement which sometimes consists of a small jet of steam passed into the mixture. The pitch is thus softened and the heated

mass is distributed on to a revolving plate which carries moulds into which the mixture is filled and then strongly compressed. The briquettes, stamped with the mark of the particular works, are automatically ejected from the mould.

Fig. 152 does not need any further explanation. In the following figure (Fig. 153) we see another machine which is used for the production of briquettes in the shape of eggs or balls for American stoves. The hot pulverised mass is distributed between two cylinders which each carry half a mould (hemisphere) corresponding exactly, in such a way that when the cylinders turn towards one another, the two moulds meet in the middle and form a sphere of coal with a smooth surface. In some works residues from cellulose manufacture are used as a binder, after evaporation, with coal, thus saving a portion of the coal-tar, pitch, glue, &c.

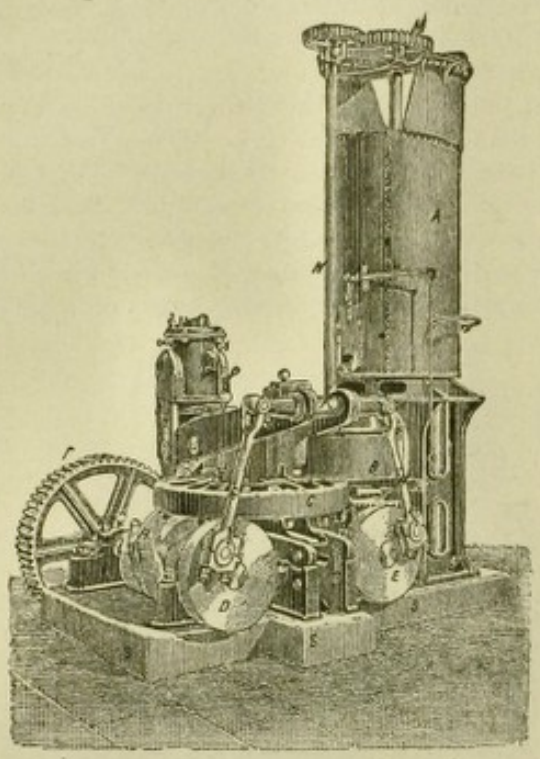


Fig. 152.

Good briquettes have a calorific power of 7700 cals. referred to the dried substance, are compact, and do not crumble in the fire. They should not contain much ash or much sulphur, and should be resistant to weathering. The pitch which is employed should not give more than 40 per cent. of coke and 74·9 per cent. of it should be soluble in carbon disulphide. It should have a calorific power of more than 8500 cals. and contain less than 5 per cent. of hydrogen. In order to discover how much pitch has been added, the composition is extracted in a Soxhlet apparatus twice per twenty-four hours with carbon disulphide, and the extract is dried for three days *in vacuo* over phosphoric acid. Good briquettes should give at least 5 per cent. of extract. They should not yield more than 8 per cent. of ash or less than 16 per cent. of volatile products.

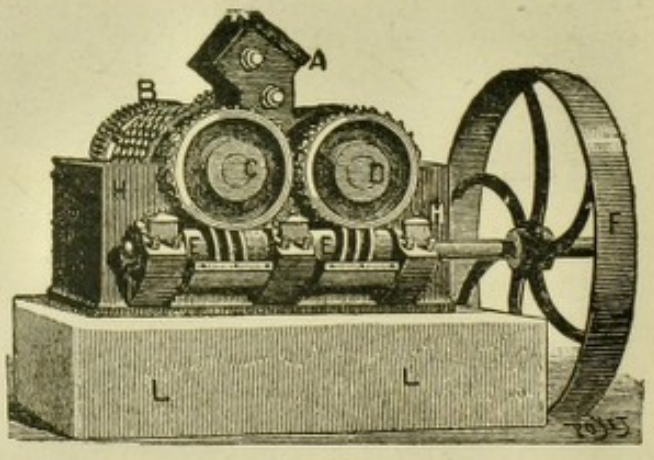


Fig. 153.

In Germany 10,476,200 tons of coal briquettes were manufactured in 1903, 13,000,000 tons in 1905, and more than 15,000,000 tons in 1907. Germany exported 940,000 tons of such briquettes in 1905, 1,090,000 tons in 1906, and 1,146,000 tons in 1909. Italy produced 829,280 tons of various briquetted fuels in 1906, and 804,700 tons in 1908, valued at £948,000; of this quantity 18,720 tons were briquettes of wood charcoal valued at £52,000. In 1907, Italy imported 945 tons of prepared carbon for electrotechnical purposes and 1570 tons in 1908.

COAL AS A SOURCE OF HEAT. The specific heat of carbon is very low and increases with elevation of the temperature; at $-50°$ it is 0·062; and at 985° it is 0·459, which shows that at ordinary temperatures the molecule is very large and complex.

The heat which is evolved on completely burning 1 kilo of pure carbon [1]

[1] In the combustion of cellulose (wood) $C_6H_{10}O_5 + 6O_2 = 6CO_2 + 5H_2O$, 17·580 Kj. (4140 Cals.) are developed per kilogramme, and this quantity was thus required by cellulose in its formation by the utilisation of the solar heat.

is 33,800 Kj. = 8080 cals., and is sufficient to melt 100 kilos of ice or to raise 80 litres of water at 0° to the boiling-point. The temperature of combustion when burnt in the air is below 1700°, whilst it is much higher when burnt in oxygen.

One h.p.-hour corresponds to 594 Cals., and the efficiency of a steam-engine varies from 500 to 1000 grms. of coal per h.p.-hour for a machine of 100 h.p., according to the efficiency of the condensation.

One kilo of good coal burnt under the boilers may, in practice, give 8 to 8½ kilos of steam. In order to determine the efficiency of boilers, these are worked for 10 hours, noting the quantity of ash and cinders and the total quantity of evaporated water by collecting the water in the measuring vessel attached to the boiler.

The determination of the *calorific power* of coal, that is, the measurement of the heat which is developed by the complete combustion of a given weight of the sample, is of the greatest importance. In order to obtain exact and concordant results in boiler tests, the analysis should be made of a well-prepared sample taken, for example, from various parts of a truck of coal and uniting the powder and the lumps so that about 100 kilos are taken altogether. This is then heaped up on a polished floor in the form of a square with sides about 2 metres high, smashing the very large pieces of coal with a hammer. Diagonal and cross lines are then drawn on the heap with a piece of wood as in the Figure, and of the eight portions so obtained four alternative portions are removed; the 50 kilos which remain are heaped up into a similar square, again crushing the larger pieces, and the sample divided in a similar manner, so that 25 kilos are obtained, and the operations are repeated until samples of 12 kilos and finally of 6 kilos are obtained. This sample is then taken into the laboratory, coarsely powdered, and reduced to half and a quarter as before. It is then finely powdered until the whole passes through a sieve such as is used for flour. From this sample portions are taken for the various analyses.

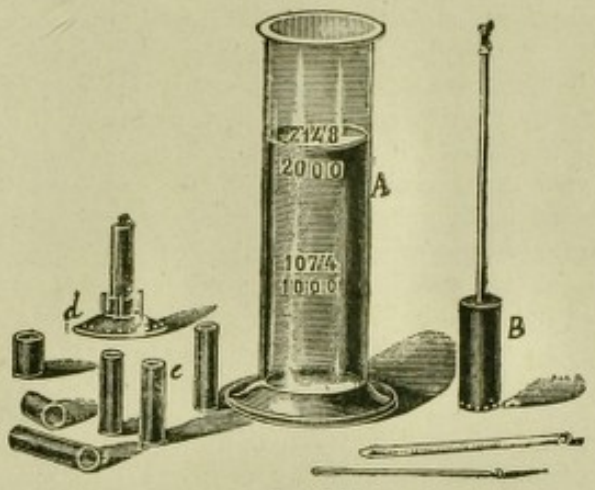


FIG. 154.

An indirect and not always exact method of determining the caloritic power of a combustible is that proposed by Berthier: 1 grm. of the powdered fuel is mixed with 40 to 50 grms. of powdered litharge (lead oxide) or 70 to 80 grms. of white lead. The whole is fused and allowed to cool after some time; the button of lead which is formed at the bottom of the crucible is then weighed. One gramme of lead corresponds to 234·2 cals., and by simple multiplication the calorific power of the fuel is obtained.

The determination is exact when the fuel is burnt in Berthelot's calorimeter or in the other sufficiently exact calorimeters of Mahler, Fischer, or Hempel. In the English and Italian coal trade, the Lewis-Thompson calorimeter is used. This is much less exact than those just mentioned and gives varying and inexact results. In this apparatus (Fig. 154) 2 grms. of the powdered coal are mixed with 20 to 26 grms. of a dry oxidising mixture of 3 parts of potassium chlorate and 1 part of potassium nitrate. The whole is introduced into a copper cylinder, *d*, and a piece of paper fuse is fixed into the surface. This is prepared by soaking filter paper in a solution of lead nitrate and then drying it. Then the temperature of the water, which should be 4° to 5° below that of the atmosphere, is exactly measured by means of a thermometer divided into twentieths of a degree at least.

The fuse, which emerges from the mixture to a height of 1 cm., is then lit, and the cylinder which is fixed in a spring foot is rapidly covered with a cylindrical copper cylinder, *B*, provided with a long delivery tube furnished with a tap, and the whole is then quickly immersed in the glass, *A*, which contains exactly 2 litres of water. As soon as the fuse ignites the mixture the development of hot gases from the combustible commences and these pass through holes in the lower part of the copper cap, passing up the column of water to which they yield all their heat. The regular combustion should last from 45 to 60 seconds, and this result is obtained by varying the quantity of oxidising mixture, the period of combustion being increased by diminishing the amount of the mixture, or lengthened by increasing it. The temperature of the water before and after the operation is then observed, and the rise of temperature so obtained. From this the number of calories evolved is deduced, knowing that 1000 cals. are required to raise the temperature of 1 litre of water up to 1°. The final result is increased by 10 per cent., to allow for the heat absorbed by the apparatus and dispersed. Certain improvements have been recently introduced into this apparatus, consisting in obliging the gases to pass through a long, thin, serpentine coil, so that all their heat may be absorbed by the water. In order to obtain reliable results, the experiment is repeated several times, always compressing the mixture in the tube to an equal extent, and the highest result is considered to be the most correct. For example, if with 2 grms. of coal a rise of 7·25° is obtained in 2 litres of water, then each litre has absorbed 7250 cals., corresponding to 1 grm. of coal, as 2 grms. have been used for the 2 litres. Adding 10 per cent. we obtain 7975 cals., which represents the calorific power of the coal.[1]

There are lignites, anthracites, cokes, and coals containing much ash which burn badly or not at all in Thompson's calorimeter, and they must then be mixed with half their weight of an easily combustible coal of known calorific power, and the heat of the lignite or anthracite then calculated. The calorific power, *C*, may also be calculated indirectly by Goutal's formula, which gives sufficiently reliable results which are generally 200 to 300 cals. higher than those obtained by Thompson's calorimeter, but accord fairly well with the values obtained with the Berthelot-Mahler calorimeter.[2]

Although not officially used in the Italian coal trade, we give a drawing of the bomb-calorimeter of Berthelot modified by Mahler (Fig. 155), and with this exact results are obtained. It is formed of a very strong steel vessel, *A*, which is platinised or varnished inside and nickel-plated outside, closed with a strong cover with a very tight screw. This cover carries a platinum crucible or boat, *m*, for the weighed sample of fuel, and is provided

[1] We here give the calorific power of several combustibles referred to 1 grm. of substance and expressed in small calories, including the heat of condensation of water vapour, which is found in the products of combustion, into liquid water. These values may vary slightly with variation of the quality of the fuels:

	Cals.		Cals.
Hydrogen	34200	Shales, paraffins, and sclid hydrocarbons	10–11000
Pure carbon (forming CO_2)	8080	Ethyl alcohol	7000
Pure carbon (forming CO)	2430	Methyl alcohol	5300
Completely dried wood	3700	Petroleum (mixed hydrocarbons)	11–12000
Air-dried wood	2900	Heavy petroleum oils	11–11500
Wood charcoal	7000	Carbon monoxide (CO)	2421
Air-dried peat	3600	Water gas (equal volumes of H and CO) per cubic metre, about	3100
Lignite	4000–5500	Lighting gas	4500–5000
Ordinary common coal	7500	Oils and fats	9300–9500
Anthracite	8000	Methane	12700
Cardiff coal No. 1	7800–8200	Ether	9027
Coke from common coal	7100		
Coke from lignite	5500–6500		

[2] Goutal's formula is $C = 82K + aV$, where *C* indicates the calorific power in calories referred to 1 grm. of fuel; *K* is the percentage of coke (after deduction of the ash) and *V* that of the volatile products (deducting the moisture); *a* is a value which varies with the amount of volatile products, and is obtained from the following table corresponding to the value of V^1, which indicates the percentage of volatile products in the coal after deducting the moisture and ash $\left(V^1 = \frac{100\,V}{K + V}\right)$; here is the Table:

V^1 =	5	8	10	12	14	16	18	20	22	24	26	28	30	34	38
a =	145	136	130	124	120	115	112	109	107	104	102	100	98	95	85

Example. A coal gives on analysis: moisture, 0·5 per cent.; coke, 85 per cent.: volatile products other than moisture, 13·5 per cent.; we then have $K = 85 - 6{\cdot}6 = 78{\cdot}4$; $V = 13{\cdot}5$ and $V^1 = \frac{13{\cdot}5 \times 100}{78{\cdot}4 + 13{\cdot}5} = 14{\cdot}6$, which corresponds in the Table to a value of $a = 118$ about, and thus $C = (82 \times 78{\cdot}4) + (118 \times 13{\cdot}5) = 8021{\cdot}8$ calories.

with two platinum wires, *h* and *g*; an iron wire of known weight dips into the crucible and may be heated to incandescence by means of the electric current. The bomb is immersed in a metal cylinder provided with a stirrer containing a definite quantity of water (1 or 2 litres), of which the temperature is measured before and after combustion by means of a thermometer divided into fiftieths of degrees; this cylinder containing the water is covered with wool or insulating felt and the whole is surrounded by a reservoir of water which surrounds the cover, in order to minimise the influence of the surrounding atmosphere. The bomb is filled with pure compressed oxygen absolutely free from hydrogen; electrolytic oxygen is therefore not suitable and oxygen obtained from liquid air is preferable; oxygen is passed in through the valve, *f*, which is connected to the cylinder, *R*, containing pure oxygen compressed to 50 to 100 atmospheres. The valve is opened to such an extent that a pressure of 15 to 20 atmospheres is present in the calorimeter as indicated by the manometer. When the current is passed the iron spiral is heated to redness and the fuel burns. A calorific determination may thus be made in a few minutes. In some bombs there are suitable apertures with valves so that the gases formed during combustion may be removed and subjected to any special analysis if required.[1]

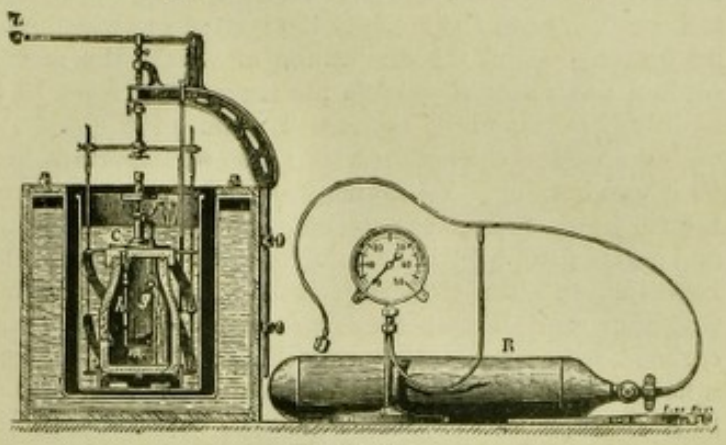


FIG. 155.

[1] The details for a practical determination are as follow:

If the bomb is perfectly gas-tight, no bubbles should escape when it is immersed in water. Before the sample is burnt, five or six temperature readings should be taken at intervals of one minute after each, until the reading of the thermometer immersed in the water in *C* remains constant. Then the current is passed from several cells for a single moment. The iron wire inside the bottom becomes heated and causes the complete and immediate combustion of the coal. The stirring is continued as at first and the readings are continued half a minute after the ignition of the charge; they are continued two or three times at half-minute intervals, and then at one-minute intervals for seven or eight minutes as the temperature rises to the maximum and decreases. By this means the mean temperature variation for each minute in the observations during ignition and before and after are obtained, and one is thus able to correct the elevation of temperature which is observed for the radiation which occurs during the period between ignition and the period of maximum temperature, because the same amount of radiation of heat will have occurred per minute as that which occurred before the maximum was reached, and thus in the first half-minute before ignition the radiation will be equal to that observed in the first half-minute after ignition. The heat of formation of the nitric acid formed from the nitrogen of the air contained in the bomb at the beginning of the operation must also be deducted; 0·23 cal. is allowed per 1 mgrm. of HNO_3, and in a bomb of 250 cu. metres capacity 48 mgrms. of HNO_3 are formed, giving rise to 11 cals.; the heat of combustion of the iron spiral or cotton thread used to start the ignition must also be subtracted. If iron wire of appropriate size is used, 1·6 cals. per mgrm. are reckoned. We will give an example. The general formula for calculating the calorific power *C* is: $C = (T + t)(a + E) - 0{\cdot}23\,n - 1{\cdot}6\,f$, where *T* is the difference of temperature observed between the point of ignition and the maximum; *t* is the temperature to be added to *T* on account of the loss of heat by radiation; *a* is the weight of water which surrounds the bomb; *E* is the *water equivalent* of the apparatus, that is, the heat expressed in grammes of water, not measured by the thermometer, which serves to heat the bomb; this is directly determined by repeated tests with a chemically pure substance of known composition and of which the theoretical calorific power is known, since the resulting heat is less than that found by the general formula in which *E* does not occur by an amount which represents the value of *E*. The heat of combustion of 1 grm. of pure naphthalene is theoretically 9692 cals., of cellulose (pure cotton) 4140 cals., of saccharine 3866 cals.; *n* is the weight in milligrammes of the nitric acid formed (48 mgrms. for a bomb of 250 cu. metres); *f* is the weight in milligrammes of the iron spiral. Here we have the practical calculations on burning, for example, 1 grm. of commercial saccharine: *a* = 1000 grms. water, *E* = 420 grms., *n* = 86 mgrms., *f* = 48 mgrms.; the temperatures observed were as follow:

Initial temperature	17·76°	After 7 minutes	20·44°
After 1 minute	17·77°	„ 8 „ (maximum)	20·60°
„ 2 minutes	17·78°	„ 9 „	20·58°
„ 3 „	17·78°	„ 10 „	20·58°
„ 4 „	17·78°	„ 11 „	20·57°
„ 5 „ (ignition)	17·78°	„ 12 „	20·56°
„ 5½ „	18·42°	„ 13 „	20·55°
„ 6 „	19·66°		

Thus we have $T = 20{\cdot}60 - 17{\cdot}78 = 2{\cdot}82$; the mean variation per minute of the temperature before ignition is $\frac{17{\cdot}78 - 17{\cdot}76}{5} = 0{\cdot}004°$, and after the maximum is $\frac{20{\cdot}60 - 20{\cdot}55}{5} = 0{\cdot}010°$; the correction for the first half-minute after ignition will be $\frac{0{\cdot}004}{2} = 0{\cdot}002°$, and for the next half-minute it will be $\frac{0{\cdot}010 - 0{\cdot}004}{2} = 0{\cdot}003$

In the *analysis of combustibles*, and especially of coal, we must also take into account the other components which may influence its value ; the *moisture* is determined by the loss in weight of 2 grms. of coal on heating for two hours at 105° ; *ash* is determined by burning 2 grms. of coal in a platinum capsule over a direct flame or in a muffle, and should not exceed 5 per cent. in coal of good quality (Cardiff 1*a*) ; in general the calorific power diminishes with increase of the ash—coal of poor quality sometimes contains 12 to 14 per cent. The volatile matter (nitrogen, hydrogen, and hydrocarbons) is found by the diminution in weight of 1 grm. of coal heated for about two minutes in a crucible which is not hermetically closed by a cover, over a gas flame, the point of which just reaches the bottom of the crucible, until the flame of the ignited gas which escapes from the crevices left by the lid ceases. From the diminution of weight the moisture must be subtracted. Coals contain quantities of volatile matter varying from 15 to 40 per cent., and of these the hydrogen is important because 1 grm. of hydrogen develops 34,200 cals. (143 Kj.) on burning, and the hydrocarbons are also important because on the average they develop 50 Kj. on burning. Deducting from the weight of the coal the volatile products, including the moisture, we find the percentage of coke. Sulphur in its various forms (as iron sulphide and organic sulphur) is harmful because on burning it produces SO_2, which attacks the boiler-plates. The total sulphur is obtained by heating 1 grm. of coal for an hour in a platinum crucible with a mixture of calcined magnesia (2 parts) and calcined sodium carbonate, free from sulphur (1 part) ; the mass is treated with water and heated with a little bromine water in order to oxidise the sulphite and obtain all the sulphur in the form of sulphate. It is then filtered, acidified with HCl, and the sulphate precipitated with barium chloride. The barium sulphate so formed is weighed and from this weight the total sulphur is deduced. Good coal should not contain more than 1 per cent. of sulphur at most.

Knowing the calorific power of a fuel, it is easy to determine the quantity of water which this can evaporate in a steam boiler, knowing that 100 Calories (418 Kj.) are required to heat 1 kilo of water from 0° to 100°, and that a further 536 Calories (2242 Kj.) are required to transform 1 kilo of water at 100° into 1 kilo of steam at 100°.

Fuels give their maximum yield of heat when combustion is complete and the carbon is completely transformed into CO_2 (1 grm. of carbon thus producing 33·8 Kj. = 8080 cals.). If, on the other hand, insufficient oxygen or air is present for complete combustion, then carbon monoxide (CO) will be formed instead of CO_2, and in this way less heat is developed (10·25 Kj. = 2449 cals.), and the CO is lost as it passes off with the chimney gases, whilst if sufficient oxygen were there to burn it a further 23·5 Kj. (5631 cals.) would be produced for each gramme of carbon which it contained. On the other hand, on practically using coal as a combustible there should be no excess of air in the furnace grate because this excess passes off unaltered through the chimney at a temperature of more than 300° and heat is thus uselessly conveyed into the atmosphere. Practical control of the proper combustion of the coal is effected by analysing the chimney gases. If carbon monoxide is present this is a sign that the draught is too weak and that the quantity of air which enters the grate is insufficient, whilst in absence of carbon monoxide

and for each minute from 6 to 7 and 7 to 8 before the maximum it will have a mean of 0·010, that is, 2 × 0·010 for these two minutes, so that the complete correction t will be (2 × 0·010) + 0·003 − 0·002 = 0·021. On introducing all these values into the general formula we have :

$$C = (2{\cdot}820 + 0{\cdot}021)\ (1000 + 420) - (0{\cdot}23 \times 86) - (1{\cdot}6 \times 48)$$
$$C = 4034{\cdot}22 - 19{\cdot}78 - 76{\cdot}80 = 3937{\cdot}6 \text{ cals. (the theoretical value being 3866).}$$

In the case of coal we must take into account the fact that the water formed in the calorimeter is, as in the above case, converted into liquid water, whilst during combustion under boilers the heat of condensation of the steam into liquid water is not comprised in the heat which is utilised. In ordinary calorimetric determinations the heat of combustion is given for the case in which the water is liquefied, but if we wish to give the effective calorific power we must deduct the heat of condensation of the water which is liquefied in the calorimeter, and this may be roughly weighed or, better still, if the calorimeter is arranged with a delivery tube, the water may be evaporated in a current of dry air by immersing the calorimeter in a bath of boiling water, and the water vapour absorbed by a weighed calcium-chloride tube. In general for 1 grm. of coal the heat of condensation of the water vapour will be about 150 to 160 cals.

the combustion is well regulated. If, however, the excess of free oxygen and air exceeds the ordinary limits, the above-mentioned disadvantages occur.

The gases to be analysed are aspirated through a tube which is applied through an air-tight hole in the flue, by means of a gutta-percha valve, *B*, into the *Orsat apparatus*, and pass into the graduated burette, *A*, which may be emptied or filled by raising or lowering the bottle of water, *C*, which communicates with it. The universal cock, *E*, is suitably turned, and the reservoir, *C*, raised or lowered in such a way that the gas is first passed into a vessel at the side containing a concentrated (30 per cent.) solution of potassium hydroxide, which is subdivided by small tubes of glass in order to increase the surface of contact, and all the CO_2 is thus absorbed; the gas is then returned to *A* and its volume measured, the volume of absorbed CO_2 being given by the difference. The remaining gas is then made to enter another vessel containing an alkaline solution of pyrogallic acid (1 vol. of a 25 per cent. aqueous solution of pyrogallic acid and 5 to 6 vols. of a concentrated solution of potassium hydroxide) or yellow phosphorus, which completely absorbs the oxygen. The remaining gas is again measured in the burette, *A*. The gas is finally passed into a third vessel containing an ammoniacal solution of cuprous chloride which absorbs the carbon monoxide, and thus the volume of nitrogen only finally remains. The cuprous chloride solution is obtained by dissolving 100 grms. of fresh cuprous chloride in a solution of ammonium chloride (1 part to 3 of water) and adding one-third of its volume of ammonia of sp. gr. 0·910; it is kept in closed bottles containing copper turnings. The gas is made to enter and leave the graduated tube by lowering or raising the water reservoir, *C*.

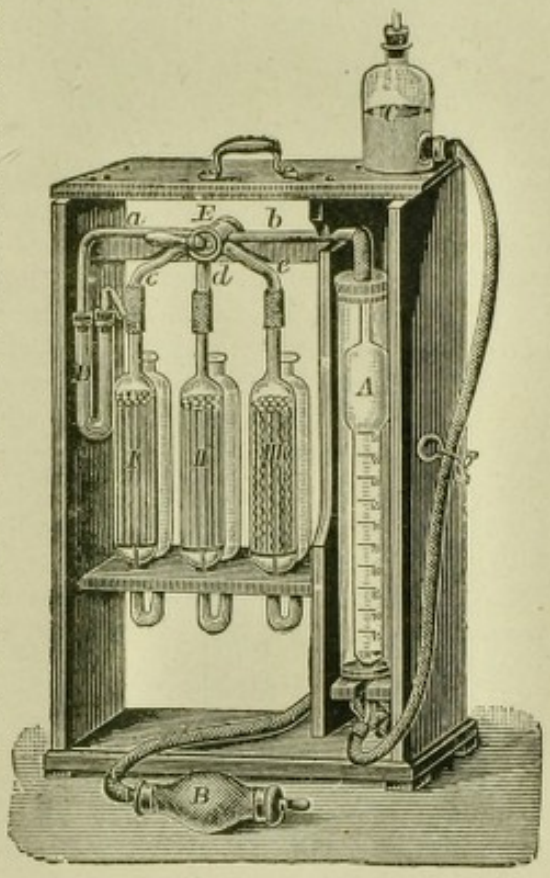


FIG. 156.

In this way the composition of furnace gases is easily determined in a very few minutes.

There are now also forms of apparatus which automatically register the composition of chimney gases, being based on the density of these.

SILICON : Si, 28.3

This element was prepared free in the amorphous state by Berzelius in 1823, by heating potassium fluosilicate with metallic potassium :

$$SiF_6K_2 + 4K = 6FK + Si.$$

Saint-Claire Deville obtained it in the crystalline condition by heating sodium fluosilicate with aluminium or with sodium and zinc; on heating powdered SiO_2 with magnesium powder and then dissolving the excess of Mg with acid, silicon is obtained as a light brown powder which is inflammable in the air. It is to-day prepared in considerable quantity in the electric furnace by reducing quartz with wood charcoal with addition of CaO and Mn_3O_4; the crude silicon which results is purified with HCl and HF and contains 90 to 91 per cent. of Si, 6 to 7 per cent. of Fe, 0·08 per cent. of Mn, about 2 per cent. of Al, 0·02 per cent. of P, and about 0·2 per cent. of carbon; the material so obtained is utilised in metallurgy to obtain iron which is hard and resistant to acids (ferro-silicon), &c. The crystals obtained by this process are lustrous, black and hard,

and form octahedra. They are separated from the fused zinc in which they are imbedded by dissolving the metal in HCl.

Silicon is one of the most abundant elements in nature, and in combination with oxygen forms silica (silicic anhydride) SiO_2, as quartz, amethyst, agate, opal, various sands, &c. In the form of silicates it is the principal constituent of the more important rocks, especially of the primitive rocks.

Silicon does not exist free in nature[1] and is obtained by heating silicon fluoride with sodium : $SiF_4 + 4Na = 4FNa + Si$; sodium fluoride is soluble in water and silicon results as a greyish-brown amorphous insoluble powder. According to Winkler it may be obtained pure by heating powdered quartz with magnesium powder : $SiO_2 + 2Mg = 2MgO + Si$.

Free silicon formed by the reduction of silica by carbon is often found in cast iron from the blast furnaces. Amorphous silicon is only soluble in HF with evolution of H, or in alkalis. It does not conduct electricity, and forms SiO_2 when burnt in the air. Crystallised silicon is, on the other hand, a good conductor of electricity and is harder than glass. Its specific gravity is 2·49 ; it does not dissolve in any one acid, but only in a mixture of HNO_3 and HF, and does not oxidise, even on heating to redness in an atmosphere of oxygen. On boiling it with a solution of sodium hydroxide it is dissolved with development of hydrogen, forming sodium silicate : $Si + 4NaOH = SiO_4Na_4 + 2H_2$.

After being heated to high temperatures amorphous silicon behaves in the same manner as crystallised silicon, perhaps because it partially melts and becomes crystalline. When burnt in an atmosphere of dry chlorine, silicon forms silicon chloride, $SiCl_4$; if the chlorine is moist a portion of it is converted into SiO_2 ; with gaseous HCl at high temperatures it also forms $SiCl_4$, but some silico-chloroform, $SiHCl_3$, is formed at the same time. It combines with fluorine even in the cold, and even with nitrogen at high temperatures. In the electric furnace it combines with various metals forming *silicides*.

CARBON COMPOUNDS

At the ordinary temperature carbon is one of the chemically more indifferent elements, and in the cold it combines with fluorine only. It does not combine with the other halogens, even on heating. At high temperatures, however, when the carbon molecules are less complex, it combines with various elements, and at the temperature of the electric arc it unites directly with hydrogen forming acetylene, C_2H_2. In the electric furnace it unites with silicon at 1400° and forms *carborundum* CSi (*see below*), and it also combines at this temperature with various metals (Ca, Ba, Mg, &c.), forming numerous carbides. With oxygen it forms two oxides, CO and CO_2, on heating, and with sulphur vapour it forms carbon disulphide, CS_2. When combined, especially with hydrogen, carbon acquires a very great capacity for reaction, and then forms thousands of compounds, the study of which is the sphere of organic chemistry.

The number of compounds which carbon can form is theoretically infinite, because the tetravalent carbon atom has the property of saturating one, two, or three of its valencies with other carbon atoms, forming more or less long chains of atoms, up to twenty and thirty atoms long, in direct, branching, or closed chains ; all the valencies which remain free are saturated by hydrogen or by elements of other groups, as is explained at length in the second volume of this work (" Organic Chemistry ").

NATURE OF FLAME. Flame is formed by a jet of combustible gas (lighting gas contains hydrocarbons, especially methane, CH_4, hydrogen, CO, &c.), which, on heating in contact with the oxygen of the air, burns and becomes incandescent, emitting light

[1] It has been calculated that one-quarter of the weight of the earth's crust is formed of silicon, whilst oxygen forms 50 per cent. of the weight of our terraqueous globe, including the atmosphere. The other elements are much less abundant ; thus it is calculated that iron forms 5 per cent. of the weight of the earth and carbon only 0·2 per cent.

and heat formed by the chemical reaction between the hot gases which form the combustible, and the oxygen of the air which acts as a supporter of combustion. The hydrogen is transformed into water and the carbon into CO_2.

A flame becomes luminous when certain hydrocarbons containing much carbon decompose with liberation of carbon particles through insufficiency of oxygen ; these particles become incandescent and very luminous. Thus, on heating, ethylene readily separates carbon : $C_2H_4 = CH_4 + C$, and so does acetylene : $2C_2H_2 = CH_4 + 3C$. In Bunsen burners, such as are used in laboratories, a luminous or colourless flame may be obtained at will by allowing more or less air to enter the tube which carries the gases to the flame.

A flame may be oxidising or reducing according to the excess or deficiency of air or oxygen which is mixed with the gas during combustion, and this property of flames is of great practical importance through the application which is made of it in various industries, in which either an oxidising or a reducing flame may be required according to the circumstances. In the colourless flame of the Bunsen burner the internal nucleus of the flame, where the gas is abundant and there is a deficiency of air, has a reducing action, whilst the external portion, and especially the point of the flame, is of an oxidising character. We

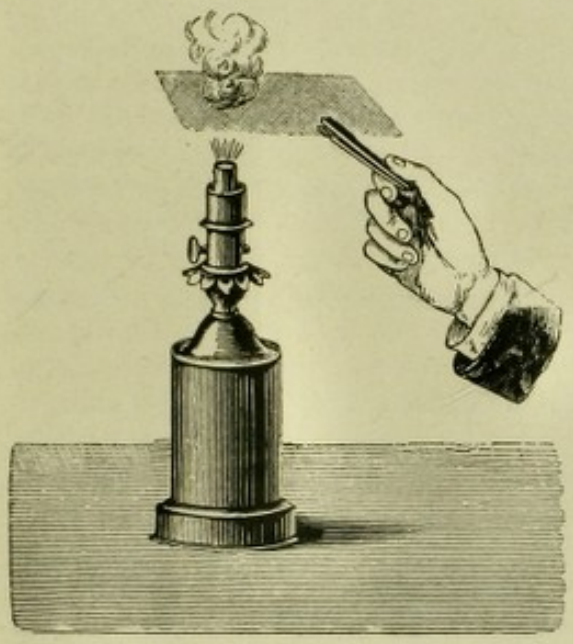


Fig. 157.

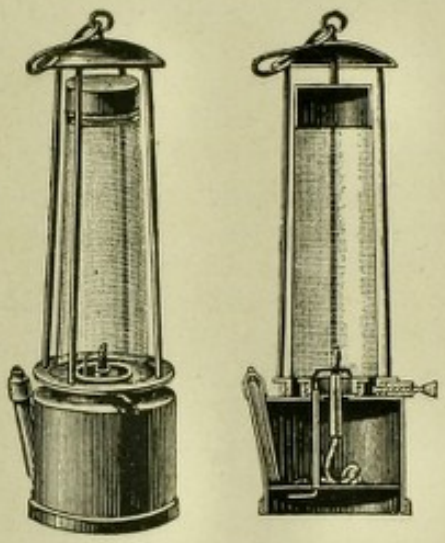


Fig. 158.

have also seen that, under different circumstances, many combustible substances may also act as supporters of combustion, for example, hydrogen, chlorine, ammonia, &c.

If a jet of lighting gas is projected on to a metallic gauze (Fig. 157) the gas may be lit above the gauze when the flame will not pass through it. Thus a flame may be isolated by means of a piece of metallic gauze from the gas supply by which it is fed, because the gauze is such a good conductor of heat that the heat produced by contact with the flame is rapidly dispersed to every side, and thus the temperature of the gauze is maintained below that which is necessary to ignite the inflammable gas on the other side of it.

This property was utilised by Davy in his miners' safety lamp (Fig. 158), which consists of a simple oil-lamp the flame of which is completely surrounded by a metallic net. If this lighted lamp is introduced into an atmosphere full of inflammable gas, this gas penetrates to the interior of the metallic gauze and is ignited, but the flame cannot communicate with the outside. These lamps are, therefore, employed by miners, because when explosive gases are formed in the mine, the lamps may be used for illumination without the risk of explosion.

Flames of oil, candles, paraffin, and alcohol are extinguished in air containing 15 per cent. of carbon dioxide, whilst a gas flame resists amounts of carbon dioxide up to 35 per cent., and a hydrogen flame will burn in an atmosphere containing 58 per cent. of CO_2, that is, in only 8·8 per cent. of oxygen. This fact may also be utilised in the construction of miners' safety lamps by causing

a hydrogen flame to burn in them simultaneously with the oil flame. When the oil flame is extinguished it is a sign of danger to the miner, because in 15 per cent. of CO_2 he would quickly be suffocated. When the miner in returning arrives at a point where the air is pure, the hydrogen which had continued to burn again lights the oil flame.

The temperature of a flame in general is lower than that deduced from theoretical calculations. Thus, in the hydrogen flame burning in oxygen, the temperature is calculated as follows: A gaseous mixture formed from 16 grms. of oxygen and 2 grms. of hydrogen develops 68,400 cals. on burning and forms 18 grms. of water vapour, and since the specific heat at constant pressure of water vapour is 0·48, then for a rise of temperature of 1° of 1 grm. of water vapour, 0·48 cal. is required, so that 68,400 cals. should heat 18 grms. of water vapour to a temperature of $\frac{68{,}400}{18 \times 0{\cdot}48} = 7909°$; in practice, however, exact measurement shows that the actual temperature of the oxy-hydrogen flame is little more than 2500°.

This abnormality is explained by the fact that the specific heat of water vapour at very high temperatures increases, but more especially because towards 1300° the water vapour which is formed commences to dissociate into its components H_2 and O, and then absorbs as much heat as is developed during its formation, so that the temperature of the flame cannot rise to 7909° as was calculated theoretically. When carbon burns vigorously in air, a temperature of about 1709° is reached, but when it burns in an atmosphere of oxygen, the temperature is much higher. The temperature of the electric arc as measured directly with pyrometers is 3690° to 3720°.

The halogen compounds of carbon are very numerous and are ordinarily studied together with organic chemistry.

CARBON TETRACHLORIDE: CCl_4

This compound is a colourless liquid of similar odour to chloroform, has a specific gravity of 1·629, boils at 77°, and solidifies in crystals at −24°; its specific heat is 0·2 and its heat of evaporation is 51 cals. (per 100 litres 9800 Cals. as for benzine). It dissolves paraffin and various resins (but not copal), especially in presence of 10 to 20 per cent. of alcohol; it is an excellent solvent for fats, even if the substance is slightly moist, in which case the fat would not be extracted by benzine, and it has the advantage of not being inflammable; when it is mixed with 10 to 20 per cent. of alcohol it is also a good solvent for resins; when mixed with sulphoricinoleic acid it dissolves in water.

It is prepared by passing dry chlorine through carbon disulphide (CS_2) which contains a little iodine in solution (or in which a catalyst formed of asbestos impregnated with $MgCl_2$ is suspended); this facilitates the chlorination: $CS_2 + 6Cl = CCl_4 + S_2Cl_2$.

On distillation CCl_4 passes over, and sulphur chloride, S_2Cl_2, remains as a residue.

In presence of a little powdered iron S_2Cl_2 is also transformed into CCl_4; thus $CS_2 + 2S_2Cl_2 = CCl_4 + 6S$, and this latter is re-utilised for the preparation of CS_2.

The tetrachloride is purified by washing it with a solution of sodium hydroxide and by then rectifying it by distillation over a solution of calcium hypochlorite, containing 6 per cent. of Cl.

It has been found that CCl_4 attacks the metals, especially in presence of water, through formation of HCl, and its high price prevented it from being used industrially on a large scale in the past as a solvent to replace benzine, &c. It is to-day, however, placed on the market in the pure state at a price of £24 to £26 per ton, and under these circumstances it is already used for degreasing wool, fabrics, linen cloth, oil-bearing seeds, bone, &c., but lead-lined or tinned

apparatus with nickel-plated cocks and valves has to be used. The vapours of CCl_4 are not more narcotic than those of benzine.

CCl_4 also renders other solvents almost uninflammable when it is added to them in the proportion of 50 to 80 per cent. During the last few years the manufacture of chlorinated derivatives of acetylene (chlorides of ethylene and ethane: $C_2H_2Cl_2$, dicline; C_2HCl_3, tricline; C_2HCl_5, pentaline; &c.) has been started in the Usines électriques de la Lonza at Geneva; these products are non-inflammable liquids which do not attack metals.

In Italy in 1907 50 tons of carbon tetrachloride were produced at £24 per ton, and although it has not yet been widely used industrially on account of its high price and of the fact that it corrodes the metals, lead-lined and tinned vessels resist it sufficiently well, and nickel resists even moist CCl_4 excellently. In 1908 the production dropped to 8 tons.

CARBON DIOXIDE: CO_2 (CARBONIC ANHYDRIDE)

This gas is also incorrectly called *carbonic acid*. It is a gas which is always found in the free state in the atmosphere in the proportion of 4 litres per 10,000 litres of air. Expired air (the product of animal respiration) contains 4 or 5 per cent.; thus the air of rooms or of places in which many people congregate rapidly becomes unsuitable for respiration through the diminution of the oxygen and increase of CO_2; for a man breathes in about 700 grms. of oxygen daily and expires about 900 grms. of CO_2 in the same period. Natural sources of carbon dioxide are found in volcanic neighbourhoods; at Bohl in the Rhine Province 300 kilos of carbon dioxide are evolved daily; large quantities of CO_2 are found at Pyrmont; in the Grotto of Dogs at Pozzuoli near Naples, the gas of which contains 61 to 71 per cent. of CO_2, about 6 per cent of oxygen and 25 per cent. of nitrogen; in the province of Arezzo there is an abundant source of CO_2 which is utilised industrially by the firm of Cesare Pegna and Sons of Florence. It is found in all active volcanoes, especially in those of South America; at Sondra in Thuringia there is a spring which yields 1000 cu. metres of pure CO_2 of 99 per cent. per hour. If the carbon dioxide in the earth's crust is present under pressure in contact with water the latter absorbs very large quantities and rises in the form of mineral springs as acidulated mineral water. This water often dissolves iron during its course and becomes ferruginous. In the form of calcium and magnesium carbonate carbon dioxide forms entire mountain ranges.

On burning carbon, coal, or organic substances in general completely, in presence of a sufficient quantity of air, CO_2 is always formed. On heating calcium or magnesium carbonate to redness CO_2 is formed abundantly: $CO_3Ca = CaO + CO_2$, whilst the alkaline carbonates are not decomposed by such treatment. On treating carbonates with dilute hydrochloric acid, the whole of the CO_2 which they contain is evolved:

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$$

In the laboratory a regular supply of carbon dioxide is obtained by the action of dilute hydrochloric acid on lumps of marble, the same apparatus being used as for hydrogen (*see* p. 131).

Carbon dioxide is formed abundantly in all fermentation processes, especially in those of sugar solutions, such as grape juice, in brewing, &c., and is utilised industrially (*see* vol. ii, "Organic Chemistry").

PROPERTIES. Carbon dioxide is a colourless gas with an acid smell and taste. Its specific gravity is 1·524 (air = 1) and 1 litre at 0° weighs 1·965 grms.; being so heavy it may be collected by displacement in air and may be poured from one vessel to another just as though it were a liquid.

A very striking demonstration of the great density of CO_2 may be based on the different velocities of diffusion of gases differing greatly in the size of their molecules (p. 39). For this purpose the Ansell apparatus with an electric bell may be used, and is also used as an automatic indicator in mines, cellars, and in all cases in which the air may become mixed with a heavier or lighter gas. In Fig. 159 one form which Ansell's apparatus may take is shown. A glass funnel with a long neck bent into a U-tube is filled with mercury up to the level, *d* ; the funnel is closed by a porous disc of plaster or unglazed earthenware. The tube, *b*, is closed by a cork stopper which carries an iron or platinum wire which does not dip into the mercury and is connected to one of the poles of a battery which is connected with an electric bell ; into the U-tube a platinum wire is sealed at *d* and communicates with the same pole of the battery, whilst another wire sealed into the U-tube at *c* is connected with the electric bell. Air is present in the funnel, *a*, and when this is surrounded outside by an atmosphere containing CO_2, the mercury rises in the tube and it comes into contact with the platinum wire in *d*, and then the current passes and the bell rings. By regulating the height of the mercury or of the metallic contact, the apparatus may be arranged to ring with any definite percentage of CO_2. If, on the other hand, the funnel is surrounded by an atmosphere of a gas lighter than air, such as lighting gas, hydrogen, firedamp, &c., the mercury is forced down and rises in the other limb of the tube until it comes into contact with the platinum point, *b* ; contact is then again made and the bell rings.

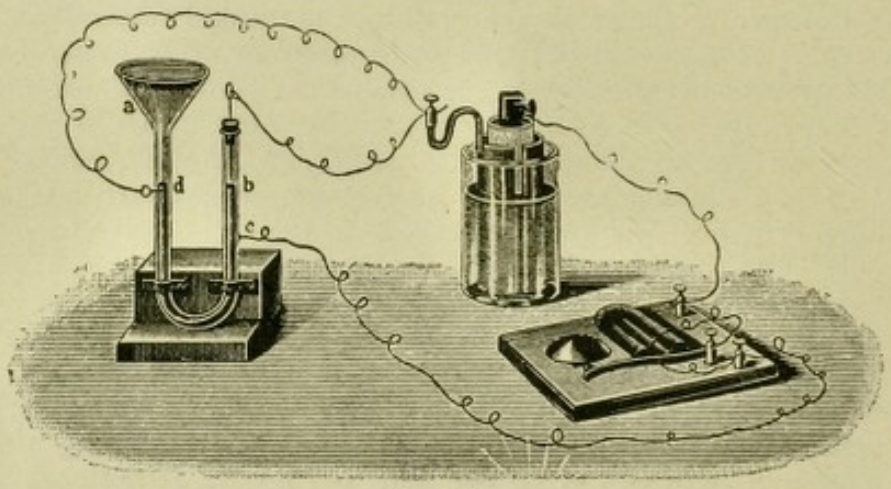


Fig. 159.

The critical temperature of CO_2 gas is 30·9° (critical pressure 77 atmospheres) and above this temperature it cannot be liquefied whatever the pressure may be. When liquefied it boils at − 78·2°, with such great absorption of heat that the remaining CO_2 solidifies. Solid carbon dioxide forms a white mass like snow which melts at − 57° under a pressure of 5 atmospheres, whilst if the pressure is less it gasifies without melting, because at ordinary pressures the boiling-point is lower than the melting-point.

These remarks also hold for all substances which have a vapour tension superior to the atmospheric pressure at their melting-points. Thus, the vapour tension of melting and liquid CO_2 is 3·5 atmospheres, and if the pressure is less than this, then it passes from the solid directly into the gaseous state (sublimes) as may be verified in the case of As_2O_3, of calomel, HgCl, and camphor, which can only be obtained liquid by melting them in sealed tubes under pressure. On the other hand, solid bodies which liquefy at the ordinary pressure, such as iodine, mercury chloride, &c., may be sublimed directly if at the melting-point the pressure is diminished below that of an atmosphere. Carnelley called the temperature at which solid bodies are no longer able to be liquefied, but pass directly into the gaseous state, the *critical pressure of solid bodies*. For ice the critical pressure is 4·6 mm., and for all other substances it indicates the vapour tension at the melting-point.

Faraday already liquefied CO_2 in 1823. The experiment was repeated by

Thilorier in 1834, and still later Natterer obtained it easily and in abundance with special apparatus at high pressures. In order to liquefy it at the ordinary temperature of 20°, a pressure of 50 atmospheres is required. It then forms a colourless, very mobile liquid which has a specific gravity of 0·726 at 22°, and of 0·91 at − 1·6°; it has thus a much greater coefficient of dilatation than the gas, and this is also true for all substances which are liquefied under strong pressure. On mixing solid carbon dioxide with a little ether a paste is formed which produces a cooling down to −140° at reduced pressure.

One volume of water at 14° dissolves an equal volume of CO_2; at 2 atmospheres pressure it dissolves 2 vols., at 3 atmospheres 3 vols., and also at greater pressures CO_2 gas exactly follows Henry's law; on diminishing the pressure the gas is again evolved.

Carbon dioxide does not burn because it is itself the product of the complete combustion of carbon, and on account of its great stability it does not maintain combustion or animal respiration. Its molecule is not dissociated even when heated to 2000°. Magnesium, however, when heated to redness continues to burn in an atmosphere of CO_2, because its chemical energy is so great that it is able to abstract the oxygen, with separation of carbon: $CO_2 + Mg_2 = 2MgO + C$; potassium, sodium, and aluminium are also able to extract two atoms of oxygen from CO_2 on heating, with separation of carbon; other metals, and carbon itself, reduce it at a red heat, removing one atom of oxygen, and forming carbon monoxide:

$$CO_2 + Zn = ZnO + CO \text{ and } CO_2 + C = 2CO.$$

Chlorophyll, which is present in plants, reduces the atmospheric carbon dioxide under the influence of solar radiation and produces more or less complex carbohydrates which are utilised in the growth of the plant, oxygen being simultaneously liberated. But vegetable cells also continuously absorb small quantities of oxygen with formation of CO_2. At a temperature of over 1300° CO_2 is partly decomposed by repeated electric discharges into CO and O, but only a certain limited amount of the gas is decomposed because the CO recombines with oxygen to form CO_2.

On burning carbon in a given volume of oxygen CO_2 is formed without increase of volume, and this partly shows the composition of carbon dioxide: C (solid) + 1 vol. O_2 = 1 vol. CO_2.

The composition of CO_2 may also be shown by burning a given weight of pure carbon (diamond or graphite) in a current of oxygen and weighing the CO_2 which is formed, after absorbing it in a weighed solution of sodium hydroxide.

The heat of formation of CO_2 starting from carbon is: $C + O_2 = CO_2 + 406$ Kj. (97,000 cals.) per 12 grms. of carbon or 44 grms. of CO_2.

Dry CO_2 does not react with litmus paper, whilst when moist or in solution it shows weakly acid reaction, although when the paper is dried the red colour disappears. Solid carbon dioxide does not react with litmus paper.

In aqueous solution CO_2 probably forms the corresponding *carbonic acid*: $CO_2 + H_2O = C : \overset{-OH}{\underset{-OH}{O}}$ which, however, has not been obtained free, and appears to be only stable at 0° under a pressure of more than 12 atmospheres (Wroblewscky); when liberated from its numerous salts it immediately decomposes into H_2O and CO_2.

It is a weakly dibasic acid which forms secondary salts (disubstituted salts, carbonates) with strong bases; these show an alkaline reaction because the acid character is very weak. Monosubstituted salts, primary salts, *dicarbonates*, are also known, for instance: $C : \overset{-OH}{\underset{-OK}{O}}$. The carbonates, other than those of the alkalis, are insoluble in water; the alkaline dicarbonates, on the other hand, are less soluble in water than the dicarbonates of the alkaline earths (Ca,

Ba, &c.). The salts of carbonic acid are all decomposed by mineral acids and also by acetic acid with evolution of carbon dioxide.

CO_2 is in itself an almost harmless gas, but since it cannot maintain respiration, it may produce death by suffocation. This occurs when the expired air contains more than 15 per cent., because the liberation of carbon dioxide from the blue venous blood cannot then occur, and the lungs are no longer able to absorb oxygen. Even when the air contains 3 or 4 per cent. of CO_2 it produces a feeling of uneasiness which is followed by unconsciousness and all the symptoms of suffocation, and it is then necessary to immediately breathe pure air in order to regain the normal condition. In cellars or elsewhere where fermenting liquors are stored it is often dangerous to enter, and frequent accidents occur when ventilation is not provided there. This danger is avoided by entering the cellar with a lighted candle, because it is extinguished by air containing more than 15 per cent. of CO_2.

For the quantitative determination of CO_2 in air, *see* p. 375.

CO_2 has also a mildly antiseptic action and this partially preserves beverages such as wine and beer, meat, &c.

On electrolysing a saturated solution of potassium carbonate at $-15°$, the potassium salt of percarbonic acid, $H_2C_2O_6$, collects at the anode, being formed in an analogous manner to persulphuric acid. K_2CO_3 is first dissociated into $K^{\cdot}$ and KCO_3' ions, and these latter are condensed at the positive pole, forming potassium percarbonate, $\begin{vmatrix} O—COOK \\ \\ O—COOK \end{vmatrix}$, which after drying forms a solid blue mass which is easily decomposed into $K_2CO_3 + CO_2 + O$, and is thus an energetic, oxidising agent, but may also act as a reducing agent for the reasons explained on p. 235. Percarbonic acid is not known in the free state.

INDUSTRIAL PREPARATION OF LIQUID CO_2

Carbon dioxide has now found such large industrial application that it is necessary to explain the principal methods of manufacture, both in the state of pure gas and more especially in the form of liquid, for the production of cold, of ice, and for other purposes (*see below*).

The sugar refineries, which do not require very pure CO_2, obtain it in the form of gas diluted with air, from limestone, by heating it with coke in kilns similar to those used for the preparation of quicklime (*see* Part III), and in this way they also obtain lime for use in refining the sugar syrup. On heating dolomite (carbonate of Mg and Ca) or, better, magnesite, $MgCO_3$, in iron retorts, pure CO_2 is obtained.

CO_2 may be obtained at relatively low temperatures (at a dark red heat) from limestone, by heating it in a retort in presence of superheated steam.

In either case, however, it has been found in practice that at high temperatures the CO_2 rapidly attacks the retort.

Under certain special conditions it is even to-day found convenient to prepare CO_2 by reacting on a carbonate with sulphuric acid. Thus, in the case of the preparation of magnesium sulphate from $MgCO_3$ and H_2SO_4 (or $NaHSO_4$, a by-product of nitric acid works), CO_2 is obtained free of cost. In breweries to-day the carbon dioxide from the fermentation vats is also used after being purified by means of solutions of potassium permanganate, &c.

Dilute CO_2 is also prepared by the combustion of pure carbon, which must not contain tarry matter or hydrogen. For this purpose the coke from gasworks is especially suitable, though sometimes anthracite or wood charcoal is also used. These products are burnt in Kindler's furnaces (Fig. 160). The carbon is introduced through the opening, *b*, and is lighted at the base, *a*, *b* being then closed with a suitable cover. The amount of air necessary for combustion is drawn through the grate, *a*, by means of a pump which communicates with the apparatus through the tube, *r*. The CO_2 which is formed passes whilst still hot, together with the nitrogen of the air, through the chamber, *c*, filled with limestone which retains the dust; and the acid substances (SO_2) develop further CO_2, which enriches the gas. This is cooled by passing over the bottom of the pans, *g* and *g'*, in which cold

water circulates, is then washed in the vessel, *d*, and finally passes through the tube, *r*, to the gasometers. As the carbon in *b* becomes less in quantity, more material is introduced above. By this method, if the air current is carefully regulated, a gas is obtained which contains a maximum of 21 per cent. of CO_2. In actual practice only 15 to 17 per cent. is obtained. For this reason the method is seldom used alone, but nearly always together with the preparation of dicarbonates which absorb all the CO_2 which is formed.

In order to prepare pure carbon dioxide, the liquefaction of the CO_2 may be used, and the method of Ozouf is then applied. He first prepares dilute CO_2 in Kindler's apparatus and then separates it from the other gases, O, N, and CO, by absorbing it in a solution of sodium or potassium carbonate at a temperature of 42° to 45° and a concentration of 20° Bé. Dicarbonates are thus formed which regenerate all the CO_2 at 100°. If the CO_2 has any smell it is first purified by passing through towers filled with animal charcoal which is cleaned occasionally by heating it to redness in a furnace.

Beins took out the first patent for obtaining liquid CO_2 directly from solid dicarbonate in 1878. He evolved the CO_2 by heating in closed vessels and thus exercised so much pressure that the gas itself was liquefied (Faraday's method, *see* p. 27).

The industrial application of the method by forming dicarbonate solutions, together with a very ingenious arrangement of the apparatus for obtaining liquid CO_2, was first effected by Luhmann. From this time the industry of liquid CO_2 extended rapidly, and numerous patents followed, all marking an interesting series of improvements which it is impossible to describe, until the more recent processes have attained great practical success. In 1898 Raydt patented a process by the dry method, that is, by absorbing the CO_2 gas with dry carbonates in presence of the necessary quantity of steam to form the dicarbonates, and decomposed these with hot CO_2. This process, however, does not appear to have been successful in practice.

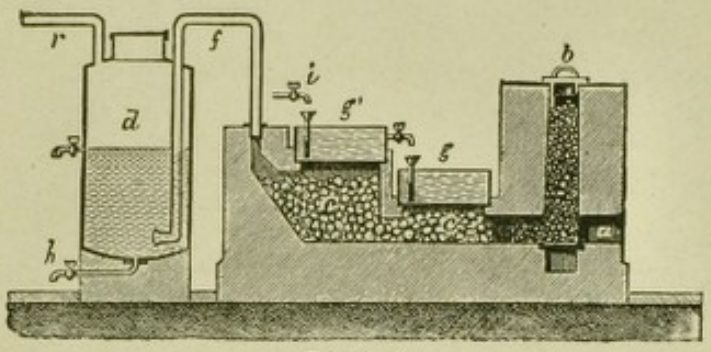


FIG. 160.

For some years the new process of Sürth has been applied, which instead of starting from dilute CO_2 of about 15 per cent. from simple coke furnaces—by Kindler's process or others—starts from a more concentrated gas free from oxygen, formed from power gas (*see below*) in a gas motor, thus obtaining 1 kilo of liquid CO_2 from 0·5 kilo of coke. The coke is burnt in presence of steam to obtain the power gas, and by means of a gas motor a quantity of energy is obtained at the same time, which is used for compression and for driving all the machinery. By the old process it is necessary to burn three times as much CO_2 as is liquefied in order to obtain the necessary power for the works. In Fig. 161 Sürth's new process is illustrated diagrammatically. It is distinguished essentially from other processes by the fact that the absorption of the CO_2 by solutions of K_2CO_3 is not effected at low temperatures of 40° to 45°, and at the ordinary pressure, but at pressures of 5 to 6 atmospheres and at 100° to 102°, the temperature of decomposition of the dicarbonate at the ordinary pressure. Under these conditions a larger quantity of CO_2 is absorbed by half the volume of potassium carbonate solution and in much smaller apparatus, because on account of the greater partial pressure exercised by the carbon dioxide in a mixture of more concentrated gas the formation of potassium dicarbonate is greatly facilitated, and also owing to the compression of the gas itself.[1]

[1] The partial pressure of CO_2 in a mixture containing 15 per cent. at the ordinary pressure would be $\frac{15}{100}$ of an atmosphere; in a gaseous mixture compressed to 5 atmospheres, on the other hand, the partial pressure of the CO_2 becomes $5 \times \frac{15}{100}$, that is, $\frac{75}{100}$ or $\frac{3}{4}$ of an atmosphere, and thus the absorption of the CO_2 is greatly increased compared with absorption at ordinary pressure. On the other hand, on working at ordinary pressure as in the other processes, if 15 per cent. of CO_2 is absorbed by a 7 per cent. solution of potassium carbonate in the first absorption tower, gas containing 8 per cent. of CO_2 will still be present in the second tower and the absorbed quantity will diminish rapidly because the partial pressure of the CO_2 is decreased from $\frac{15}{100}$ to $\frac{8}{100}$ of an atmosphere, and the absorption in a third tower is rarely attempted. This explains how a considerable portion of the CO_2 produced in the coke furnaces is lost in the old processes, because it is not all absorbed by two or three potash towers. It may also be noted that only about half of the carbonate is transformed into potassium bicarbonate, and that above this limit the absorbing power of the potassium carbonate for CO_2 diminishes rapidly.

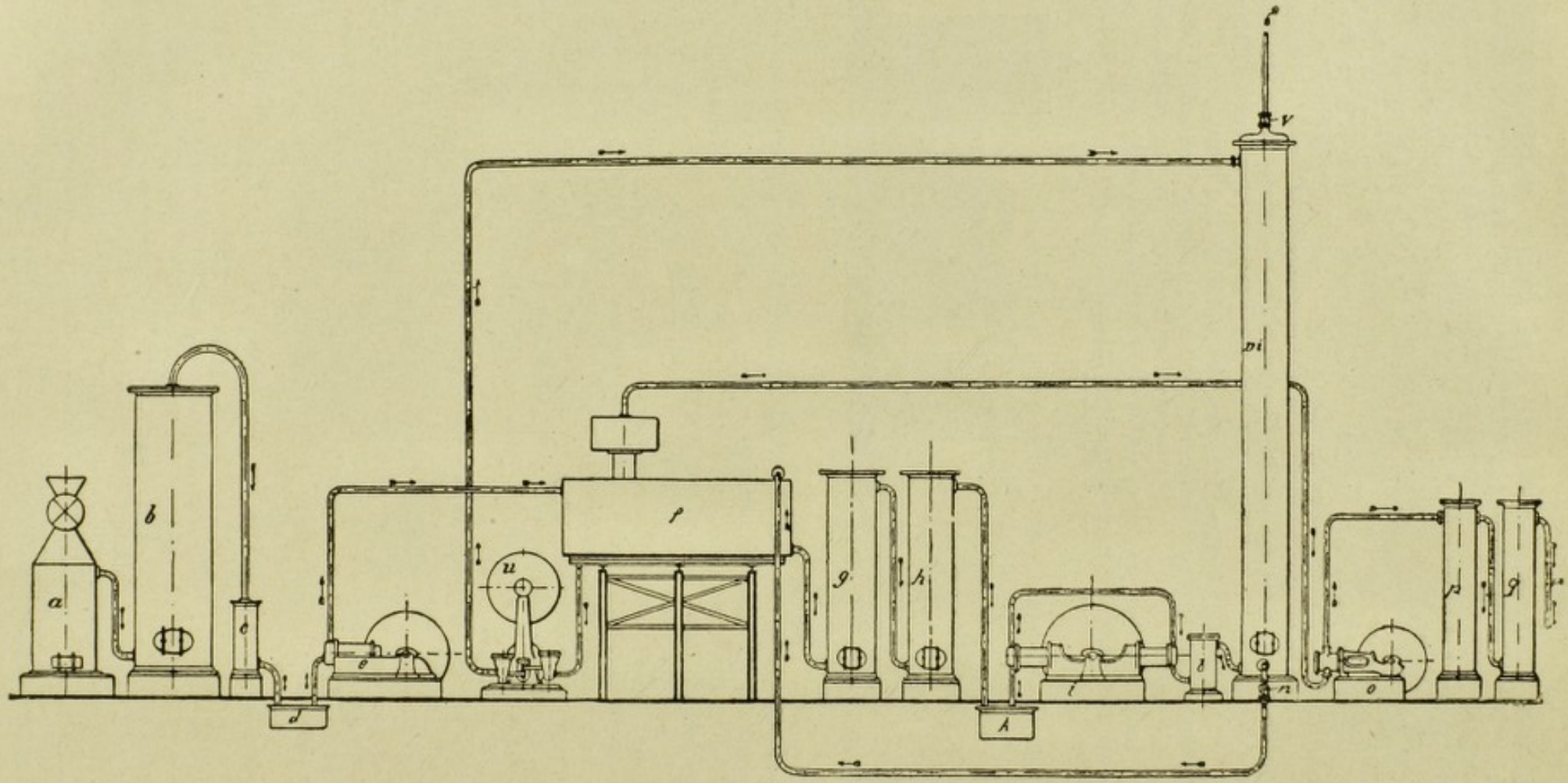


Fig. 161.

free CO_2 is also absorbed at such pressures together with the combined CO_2. It is evident that in order to recover all the CO_2 from the bicarbonate it is necessary to diminish the pressure whilst maintaining the temperature of the solution at 102°. The regenerated solution of K_2CO_3 is then quite ready for fresh absorption of CO_2 without any necessity for reheating or recooling it. In *a* power gas is produced, which is washed or cooled with water in the scrubber, *b*, and freed from tar in *c*; in *d* the water which is carried over with it is condensed and separated and it then enters the gas motor, *e*, with exactly the right quantity of air. It is here completely burnt, producing the power necessary to drive the works, and the resulting gases (exhaust gases) which are very hot (400°) are first utilised by circulating through tubes which keep the solution of bicarbonate contained in the gasifier, *f*, hot. These gases are then drawn by the pump, *i*, through the cylinders, *g* and *h*, which are filled with limestone and siliceous stones respectively. In the first of these they encounter a spray of water; and in *h* sulphur dioxide, which is always present, is absorbed by a weak solution of soda, and thus nothing is left but CO_2 and N. The same pump, *i*, which is both a compressor and an exhaust pump, then compresses the gas and, after separating the lubricating oil carried in with it, it is passed into the absorption tower, *m*, from the top of which the hot solution of potassium carbonate falls, which is provided by the degasifier, *f*, and forced in by the pump, *u*. The CO_2 is completely absorbed whilst the nitrogen escapes through the valve *v*, at the top of the tower where its pressure may be eventually utilised to drive a gas turbine, in which manner a considerable portion of the power used in compression may be recovered, or in certain cases the nitrogen may be also utilised chemically for the manufacture of calcium cyanamide (*see* p. 309).

The solution of potassium carbonate saturated with CO_2 (potassium dicarbonate) is collected at the base of the tower, and being under pressure is easily raised, without any necessity for pumping, through the tube, *n*, into the degasifier, *f*, where all the absorbed CO_2 is evolved, because it is here no longer under pressure and the temperature is maintained at 100° to 102°. The carbon dioxide is collected by the suction and compression pump, *o*, and passed at a pressure of 1 to 2 atmospheres through the cylinder, *p*, filled with lumps of fused calcium chloride, where it is dried, and then through the cylinder, *q*, filled with wood charcoal, where it is deprived of any smell. The pure, dry, and odourless CO_2, which is thus obtained, finally passes into the true *compressor* for liquefaction.

One of these plants was at work in Genoa in 1906, and others are projected for other places.

The new *Schütz process* has also been applied in Italy (Dr. Candiani & Co. of Milan erected a works at Naples in 1908), and it differs from other processes in the fact that CO_2 and a certain quantity of pure distilled water are produced simultaneously. The latter is used for steam boilers, thus avoiding incrustations, and to dilute the solutions of soda, thus avoiding the accumulation of impurities by the continued evaporation and dilution. The principle of lubricating the steam-engine with the same solution of potassium carbonate is also employed, thus avoiding lubricating oils and the consequent defilement of the condense water, which may thus also be employed for rediluting the solution of potash, &c. The heat which is developed through the combustion of the coke is sufficient to drive all the machinery; in fact the carbon is burnt in a semi-stationary engine of great efficiency and the combustion gases are utilised. The arrangement of the machinery and the stages of the process are shown diagrammatically in Fig. 162. The coke which is burnt on a hearth heats the boiler, *a*, which supplies steam for driving the motor, *b*, which is lubricated with a solution of potassium carbonate. The gases from the coke are washed with a spray of water in the tower, *c*, filled with coke. They escape from the top of this and are driven by the pump, *d*, through the saturating tower, *e*, from the top of which a spray of hot water falls. The hot gases are thus saturated with water vapour and enter the lower part of the absorption tower, *f*, from the top of which a spray of a cold potassium carbonate solution falls. This not only absorbs the CO_2, but also condenses a part of the moisture on account of the lowering of the temperature of the gases, and, therefore, no concentration of the potassium carbonate solution occurs, but, on the other hand, it is diluted. The gases which are not absorbed escape from the top of the tower, *f*, and consist mainly of nitrogen which may be used as indicated above, whilst the solution, which is saturated with CO_2, is forced by the pump, *g*, through the gasifier, *h*, where the combined CO_2 is liberated by means of a bundle of tubes in which steam escaping from the motor circulates. A certain amount of steam is liberated together with the CO_2, and this is condensed in the

cooler, *i*, by means of a counter current of water, the CO_2 being collected in the gasometer, *k*. The condensed water is used for the boiler, *a*, and the water which circulates in the cooler issues hot from the top and feeds the saturation tower, *e*, as has been described above. That part of the vapour which is condensed after having heated the gasifier, *h*, is utilised by collecting the condensed water in *l*, in order to use it for feeding the boiler, *a*. From the Figure we also see how the potassium carbonate solution freed from CO_2 is collected and then pumped afresh into the absorption tower, *f*.

By this process also the heat produced by the combustion of the coke is rationally and almost totally utilised, and thus a yield of 1 kilo of pure liquid CO_2 of 99 per cent. is obtained from 500 to 700 grms. of coke burnt, according to the size of the plant. During late years the Schütz process has undergone many improvements and is now gradually displacing the Sürth process.

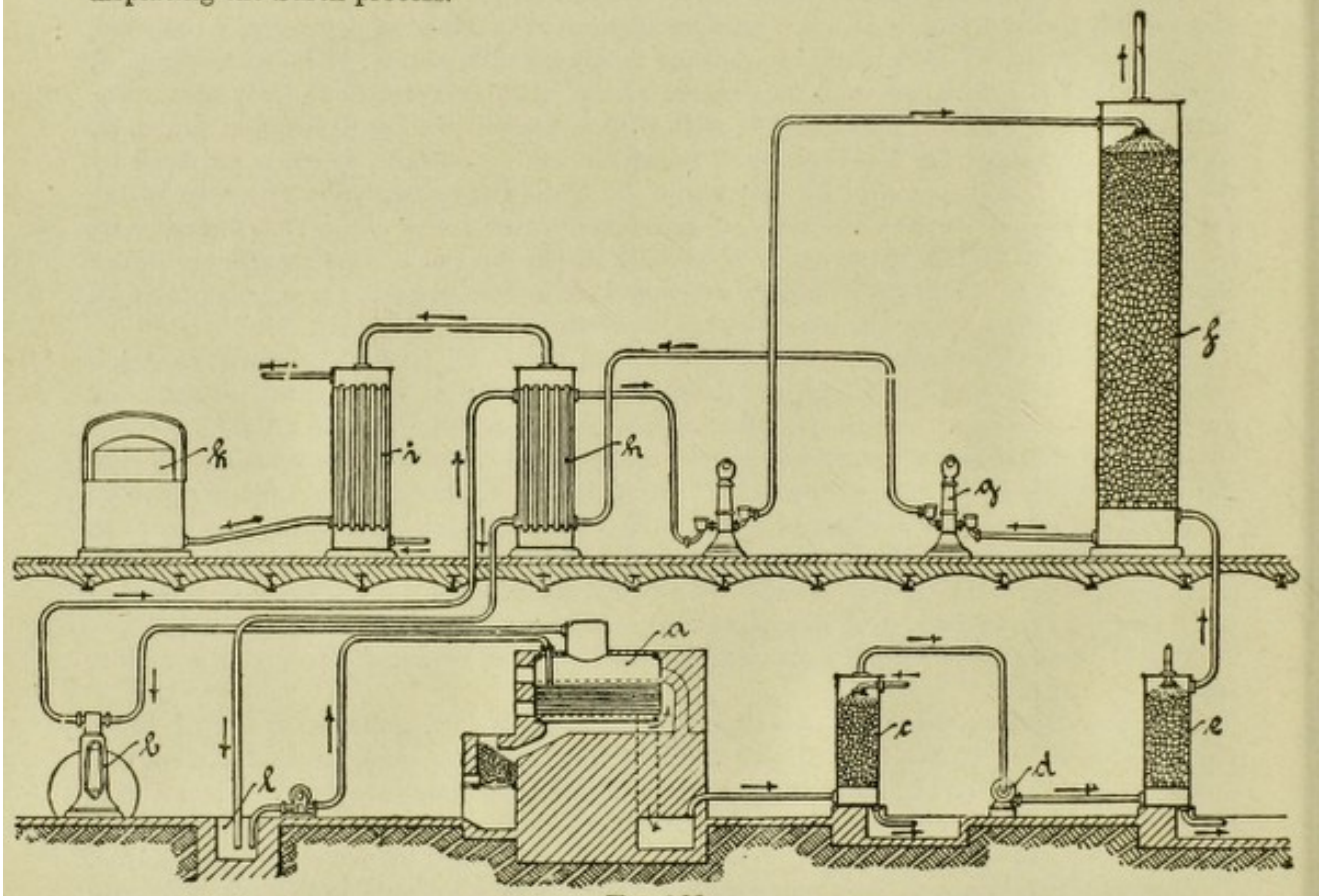


FIG. 162.

The compressors which are used for the liquefaction of pure CO_2 gas are analogous to those used for the liquefaction of air (p. 294). One type which has been used for some years, but which has undergone several improvements, is that indicated diagrammatically in Fig. 163. The dry CO_2 gas, free from air, proceeds from the gasometer by means of the tube, *M*, enters the body of the pump, *B*, is compressed to 30 atmospheres and escapes through the tube, *N*. It is cooled with water in the serpentine coil, *D*, and then passes through the tube, *P*, into the second portion of the pump, *C*, where it is compressed to 60 atmospheres. At this pressure it enters the cooling coil, *F*, where it is cooled with water, and accumulates as a liquid in the vessel, *H*, from which it is passed into the usual steel cylinders, *I*, which are used for transport. The compressors, the cooling coils and the steel bombs are all surrounded by cold water which circulates through the tubes 1 to 8. For the production of 10 kilos of liquid CO_2 per hour, the serpentine coil, *D*, has a length of 80 metres and *F* a length of 150 metres. With 6 h.p. 20 to 25 kilos of liquid CO_2 may be produced. The cylinders containing the CO_2 are similar to those used for compressed gases (pp. 130 and 177); they are cast in a single piece and when of a capacity of 10 litres should not contain more than 8 litres of liquid CO_2 (= 4360 litres of gas) in order to avoid accidents through the very great dilatation of the liquid CO_2 (*see* p. 381).[1]

[1] The cylinders weigh 37 kilos; after being made they must be heated to redness before being subjected to the Italian official test of resistance to a pressure of 250 atmospheres, although ordinarily they have only to sustain a

We will now illustrate by a practical example the thermal balance of an industrial process in this case, as has already been done for the manufacture of hydrochloric acid (p. 164).

For a factory which produces 50 kilos of liquid CO_2 per hour by the coke furnace process, about 15,000 litres of potassium carbonate solution of 20° Bé. are required, weighing 17,430 kilos, the whole of which has to be heated from 45° to 102° in order to regenerate the CO_2 which is absorbed. In order to raise the temperature in this manner by 57° about 993,500 Cals. will be required, that is, 17,430 × 57 Cals. (*a*), to which we must add about 53,600 Cals. (*a'*) because about 100 kilos of water are evaporated together with the CO_2, and the heat of evaporation of water is 536 cals.

Furthermore, for working the compressors, pumps, transmitters, &c., a steam-engine is required of about 25 h.p. which consumes 375 kilos of steam per hour at 5 atmospheres pressure, that is, 15 kilos per h.p.-hour. For this production of steam, 62·5 kilos of coke are required, as, generally speaking, 1 kilo of coke produces 6 kilos of steam, that is, 1·25 kilos of coke (*b*) are required for each kilo of liquid CO_2 which is manufactured ($\frac{62}{50} = 1{\cdot}25$).

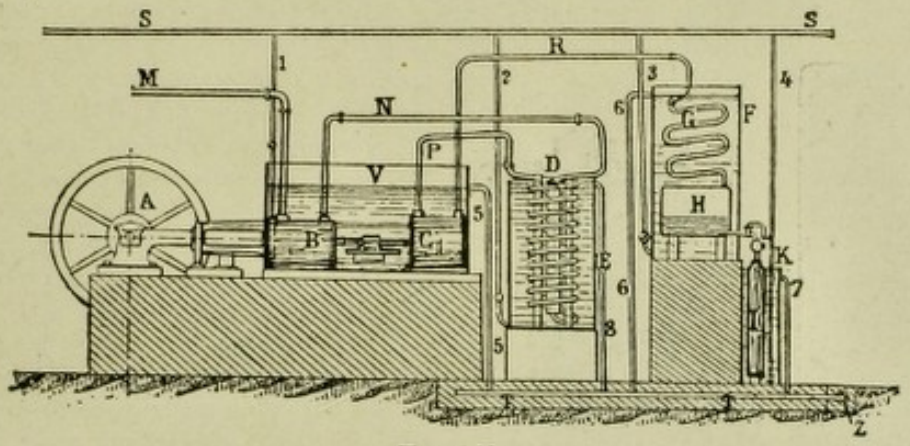


FIG. 163.

A portion of the heat produced during all these processes is recovered in the following manner: The 62·5 kilos of coke produce on burning 312,000 Cals. (*e*) (5000 for each kilo) and of this only 251,000 Cals. (*d*) are utilised for the production of 375 kilos of steam at 5 atmospheres pressure, that is, at a temperature of 153°; for in order to raise 1 kilo of water from 20° to 153°, 133 Cals. are required, and to convert this into steam at 5 atmospheres a further 536 Cals. are needed, being 669 Cals. altogether, and thus for the 375 kilos of steam we require 375 × 669 = 251,000 Cals.; the remaining 61,000 Cals. (*e*) remain in the hot furnace gases from the coke furnace, and of these about 50,000 Cals. (*f*) are recovered by heating the solution of potassium dicarbonate. On the other hand, the degasified solution of carbonate at a temperature of 102° must be cooled to 45°, and during this process serves to heat the dicarbonate solution which is to be gasified in a counter-flow apparatus. It is calculated that about 44° of this temperature difference can be utilised, and for 17,430 kilos of solution this gives a recovery of heat of 766,900 Cals. (*g*). Finally, we may calculate the recovery of the heat which escapes from the steam-engine, supposing that 10 per cent. of this is lost by prior condensation, leaving 338 kilos of steam at 100°; this 338 kilos of steam may be condensed in heating coils in the degasifier and thus regenerates 338 × 536 = 181,170 cals. (*h*). We thus obtain the following summary:

	Heat employed		Heat recovered
(*a*)	993,500 Cals.	(*f*)	50,000 Cals.
(*a'*)	53,600 ,,	(*g*)	766,900 ,,
(*c*)	312,000 ,,	(*h*)	181,170 ,,
Total	1,359,100 Cals.	Total	998,070 Cals.

The difference is, therefore, 361,030 Cals., which are necessary for the production of 50 kilos of CO_2; since 1 kilo of coke yields 5000 Cals. 72·2 kilos of coke will be necessary

pressure of 60–70 atmospheres. They are so safe that the railways (in Italy) to-day allow them to be carried on all trains, whereas at first they were classed with inflammable and explosive materials

for this purpose, that is to say, in order to produce 1 kilo of liquid CO_2, we require by this process 1·44 kilos of coke altogether, and this result is confirmed by actual experience.

Liquid CO_2 is placed on the market, as we have already said, in steel cylinders of various sizes (*see above*). These are closed above by means of various pieces strongly screwed together, as is seen in Figs. 164 and 165, which require no further explanation, because one can see how by turning the upper valve the escape of CO_2 may be readily regulated, and how a side-piece may be attached containing a pressure-reducing valve. For each kilo of CO_2 2 kilos by weight of steel cylinder are needed, from which it is evident that it is not profitable to transport CO_2 to great distances, because whilst the product itself costs 1*d.* to 1½*d.* per kilo, the freight and return of the empty cylinders to distances of 300 to 400 km. cost 1*d.* to 1¼*d.* (in Italy) by goods train and 3*d.* to 3½*d.* by passenger train.

The factory of Rommenhöller in Berlin alone possesses 155,000 steel cylinders for the transport of liquid CO_2.

SOLID CARBON DIOXIDE. This is formed with relative ease as a white mass similar to snow, by allowing liquid carbon dioxide to rapidly and freely expand in the air. Natterer allowed liquid CO_2 to expand in a brass chamber, whilst Landolt in 1884 obtained solid CO_2 in a much simpler manner by placing a woollen bag over the mouth of a cylinder of liquid CO_2 which was inclined downwards; on opening the valve, the CO_2 solidified as a snow in expanding and was retained by the bag, whilst the gas passed out through its pores. On then compressing this solid CO_2 in cylinders it is obtained as blocks of solid CO_2 which are very compact and have a specific gravity of 1·2; they evaporate very slowly, and by simply wrapping them in cardboard, cotton-wool, or other substances, they may even be despatched without any danger by rail, just in the same manner as ordinary ice. By spontaneous evaporation their temperature remains at − 65°. Attempts have been made in England to establish a trade in this product (Eng. Pat. 21,861 of 1899) and it is probable that it may acquire importance in the future, because it would be easy in this manner to produce great cold very cheaply without danger and without machinery, by means of the use of solid CO_2, the cost of transport being greatly reduced because heavy and costly steel cylinders are dispensed with. Recently, in 1905, a company for the preparation and sale of solid carbon dioxide was established at Charlottenburg, using the process of Heyl and Wultze (Ger. Pat. 157,403); the compressed product is placed in receivers in which a pressure of one atmosphere only is maintained, which are surrounded by a freezing mixture and communicate with a small compressor.

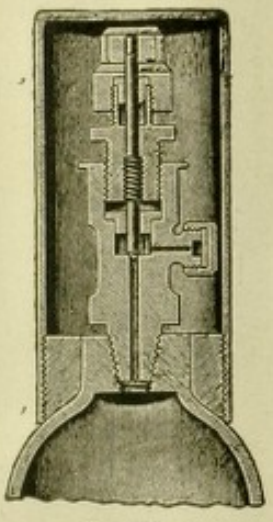


Fig. 164.

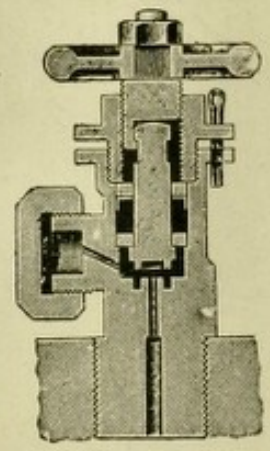


Fig. 165.

APPLICATIONS OF CARBON DIOXIDE. The gas is used in sugar refineries for separating from the sugar juice the lime which has been used for defecation. It is also used in white lead factories and in the manufacture of dicarbonates and of Solvay soda.

Liquid carbon dioxide is also used for effervescing drinks, such as soda water, mineral waters, sparkling wines, &c., because it holds certain salts in solution which would otherwise be precipitated (*see* p. 228); in beer and wine it has also a preservative action and hinders decomposition.

In restaurants the beer is raised from the cellar by connecting the barrel with a cylinder of liquid CO_2 furnished with a reducing valve, *B* (Fig. 166), and thus forcing it through the concentric tube, *G*, to the delivery tap. It is thus kept saturated with CO_2.

Raydt suggested the use of liquid CO_2 contained in iron cylinders at great

pressure, about 60 atmospheres, for motors and also for projecting water to great distances in case of fire without the use of a pump. Liquid CO_2 is largely used in breweries for the preservation and saturation of the beer and in the pressure apparatus which serves to convey it. It is used in ice factories (p. 234), and its use has been proposed for removing boiler scale by saturating the feed water. It is now used in large quantities for hardening white meta and steel and for obtaining large steel castings without blowholes ; for this purpose liquid CO_2 is poured on to the steel castings in gas-tight vessels, enormous pressures being thus produced at high temperatures (about 700 atmospheres at 100° and about 2000 atmospheres at 200°). Under these conditions the solidified casting is free from blowholes. The firm of Krupp of Essen use about 100 kilos of liquid CO_2 per hour for this purpose, especially for the casting of guns of large calibre. It is also used as an anæsthetic and generally for producing cold for surgical operations.

During the last few years baths of gaseous carbon dioxide have been applied therapeutically.

It is also employed to freeze sandy or crumbly soil before this is bored or excavated for wells, canals, foundations for the pillars of bridges under the water level, &c. At points where boring is to be carried out, a series of communicating vertical tubes are driven into the ground forming a ring arranged about a circumference of a diameter about two metres wider than the proposed boring. In these tubes brine from an ice machine is circulated or liquid carbon dioxide is evaporated. The previously moistened soil freezes and the whole forms a rigid block which may be easily and safely excavated. The great pressure of CO_2 in steel cylinders is also used for raising sunken ships, to which a deflated balloon is attached which is then filled with compressed gas—CO_2, hydrogen, &c.—under water, the balloon thus raised carrying the submerged vessel to the surface. Pure compressed CO_2 is also used for decanting inflammable liquids (benzene, &c.).

FIG. 166.

PRICES AND STATISTICS. In Germany in 1891 there were 23 works manufacturing liquid carbon dioxide which produced 2000 tons and exported about 1000 tons. In 1899 there were 60 works producing 14,000 tons of liquid CO_2, more especially provided by natural springs and the combustion of coke, and a similar quantity by heating carbonates. Practically none is to-day prepared from carbonates with mineral acids. In 1905 the production rose to 30,000 tons, two-thirds of which was obtained from natural gas, of which 7332 tons were exported at a price of 1*s.* 2*d.* per kilo in steel cylinders supplied by the purchaser ; it costs ½*d.* a kilo more when the cylinders are supplied by the manufacturer. In 1908 the production increased to 45,000 tons and the exports diminished to 2641 tons in 1909.

In France there are fewer works. The Carbonique Lyonnaise produces 150 kilos of liquid CO_2 per hour, and always maintains a stock of 13,000 cylinders of CO_2. The works at Bobigny produce 100 kilos per hour by burning coke. In 1897 France produced barely 1000 tons of liquid CO_2, in 1900 it produced 8000 tons, and the price descended from 1*s.* 3*d.* per kilo to less than 4*d.* per kilo, through competition. In Germany small quantities of liquid CO_2 are also sold at 2½*d.* to 4*d.* per kilo. In 1906 there were 40 works in the United States of America with a production of 15,000 tons. Switzerland produced 350 tons in 1905.

In Italy 183 tons of liquid CO_2 were produced in 1903 of which 135 tons came from Arezzo and the rest from Avigliana ; the commercial price was 7*d.* per kilo and 4 tons were imported. In 1904 the production rose to 196 tons and the imports decreased to 2 tons. Then a large number of works were erected in 1905–1906, and there is just at present over-production, which has obliged the manufacturers to seek for an outlet which is not always profitable, in the form of exportation, and a lowering of prices in order to increase the internal consumption ; thus in 1905 the production was 308 tons, in 1906 469 tons, in 1907 660 tons, in 1908 1200 tons, in 1909 1500 tons. The imports have completely ceased and the exports were 29 tons in 1906, 50·5 tons in 1907, and 42·4 tons in 1908. The price decreased continuously and at present the great competition between the various works has brought it down to 3½*d.* per kilo.

In order to *analyse* liquid CO_2 a sample is taken in a weighed glass tube with two cocks, by connecting it with the inverted steel cylinder so that liquid CO_2 is removed and not the gas mixed with air which is above it. From the weighed glass tube a portion of the gas is then passed into an Orsat apparatus in order to be analysed in the ordinary way (*see* p. 375).

CARBON MONOXIDE : CO

When carbon is heated to a temperature of 700°, or better still to above 1000°, in presence of air, carbon monoxide is mainly obtained instead of the dioxide, and at this same temperature CO_2 is decomposed in presence of excess of carbon : $CO_2 + C = 2CO$.

It was once believed that during the combustion of carbon between 400° and 700° CO_2 only was formed, but it has recently been shown that at 500° a little CO is already formed, together with the CO_2, and in presence of finely divided metals CO is formed even at 300°. This is explained by the fact that the reaction is reversible : $C + CO_2 \rightleftharpoons 2CO$, between the temperature limits indicated. In general, CO is formed whenever carbon is burnt in presence of an insufficient quantity of air.

PROPERTIES. It is a colourless, odourless gas, almost insoluble in water, but is very soluble in an ammoniacal or hydrochloric acid solution of cuprous chloride, with which it forms a crystalline compound, $2CuCl.CO + 2H_2O$, which on heating with potassium hydroxide liberates CO again, and is separated as a black precipitate.

Even small quantities of CO produce a black precipitate with a solution of palladium chloride ; 0·5 per cent. of CO in air already gives a brown coloration with an ammoniacal solution of silver nitrate, which then gives a black precipitate on boiling.

With iodine pentoxide, I_2O_5, it gives a fairly sensitive reaction by liberating iodine which forms a violet solution with chloroform or carbon disulphide :

$$5CO + I_2O_5 = I_2 + 5CO_2.$$

It is lighter than air (0·9672), and 1 litre weighs 1·2508 grms. Its critical temperature is −141°, and its critical pressure 35 atmospheres. Liquid CO boils at −190°, and is solid at −212°.

In the gaseous state it burns with a fine bluish flame.

On mixing 2 vols. of CO with 1 vol. of oxygen in a cylinder and lighting it with a powerful flame, a detonation is obtained : $2CO + O_2 = 2CO_2$. If the gaseous mixture is moist it is ignited very easily and at a lower temperature, perhaps because the CO reacts with water vapour forming hydrogen : $CO + H_2O = CO_2 + H_2$, and the hydrogen in turn combines with the oxygen of the mixture, regenerating water, so that in this case the latter would exert a pseudo-catalytic action. The flame of CO is extinguished in perfectly dry air.

Being a gas which is still oxidisable it has the property of reducing various metallic oxides, for example, copper oxide, at a red heat :

$$CO + CuO = CO_2 + Cu.$$

It also reduces certain oxides and chlorides of the noble metals even in the cold. A sensitive reaction for CO is thus obtained with a piece of paper impregnated with palladium chloride which blackens in presence of traces of the gas.

CO does not maintain combustion because it yields up its oxygen with difficulty, only separating carbon by the action of potassium at a red heat. A mixture of CO and H yields formaldehyde under the action of the dark electric discharge. Formaldehyde is one of the simplest organic compounds known : $CO + H_2 = HCOH$.

It is a very poisonous gas even in small quantities, as 1 litre of CO in 100 cu. metres of air produces symptoms of poisoning, and 1 litre in 779 litres of air is capable of killing a man in half an hour. It may be recognised when absorbed by the blood by means of the spectroscope. It combines with the hæmoglobin of the blood, thus preventing the formation of oxyhæmoglobin and the vital functions of the blood, through anoxæmia.[1] The symptoms of carbon monoxide poisoning are headache, unconsciousness, convulsions, &c. Air which only contains 0·05 per cent. is already poisonous for human beings, and cases of poisoning in badly ventilated rooms in which coal is burnt and where the stove is made of iron which becomes porous when hot are thus explained. In such cases the fuel is burnt with an insufficient quantity of air and at very high temperatures. In speaking of oxygen (p. 175) we have noted the experiments of Mosso, who showed that in compressed oxygen animals still resist the action of 6 per cent. of CO, and that when this pressure is released the animals immediately died.

On considering the thermochemical behaviour of carbon with respect to oxygen, it is interesting to note that whilst ordinarily, when simple elements combine with one or more atoms of oxygen, they give a maximum development of heat when combining with the first atom of oxygen, in the case of carbon the reverse is the case. Thus we know already that when carbon unites directly with two atoms of oxygen to form CO_2, 406 Kj. (97,000 cals.) are developed, and we also know that when CO + O forms CO_2, 284 Kj. (67,850 cals.) are formed and consequently, during fixation of the first atom of oxygen C + O = CO, 122 Kj. (29,150 cals.) will be developed.

This difference in the amount of heat evolved by combination with the first and with the second atom of oxygen is probably explained by the hypothesis that the whole of the heat liberated during combination with the first atom of oxygen is not indicated by the thermometer as heat of reaction, but that one portion remains absorbed by the intermolecular work necessary to disintegrate and volatilise the complex molecule of solid carbon.

When, on the other hand, CO and O react, the CO molecules are already free and consequently we may conclude that in order to disintegrate the molecules of solid carbon, at least 162 Kj. (= 38,700 cals., that is, 67,850 − 29,150) are required, assuming that the combination with the first atom of oxygen really causes an evolution of at least as much energy, namely, 67,850 cals., as combination with the second atom.[2]

[1] P. Giacosa maintains, on the other hand, that death occurs from a different cause, namely, through a reflex paralysis of the nervous centres governing respiration, caused by contact of the carbon monoxide with the sensitive terminals of the respiratory passage. Thus it is a case of poisoning, not by chemical, but by nervous action.

Many theoretical considerations and certain experiments of Marcacci also point in this direction. The experiment conceived and carried on by Giacosa is of interest in this connection. He first removed the blood from a dog and then, when it was at the point of death through acute anæmia, he introduced into its circulatory system the blood of another dog which had already been treated with carbon monoxide, so that its red blood-corpuscles no longer contained any oxygen. The entry of this blood into the respiratory system of the dog caused the respiratory activity to be revivified at once, and then the dog immediately regained normal respiration and passed in a few minutes from death to life. Thus, as in this case the blood which circulated in the body of the revived dog contained, at least at the beginning, quantities of oxygen much less than those which remained in the blood of an individual killed by poisoning with carbon monoxide, we may conclude that in such individuals death occurs through other causes.

[2] In these cases we are always speaking of the *molecular* calorific power, that is, the heat developed by the combination of 12 grms. of carbon with 32 grms. of oxygen to form 44 grms. of CO_2 (1 mol.) with development of 406 Kj., whilst in the case of combustibles in general the calorific power in large or small calories is practically referred to 1 grm. or 1 kilo of the combustible. Thus, as 12 grms. of coal give 97,000 cal., 1 grm. will give 8080 cals.; for CO − 28 grm.—the molecular calorific power when burnt to form CO_2 is 67,850 cals.; for 1 grm. of CO the heat of combustion will thus be 2423 cals.

PREPARATION. When an electric arc is passed between carbon electrodes under water CO is formed at the expense of the carbon of the electrodes : $C + H_2O = CO + H_2$.

Various organic acids, such as citric, malic, and formic acids, when treated on the water-bath with strong sulphuric acid monohydrate, develop a strong current of carbon monoxide mixed with very little carbon dioxide (CO_2). In the laboratory oxalic acid is always used and the traces of CO_2 are separated by passing the gas through a solution of sodium hydroxide. (*Translator's note.*—In these cases the amounts of carbon dioxide formed may be considerable and from oxalic acid equal volumes of CO and CO_2 are formed.)

The preparation from potassium ferrocyanide (1 part) with strong sulphuric acid (9 parts) is even more convenient. In this case the gases are passed through a solution of sodium hydroxide to absorb the traces of CO_2, SO_2, and prussic acid which are always formed.

CO may be obtained from CO_2 by powdered metallic zinc heated to dull redness : $CO_2 + Zn = ZnO + CO$, or more easily by heating magnesium carbonate mixed with zinc dust in a retort ; a mixture of $CO_2 + CO$ is first formed, but pure CO is obtained later ; the magnesium carbonate may be advantageously replaced by calcium carbonate :

$$CaCO_3 + Zn = ZnO + CaO + CO.$$

On heating carbon with metallic oxides CO is also formed, thus $C + ZnO = CO + Zn$, and this reaction explains the reducing action of carbon on heating with various metallic oxides, which is utilised in the preparation of metals. In 1794 already Courbelle found that steam in presence of carbon heated to about 600° forms CO_2 and H ; $C + 2H_2O = CO_2 + 2H_2$, but that above 900° CO is mainly formed : $C + H_2O = CO + H_2$, and $CO_2 + C = 2CO$. It is necessary to remember that during this reaction, and in the production of water gas, absorption of heat occurs.[1]

One kilo of coke containing 90 per cent. of carbon produces up to 2·5 cu. metres of water gas ; 1 kilo of ordinary coal produces about 2 cu. metres and of lignite 1 cu. metre. Crude water gas from coke contains 45 to 50 per cent. by volume of H, 40 to 50 per cent. of CO, 4 to 7 per cent. of CO_2, 4 to 5 per cent. of N, and about 1 per cent. of oxygen ; the calorific power is about 2500 cals. per cubic metre, and the gas costs from ·3*d.* to ·5*d.* per cubic metre.

The excess of water vapour proposed by Fayes and applied by Hembert and Henry

[1] The mixture H, CO and CO_2 with a little nitrogen from the air is called *water gas* ; in 1832 Jobard, of Brussels, used this gas for illuminating purposes. Water gas alone is, however, only very slightly luminous, and it is very poisonous on account of the large quantities of CO which it contains.

In spite of the improvements of Selligne and then of Witte, Leprence, Baldamus, Grune, Isoard, Kirkham, &c., by which the gas was rendered luminous by mixing it with hydrocarbons such as benzene, it was not used in large quantities. In 1860 Fayes constructed an apparatus by which a water gas containing little CO was prepared by employing an excess of steam in order to partly transform the CO into CO_2 : $CO + H_2O = CO_2 + H_2$ (for percentage composition, *see below*).

On cooling, this gas separates the excess of steam, and on then passing it over calcium hydroxide the CO_2 is absorbed, leaving almost pure hydrogen. By means of his apparatus Fayes produced as much as 1200 cu. metres of hydrogen per twenty-four hours at a cost of about ½*d.* per cu. metre, exclusive of labour and the cost of plant. This method was fairly successful at first, but was abandoned on account of the not inconsiderable technical difficulties and also probably on account of the presence of a little CO in the resultant gas. The method was only taken up again about the year 1880, first by C. Hessel in Kilburn (Eng. Pat. 3584 of 1880), then by G. E. Moore of New York in 1886 (Ger. Pat. 35,203 of 1886), and finally by Hembert and Henry in 1886 with a very ingenious arrangement of plant.

In the latter apparatus the superheated steam in small jets is first brought into contact with red-hot coke in the first retort ; equal volumes of CO and H_2 are thus formed and are passed into a second red-hot retort filled with lumps of refractory fireproof stone, and the reaction is completed by means of jets of superheated steam $H_2O + CO = H_2 + CO_2$. The gas finally contains H_2 and CO_2 only. Boulogne-sur-Seine is lighted on this system. The gas is rendered luminous by placing a small platinum net in the middle of the flame, as had been proposed by Gillard in 1846. This gas costs about 1½*d.* per cu. metre.

According to Eng. Pat. 2523 of 1909 carbon monoxide may be economically removed from water gas and replaced by hydrogen by passing the gas mixed with steam at 500° into a hot solution containing calcium hydroxide, $CaCO_3$ and H_2 being thus obtained. CO is also absorbed by the lime

in order to obtain less CO is advantageous on account of the law of mass, because, given the following systems in equilibrium, the following reactions are possible :

(1) $C + H_2O = CO + H_2$ (3) $CO_2 + C = CO + CO$

(2) $C + 2H_2O = CO_2 + 2H_2$ (4) $CO + H_2O = CO_2 + H_2$

The simplest and most economical means of displacing the equilibrium in such a manner as to produce less CO (1 and 3) and produce more hydrogen, is by increasing the velocity of the reactions (2) and (4), that is, by increasing the quantities of steam or by removing the CO_2 as was actually done later. It is not necessary to deny that the reaction (1) occurs at high temperatures with absorption of heat corresponding to 133 Kj. (= 31,800 cals.), and that reaction (2) occurs at lower temperatures, but also with absorption of heat, namely, of 91 Kj. = 21,750 cals. In order to start the reaction it is necessary at the beginning to supply heat by means of superheated steam or to introduce a little air which unites with the carbon to form CO and thus develops heat.

The disadvantage of this process is the presence of a larger or smaller quantity of CO ; excess of steam is eliminated by drying the gas with H_2SO_4—1 kilo per 100 cu. metres of gas.

The elimination of CO was also attempted by Bauer (1887) by adding iron oxide to the fuel. This was reduced to metallic iron partly by the carbon and partly by the CO.

Pritschi and Beaufils in 1887 proposed the absorption of the CO by means of a solution of cuprous chloride, Cu_2Cl_2, which was then recovered by liberating the absorbed CO *in vacuo* (*see* preceding Note).

A *water gas* obtained by the interaction of steam and carbon and purified with CaO only, in order to absorb the CO_2, gave the following results on analysis : H = 36 per cent. ; CO = 51 per cent. ; N = 7 per cent. ; CO_2 = 4 per cent. A gas of this kind, on account of the high temperatures produced during combustion and the enormous quantities of CO, cannot be used for illuminating purposes. In certain cases the CO forms 40 per cent. and hydrogen 50 per cent. of the mixture.

In 1893 the firm of Krupp of Essen (Ger. Pat. 67,827 of 1893) improved the process by also using the method of Tessié du Motay and Marechal (1868). They mixed calcium oxide with the fuel so that the CO_2 was at once fixed as fast as it was formed, and the production of CO thus prevented.

Krupp obtained considerable advantages by mixing the fuel with carbonates and hydroxides of the alkalis or alkaline earths ; in this way a gas composed of H and CO_2 only was at once obtained as soon as the action of the steam commenced at a fairly low temperature. In this reaction air is excluded and thus no nitrogen is present in the resulting gases.

This water gas is not poisonous and may be employed directly as a fuel gas and for heating. From this gas pure hydrogen and pure CO_2 may be obtained if desired by liquefying the CO_2 by pressure and refrigeration.

In North America water gas has been advantageously employed instead of ordinary lighting gas, by carburetting it with light petroleum in order to render it luminous, as had been shown by Lowe, helped by the discoveries of Faraday, who had shown that the flame of methane gas may be rendered luminous by passing it over liquid hydrocarbons. Water gas may be employed with great advantage to-day by rendering it luminous by means of the Auer mantle which is formed of oxides of zirconium, thorium, &c., which easily become incandescent, emitting a very white light.

In other cases *producer gas* (air gas, Siemens gas, or generator gas) is used for heating and power. It is prepared by passing a current of air, together with a spray of water, over an excess of red-hot carbon in such a manner that a gas containing 28 to 33 per cent. of carbon monoxide, very little hydrogen (1·5 to 4 per cent.), 0·8 to 4 per cent. of CO_2, and 62 to 64 per cent. of N is obtained.

Finally *suction gas* or *Dowson gas* may be prepared, which has a composition intermediate between that of the two gases last referred to—about 30 per cent. of carbon monoxide and 15 per cent. of hydrogen. It is obtained by passing a current of superheated steam, together with a current of air, over red-hot carbon. *Mond gas* is, in general, obtained from peat, &c. (*see* p. 326).

It has been our desire to mention these gases because they have effected a small revolution in the production of energy, and in many cases

they advantageously displace steam-engines in countries where fuel is dear, as in Italy.

We will also mention another gas which is obtained during the dry distillation of wood (*Riché gas*). This industry cannot be carried on unless the secondary products which result, namely, methyl alcohol, acetic acid, tar, wood charcoal, &c. (*see* vol. ii, "Organic Chemistry"), are rationally utilised. Riché gas is of varying composition, but often contains about 60 per cent. of CO_2, 25 per cent. of CO, 15 per cent. of methane and a very small quantity of hydrogen.

All these gases are employed as a source of power by means of gas motors. The cost of a h.p.-hour obtained from these varies greatly according to the size of the motor, and may oscillate from 0·15*d.* to 0·4*d.*, whilst an electric h.p.-hour costs from 0·3*d.* to 1·2*d.*, according to the locality, and a h.p.-hour obtained by steam costs from ·8*d.* to 1·5*d.* and even more according to the size of the boiler and steam-engine. A h.p.-hour can sometimes be produced with 800 litres of good water gas, but in the case of certain other gases 3 cu. metres are required. The calorific intensity of these gases varies from 2600 to 3500 cals. per cubic metre. The calorific intensity of producer gas is sometimes as low as 1000 cals. per cubic metre.

When water gas is carburetted with benzene, &c., its calorific power rises to 5000 cals., and it may be advantageously mixed with illuminating gas.

CARBON SUBOXIDE : C_3O_2, the constitution of which is probably: OC : C : CO, was first obtained by Diels and Wolf in 1906 by decomposing malonic ester, and later in 1908 from malonyl chloride. It is a gas of disagreeable odour, which liquefies at + 7°. It yields CO_2 with oxygen on heating. With cold water it forms malonic acid:

$$C_3O_2 + 2H_2O = CH_2(COOH)_2.$$

It reacts with NH_3 and aniline even below 0°, and also reacts with gaseous HCl. The liquid is transformed in a few days into an amorphous blackish-red solid mass which liberates a quantity of carbon monoxide at 37°. Berthelot appears to have obtained an oxide, C_4O_3, in 1876.

NICKEL TETRACARBONYL : $Ni(CO)_4$. This compound was obtained by L. Mond in 1890 by the action of CO gas on finely divided nickel at a temperature of 25° to 30°. The CO acts as a diatomic residue, called *carbonyl*. Nickel tetracarbonyl is a colourless liquid, very refractive to light. It boils at 43° at a pressure of 751 mm. and crystallises at −25°. Its vapours decompose at 60° with explosion. The *ferrocarbonyls* $Fe(CO)_4$ and $Fe(CO)_5$ are also known.

CARBONYL CHLORIDE : $COCl_2$ (phosgene or carbon oxychloride). As seen in the preceding compound the radical CO has free carbon valencies which may also be saturated with chlorine. Carbonyl chloride compound is obtained by the direct action of sunlight on a mixture of carbon monoxide and chlorine: 1 vol. CO + 1 vol. Cl_2 = 1 vol. $COCl_2$; it is also obtained by passing this gaseous mixture over red-hot spongy platinum, or more easily over animal charcoal (Paternò). It is also formed from CO and $SbCl_5$ as the latter liberates two atoms of chlorine on heating, which enter into reaction: $CO + SbCl_5 = COCl_2 + SbCl_3$. Since 1906 it has been manufactured by the process of Michalske (U.S. Pat. 808,100) by heating a mixture of quicklime, calcium chloride and powdered coke in the electric furnace. Calcium carbide remains and $COCl_2$ is evolved and is condensed as a liquid at 7°.

It is a colourless gas of suffocating odour. At 7° it is transformed into a liquid of sp. gr. 1·432; the gas is soluble in benzene and in acetic acid. It is readily decomposed by water: $COCl_2 + H_2O = 2HCl + CO_2$

It is employed in various industries for the manufacture of organic products, especially of aniline colours. It is sold at £1 8*s.* per kilo in steel cylinders.

CARBONYL NITRIDE : $CO(N_3)_2$. This compound was prepared by Curtius in 1894, and is formed of divalent carbonyl saturated with two residues of hydrazoic acid: $\begin{matrix}N\\ \vdots\\ N\end{matrix}\!\!>N - CO - N<\!\!\begin{matrix}N\\ \vdots\\ N\end{matrix}$ It is a crystalline substance which is very volatile and rather explosive.

CARBON DISULPHIDE : CS_2

This compound is formed by the action of sulphur vapour on red-hot carbon ; the vapours of carbon disulphide then condense to form a liquid which when pure is almost colourless, has a distinct odour and is very mobile and refractive. It has a specific gravity of 1·262 at 20°, and boils at 46·5°. It is insoluble in water, but dissolves in all proportions in alcohol and ether and is also soluble in oil to the extent of 60 per cent. It is an endothermic compound : $C + S = CS_2 - 5{\cdot}3$ Kj., and is therefore only formed on heating. It easily catches fire and burns with a bluish flame :

$$1 \text{ vol. } CS_2 \text{ (vapour)} + 3 \text{ vol. } O_2 = 1 \text{ vol. } CO_2 + 2 \text{ vol. } SO_2.$$

The vapour of CS_2 also burns in an atmosphere of nitric oxide with an intense bluish-white flame very rich in actinic rays. It is a very good solvent for iodine, with which it gives a violet solution, for sulphur, phosphorus and india-rubber, and also for many fats. Carbon disulphide vapour is harmful to the system, and if inspired often produces fatal cases of poisoning.

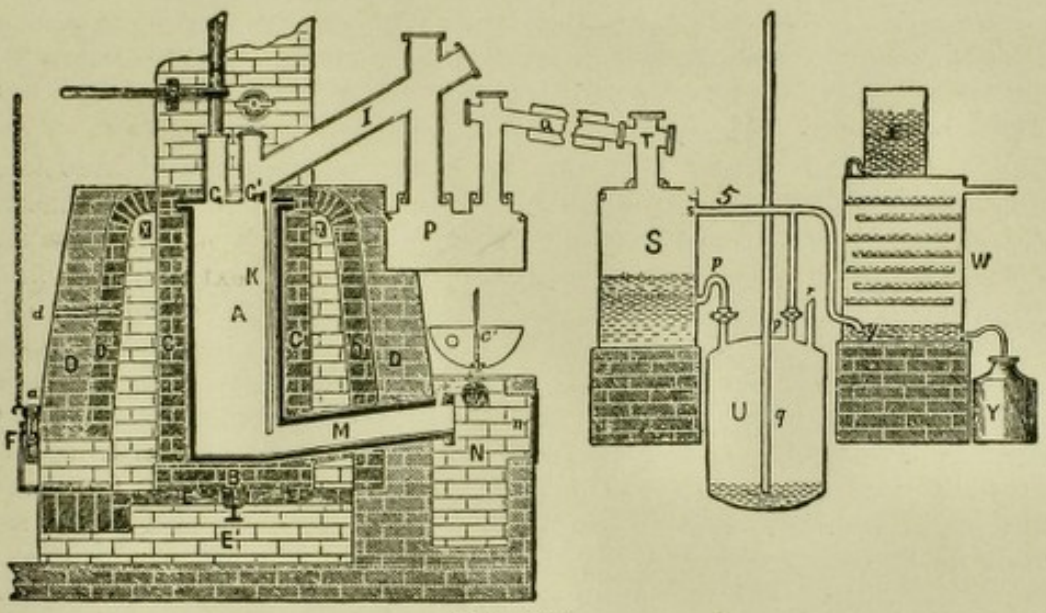


Fig. 167.

INDUSTRIAL MANUFACTURE. In certain localities iron, zinc, or antimony sulphides are mixed with carbon and heated, but the largest quantities of carbon disulphide are prepared by heating sulphur directly with carbon. The first important industrial plant was devised by Deiss, and whilst CS_2 still cost £2 per kilo in 1840, in 1848 Deiss prepared it at 6*s.* 4*d.* per kilo, and the price descended later to 5d. per kilo. Deiss' apparatus was often modified, and the arrangement most used to-day is that of Singer (Fig. 167). A cast-iron retort, *A*, 1·7 metres high, the walls of which are 5 to 7½ cm. thick, is filled with gas coke or beechwood charcoal, and heated in a furnace with double walls,[1] between which the furnace gases circulate.

The sulphur is melted apart in the pan, *c'*, and is allowed to slowly drop into the lower tube, *M*, of the retort. It then evaporates and passes through the carbon which is heated to dull redness, forming vapour of carbon disulphide mixed with sulphur vapour and a few other impurities, such as CO_2, H_2S, &c. In the delivery tube, *I*, which is slightly inclined, a great part of the sulphur condenses and runs back to the bottom of the retort through the tube, *K*. The remaining sulphur vapours are deposited and condensed in the vessel, *P*.

The carbon disulphide vapours are condensed, on the other hand, in a condenser, *Q*, which is about 9 metres long, and round which cold water passes. The liquid CS_2

[1] The walls of the retort are made so thick because a portion of the iron is attacked. It is found that in a retort weighing 1500 kilos 20 tons of CS_2 may be produced. If, however, the furnace is badly constructed or the cast iron of the retort is of poor quality, it may become corroded in a few days. Retorts weighing 4 tons last six or seven months.

accumulates in the vessel, *S*, and continuously passes into the reservoir, *U*, from which it is forced by air pressure into large settling tanks. The miscellaneous gases, especially H_2S, which are mixed with the CS_2 are not condensed in the vessel, *S*, but bubble through the tube, *sy*, into oil, which extracts the remaining CS_2 vapours. They then pass through the purifier, *W*, consisting of several trays over which oil from the reservoir, *x*, runs. This oil removes the last traces of CS_2, and is collected in the reservoir, *Y*. The gases which escape from the purifier are then passed through solutions of alkali or ferrous sulphate in order to absorb the H_2S. Laming's material may also be used for this purpose as in gasworks. Various more perfect systems of condensation for the CS_2 vapours have been proposed and reduce the losses to a minimum.

If the operation is well conducted 90 per cent. of sulphur is transformed into CS_2.

The crude carbon disulphide contains in solution 8 to 10 per cent. of sulphur and certain gaseous impurities which are not separated by direct distillation. It is, therefore, first shaken with lime water and then placed in a still together with 1 per cent. of oil, a little water, and a little lead acetate. It is then distilled from a water-bath. Fairly pure CS_2 is thus obtained and may be further purified by distillation.

In America much carbon disulphide is to-day prepared by the process of Taylor (U.S. Pat. 688,364 and Ger. Pat. 706,128 of 1902) in a special electric furnace in which the carbon and sulphur are heated to high temperatures. These furnaces have been constructed to yield 12 tons of carbon disulphide per twenty-four hours, using 400 h.p., and the most suitable form has been shown to be that with a very large diameter equal to half the height.

USES OF CS_2. Until 1850 this body was only employed industrially for vulcanising and dissolving india-rubber, but its use as a solvent has now greatly extended in many industries. Attempts have been made to use it for the extraction of sulphur from poor ores. It is used for extracting aromatic oils from drugs. It is also used in large quantities for the extraction of oil from seeds and from oily seed residues and rags. It is also used for degreasing vegetable and animal residues, such as rags, bones, meat, hides, wool, &c. It is used for preparing solutions of wax for coating plaster casts and for the preparation of wax paper. It is also used for dissolving out the tar from many industrial by-products, for preparing various chemical products, for making Greek fire (phosphorus dissolved in CS_2), for killing insect pests, and more especially, in large quantities, for destroying phylloxera in vineyards by injecting it into the earth with suitable pumps. Large quantities are, however, lost in this way, even if it is used as a 5 per cent. emulsion in water, on account of its great volatility. To-day it is almost entirely replaced with advantage for this purpose by potassium trithiocarbonate (*see* Part III). In 1906 it was used with good results for destroying the nematodes which attack beetroot.

In France about 550 tons of carbon disulphide were produced in 1900, and 650 tons in Germany ; Hungary produced 2760 tons in 1905.

In Italy 2000 tons of carbon disulphide were produced in 1903 of the value of £22,760 (£11 12*s*. per ton) ; 2306 tons in 1905, valued at £27,600 ; 2256 tons in 1906, and 3560 tons in 1907 ; the exports were 317 tons in 1904, 337 tons in 1906, 782 tons in 1907, and 1075 tons in 1908.

Its market price is about £16 per ton, although during certain years it was often sold at £12. It is placed on the market in sheet-iron vessels and is carried as inflammable goods.

CARBON MONOSULPHIDE, CS, was prepared by Dewar and Jones in 1910 by acting on nickel tetracarbonyl with thiophosgene in the cold :

$$CSCl_2 + Ni(CO)_4 = NiCl_2 + 4CO + CS.$$

This sulphide polymerises to an amorphous blackish-brown mass which dissolves slightly in phenol and in carbon disulphide with a brown colour. It has a specific gravity of 1·6, is unchanged at 360° and forms CS_2 and carbon at a red heat. It dissolves in strong sulphuric acid to a purple solution and is regenerated unchanged on dilution with water, It also dissolves in alkalis and is generated on addition of acids.

TRITHIOCARBONIC ACID : $CS\begin{matrix}-SH\\-SH\end{matrix}$. This compound is easily obtained in the form of potassium trithiocarbonate, by dissolving potassium sulphide in carbon disulphide, $CS_2 + K_2S = CS\begin{matrix}-SK\\-SK\end{matrix}$; this salt is used for destroying phylloxera (*see* Part III, Potassium Salts). The acid is liberated by HCl and forms a reddish-brown and somewhat unstable oil. It may be considered to be derived from carbonic acid by imagining all the oxygen replaced by sulphur.

CARBON OXYSULPHIDE : COS. This compound is obtained in small quantities by passing a current of sulphur vapours and CO through a red-hot tube. It is prepared more easily by the action of dilute sulphuric acid on potassium sulphocyanide CNSK. It is a colourless gas of similar odour to hydrogen sulphide and is found free in certain sulphuretted waters. It dissolves in an equal volume of water and slowly decomposes : $COS + H_2O = CO_2 + SH_2$. It burns easily, forming SO_2 and CO_2.

CYANOGEN COMPOUNDS. These are compounds of carbon with nitrogen which are always formed when nitrogenous organic compounds are heated with potassium hydroxide.

Potassium cyanide is first obtained, from which potassium ferrocyanide, $K_4Fe(CN)_6$ (yellow potassium prussiate), is formed with ferrous oxide.

All these cyanogen compounds contain the characteristic CN group, called *cyanogen*, which acts as a monovalent radical. From potassium cyanide and ferrocyanide all the numerous other cyanogen compounds, which are studied in organic chemistry, are formed.

HYDROCYANIC ACID : HCN (prussic acid) is the acid corresponding to potassium cyanide. It is a colourless liquid which boils at 27°, and is obtained by distilling a concentrated solution of potassium cyanide or potassium ferrocyanide with dilute sulphuric acid (with strong sulphuric acid CO would be formed). Both hydrocyanic acid and its salts are among the most powerful poisons known, with the exception of the ferrocyanides, which are not poisonous at all. HCN is an endothermic compound.

Other cyanogen compounds are described in the chapter on Iron, and also among the organic compounds in vol. ii of this work (" Organic Chemistry ").

SILICON COMPOUNDS

SILICON HYDRIDE : SiH_4 (Silicomethane). This compound is formed on dissolving an alloy of magnesium and silicon in hydrochloric acid. The alloy is obtained by heating 1 part of powdered quartz with 1·5 parts of magnesium powder. Thus the gas is obtained in an analogous manner to AsH_3 and SbH_3 which are obtained from an alloy of As or Sb with zinc :

$$Si + Mg_2 + 4HCl = SiH_4 + 2MgCl_2.$$

Silicon hydride is evolved mixed with hydrogen and catches fire in the air because it contains small traces of silicoethane, Si_2H_6, and forms H_2O and SiO_2 in the form of smoke rings in the same manner as PH_3. It is also obtained by the electrolysis of various chlorides, employing an aluminium cathode containing silicon. It may be obtained free from hydrogen from various organic silicon compounds, for example, by heating the triethyl ester of silicoformic acid, $SiH(OC_2H_5)_3$, and then only catches fire on heating. It liquefies at −1° under 100 atmospheres pressure. It combines with chlorine with formation of flame. If it is passed into a glass tube and lit at the end, a brown spot of amorphous silicon is obtained on introducing a cold porcelain surface into the flame ; also if the glass tube is heated at any point a brown mirror of silicon is obtained analogous to that which is obtained with As and Sb, showing the ease with which it is decomposed into Si and H_4. With solutions of alkali hydroxides it forms alkali silicates :

$$SiH_4 + 2NaOH + H_2O = 4H_2 + SiO_3Na_2.$$

SILICON TETRACHLORIDE : $SiCl_4$. This compound is obtained on passing a current of dry chlorine over silicon and heating to 300°, or over magnesium silicide, or more easily over a red-hot mixture of SiO_2 and carbon : $SiO_2 + 2C + 2Cl_2 = 2CO + SiCl_4$. A little **Silicon Hexachloride,** Si_2Cl_6, is always formed at the same time.

Silicon chloride formed in this manner distils as a colourless liquid of sp. gr. 1·52; it boils at 59·5°. It fumes in the air and is easily decomposed by water into hydrochloric acid and silicic acid: $SiCl_4 + 4H_2O = SiO_4H_4 + 4HCl$, whilst the chlorides of carbon are stable in contact with water.

Since silicon chloride evaporates without alteration, the atomic weight of silicon may be deduced indirectly from its density and percentage composition.

Silicon Oxychloride: Si_2OCl_6, that is, $Cl_3 \equiv Si.O.Si \equiv Cl_3$, is also known, and so is a compound analogous to chloroform, $CHCl_3$, namely, **Silicochloroform**, $SiHCl_3$, which is a liquid boiling at 34°, and is obtained by the action of silicon hydride on phosphorus or antimony pentachloride. It is also formed together with $SiCl_4$ on heating silicon with dry HCl. In contradistinction to ordinary chloroform it is decomposed by water.

Silicon Bromide and Iodide: $SiBr_4$; SiI_4. These substances are obtained in an analogous manner to the chloride and possess similar properties. The bromide is a colourless liquid; the iodide forms colourless octahedra. **Silicobromoform, $SiHBr_3$, Silico-iodoform, $SiHS_3$,** and **Silicon Hexaiodide, Si_2I_6,** are also known.

SILICON FLUORIDE: SiF_4, and FLUOSILICIC ACID: H_2SiF_6. The first compound is obtained on heating calcium fluoride mixed with silica or silicates (sand, powdered glass, &c.) with sulphuric acid; hydrofluoric acid is first formed and immediately reacts with the silica:

$$SiO_2 + 4HF = 2H_2O + SiF_4.$$

It is a colourless gas which fumes strongly in the air and has a pungent odour. It is liquid at $-160°$, and does not attack glass when completely dry. It is formed in large quantities during the manufacture of superphosphates, and since it is harmful to respiration and to vegetation, especially to mulberry trees, these works to-day recover it all in the form of fluosilicic acid (*see* Superphosphates, Part III). It is characterised by the fact that it is immediately decomposed by water, forming gelatinous silicic acid, H_4SiO_4, and fluosilicic acid, H_2SiF_6, which remains dissolved in the water:

$$3SiF_4 + 4H_2O = SiO_4H_4 + 2H_2SiF_6.$$

In the preparation in the laboratory of fluosilicic acid the mixture of $CaF_2 + SiO_2 + H_2SO_4$ is heated in a flask, and the SiF_4 gas which is evolved is passed through a thin layer of mercury at the bottom of a cylinder of water so that the gelatinous silicic acid which is formed cannot obstruct the delivery tube. The gelatinous silicic acid is then collected on a filter; the filtrate consists of an aqueous solution of fluosilicic acid which cannot be separated unchanged because on evaporating the water SiF_4 escapes and a solution of HF remains. The aqueous solution of H_2SiF_6 behaves like a halogen acid. It dissolves the metals with evolution of hydrogen and forms salts with bases, behaving as a dibasic acid. Barium fluosilicate is insoluble in water. Potassium fluosilicate is soluble with difficulty, and the other fluosilicates are almost all soluble.

Silicon fluoride forms a *hydrate*, $H_2SiF_6 + 2H_2O$, with a concentrated solution of HF, which is obtained solid and melts at 19°.

Fluosilicic acid does not attack glass and is used for hardening pastes of plaster of Paris or cement, perhaps because it forms calcium fluoride and separates SiO_2. It has a powerful antiseptic and anticryptogamic action, and is used for preserving wood and oil pigments.

Solutions of fluosilicic acid of 20° Bé. cost about £18 per ton, and sodium fluosilicate costs about £26.

SILICON CARBIDE: SiC, ordinarily called **Carborundum.** This substance was accidentally obtained by Acheson whilst endeavouring under Edison's advice to prepare artificial diamond by dissolving carbon in fused aluminium silicate at very high temperatures in the electric furnace. He actually produced carbon silicide which was studied in 1892–94 by Mühlhäuser, who determined its composition. It is now known that the temperature of formation of carborundum is from 1920° to 1980° and that its decomposition into graphite and silicon (*see* p. 360) occurs at 2220°. It is to-day prepared in large electric furnaces

at 3500° from a mixture of 3 tons of powdered coke, 6 tons of siliceous sand, and 1·5 tons of sodium chloride which is used as a flux : $SiO_2 + 3C = 2CO + SiC$. The silica is then eliminated with a boiling mixture of nitric and hydrofluoric acids. A crystalline mass remains, of greenish-blue colour, which is extremely hard, only slightly softer than diamond, and in the form of powder and of grindstones it has advantageously replaced emery for all polishing purposes. Scarcely any solvents dissolve it, but it is attacked by fused sodium hydroxide or sodium carbonate.

As it is very resistant to high temperatures and a better conductor of heat than many other substances, endeavours have been made to utilise it as a refractory material or for ingot moulds for molten aluminium, more especially as it is not altered by great variations of temperature. Since, however, it is still very dear, it is only used to-day in the form of a cement or varnish for coating the ordinary refractory materials.

In 1905 Bölling prepared a product similar to carborundum which is called *silundum* and is used for the preparation of electrodes. It is formed of carbon which is combined with silicon vapour at a temperature of 1800° to 1900°. Thus on placing pieces of carbon shaped into any desired form in the electric furnace and covering them with silicon carbide and silica, at 1900° silicon is transformed into vapour and penetrates all the pores of the carbon combining with it and also depositing in it. A compact non-porous mass of suitable form results which conducts the electric current and transforms it into thermal energy at the highest temperatures, for which platinum can no longer be used. It offers greater resistance than carbon to the passage of the current. Perhaps it will also be applied for electric heating for domestic purposes.

In 1903 the production of carborundum at Niagara was 2370 tons and in 1904 it rose to 3500 tors of the value of £140,000. In Italy in 1905 850 tons were produced, and in 1906 about 1100 tons of the value of £13,520.

Carborundum containing 68·3 per cent. of silicon costs about £64 per ton, and when powdered it costs as much as 2*s.* per kilo and in large quantities 9½*d.* per kilo. When spread on sheets of paper it costs 7*s.* 2*d.* per 100 sheets and on sheets of linen 12*s.* 10*d.*

CALCIUM SILICIDE : $CaSi_2$, is used for reducing and desulphurising metals. It is obtained by heating the following mixture in the electric furnace : 64 parts of calcium carbide, 120 parts of silica, and 24 parts of coal : $CaC_2 + 2SiO_2 + 2C = 4CO + CaSi_2$ (Ger. Pat. 206,785).

IRON SILICIDE or **FERROSILICON.** *See* chapter on Iron.

SILICON DIOXIDE : SiO_2 (SILICIC ANHYDRIDE, SILICA)

Until a short time ago this compound was the only one known of silicon and oxygen; now, however, a monoxide of silicon, SiO, has also been prepared. The dioxide is found abundantly in nature in the form of *quartz* or *rock crystal* and of *flint*. Quartz is often pure silicon dioxide and crystallises in hexagonal prisms and pyramids. It is generally almost colourless, but is called by various names according to the colour produced by various impurities. In the state of amorphous hydrates ($SiO_2.nH_2O$) it is found in various minerals, such as *agate, chalcedony, flint,* &c. In the form of silicates it forms entire mountain ranges.

Amorphous silica is formed artificially by heating amorphous silicon in oxygen or air, or by heating silicic acid. It then forms a white amorphous powder of sp. gr. 2·2, which melts at very high temperatures in the oxyhydrogen flame and may be volatilised at the temperature of the electric arc.

It is insoluble in water and in all acids excepting hydrofluoric acid, which transforms it into silicon fluoride, SiF_4, and then into fluosilicic acid. At high temperatures it is partially reduced by sodium and potassium to silicon. This reduction occurs more easily with magnesium and aluminium :

$$SiO_2 + Mg_2 = Si + 2MgO.$$

Whilst natural silica dissolves in hot solutions of sodium hydroxide when in a state of extremely fine division only, artificial silica dissolves much more readily. All the varieties of silica are transformed into a glassy mass, soluble

in water, called *soluble glass*, by fusion with the alkali hydroxides or carbonates. This substance consists of alkali silicates, Na_4SiO_4 and Na_2SiO_3.

Certain forms of apparatus are to-day made of quartz, for instance, crucibles, flasks, and thermometers in which the mercury is replaced by tin, &c., because they are very resistant to extremely high temperatures, up to 1600°, and to abrupt temperature changes. When such bodies are heated to redness they may be immediately immersed in water or even in liquid air without breaking, owing to the very small coefficient of dilatation of the quartz. In preparing such apparatus the quartz is melted in iridium vessels heated with a strong oxyhydrogen or oxyacetylene flame to 1850° to 2000°. Such apparatus costs as much as platinum apparatus. (The price has recently been much reduced.—*Translator's note.*)

More economical forms of quartz apparatus are obtained by heating the powdered quartz until it becomes soft and the particles adhere to one another. The articles thus formed are not transparent and are glazed on the surface with the oxyacetylene flame.

Much quartz is used in the manufacture of glass, porcelain, sodium silicate, &c. For such uses the price varies from 14*s.* to £1 4*s.* per ton.

The cheaper quartz articles for laboratories cost four or five times more than similar articles of the best porcelain. It is found that during its use, for instance, for large vessels for the concentration of acids, very fine cracks are formed which slowly allow the acid to escape. This industry is still in its youth and further improvements will certainly take place.

SILICON MONOXIDE : SiO. In 1907 H. N. Potter reported that he had obtained this compound in the electric furnace according to the reaction $SiO_2 + C = SiO + CO$, or $2SiO_2 + SiC = 3SiO + CO$. Up to the present, however, it is not very easy to distinguish chemically and physically between SiO and SiO_2.

SILICIC ACID : H_4SiO_4 (ORTHOSILICIC ACID)

The soluble alkali silicates when treated with hydrochloric acid separate a gelatinous mass of orthosilicic acid of the same character as that obtained with silicon fluoride and water :

$$Na_4SiO_4 + 4HCl = 4NaCl + Si(OH)_4.$$

This normal silicic acid, when washed and dried in the air, loses one molecule of water and is transformed into amorphous *metasilicic* acid, SiO_3H_2, which on heating to redness loses a further molecule of water, leaving silicon dioxide, SiO_2.

Since gelatinous silicic acid is slightly soluble in water, in dilute hydrochloric acid, and in soda, if a little sodium silicate is poured into dilute hydrochloric acid, gelatinous silicic acid is not separated but remains in solution together with the NaCl which is formed and the excess of HCl. In order to separate the aqueous solution of NaCl and HCl from the silicic acid, a dialyser is employed, using the osmotic phenomenon studied by Graham (*see* p. 102).

Numerous *polysilicic acids* are known, corresponding to salts or to natural silicates, and they may be supposed to be formed by the condensation of two or more molecules of silicic acid with simultaneous loss of one or more molecules of water. All these acids may be derived from the general formula, $mSi(OH)_4 - nH_2O$, where m indicates the number of molecules of orthosilicic acid which condense with separation of n molecules of water.

It is these polysilicates or polysilicic acids which actually exist in opal, agate, chalcedony, amethyst, &c. ; on heating to redness these substances lose 5 to 15 per cent. of water.

The more widely diffused corresponding higher acids are : $H_2Si_2O_5$, $H_4Si_3O_8$, $H_2Si_3O_7$, $H_4Si_4O_{10}$, &c.

SILICON DISULPHIDE : SiS_2. This compound is obtained in an analogous manner to CS_2 by passing sulphur vapours over hot amorphous silicon or by passing carbon disulphide vapours over a red-hot mixture of SiO_2 and carbon.

It is a solid substance which sublimes in the form of white silky needles, and is decomposed by water into silicic acid and H_2S.

A **SILICON NITRIDE, Si_2N_3**, is also known and is formed by passing dry nitrogen over red-hot amorphous silicon.

TITANIUM : Ti, 48.1 ; ZIRCONIUM : Zr, 90.6 ; THORIUM : Th, 232.42

These three elements belong to the group of the rare elements ; they have the same analogy to the group of carbon and silicon as vanadium, columbium, and tantalum have to the elements of the phosphorus group.

They are also analogous to tin ; thus they also form basic compounds which are the more basic the higher their atomic weight. These compounds react with acids, forming fairly stable salts. They are tetravalent elements, and form compounds of the type, MX_4, whilst none of the type MX_2 are known, though such have been studied in the case of tin.

In the group of the rare earths, Urbain in 1909 was able to detect the presence of at least 16 rare elements, samarium, europium, gadolinium, neodymium, praseodymium, terbium, dysprosium, holmium, &c.

TITANIUM : Ti, 48.1

This is a rather rare element which is found in certain minerals such as *rutile*, *anatase* and *brookite*, which contain titanium dioxide, TiO_2 ; *perowskite* contains calcium titanate, and ferrous titanate, $FeTiO_3$, is also known.

Titanium was first obtained in the free state by Berzelius. It was recognised and studied as a simple element by Wöhler, who obtained it by heating potassium fluotitanate TiF_6K_2, with potassium. It is obtained to-day from its oxide by heating it with finely divided aluminium. In 1910 Hunter obtained it in the pure state by heating titanous chloride to redness in a closed vessel with sodium. It forms a grey metallic powder or a metallic mass similar to steel, which is fairly hard and melts with difficulty, but may be worked at a red heat. It decomposes boiling water and dissolves in HCl or H_2SO_4 with evolution of hydrogen in the same manner as metals. It has a specific gravity of 4.50 and melts between 1800° and 1850°. It burns on heating in the air. On account of its affinity for oxygen and nitrogen on heating, it is used by being added to steel in proportions up to 10 to 15 per cent., by which means the metal becomes much tougher that ordinary steel.

Certain titanium compounds are used in the dyeing of cotton with basic colours and on tannin mordant.

TITANIC CHLORIDE : $TiCl_4$. This is formed in the same manner as $SiCl_4$, by heating a mixture of titanium dioxide and carbon to redness in a current of chlorine.

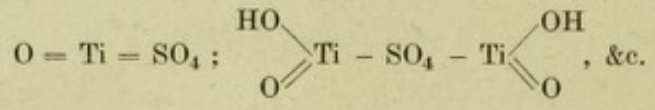
It is a colourless liquid which boils at 136° and fumes in the air forming HCl and titanic acid. Its specific gravity is 1·76. It decomposes with water into metatitanic acid, H_2TiO_3, and HCl.

Ti_2Cl_4 and Ti_2Cl_6 are also known, and so is fluotitanic acid, H_2TiF_6, and the corresponding salts,

TITANIUM DIOXIDE : TiO_2. This compound is obtained by heating the acid or hydroxide to redness. It is a white amorphous powder which is found crystalline in nature as *rutile*, *brookite*, and *anatase*. It is insoluble in acids except in HF, with which it forms the fluoride. When fused with alkalis it forms titanates, and on heating with gaseous ammonia it forms titanium nitride, TiN_2, which is a powder of an intense violet colour. **Titanium cyanonitride, Ti_5CN_4**, is also known, being formed in the slag of blast furnaces in which titaniferous iron ore is worked. It is there found in the form of cubes with a coppery-red metallic lustre.

TITANIUM PEROXIDE : TiO_3. This is obtained from solutions of titanic acid with hydrogen peroxide (*see* p. 235).

TITANIC ACID : H_4TiO_4. This compound is obtained in the free state from hydrochloric acid solutions of the titanates by treating them with ammonia. When dried over sulphuric acid it loses 1 mol. of water forming *titanium hydroxide*, TiO_3H_2, which may be considered as a *metatitanic acid*, because it forms salts with energetic bases (K_2TiO_3 ; $FeTiO_3$, &c.). Polyacids are also known. But these compounds of titanium may also be considered as hydroxides, $Ti(OH)_4$ and $TiO(OH)_2$, because they have basic properties, and therefore also form salts with acids. Thus various sulphates are known, for example:



ZIRCONIUM : Zr, 90.6

This element is rare and is found in the form of silicate, $ZrSiO_4$ (*zircon*). It is obtained in the free state by a process analogous to that for obtaining titanium, and forms a black powder which burns easily ; two other allotropic forms are also known, one crystalline and the other graphitic.

The *tetrachloride* and *tetrafluoride of zirconium* are known, $ZrCl_4$ and ZrF_4, and also *zirconium hydroxide*, $Zr(OH)_4$, which is obtained by precipitating a solution of its salts with strong acids by NH_3, and forms a voluminous mass, insoluble in alkaline solutions. On fusing with alkalis, however, *sodium metazirconate*, Na_2ZrO_3, and *sodium zirconate*, Na_4ZrO_4, easily decomposable by water, are formed. The basic character of the hydroxide is shown by the salt which is obtained with sulphuric acid, $Zr(SO_4)_2$. On heating to redness the hydroxide forms *zirconium dioxide*, which is also found crystallised in nature, and dissolves in hot strong sulphuric acid only, forming the above-mentioned sulphate ; on fusing with alkalis it forms alkali zirconates and metazirconates, mentioned above.

On heating the oxide to redness it emits a very intense white light which was used for preparing the first incandescent mantles for illumination. It is now also used for electric lamps.

THORIUM : Th, 232.42

Until a few years ago very little of this element had been found ; to-day, however, considerable quantities of its derivatives are produced for the preparation of the Auer incandescent mantles.

It was first extracted from *thorite*, $SiO_4Th.2H_2O$, which is somewhat rare, although it contains 52 per cent. of thorium. To-day it is obtained from the more abundant *monazite*. In 1906 a very important monazite deposit was discovered in the Transvaal containing up to 13·5 per cent. of thorium oxide. In the United States of America 650 tons of monazite sand were produced in 1905, valued at £64,000 ; but in 1908 the production had already fallen to 200 tons, whilst 300 tons of thorium nitrate were imported. Free *thorium* is obtained by heating the double chloride or double fluoride of thorium and potassium with metallic potassium or sodium. It forms a powder of metallic lustre of sp. gr. 11. It keeps well in the air up to temperatures of 100° to 120°, but on heating to higher temperatures it burns with a strong light producing the dioxide, ThO_2, also called *thoria*.

The oxide, and also the hydroxide, $Th(OH)_4$, no longer possess any acid characteristics, as they do not dissolve or form salts with the alkalis, whilst, on the contrary, ThO_2 only dissolves in concentrated acids such as HCl, H_2SO_4, HNO_3, but not in dilute acids, forming, for example, thorium sulphate $(SO_4)_2Th.9H_2O$, which is soluble in cold but insoluble in hot water. Both the oxide and the sulphate are isomorphous with the oxide and sulphate of uranium. With regard to the radio-activity of thorium minerals, *see* p. 121.

THORIUM NITRATE is the salt most employed in the manufacture of Auer incandescent mantles and has the formula $Th(NO_3)_4 + 6H_2O$ when crystallised from hot solutions, but it sometimes only contains $5H_2O$, whilst from cold solutions it separates with $12H_2O$; these crystals lose $8H_2O$ at 100° and a nitrate containing $4H_2O$ remains, which is that commonly placed on the market, and contains 47 to 49 per cent. of ThO_2. The anhydrous nitrate contains 55 per cent. of ThO_2, but it is not suitable as a commercial product, because on drying and heating it a portion may be decomposed. On heating to redness it is completely decomposed forming the oxide ThO_2. The pure nitrate costs about £1 12*s*. per kilo, the oxide costs £40 (?). In 1894 the nitrate cost £100 per kilo ; in 1895 £26 ; in 1896 £6 8*s*. ;

in 1898 £2. The world's consumption of thorium salts is about 160 tons, obtained from 2000 tons of monazite which contain 5 per cent. of ThO_2 on the average.

THORIUM CHLORIDE : $ThCl_4$. This compound is obtained from thorium with HCl gas. It melts at a white heat and then sublimes in white crystals. It is soluble in water from which crystals of $ThCl_4,8H_2O$ may be re-obtained. It forms double salts with other chlorides.

THORIUM HYDROXIDE : $Th(OH)_4$. This is obtained as a gelatinous precipitate by precipitating soluble thorium salts with ammonia. On reheating to redness it forms a mass of thorium dioxide, ThO_2. The hydroxide, $ThO(OH)_2$, is not known.

RARE EARTHS FOR INCANDESCENT LIGHTING

The first use of rare earths for this purpose was in the lime-light, in which a very vivid white light is obtained by heating a piece of calcium oxide in the oxy-hydrogen flame, but the quicklime soon crumbles because it rapidly absorbs moisture and carbon dioxide from the air.

In 1880 Auer von Welsbach [1] utilised the property of thorium oxide of emitting an intense white light at a lower temperature than zircon in the ordinary Bunsen gas flame.

It was then found that pure thorium dioxide gives a less intense light than when it contains very small quantities (1 to 2 per cent.) of cerium oxide, which fact is probably explained by the catalytic action which this latter compound exercises during the combustion of the gas, which it accelerates greatly, since the temperature is higher than that obtained by ordinary combustion, and thus at this higher temperature the thorium oxide emits more light.

Auer prepared a netted fabric of cotton or linen, which is to-day made of artificial silk, and formed a species of lengthened cone (mantle). He then soaked this in a concentrated solution of thorium nitrate containing 1 to 2 per cent. of cerium oxide, allowed it to dry and then burnt away the cotton fabric ; the remaining skeleton, which has the same form as the fabric, is heated to redness in a strong Bunsen flame, using compressed gas. A maximum contraction and a certain consistency are thus obtained, which are still further increased by immersing the mantle in an ethyl alcoholic solution of collodium and then drying it in suitable chambers. These mantles are mounted on special burners of ordinary gas and then show the intense incandescence which we all know. Thorium oxide gives a bluish-white light ; lanthanum oxide a pure white light ; yttrium, yellowish-white ; zircon, very white ; cerium, reddish-white. By using different mixtures of these oxides the various lights may be modified or corrected.

The original source used for obtaining the rare earths is *monazite*, of which large deposits have been found in Brazil and North Carolina, and these discoveries have made the rapid spread of lighting by means of incandescent burners possible. This discovery has in this way saved the lighting gas industry from the extremely sharp competition of the electric light, and to-day in many places illumination with incandescent gas mantles is more advantageous than with incandescent electric lamps, or in some cases even than the electric arc.

The monazite, which is largely composed of phosphates of cerium, didymium, and lanthanum, contains mixed with it various quantities of thorium minerals. The analysis of this mixture is, up to 28 per cent. of cerium oxide, 15 per cent. of didymium oxide, 13 per cent. of lanthanum oxide, 26 per cent. of phosphoric acid, 5·5 per cent. of alumina, and 3 per cent. of titanic acid.

The cerium and aluminium are separated by forming the corresponding basic sulphates, which are insoluble. Didymium and lanthanum remain together in solution and are transformed into double nitrates, that is, nitrates of the metal and ammonia. The separation of all these elements of the rare earths is somewhat complex, but is performed by utilising the properties which their various salts (sulphates, nitrates, &c.) have of being more or less soluble in the heat or in the cold, and of certain other salts (nitrates) of being more or less resistant to heat. The purity of the separate salts is then controlled spectroscopically.

[1] Berzelius had already observed that when zircon is strongly heated much light is emitted. In 1868 Caron determined the luminous intensity of the light at the temperature of the oxy-hydrogen flame, and then Tessié du Motay at once attempted the first application of this light by employing the hydrogen flame in order to render zircon incandescent. In 1885 Linnemann prepared small discs of zircon and of zirconia adapted for incandescent burners, and W. Kocks discovered methods of giving any desired form to the oxide.

Pictet has prepared special mantles which can be used with gas mixed with oxygen, and which are capable of resisting the highest temperatures up to about 3000°.

During the last few years Nernst has brought out a new electric incandescent lamp based on the fact that a filament formed of magnesium oxide mixed with a little zirconia, thoria, yttria, &c., does not conduct the electric current in the cold, but passes the current when gently heated, the filament then becoming incandescent.

Electric lamps formed with very fine filaments of osmium and of tantalum have recently been introduced in practice and possess great advantages.

In 1908 Italy imported 898 kilos of salts of thorium, cerium, and zirconium, of the value of £3512, and 9567 kilos of incandescent gas mantles, either burnt or on a collodium basis, of the value of £9560. The world's production of Auer and other similar mantles is stated to have been 220,000,000 mantles in 1908, of which about 100,000,000 came from Germany, 55,000,000 from America, 35,000,000 from England and British Colonies, 15,000,000 from France, 3,000,000 from Austria, 2,500,000 from Italy, 2,000,000 from Belgium, and 1,500,000 from Russia.

In 1906 Germany exported Auer mantles to the value of £460,000. Smaller quantities are exported to-day as large numbers of works have been erected in almost every country. Mantles of very poor quality at very low prices are to-day placed on the market, but the price is always disproportionate to the value. In dealing with these products it would be advisable always to determine their illuminating value by means of photometric measurements.

BORON : B, 11

This is a substance which it is difficult to connect with the other groups of elements. It has many resemblances to the metals, although it has decided non-metallic properties. Thus its oxy-compounds have an acid character. In nature it is found in a state of combination only, as boric acid, $B(OH)_3$, sodium tetraborate (*tinkal*), $Na_2B_4O_7 + 10H_2O$, *borocalcite*, B_4O_7Ca, of which the largest deposit has recently been found in the Argentine, as *boracite*, $2(Mg_3B_8O_{15}) + MgCl_2$, at Stassfurt, as *larderellite*, $(NH_4).B_8O_{13}.4H_2O$, and as *colemanite*, $Ca_2B_6O_{11}.5H_2O$, in California.

These boron compounds are employed for various purposes, such as in medicine, in connection with soldering, in the preparation of fusible enamels, glass, earthenware, &c.

These minerals are abundant in volcanic territories, such as California, India, Chili, and the Argentine, and their origin is explained by the property, which many of these salts which accumulate at the bottom of dried-up seas possess, of being easily carried through the strata of the terrestrial crust by means of steam. Sea water contains about 0·2 grm. of boron per cubic metre. Boron is widely diffused in small quantities throughout the earth and is thus found in the ash of many plants. It was discovered in 1807 simultaneously by Davy in England and by Gay-Lussac and Thénard in France.

Free boron is obtained by reducing boric acid or borax with K, Na, Mg, Al, or P on heating. Moissan has recently obtained it in the electric furnace. It forms masses of a red or yellow colour, but sometimes colourless, which dissolve in molten aluminium and gradually separate "*crystalline boron*" on cooling; this was obtained long ago by Wöhler and by St. Claire Deville, and resembles diamond in its refractive power, hardness, brilliance, resistance to heat and to chemical reagents. Its specific gravity is 2·68. "Crystalline boron" is more stable than amorphous boron and only volatilises at the temperature of the electric furnace. In 1909 Binet de Jassoneix showed that "crystalline boron" is really aluminium boride, AlB_2, which sometimes forms mixed crystals with aluminium carbide, Al_4C_3. Amorphous boron forms a brown powder which when finely powdered easily absorbs gases and has a marked catalytic influence on various reactions. It burns at 300° with a green light, forming B_2O_3 and BN, boron nitride. Crystalline boron is not attacked by acids and by dissolved alkalis, but is only dissolved on fusing it with hot alkali hydroxides or carbonates. On heating it to redness in presence of steam or of H_2S, hydrogen is evolved. It has a very low specific heat and, therefore, a very low

atomic heat, which increases at high temperatures (*see* p. 109), indicating that at low temperatures boron has a very large complex molecule.

Graphitic boron costs up to £400 per kilo, crystallised boron £260, and amorphous boron £32.

BORON HYDRIDE : BH_3. This compound is a gas which is obtained mixed with hydrogen by heating magnesium with boron trioxide, and then treating the resulting mass with HCl ; the gas, which contains BH_3 and H, is only slightly soluble in water, burns with a green flame and is decomposed by $AgNO_3$. At a red heat it is dissociated into H_3 and B, and in a red-hot glass tube deposits of boron are formed.

BORON TRIOXIDE, BORIC ANHYDRIDE : B_2O_3. This compound is formed on burning amorphous boron in oxygen, and practically by heating boric acid to redness :

$$2B(OH)_3 = B_2O_3 + 3H_2O.$$

It forms a hard, amorphous, glassy mass which only volatilises at a white heat, and on heating displaces even the more energetic acids from various salts and dissolves many metallic oxides, forming a kind of glass, which is often coloured (*borax beads* by which various metals may be recognised in chemical analysis). In the air it is slowly transformed into boric acid.

BORIC ACID : BO_3H_3 (BORACIC ACID)

In the Tuscan marshes and especially at Larderello and the vicinity, *soffioni* of very hot steam escape from certain crevices in the ground and are also called *fumaroli*. These contain a small quantity of boric acid together with CO_2, NH_3, SH_2, and a little ammonium sulphate. On condensing these vapours in vats of water called *lagoni*, and concentrating the dilute 2 per cent. solution, crystalline boric acid separates. During the last few years, thanks to the work of Professor Nasini, the utilisation and treatment of these *soffioni* have been rendered more rational and the heat of these gases has also been employed in suitable motors and the boric acid finally refined. Crystallised boric acid is also found in the earth in Tuscany under the local name of *sassolino*. It is abundant in Thibet and California in the form of sodium borate (tinkal).

Considerable quantities of boric acid are prepared to-day, and compete with that obtained from Tuscany, by decomposing the boracite which is abundant in the upper layers of the Stassfurt salts (*Abraumsalze*). The powdered boracite is mixed to a paste with a little dilute HCl and then poured into boiling water. The clear solution is decanted off, saturated, and whilst still hot is poured into lead-lined vessels where the boric acid crystallises on cooling. It is then recrystallised from boiling water in stone vessels which are slowly cooled. In the laboratory the whole of the boric acid may be extracted from mother liquors or other impurities by shaking the liquid with ether or with chloroform, which dissolves all the boric acid, and does not mix with the water ; on decanting the new solution and evaporating the solvent, which may be recovered in a condenser, pure boric acid remains.

Th. Heidlberg proposed the following economic process in 1907 : 500 kilos of finely ground borocalcite are poured with efficient stirring into a boiling solution of sodium disulphate of 15° Bé, containing 850 kilos of crude disulphate ; after an hour the whole is passed through a filter press and the calcium sulphate which is retained is washed with hot water. The whole of the liquors are then concentrated to 30° Bé., after which 430 kilos of crude boric acid separate on cooling and are converted into commercial quality by one recrystallisation. The mother liquors after further concentration separate very fine crystals of sodium sulphate ; the last mother liquors are used for treating new portions of boracite.

The minerals contain from 5 to 35 per cent. of B_2O_3 and two to four tons of crude borax are needed for the preparation of one ton of boric acid.

Pure boric acid is obtained by mixing a saturated boiling solution of sodium borate with HCl or H_2SO_4 ; on cooling, crystals of boric acid are obtained,

which are purified by recrystallisation from water. It is obtained in large, light, shining crystalline scales if a small amount of an albuminous substance is added to the solution in certain definite proportions. In the cold it dissolves in water to the extent of 4 per cent., and on heating up to 33 per cent.

The solution turns blue litmus paper feebly red and turns yellow turmeric paper brown in common with bases which, however, do not redden litmus, and very small quantities of boric acid may be detected with turmeric. When dissolved in alcohol it burns with a green flame and may be distilled in considerable quantities in a current of steam. Boric acid is used in large quantities in medicine, especially by oculists, as a useful though mild antiseptic. Its use is greatly abused as a preservative for foodstuffs, such as vegetables, tomatoes, &c. On heating for a long time to 80° to 100° it loses one molecule of water and forms metaboric acid.

Crude boric acid costs from £14 to £16 per ton. Refined boric acid costs £20 to £24, and when in large scales £32 to £34 per ton. In 1893 87 tons were produced in Italy, 166 tons in 1898; in 1901 more than 347 tons of refined boric acid, in 1905 749 tons, in 1906 562·1 tons, in 1907 466·4 tons, and in 1908 429·2 tons. The production of the crude acid is stated to have been 2763 tons in 1901, valued at £35,400, and about as much in 1908. The exports of crude boric acid were 738·4 tons in 1904, together with 220 tons of the refined product, whilst in 1906 1675 tons of the crude and 494 tons of the refined acid were exported, and in 1908 635·8 tons of the crude and 339 tons of the refined. The imports, in spite of a protective tariff of £1 8*s*. per ton, were 14·6 tons in 1906, 49·6 tons in 1907 and 74·6 tons in 1908 of the value of £1496.

In 1908 Germany imported 1900 tons, and in 1909 2550 tons of boric acid and borax. It exported 2750 tons. Turkey consumes 120 tons of boric acid per annum.

METABORIC ACID : BO.OH, is vitreous and is obtained from boric acid (*see above*). It melts at 60°, being transformed into

TETRABORIC ACID : $H_2B_4O_7$, according to the following equation :

$$4BO_2H = H_2O + H_2B_4O_7.$$

This in turn finally loses one molecule of water at a red heat, forming two molecules of boric anhydride, B_2O_3.

The more important salts are formed from tetraboric acid, and **Borax**, which is the commonest salt, is a sodium tetraborate, $B_4O_7Na_2$, which crystallises from water, in which it is not very soluble, with 10 mols. of water if the temperature is low, or with 5 mols. of water if the temperature approaches 60° (*see also* Part III).

HALOGEN DERIVATIVES OF BORON

BORON CHLORIDE : BCl_3, is obtained by heating boron in a current of chlorine, or a red-hot mixture of B_2O_3 and carbon in presence of chlorine. It is a liquid which boils at 18°, has a specific gravity of 1·25, and is decomposed by water :

$$BCl_3 + 3H_2O = BO_3H_3 + 3HCl.$$

The *bromide*, *iodide*, and *fluoride* of boron are also known.

The latter is a gas which is very soluble in water and is obtained in an analogous manner to silicon fluoride. With HF it forms *fluoboric acid*, BF_4H, which is a very energetic monobasic acid, more especially known in its salts, which are not very soluble.

BORON NITRIDE : BN. Amorphous boron is one of the few elements which combine directly with nitrogen when heated to redness with formation of a nitride. With NH_3 boron also forms BN, and develops H. Thus also boron burns with a bright light in an atmosphere of nitrous oxide, forming B_2O_3 and BN.

BN is prepared in practice by heating to redness in a platinum crucible 1 part of boric anhydride with 2 parts by weight of ammonium chloride or with urea, and washing the residue with HCl.

It forms a white amorphous powder which is not altered even on heating to redness in the air. It is insoluble in water, in acids, and in dilute alkalis. It is decomposed by steam at 200° : $BN + 2H_2O = BO_2H + NH_3$. It combines with HF, forming ammonium fluoborate : $BN + 4HF = BF_4NH_4$. On heating under the blowpipe BN forms B_2O_3.

BORON SULPHIDE : B_2S_3, is also known, and is obtained by burning boron in sulphur vapour, or by heating amorphous boron to redness in a current of H_2S ; also from a mixture of B_2O_3, carbon and carbon disulphide vapours. It forms silky white crystals, which are violently decomposed by water : $B_2S_3 + 6H_2O = 3H_2S + 2B(OH)_3$.

BORON CARBIDE : B_2C_2, has been more closely studied than the carbide B_6C, which is prepared in the electric furnace from boron and carbon in presence of copper. The copper is then removed from the fused mass by the action of HNO_3, and black shining crystals of extraordinary hardness, greater than that of carborundum, remain.

A **BORON PHOSPHIDE : BP**, also exists.

PART III. METALS.

The distinction of this numerous group of elements, the metals, from those which we have already studied as non-metals, is not very rigorous, and although for some elements many of the physical and chemical properties differ very greatly, other properties are common ; various members of the one group or the other possess both metallic and non-metallic properties, so that they cannot be rigorously considered to belong to the one group much more than the other.

The more or less metallic external appearance and conductivity for electricity and heat are differential characteristics only in a relatively quantitative sense, and the same may be said of the fact that oxygen compounds of the non-metals ordinarily form acid substances, whilst the oxidised compounds of the metals in general are basic substances, for here also the exceptions are numerous. The valency of the metals with respect to oxygen diminishes with elevation of the temperature, and in general the compounds containing the minimum of oxygen are the more stable at higher temperatures, whilst at ordinary temperatures those containing the maximum of oxygen are more stable.

The metals do not form gaseous hydrogen compounds and form chlorides which are stable in contact with water. When any substance which contains both a metal and a non-metal is decomposed by electrolysis, the metal is always formed at the negative pole, whilst the non-metal separates at the positive pole. Excepting mercury the metals are all solid and have a specific gravity which varies from 0·59 to 22·5 (*see* Table on p. 411), and which ordinarily increases with increase of the atomic weight. This relation becomes more evident if the atomic volumes of the metals are compared, that is, the ratios between the atomic weight, A, and the specific gravity, d: atomic volume $= \frac{A}{d}$.

Those metals which have a specific gravity lower than 5 are called the *light* metals and the others the *heavy* metals.

Almost all the metals are more or less ductile and malleable.

The *malleability* of metals, that is, the property of being converted into very thin sheets by hammering, and the ductility, that is, the capacity for being drawn into very thin wires, vary with the temperature. For iron they attain a maximum at a red heat, whilst zinc is malleable between 100° and 150°, and becomes brittle at 205°. In the scale of ductility and malleability all metals do not follow the same order, and thus two metals which are very close together in the scale of malleability may be somewhat far apart in the scale of ductility and *vice versa*. With suitable precautions, gold leaf has been obtained of a thickness of only 0·0001 mm. and platinum wires of a diameter of 0·000,08 mm. ; gold and silver leaf of these very small orders of thickness are almost transparent between 200° and 500°.

On cooling molten metals in a suitable manner crystals of the regular or hexagonal rhombohedric systems are sometimes obtained.

Metals may also occur in allotropic forms, crystalline or amorphous. In certain cases the same metal may possess various specific gravities according as it has been rolled, hammered, or molten, and they acquire different degrees

of brittleness at various temperatures; also the heat of oxidation is not always equal. Allotropy also includes the passive form of certain metals. In the allotropic passive form under certain conditions the metals resist the action of acids and behave electrolytically in a different manner from the active form.

The hardness and brittleness of metals are extraordinarily modified by minimal traces of impurities. Thus gold becomes extremely brittle when it contains $\frac{1}{2000}$ of lead; iron containing minimal quantities of carbon becomes very hard (steel), and acquires well-marked special properties with traces of vanadium, Mn, &c.; lead containing three parts per 1000 of antimony becomes very oxidisable when liquefied, so that it even catches fire. We will see later, on studying alloys, what a great influence even small quantities of a given component may have in modifying not only physical properties, but also the chemical properties of the alloy.

Kahlbaum in 1902 and Moissan in 1906 succeeded in distilling numerous metals in porcelain tubes with the oxy-hydrogen flame in an almost absolute vacuum (down to two-millionths of a millimetre). Kahlbaum thus obtained about 25 metals in an extremely pure condition, often crystallised in an allotropic form. It has been sometimes observed that certain easily fusible metals volatilise with difficulty (tin); osmium volatilises without melting, whilst in general when comparing two metals that one which boils first also melts first. Certain metals, such as copper and silver, absorb oxygen during fusion and liberate it again at the moment of solidification (*recalescence*).

The metals are more porous when hot, and gases then pass through their pores with greater facility. Palladium is capable of absorbing 936 vols. of hydrogen.

The *specific heat* of metals is influenced by the temperature, and in general it is diminished by lowering the temperature, the diminution being greater the smaller the atomic weight (*see* p. 109).

It has now been shown that the molecules of the metals are monatomic. This result is obtained from their vapour densities, from the diminution of the vapour tension of mercury in which they are dissolved, and from the freezing-point of the metallic alloys which are true solutions of metals.

Metals may thus be considered as elements the molecules of which are formed of a single atom, and this explains the great power of reaction of most of them and their electric conductivity.

Metals act as cations and conduct the electric current without simultaneous transference of matter, and without alteration. They are, therefore, called conductors of the first class in distinction to electrolytic conductors (solutions) which are conductors of the second class and decompose, matter being transported during conduction. The electric conductivity of metals increases with diminution of the temperature, and it appears that in the vicinity of absolute zero their conductivity is very great, whilst on the other hand the conductivity of electrolytes (solutions) diminishes with diminution of the temperature.

Endeavours have recently been made to explain the electric conductivity of metals by the hypothesis that in the metals themselves there are very numerous non-material electric particles, similar to ions, which impart to them the property of conducting the current. The metals may then almost be considered as solutions of electric particles.

The magnetic elements, which are attracted by the magnet, are the following, arranged in decreasing order: Fe, Ni, Co, Mn, Cr, Ce, Ti, Pd, Pt, Os.

The non-magnetic metals, which are not attracted by a magnet, may be arranged in the following order, commencing with those which are least magnetic: Bi, Sb, Zn, Cd, Na, Hg, Pb, Ag, Cu, Au, As, U, Rh, Ir, W, and

naturally the final terms of the two series approach one another in properties, so that uranium and iridium are sometimes classed amongst the magnetic metals. Certain metallic compounds, such as certain oxides and peroxides, are also magnetic. The magnetism of iron disappears at 740°, that of nickel at 340°, and that of cobalt at 900°. The spectroscopic behaviour of metals has already been discussed at length in Part I (p. 54).

We give on the opposite page a Table in which the most important physical constants of the metals are shown.

METALLIC ALLOYS

All the metals form alloys more or less easily, which cannot be considered as simple mechanical mixtures as the union is more intimate, occurs between molecule and molecule through the agency of fusion, and it is then no longer possible to separate the components mechanically. Alloys may be compared rather to solutions, and may thus be considered as true solid solutions, and when they are melted consist of nothing else than liquid metallic solutions.

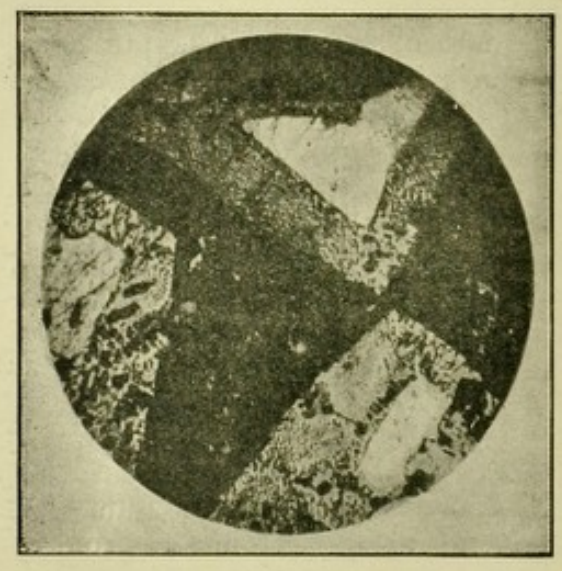


Fig. 168.

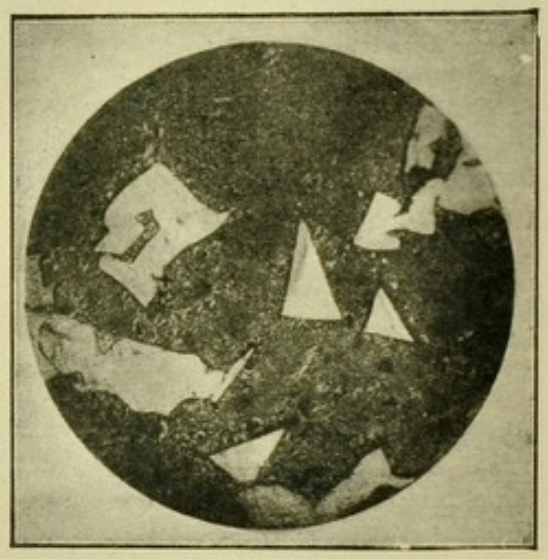


Fig. 169.

On the other hand, the alloys are not homogeneous chemical combinations, that is, the components are not merely mixed in the ratio of their atomic weights, but also in the most varied proportions, and just as in ordinary solutions of salts the solubility varies with the nature of the solvent and of the dissolved substance, so also is this the case for two or more molten metals. These sometimes mix in any proportion whatever, but in certain cases only in well-defined proportions.

The rules which regulate solutions, chemical equilibria and the phase rule may also be applied with proper precautions to molten alloys.

The eutectic temperature of alloys corresponds to the cryohydric temperature of ordinary solutions (pp. 117 and 229).

Guillemin, Sorby, Martens, Widmanstätten, and others have conducted micrographic analyses by attacking the surfaces of well-polished alloys with cold dilute nitric acid or with dilute sulphuric acid (1/10), under the influence of a weak electric current (2 volts at $\frac{1}{10}$ of an ampère) ; they then examined the washed corroded surfaces under the microscope and photographed it, because in this way curious figures and crystalline portions are rendered evident which are constant and characteristic for definite compositions of each alloy.

Microphotographs of alloys of bismuth, tin, and antimony are illustrated in Figs. 168 and 169, which we will study later, and in these crystals of characteristic

PHYSICAL CONSTANTS OF METALS

Metal	Melting-point	Boiling-point approx.	Hardness Pb=1	Density Water=1	Specific heat	Linear coefficient of expansion between 0°–100° per 10,000,000	Electric conductivity Ag=100	Thermal conductivity Ag=100
Aluminium .	660°	1800°	17·3	2·56	0·2143	234		
Antimony .	625°	1440°		6·72	0·0523	116	4·62	
Arsenic . .	500°			5·67	0·0830	60	4·76	
Barium . .	1000°			3·75				
Beryllium .	1000°			1·64	0·4084			
Bismuth . .	265°	1420°	3·3	9·82	0·0308	137	1·25	
Cadmium .	320°		6·9	8·65	0·0567	310	32·72	1·8
Caesium . .	26·4°			1·88				
Calcium . .	760°		1·9 (?)	1·83	0·1722			
Cerium . .	440°			6·63	0·0448			
Chromium .	3000° (?)			6·8	0·1216			
Cobalt . .	1600°			8·5	0·1067	124		
Columbium .				6·27				
Copper . .	1081°	2310°	19·3	8·93	0·0952	70	99·95	73·0
Gallium, solid .	30°			5·96	0·079			
Germanium .	900°			5·47				
Gold . .	1064°		10·7	19·3	0·0324	145	77·96	53·2
Indium . .	176°			7·42	0·0574	459	18·61	
Iridium . .	1950°			22·42	0·0326	70		
Iron .	above 1800°	2450°		7·8	0·1138	123		11·9
Lanthanum .				6·19	0·0448			
Lead . .	326°	1525°	1	11·38	0·0315	280	8·32	8·5
Lithium . .	186°			0·59	0·9408			
Magnesium .	632·5°	1120°		1·74	0·2499	276		
Manganese .	1247°	1900°		8·0	0·1217			
Mercury . .	−39·4°			14·4	0·0319		1·61 (liq.)	
Molybdenum .	1800° (?)			8·6	0·0722			
Nickel . .	1600°			8·8	0·1092	129		
Osmium . .	2500° (?)			22·48	0·0311	66		
Palladium .	1500°			11·5	0·0593	119		
Platinum . .	1770°		24·0	21·5	0·0324	91		8 4
Potassium .	62·5°			0·86	0·1655	842	22·62	
Rhodium . .	1850° (?)			12·1	0·0580	85		
Rubidium .	38·5°			1·52				
Ruthenium .	1950° (?)			12·26	0·0611	99		
Silver . .	962°	1955°	13·3	10·51	0·0570	194	100	100
Sodium . .	97·6°			0·97	0·2934	711	40·52	
Strontium .				2·50				
Tellurium .	- 455°			6·25	0·0525	173		
Thallium . .	270°			11·86	0·0336	302	9·16	
Thorium . .				11·1	0·0276			
Tin . . .	232°	2270°	1·7	7·29	0·0562	227	12·36	14·5
Tungsten .				19·13.	0·0334			
Uranium .	1500° (?)			18·69	0·0277			
Vanadium .				5·5				
Zinc . .	419°		11·7	7·15	0·0956	291	29·02	19
Zirconium .				4·15	0·0660			
Brass . .								23·1
White Metal .								6·3

form are clearly shown. Other microphotographs are reproduced and explained in detail later in the chapter on Iron.

The microscopic study of alloys has greatly helped the elucidation of their internal constitution. In solidified alloys certain crystals of constant chemical composition different from that of the alloy may sometimes be isolated by suitable solvents and may be considered as true chemical combinations. From an alloy of 1 part of copper with 2 parts of tin, shining scales, unattacked by the acid, and of the formula, $SnCu_3$, may be obtained by treating it with concentrated cold HCl.

In metallic alloys the electric conductivity is generally lower than the mean conductivity deduced from that of the component metals, because the alloy may be considered as a thermo-couple formed by its components, the electromotive force of which acts in opposition to that producing the current. From

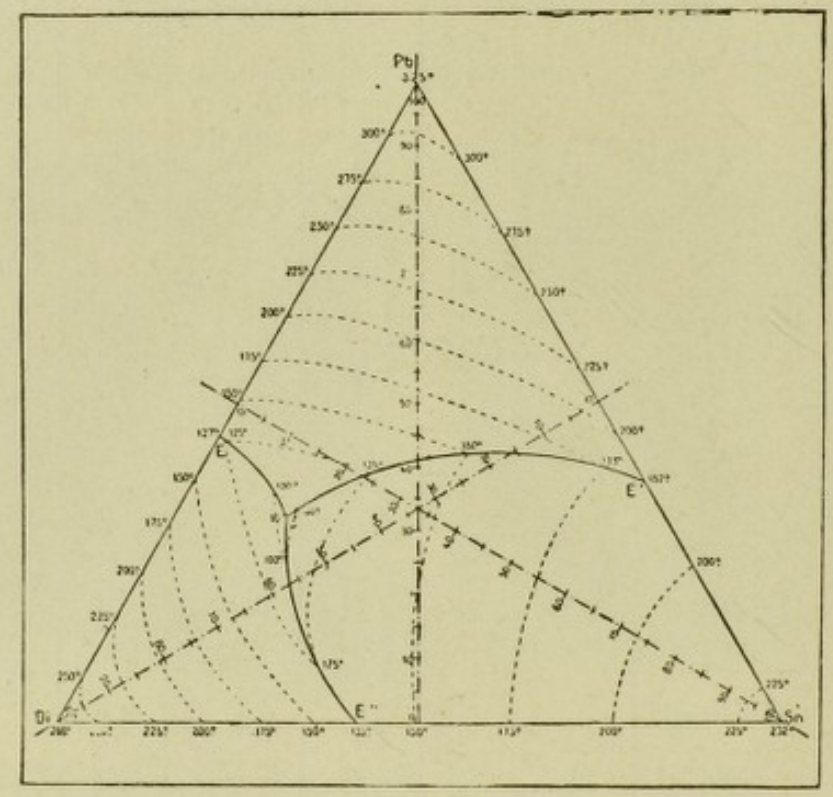


Fig. 170.

the electric conductivity of an alloy its composition may also be deduced, and one may decide whether the metals are present in combination or not by remembering that chemical combination tends to lower the conductivity. The compound $SnCu_3$ was detected in this particular manner.

Alloys generally melt at temperatures below that of their components thus on mixing 8 parts of lead, 15 of bismuth, 4 of tin, and 6 of cadmium, an alloy is obtained which melts at 68°, although none of its components melt below 200°. By thermal examination the composition of the various substances which are formed in the alloy may be deduced.

Information may be also obtained as to whether the alloy contains or is capable of forming a definite chemical combination by comparing the solidifying points of various alloys.

Thus, if small quantities of another metal are contained in a metal, the solidifying point of the first will generally be lowered. On gradually adding further larger quantities of the second metal, the solidifying point will be further lowered until a minimum is reached, called the *eutectic* point, and up to this point there has been no chemical combination, because such combination would, on the other hand, raise the solidifying point. Those

metals which do not form chemical combinations, but which form mixed crystals (p. 87) varying continuously in composition as the proportion of the components is varied, do not show minima of melting-point, that is, eutectic-points, but the diminution or increase of the temperature of solidification follows a continuous curve, rising or descending according to the metal which predominates at the beginning. In the preceding case, on the other hand, in which a eutectic-point was found, we have an indication that these two metals are able to combine in definite proportions to form true chemical combinations. Thus, on continuing to increase the quantity of the second metal after attaining the eutectic-point, the temperature of solidification steadily rises until a maximum is reached, and at this point the two metals form a chemical combination of definite formula. If now the quantity of the second metal is still further increased, the temperature of solidification is lowered because we have an *alloy* between the combination already formed and the excess of the second metal. A further minimum melting-point, that is, a new eutectic-point (eutectic alloy), will again be obtained, but on continuing the addition of the second component, the melting-point will rise again until it reaches the melting-point of the second metal Sometimes the two metals are able to form several successive chemical combinations, and then before the melting-point of the second metal is reached further maximum and minimum melting-points are passed through.

When two metals do not form combinations or even mixed crystals, then the *melting-point curve* may descend without passing through a true eutectic-point, but will then rise continuously until the melting-point of one of the metals is reached.

The following alloys, which consist of true chemical combinations, are well known: $SnCu_3$, $PtHg_2$, $PtZn$, $PtSn_4$, Al_3Mn, Zn_3Hg, Cd_3Tl, Hg_6Na, and Hg_2Na.

In 1908 Tamman published a complete study of more than 150 binary alloys.

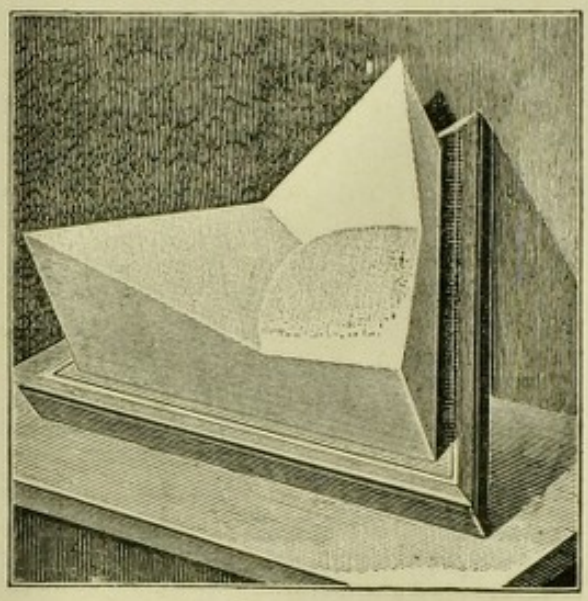


FIG. 171.

In Figs. 170 and 171, we show a diagram in plan and in relief of the melting-points with the relative eutectic-points of alloys of lead, tin, and bismuth.[1]

[1] A diagram of fusibility for alloys of three metals—Pb, Sn, and Bi—may be represented as in Fig. 170, in which the vertices of an equilateral triangle correspond to the pure metals respectively. The proportion of each metal which enters into an alloy of any definite melting-point is indicated by the line which forms the height of the triangle corresponding to the vertex of that particular metal. The sides of the triangle show the binary alloys and all the internal points correspond to ternary alloys.

The melting-points of the ternary alloys may be represented by dotted curves which unite all the alloys of varying composition which solidify at the same temperature. Generally these curves form triangles of which the angles are arranged along three lines, E_ε, E'_ε, E''_ε, corresponding to the relative temperature minima. These three lines meet at a single point $_\varepsilon$, which represents the alloy of the three metals which has the lowest melting-point.

In Fig. 171 the diagram of the preceding Figure is indicated in relief, and comprises all the alloys which can be formed from the three metals mixed in varying proportions. The three extreme highest points correspond to the melting-points of the respective pure metals. The surface which starts from these points is divided into three slopes separated by three depressions or valleys, which represent the lines of relative eutectic-points converging towards the absolute eutectic-point. In each of these three regions, on cooling, the pure metal which corresponds to the vertex of that region gradually separates in the solid state; along the relative eutectic-points the binary alloy of the metals corresponding to the two adjacent regions separates on cooling, and at the absolute eutectic-point, which corresponds to the cryohydric-point of salt solutions, &c., the whole of the ternary alloy solidifies on cooling. It is evident that in order to prepare such a diagram or model, numerous exact determinations are necessary, which then give complete and exhaustive information on everything which can be done with an alloy of the three metals.

Fig. 168 is a microphotograph of one of the alloys in which the light crystals of bismuth, which have separated between 175° and 125°, are clearly evident. Round each crystal one sees crystals of bismuth or tin deposited along the relative eutectic lines between 125° and 96°. The black part of the figure represents the homogeneous ternary alloy of the three metals corresponding to the absolute eutectic temperature. In Fig. 169, on the other hand, we see the angular crystals of antimony.

These crystals are of very great importance in the alloys which are used for bearings for machinery, because only the softer portions of the alloy remain in a condition which is slightly adhesive to the shafting, whilst the points of contact which carry the weight of the whole shaft revolving in the bearings are formed by these harder crystals, which present a minimum of surface and thus give a minimum amount of friction.

The coefficient of elasticity of an alloy is generally equal to the mean of those of its constituent metals, and is the larger the more fine and homogeneous its grain.

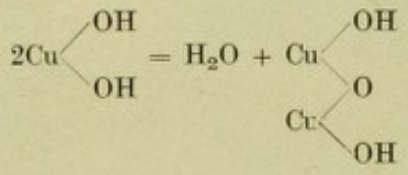
When an alloy is melted and allowed to cool slightly, certain of its components sometimes separate, forming solid layers of different composition. This phenomenon is called *liquation;* the Germans call it "*Saigerung.*"

The chemical behaviour of an alloy is sometimes very different from that of its components. Thus an alloy of 56·5 per cent. of copper and 43·5 per cent. of zinc is not attacked by nitric acid, whilst copper or zinc alone are rapidly dissolved; thus also an alloy of gold and silver containing less than one-third of silver is insoluble in HNO_3, whilst free Ag is soluble; thus also platinum is not soluble in nitric acid, whilst an alloy of platinum and silver dissolves completely.

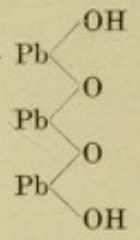
The alloys of other metals with mercury are called *amalgams.*

SALTS, ACIDS, AND BASES

We have already seen how several molecules of a polybasic acid are able to condense and form polyacids, such as pyroantimonic, pyrophosphoric, and pyrosilicic acid, &c., and in the same way it is known that the polyacid bases, also called polyhydric bases, condense to form polybases or polyhydroxides:



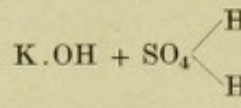
; $3Pb(OH)_2 = 2H_2O +$



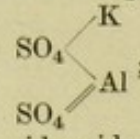
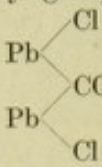
From these polyhydroxides basic salts are obtained by the replacement of a portion of the hydroxyl groups by acid residues.

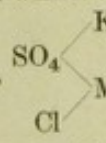
The metals easily form halogen combinations (chlorides, bromides, iodides, &c., which are non-oxidised salts) either by the direct interaction of their elements or by the action of the halogen acids on the metals or the corresponding oxides and carbonates; some of these combinations are easily obtained by the action of the halogen on a mixture of metallic oxide and carbon.

In the formation of salts from acids and bases there is generally separation of one or more molecules of water formed from one or more atoms of hydrogen of the acid and one or more hydroxyl groups of the base:



; $K.OH + HCl = KCl + H_2O.$

Mixed salts or *Double salts* are obtained when hydrogen atoms of a polybasic acid are replaced by atoms of more than one metal, for example,  ; $PO_4\begin{cases}K\\NH_4\\Na\end{cases}$; or also when the hydroxyl groups of a polybase are replaced by acid residues of varying character, for example,  ; however, such constitutions of double salts can only be admitted in the solid crystallised state, because in aqueous solution only the corresponding characteristic ions occur, and these ions are the same as those of the simple salts, that is, of potassium sulphate, aluminium sulphate, potassium phosphate, ammonium phosphate, &c. In dilute solution the size of the molecule is actually found by cryoscopic determination not to correspond to that of the double salt, but to those of the simple salts. The double salts are, however, separated from concentrated solutions of the simple salts when

one of these salts is in excess. In general double salts have two similar metallic or acid residues. Very occasionally double salts are met with which simultaneously contain both acid and basic residues which are all different, such as,  , and the formulæ of these special double salts are written as molecules of the component salts, separated by a point: $SO_4Mg.KCl$. Certain complex double salts are also known which dissociate in solution into special ions different from those of the corresponding simple salts.

The property possessed by certain substances of forming double or complex salts which are more soluble than those of the individual simple salts is practically utilised, as in some cases the solubility of a given salt can thus be considerably increased.

NOMENCLATURE OF SALTS, ACIDS, AND BASES. In the denomination or nomenclature of salts, the name of the acid is formed from the name of the corresponding elements modified by a suffix. The names of the more stable and better known acids terminate in *ic*, for example, hydrochloric, hydrosulphuric, chloric, sulphuric, and nitric acids, &c.; the salts corresponding to the non-oxygenated acids change the suffix *ic* into *ide* (chloride, sulphide, iodide, &c.); whilst in those derived from the oxy-acids, the suffix is changed to *ate* (chlorate, sulphate, arsenate, carbonate, &c.). The acids which contain less oxygen have the suffix *ous* (nitrous, sulphurous, arsenious, &c.), and the names of the salts corresponding to them end in *ite* (nitrite, sulphite, arsenite, &c.). On the other hand, the acids containing more oxygen take the prefix *per* (persulphuric, perchloric acids, &c.), and the corresponding salts change their suffix into *ate* whilst retaining the prefix *per* (persulphate, perchlorate). Acids containing a minimum of oxygen take the suffix *ous*, together with a prefix *hypo* (hyposulphurous, hypochlorous, hyponitrous acids, &c.), and in their salts the suffix is replaced by *ite* (hyposulphite, hypochlorite, hyponitrite, &c.). Many metallic oxides which contain a maximum amount of oxygen and which are able to readily give up a part of it, so that they act as energetic oxidisers, are called peroxides.

ELECTROCHEMISTRY

This branch of chemistry has acquired great importance on account of its practical application in recent years. In many countries the importance of electrochemical industrial processes has been exaggerated and will lead to bitter and disagreeable or even costly disappointments. Under the conditions of science and industry to-day we may safely affirm that calcium carbide, potassium chloride and hydroxide, and in certain cases sodium hydroxide, the hypochlorites, aluminium, copper, &c., can be produced electrolytically with advantage. But it is not to be denied that present-day electrochemical industry cannot afford to pay for expensive electrical energy, and that sometimes a price of £2 or £2 8*s*. per h.p.-year for this commodity is already too expensive. It is also necessary to remember that in Italy, where fuel is scarce, certain interests are always ready to buy electrical energy for transformation into light and power, even at a price of £6 to £8 per h.p.-year. Under these conditions, it cannot be advantageous to develop electrochemical industries in all localities. It is not, however, impossible that in the future, when the yields and the production of electrical energy have been improved, the electrochemical industry will acquire much more importance than can at present be foreseen. The water-power utilised to-day by the various nations is altogether about 4,000,000 h.p., of which there are more than 500,000 in Italy, more than 750,000 in France, about 1,000,000 in Norway and Sweden, 1,000,000 from Niagara Falls, 300,000 in Germany, and 250,000

in Switzerland. The sources of water power which have not yet been utilised are, however, much more important. It is estimated that in Norway and Sweden 14,000,000 h.p. is available, in Italy 6,000,000, in France 5,000,000 (for 9 months in a year, and 3,000,000 in the 3 less productive months), in Switzerland 1,250,000, in Austria 2,000,000, in Great Britain about 900,000, in Russia about 11,000,000, in America more than 25,000,000 (5,000,000 of which can be obtained from Niagara Falls).

Many chemical phenomena are closely connected with electrochemical phenomena. It will suffice to mention the electrolytic dissociation of many substances when dissolved in water, such as salts, acids, bases, &c., and also many chemical reactions under the influence of the electric current. Volta's cell was the first demonstration of the transformation of chemical into electrical energy, and a similar phenomenon is easily produced under the most varied chemical conditions (*see below*, Daniell's Cell). Volta actually believed that with his cell he had discovered a new infinite source of gratuitous energy with which it would be possible to produce perpetual motion without any corresponding consumption of energy. The law of the conservation of energy was not then known, and it was only much later that it had to be admitted that the electrical energy of the Volta cell was provided by energy resulting from a chemical reaction. In order to be able to study the relation between phenomena of these two kinds, it is necessary to be able to compare them quantitatively in terms of the same unit of measurement, and to know the various units which are used, and among the most important for our purpose are the following.

The UNIT QUANTITY OF ELECTRICITY is the INTERNATIONAL COULOMB, and it is found experimentally that 96,540 coulombs are required to evolve 1·008 grms. of hydrogen from an electrolyte, such as acidified water.

An electric current which transports one coulomb per second has an intensity of one *ampère*, therefore an electric current of *one ampère* carries a quantity of electricity equal to 3600 coulombs in one hour. The INTERNATIONAL AMPERE is the unit of current strength. If we wish to understand the significance of this current strength a little more clearly, we may compare it with a current of water which we will suppose to have a value of 1 when it transports, for example, 500 litres of water per second. The strength of this current will be doubled, that is, its velocity will be doubled, if it transports 1000 litres of water per second, and it will be trebled if it transports 1500 litres per second, the section of the outlet remaining equal.

A current of 1 amp. strength, in order to develop 1·008 grms. of hydrogen, must pass through the electrolyte for 96,540 seconds, that is, 26 hours and 49 minutes, because this current transports 1 coulomb per second.

The work which is produced by an electric current does not depend on the intensity only, but also on the tension or difference of potential of the current itself.

This tension may be compared, up to a certain point, with the height at which a given quantity of water is stored ; the work which it produces in falling then varies with the *head* of water.

But in order that a current may pass along a conductor (hydraulic or electric), it is necessary that a difference of level should exist, and the work produced by the same quantity of electricity will be the greater the greater the potential difference or electrical level between the extremities of the conductor. This potential difference is the *electromotive force* of the current, and the practical unit of electromotive force is given by the potential difference which exists at the extremities of a conductor which has a resistance of 1 ohm (*see below*), and is traversed by a current of 1 amp. ; this tension is equal to 1 VOLT or the INTERNATIONAL VOLT.

If we pass the same current through different solutions of various salts, such as copper sulphate, zinc sulphate, silver nitrate, &c., then after a certain time 31·8 grms. of copper will have been deposited and at the same moment 32·7 grms. of zinc and 107·92 grms. of silver will have been deposited in the other voltameters. We immediately see that these weights exactly represent the equivalent or combining weights of these metals, and thus it is possible to measure the intensity of a current by weighing the quantity of material which is deposited at the electrodes in unit of time, and it has thus been found experimentally that a current of 1 amp. in one second deposits exactly 1·1175 mgrms.

of silver, or 0·0104 mgrm. of hydrogen, or 0·6589 mgrm. of copper from a cuprous salt, or 0·3200 mgrm. of copper from a cupric salt, 0·3385 mgrm. of zinc, &c., and these quantities are in the same ratio to one another as the respective combining weights (p. 21), and we may also measure the quantity of hydrogen gas evolved by 1 amp. in a voltameter containing dilute sulphuric acid.

These facts, which were already studied by Faraday in 1833, led to an important and universal law called by his name, according to which, under equal conditions, the quantity of matter separated is exactly proportional to the current strength, and the same current passing through several separate electrolytes separates from each quantities of matter which are in the same ratio as their equivalent or combining weights.

The work done by a continuous current per second is measured by the product of the current strength in ampères, and its potential difference in volts. The product of 1 amp. and 1 volt is 1 **watt**, which is thus the unit of measurement of electrical energy. One watt corresponds to 10^7 ergs per second, that is, 1 joule per second (p. 59), that is, it is almost equal to the work produced by 100 grms. of water falling from a height of 1 metre. Since this value is small, the kilowatt (kw.) = 1000 watts = 10^{10} ergs per second, that is, a Kilojoule per second, is used in practice, and a horse-power corresponds to 736 watts.

From these data it is easy to calculate the electrothermic equivalent, knowing that a calorie corresponds to 41,800,000 ergs (p. 59), and thus the work produced by 1 watt per second corresponds to $\frac{10^7}{41{,}800{,}000} = 0{\cdot}2991$ cal. It is thus possible to calculate the *electrochemical equivalent* as we have found above that 96,540 coulombs correspond to 1·008 grms. of hydrogen or 107·938 grms. of silver, being the chemical equivalents or combining weights expressed in grammes; thus one coulomb corresponds to 0·001,118,1 grm. silver.

An electric current passing through a conducting wire or a solution encounters a certain resistance which may be compared with the resistance encountered by water flowing through a tube, a resistance which increases with the length of the tube and decreases with its cross-section.

The unit of resistance is the INTERNATIONAL OHM, which represents the resistance offered to the passage of a constant current by a column of mercury 106·3 cms. long and of a weight of 14·4521 grms. at 0°, the uniform cross-section thus resulting being 1 sq. mm.

An electrolytic process depends upon the current strength, I, which, according to Ohm's law, is found by dividing the electromotive force, E, by the resistance, R: $I = \frac{E}{R}$.

The total resistance of a cell is made up of the sum of its internal resistance, R_1, and the resistance of the external circuit, uniting the two poles, R_2, so that $I = \frac{E}{R_1 + R_2}$.

If, for example, we wish to calculate the current strength, I, passing through a system in which there is an electromotive force, E, of 3·4 volts, when the circuit is broken, with an internal resistance, R, of 0·6 ohm and an external resistance of the circuit uniting the two poles, $R_2 = 4$ ohms, then on applying the general formula, we find

$$I = \frac{E}{R_1 + R_2} = \frac{3{\cdot}4}{0{\cdot}6 + 4} = 0{\cdot}74 \text{ ampère.}$$

If the electromotive force, E (voltage), of a source of electricity remains constant, the current intensity (ampérage) may be modified by varying the resistances, R_1 and R_2, and since the resistance of a homogeneous wire is proportional to its length, l, and in inverse proportion to its cross-section, S, the resistance of any conductor (rheostat) can be calculated thus: $R = k\frac{l}{S}$, where k is a constant factor called *specific resistance*, which depends only on the nature of the conductor, and which is defined for any substance as the resistance of a length of 1 cm. of 1 sq. cm. cross-section. In the case of copper, $k = 1{\cdot}584$ millionths of an ohm. If k is the specific resistance of a substance, then $\frac{1}{k}$ is its *specific conductivity*, which in the case of metals increases with diminution of the temperature, whilst in solutions it generally increases as the temperature rises.

ELECTROMOTIVE FORCE OF METALS; VOLTAIC SERIES OF THE ELEMENTS

If a zinc plate is immersed in a solution of copper sulphate it is noticed that copper is immediately deposited on the zinc, whilst a part of the latter passes into solution with formation of zinc sulphate.

This phenomenon is due to the fact that the electric charges of the copper ions are given up to the zinc plate which then liberates zinc ions charged with electricity, which in presence of SO_4'' anions replace the copper forming zinc sulphate. Thus the process continues with deposition of copper ions and formation of zinc ions. Although there is thus an exchange of electric charges, we cannot detect an electric current in this liquid because this continual transformation occurs at all points inside the liquid. If, on the other hand, we arrange the experiment in another manner as a Daniell cell (Fig. 172), we may study this phenomenon more closely; K is an open copper cylinder immersed in a cylinder, P, of porous earthenware closed at the bottom, which contains a solution of copper sulphate and retains it, but allows the current to pass. Z is an open cylinder of zinc, immersed in a glass vessel which contains zinc sulphate. If the copper cylinder is united with the zinc cylinder by means of a metallic wire, L, then deposition of copper immediately commences on the cylinder, K, and simultaneously the corresponding quantity of zinc dissolves in Z. If we insert a current indicator in the wire circuit, we are able to detect an electric current passing through it in the direction from the copper to the zinc in the external circuit, that is, in the wire connecting the two poles, and consequently from the zinc to the copper inside the cell. The copper is thus the cathode and the zinc the anode. By means of an electrometer we may also observe that the zinc pole has a potential (voltage) lower than that of the copper pole, and thus the current passes from the former to the latter inside the liquid in order to then continue from the copper to the zinc in the external circuit. The potential difference between the two metals remains constant even if the surface and the distance between the electrodes are varied, and within certain limits even when the nature of the anion is varied. If one of the metals and the corresponding salt are replaced by another metal, which has a distinct, definite and constant potential, the difference of potential between the two metals of the elements in the Daniell cell remains constant under all circumstances. Each couple of metals has a constant potential difference which is characteristic compared with that of other metals and is called the electromotive force of the metals themselves.

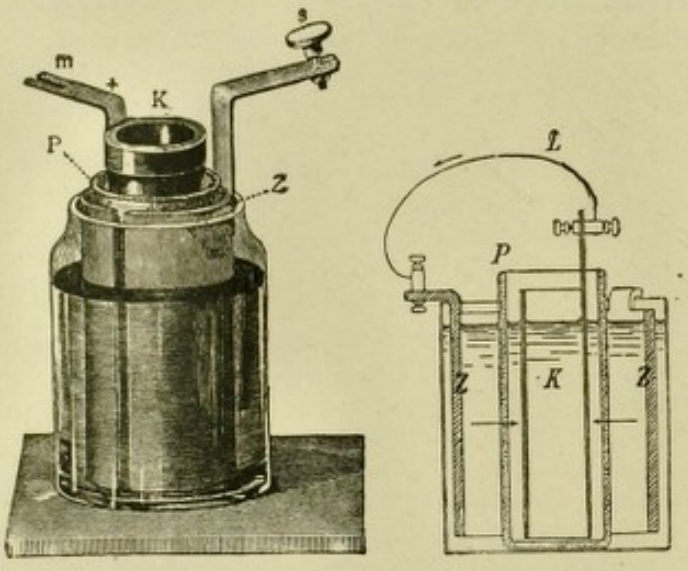


FIG. 172.

The metal of lower potential acts as a precipitant, passing into solution, becoming oxidised and acting as an anode, for example, zinc, whilst the precipitated or reduced metal acts as a cathode or negative pole to which the metallic cations pass, for instance, copper. It is thus possible to establish voltaic series, that is, to arrange the metals in such a manner that they follow one another

in a series in which one metal functions as precipitant or anode compared to another of higher potential which is precipitated in turn as cathode by another metal of still higher potential, thus, for example, cadmium precipitates metallic copper from copper sulphate, forming cadmium salts, but zinc precipitates cadmium from cadmium sulphate, &c.

By Faraday's law a certain quantity of zinc always produces the same quantity of electricity and precipitates different quantities of other metals in proportion to their equivalents, that is, it liberates an equal number of their ions. A given quantity of zinc—which corresponds to a definite quantity of electricity—in order, for example, to separate various weights of cadmium and of copper, must necessarily perform different amounts of electrical work, but the quantity of electricity being constant, it must act with a different potential, different in the case of two different metals, in exactly the same way as, in order to produce different amounts of work with the same quantity of water, it is necessary to allow it to fall from different heights.

For a silver-zinc	couple	there	is	a	potential difference of	1·57 volts
„ copper-zinc	„	„	„	„		1·10 „
„ cadmium-zinc	„	„	„	„		0·35 „

In order to obtain the relative value of the potentials of the elements it is necessary to choose as an arbitrary zero the potential of any one element, and we can then calculate the values of the others ; if, for example, in such a series we take the value for zinc as zero, then the potential of silver will be 1·57, that of copper 1·10, that of cadmium 0·35. Starting from a zero which is not that of zinc, it has been possible to determine the tension of all the metals, and we can thus establish the following electrochemical series of the elements which commences with the electropositive alkali metals and becomes more negative as we approach the non-metals up to fluorine.[1]

	Volts		Volts		Volts
Cs	+	Tb	+ 0·11	As	− 0·55
Rb		Fe	+ 0·09	Cu	− 0·59
K		Co	− 0·02	Hg	− 1·03
Na		Ni	− 0·02	Ag	− 1·06
Mg	+ 1·24	Sn	− 0·09	Pd	− 1·07
Al	+ 1·03	Pb	− 0·10	Pt	− 1·14
Mn	+ 0·82	H	− 0·25	Au	− 1·36
Zn	+ 0·51	Sb	− 0·38	⋮	
Cd	+ 0·16	Bi	− 0·50	F	—

This electrochemical series is interesting from various standpoints ; thus the more electropositive metals are able to separate those which are less electropositive or more electronegative from solutions of their salts. Also those metals which are more electropositive than hydrogen have a solution tension greater than that of the $H^{\cdot}$ ions, and evolve hydrogen from dilute acids, whilst this cannot occur with those elements which are more electronegative, that is, which have a smaller potential. Thus copper and mercury do not evolve hydrogen with acids, and mercury is purified in practice by washing it with nitric or sulphuric acid because the impurities consisting of other metals dissolve rapidly in these acids. It also explains why it is not possible to transform copper directly into sulphate by the action of sulphuric acid, so that in order to obtain this salt it is necessary to first oxidise the copper. It also explains why copper is frequently used industrially for the construction of the most varied apparatus to resist the action of acids (in dyeing, sugar refining, &c.).

We may also infer *a priori* how metallic alloys or metallic coatings, such as galvanised iron wire, tin-plate, &c., will behave in presence of an electrolyte

[1] *Translator's note.*—In this series the *electropositive* elements, *i.e.*, those with the (+) sign, are those which form the *negative* pole of a cell, and *vice versa*, as the more positive ions travel through the internal circuit *with* the current.

or even in presence of rain water, which always contains small amounts of salts and of carbon dioxide in solution. In the case of "galvanised" (zinc-covered) iron wire, the zinc will go into solution (become oxidised) but not the iron, even though the latter is partially laid bare; whilst, on the other hand, tin-plate will easily form iron rust although well covered by tin at certain points, because the potential of the iron is higher than that of the tin, and it will therefore readily go into solution and become oxidised.

These theoretical deductions are strictly confirmed in daily practice.

ELECTROLYSIS: PRIMARY AND SECONDARY PRODUCTS. When a sufficiently concentrated solution of sulphuric acid is decomposed by electrolysis, then at the anode, instead of the formation of oxygen and repeated regeneration of sulphuric acid as occurs in the case of slightly acidified water, persulphuric acid and oxygen are formed through the condensation of two SO_4 anions with 1 mol. of water:

$$2(SO_4) + H_2O = O + H_2O_8S_2.$$

Those products of electrolytic decomposition which result directly from the ions are called primary products. Thus, in the case of HCl the primary products of the electrolytic dissociation are hydrogen and chlorine formed from the H and Cl ions. In the dissociation of sulphuric acid the oxygen may be considered as a secondary product of the electrolysis because it is formed by the interaction of one of the ions with another substance, water. On electrolysing HCl in very dilute solution oxygen is formed instead of the chlorine at the anode as a secondary product, because $2Cl + H_2O = 2HCl + O$, and thus one may have both primary and secondary decomposition of water. In the electrolysis of concentrated solutions of NaCl, the Cl anion is carried to the anode where it escapes as molecular chlorine, but at the cathode metallic sodium is not formed, but hydrogen instead, because the metallic Na cation decomposes water as soon as it is formed and evolves hydrogen ($Na + H_2O = NaOH + H$). In this case Na is a primary product and H and sodium hydroxide the secondary products.

In order to separate the ions from an electrolytic solution at the cathode and the anode, it is necessary to use an electromotive force which increases with increase of the solution tension of the two kinds of ions, and with decrease of their osmotic pressure.

Therefore, in order to separate metals electrolytically it is necessary to take into account the potential difference at the electrodes and not merely the current intensity. In a solution containing both zinc and copper ions it is possible to separate the copper only by means of a current of low electromotive force, but with a current of higher electromotive force (greater difference of potential) zinc may also be separated.

The decomposition voltage of certain cations and anions referred arbitrarily to that of hydrogen, which is considered as zero, is the following: *Cations:* $Zn^{\cdot\cdot} + 0{\cdot}770$ volt; $Cd^{\cdot\cdot} + 0{\cdot}420$; $Pb^{\cdot\cdot} + 0{\cdot}148$; $Cu^{\cdot\cdot} - 0{\cdot}320$; $Ag^{\cdot} - 0{\cdot}771$. *Anions:* $SO_4H' - 2{\cdot}6$ volts; $SO_4'' - 1{\cdot}9$; $OH' - 1{\cdot}68$; $Cl' - 1{\cdot}417$; $O'' - 1{\cdot}08$; $Br' - 0{\cdot}993$; $I' - 0{\cdot}520$. From these data the decomposition voltage of the most varied electrolytes may easily be calculated. Thus, in order to electrolytically decompose zinc iodide of normal concentration, a voltage of $0{\cdot}520 + 0{\cdot}770 = 1{\cdot}290$ volts will be necessary, and for copper sulphate, $1{\cdot}9 + 0{\cdot}329 = 2{\cdot}229$ volts.

In order to interpret the electrochemical phenomena which we have noted in the Daniell cell, that is, the potential difference which arises between a metal and a solution of a salt, Nernst compared it to the vapour pressure which is produced by a liquid in a closed vessel, a pressure which increases until equilibrium is attained with the vapour tension of the liquid itself (*see* p. 81) or the osmotic pressure which a salt exercises when dissolved in water, a pressure which increases with the quantity of the salt until it is in equilibrium with the solution tension. Thus, each metal immersed in a solution has a tendency, which varies according to its nature, to give off ions to the solution. This electrolytic solution tension is the greater the smaller the number of metallic cations already present in the solution, that is, the smaller the osmotic pressure of the dissolved cations. In reality, however, the number of cations which a metal gives up to a solution is extraordinarily small, because as these are positively charged and the metal remains negatively charged, it attracts these cations and equilibrium occurs when as many ions enter into solution as are deposited at any given moment. But since the electric charge

of a few metallic ions in solution is very large, a potential difference between the metal and the solution may be immediately observed, a difference which is constant for each individual metal. In the Daniell cell, we have a potential difference between each of the two metals and the respective solutions. The electromotive force of the Daniell cell does not depend on the solution tension of each of the two metals only, but also on the osmotic pressure of the dissolved ions of each metal, and since this pressure is almost equal for the zinc and the copper ions, whilst, on the other hand, metallic zinc has a solution tension much greater than metallic copper, the current will pass from the zinc to the copper in the internal circuit and the zinc will remain negatively charged (negative pole), because it gives off positive cations. The copper, on the other hand, will be positive because positive copper cations are deposited on it. If we now diminish the osmotic pressure in the copper sulphate by diminishing the number of the $Cu^{\cdot\cdot}$ cations by means of the addition of potassium cyanide, which forms less ionised, complex $Cu(CN)_2$ with $Cu^{\cdot\cdot}$, we will increase the tension of the copper solution and a larger number of cations will thus pass into solution until they reverse the direction of the current. The electromotive force of a galvanic cell and the electric current which is caused by it depends more particularly on the solution tensions of the two metals and we may thus consider the cell as a machine in which free chemical energy is transformed into free electrical energy. The process may be represented by the chemical equation $Zn + CuSO_4 = ZnSO_4 + Cu$, that is, the zinc which displaces the copper ions dissolves, that is, becomes converted into ions, and, on the other hand, converts copper ions into neutral deposited copper: $Zn + Cu^{\cdot\cdot} = Zn^{\cdot\cdot} + Cu$.

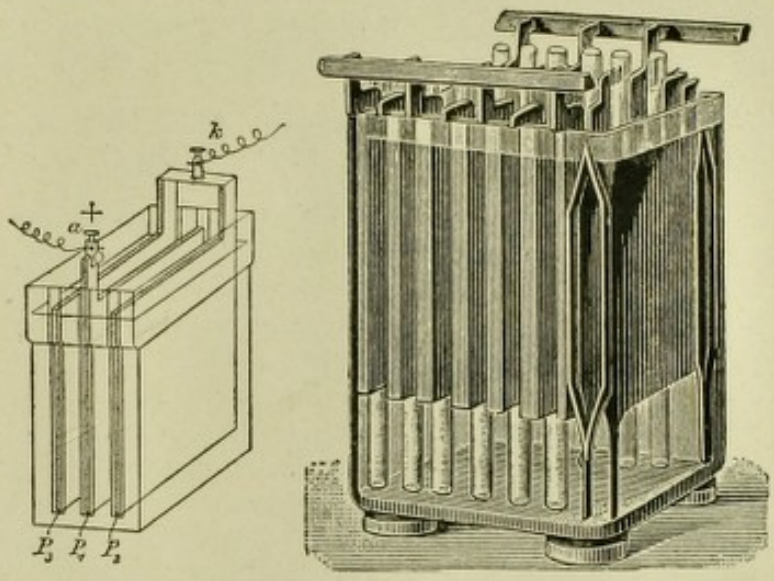


FIG. 173.

ACCUMULATORS. A very important type of reversible cell is that of the common lead-plate accumulator, which consists of a large number of porous leaden plates (Fig. 173) arranged in parallel in a closed reservoir containing very pure dilute sulphuric acid of 20 to 25 per cent. The lead plates are alternately covered with lead peroxide, PbO_2, and with lead sulphate, $PbSO_4$. All the plates (P_1) covered with lead peroxide are connected to one another and form an anode or positive pole, a, whilst those covered with lead sulphate, P_2 and P_3, are also connected together forming a cathode or negative pole, k. By passing a current in through the positive plate, it passes through the acid and out at the negative plate. During this process the lead sulphate on the latter is reduced to metallic lead, whilst a corresponding quantity of lead peroxide accumulates on the other plate; when hydrogen commences to be evolved from the lead plate and oxygen from that coated with peroxide, this indicates that the cell is charged, that is, it has stored up electrical energy (potential energy: *see* p. 5); this charge is retained for a long time, so long as the two poles are not brought into metallic connection. When this is done an electric current passes in the reverse direction, because the lead peroxide plate, by its solution tension, liberates free negative ions of PbO_2'', which neutralise the positive ions of $Pb^{\cdot\cdot}$ formed by the plate of spongy lead, forming neutral molecules of PbO which combine with sulphuric acid and form lead sulphate, which is deposited on the cathodic plate until the accumulator is discharged. During charging the following chemical reaction occurs: $2PbSO_4 + 2H_2O = 2H_2SO_4 + Pb + PbO_2$, and, on the other hand, during the discharge we have firstly: $PbO_2'' + Pb^{\cdot\cdot} = 2PbO$, and then $2\,PbO + 2H_2SO_4 = 2\,PbSO_4 + 2H_2O$.

Accumulators are of great practical importance because they allow hydro-electric energy to be utilised at moments in which it would otherwise be lost, for example, at night, so that it may be used at times when a large supply of current is required in addition to

the ordinary dynamo, which does not thus require to be so large because it can be built of a size proportionate only to the hydraulic power which can be utilised by day.

The Bunsen and Leclanché cells are irreversible cells having cathodes of zinc and anodes of carbon, and when a current is passed through them in the reverse direction they do not regain their original condition. All cells, however, are sources of electrical energy provided by reaction between ions, and in every chemical reaction it can be shown by suitable apparatus that an electrical current is produced if the substances and the solutions taking part in the reaction are kept separate ; then the ions of the one portion pass on their electrical charge to the other electrode by means of the interpolar circuit, causing the formation of new ions which are formed from the neutral metallic molecules or neutralising ions, already free, of opposite charge.

The valency of metals is well indicated by their oxygen compounds in which the oxygen is always divalent, and thus the metals may be divided into 8 groups according to their valency. These groups are evident in the periodic system of the elements which will be considered at the end of this volume. The metals form the following various forms of oxides commencing with the group of the monovalent metals and rising up to the metals with a valency of 8 :

I	II	III	IV	V	VI	VII	VIII
K_2O	MgO	Al_2O_3	SnO_2	Bi_2O_5	CrO_3	Mn_2O_7	OsO_4

The hydroxides corresponding to the first two groups are strong bases such as KOH and $Mg(OH)_2$, substances, that is, which show a strongly alkaline reaction and form salts with metals. The bases are substances formed from metallic cations united with hydroxyl residues (OH anions) and have an opposite chemical action to the acids (p. 92) ; the acids on the other hand are characterised by their acid taste, by their property of reddening blue litmus solution and of evolving hydrogen in contact with almost all the metals even in the cold, especially with magnesium powder. The fundamental properties of bases when dissolved in water are due to the OH (anions) independently of the nature of the metal which they contain, and the OH group in solutions of the bases is present in the state of free ions and produces the alkaline reaction.

The hydroxides of the third and fourth groups possess both basic and acid characters, so that they form salts both with acids and with bases. The hydroxides of the fifth and seventh groups are not known, but the corresponding salts are well defined, and they may thus be considered as anhydrides which have an acid character.

The metals of the first and second groups form peroxides, such as Na_2O_2, BaO_2, &c., which are more highly oxidised and do not form salts, but easily lose one atom of oxygen when heated with oxy-acids, and form chlorine when heated with HCl ; the peroxides of lead and manganese, PbO and MnO_2, behave in the same manner.

Acids unite with bases (or oxides) to form salts with separation of water, and thus also the metallic oxides combine with acid anhydrides forming salts, but without separation of water. On dissolving metals in dilute acids, salts are also formed : $Zn + H_2SO_4 = ZnSO_4 + H_2$. However, the hydrogen of the acid which is thus evolved may sometimes act as a reducing agent on the acid itself. Thus, if we treat zinc with strong sulphuric acid, sulphurous acid and even hydrosulphuric acid are also formed :

$$SO_4H_2 + H_2 = 2H_2O + SO_2, \text{ and also } SO_4H_2 + 4H_2 = 4H_2O + SH_2.$$

Nitric acid is also reduced in dilute solution ; on the other hand, the acids of arsenic and antimony are more stable, and phosphoric acid still more so. In the formation of salts it is supposed that one or more atoms of the hydrogen of the acid are substituted by one or more atoms of a metal, but when the salt

is formed by the action of an acid on a base which has more than one hydroxyl (OH) group, that is, in the case of polyacid bases, such as $Bi(OH)_3$, $Pb(OH)_2$, $Zn(OH)_2$, &c., in contradistinction to polybasic acids, various types of salts may be formed, namely, *neutral salts*, in which all the OH groups of the polyacid bases are replaced by acid residues, or *basic salts*, in which only a part of the (OH) hydroxyl groups are replaced as may be seen from the constitution of the following salts :

$Bi\{OH, OH, NO_3$	$Bi\{OH, NO_3, NO_3$	$Bi\{NO_3, NO_3, NO_3$	$Pb\{OH, NO_3$	$Zn\{OH, Cl$
Dibasic bismuth nitrate	Monobasic bismuth nitrate	Neutral bismuth nitrate	Basic lead nitrate	Basic zinc chloride

FIRST GROUP OF THE METALS

ALKALI METALS

	(*a*) Atomic weight	(*b*) Specific gravity	(*c*) Atomic volume, c = a : b	(*d*) Melting-point	(*e*) Boiling-point
Lithium . Li	7·00	0·59	11·9	180°	—
Sodium . Na	23·00	0·97	23·7	96°	742°
Potassium . K	39·10	0·87	45·0	62·5°	667°
Rubidium . Rb	85·45	1·52	56·1	38·5°	—
Caesium . Cs	132·81	1·88	70·7	26·5°	270°

As the atomic weight of these metals rises, so does the specific gravity, and even more so the atomic volume, whilst, on the other hand, the melting- and boiling-points become lower.

As in the case of the first group of non-metals—that of the halogens—the acid character was most pronounced, so also the first group of the metals has a more pronounced alkaline (basic) character than the others.

These metals oxidise in the air, and decompose water already in the cold forming hydroxides [1] soluble in water and of strongly alkaline reaction, which are not decomposed even on heating to redness. They have an alkaline reaction which is the greater the higher their atomic volume ; lithium has the least markedly basic reaction. All the metals of this group are in general monovalent.

These elements can be divided, according to their chemical resemblances, into two sub-groups. Caesium, rubidium, and potassium have a more alkaline character and form comparatively insoluble tartrates and chloroplatinates, which are used to separate them from the other sub-group, forming tartrates and chloroplatinates, which are more soluble. Also the carbonates and bicarbonates of Cs, Rb, and K are deliquescent, whilst those of sodium and lithium are not deliquescent in the air, and lithium carbonate is not very soluble in water.

[1] The heat of formation of the hydroxides dissolved in water, starting from the elements, is as follows : Li.OH aq. = 491 Kj. (117,400 cals.) ; NaOH aq. = 467·8 Kj. (111,800 cals.) ; KOH aq. = 487 Kj. ; whilst the heat of formation of water from its elements is 286 Kj. Therefore, by the thermochemical law of the tendency to the formation of more stable compounds with the maximum evolution of heat, the reason why the alkaline oxides decompose water forming the more stable alkali hydroxides is explained, and thus in general all metals which form hydroxides having a heat of formation greater than 286 Kj. are able to decompose water either on heating or in the cold, and do so the more energetically the greater is the heat of formation of the respective hydroxides.

POTASSIUM: K, 39.10

Whilst various potassium salts, such as the carbonate and nitrate, have been known since the most remote antiquity and have been studied for some time, free potassium was obtained for the first time by Davy in 1807 by decomposing potassium hydroxide, which was then believed to be a simple substance, by means of a powerful electric current. Potassium in combination is abundant and widely distributed in nature. It is found in all soils, because it is a constituent of many rocks, especially of felspar, a double silicate of aluminium and potassium, which by weathering, together with the other constituents of granitic rocks, is continuously forming constituents of new arable soil. It is thus found as a normal constituent of all vegetables in the form of organic salts, and remains accumulated in the ashes of plants in the form of carbonate.

It is found as chloride and sulphate in sea water,[1] 1 cu. metre of which contains 0·6 grm. of KCl, being carried into the sea by the rivers which annually transport about 50,000,000 tons of potassium salts.

At one time potassium salts were obtained from wood ashes which were specially produced by the destruction of enormous Russian and American forests, but since Frank, in 1860, showed the extraordinary importance of the immense saline deposits at Stassfurt, near Magdeburg, by his memorable work, potassium salts have been prepared from the salts in these deposits and the numerous other deposits which are found in North Germany.

The origin of the saline deposits of Stassfurt is explained in the following manner. Rain water dissolves potassium salts from the soil and the rocks, and those which are not absorbed by plants are carried out to sea. By the natural evaporation of the water of bygone seas, large deposits of salts were formed arranged in the order of their solubility.

The lowest strata of these deposits consist of sodium chloride (rock salt) and in some localities their thickness is more than 1000 metres. Above the sodium chloride strata of carnallite, a double chloride of magnesium and potassium, $MgCl_2 + KCl + 6H_2O$, are formed of a thickness of 20 to 40 metres. After the complete evaporation of these seas, the carnallite would certainly be easily redissolved by rain water excepting where, through the action of the wind or through foldings of the earth's crust, these strata were covered by other strata of earth or rocks impermeable to water, which preserved them until to-day. Where, however, water was able to penetrate to the carnallite, this dissolved the magnesium chloride by preference and left the important deposits of *sylvine*, which consist of almost pure KCl and are very valuable. The water saturated with $MgCl_2$, on filtering through strata of gypsum, became saturated with calcium sulphate and then in contact with other salts of magnesium and potassium, such as carnallite, new salts were formed which collected as large deposits of *kainite*, $MgSO_4.K_2SO_4.MgCl_2 + 6H_2O$.

The importance and the great development of the industry of the potassium salts in Germany may be seen from the following Tables which show the annual production :

In 1865 about	100,000	tons of various potassium salts were obtained
1875	500,000	,, ,, ,, ,, ,,
1885	1,000,000	,, ,, ,, ,, ,,
1895	1,600,000	,, ,, ,, ,, ,,
1901	3,500,000	,, ,, ,, ,, ,,
1904	4,085,000	,, ,, ,, ,, ,,
1906	5,650,000	,, ,, ,, ,, ,,
1908	6,100,000	,, ,, ,, ,, ,,
1909	6,900,000	,, ,, ,, ,, ,,

The salts extracted in 1906 were valued at about £4,400,000 ; the salts extracted in 1904 consisted of 1,906,000 tons of kainite and 2,179,000 tons of other potassium salts, that is, carnallite, schönite, and sylvine. 12 to 14 per cent. of the potassium salts are used industrially, and the rest for agricultural purposes, of which more than two-fifths are

[1] In Sardinian salt, Pavesi found 7·85 per cent. of potassium sulphate and 6·72 per cent. of potassium chloride ; in that from the saline spring of Volterra, Funaro found 12·5 per cent. of potassium sulphate and 0·55 per cent. of potassium chloride.

exported. In 1909 148,500 tons were exported to the United States, 13,330 tons to Austria, 8900 tons to Russia, 17,700 tons to France, 4130 tons to Italy, &c.[1]

For several years a syndicate of the potassium salt works has been formed, dissolved and reformed several times, and undertakes the sale of the products of Leopoldshall and Stassfurt. In 1910 the syndicate was reconstituted and comprises 65 works which control almost the entire production, only 3 works being excluded. The convention will last until 1915, but may be prolonged to 1925.

It is interesting to note how this enormous consumption of potassium salts for agricultural purposes is distributed among the various countries, and in order to make the comparison clear, we will express the amounts of various salts in kilos of potassium oxide, K_2O, per 1000 inhabitants and per square kilometre of arable land. We then obtain the following results for 1895 and 1901 :

Countries	Consumption in kilos of K_2O per 1000 inhabitants		Consumption of potassium salts—K_2O—per sq. km. of arable land	
	1895	1901	1895	1901
Holland	515·6	1900·6	125·3	461·9
Germany	1151·2	2638·5	171·0	391·9
Belgium	443·4	970·4	136·0	297·7
Sweden	1019·7	1874·6	145·0	266·6
Scotland	102·3	889·5	14·0	254·6
Switzerland	271·0	550·0	39·2	79·5
England	85·0	135·6	7·0	61·5
United States of America .	465·7	1045·8	24·1	54·0
Austria	41·0	130·0	5·6	17·8
France	130·7	163·2	13·4	16·8
Spain	20·0	139·4	1·3	8·5
Italy	28·0	41·7	4·3	6·4
Russia	4·5	20·1	0·2	1·0

If, on the one hand, it is disquieting to find Italy almost at the bottom of this thermometer of agricultural progress, it will, on the other hand, serve as a stimulus to more rapid progress in order to equal that of the other nations. It is necessary, however, to say that during the last few years a very considerable increase in the consumption of potassium salts has also occurred in Italy (*see below*, Chloride and Sulphate). In 1903 1000 tons of kainite were imported, and about 2000 tons in 1908 at £2 8*s*. per ton delivered at Genoa.

Free metallic potassium is prepared by heating a mixture of 30 parts of potassium carbonate with 13 parts of wood charcoal and 5 parts of gypsum : $K_2CO_3 + 2C = 3CO + K_2$.

[1] The potassium salts were used in Germany and other countries in 1908 for the following purposes :

		For potassium carbonate and hydroxide	For conversion saltpetre	For potassium chromate	For potassium chlorate	For alum	For manures	For various purposes
		Tons	Tons	Tons	Tons	Tons	Tons	Tons
Potassium chloride of 80 per cent. strength .	in Germany .	78,425	20,158	678	517	—	100	5402
	in other countries .	4,440	20,736	3,118	17,582	480	132,136	4750
Potassium sulphate of 90 per cent. strength .	in Germany .	—	—	—	—	494	92	2235
	in other countries .	—	—	—	—	2,183	49,608	140

The industrial methods are almost the same as those employed in the manufacture of metallic sodium, and will be described when speaking of that metal. At one time, tartar, that is, potassium bitartrate, which already contains sufficient quantities of lime, was used, being heated to a white heat in iron retorts, and the vapours of potassium were condensed in vessels containing mineral oils (petroleum) which protected the potassium from oxidation or from catching fire in the air. Potassium carboxide $(KOC)_6$ was generally obtained, together with the potassium, and is explosive ; it also obstructed the pipes and diminished the yield. According to C. Winkler (1890) the production of this product is avoided by directly reducing fused potassium hydroxide with red-hot magnesium :

$$KOH + Mg = MgO + H + K.$$

To-day, however, potassium is mainly prepared from potassium chloride by electrolytic means, by an industrial process analogous to that which we will describe in the case of sodium. It appears, however (Ger. Pat. 140,737 of 1902), that pure potassium may be obtained at a low price by distilling a mixture of potassium fluoride or fluosilicate with aluminium at a comparatively low temperature.

Potassium is purified by redistillation and by squeezing it through cloths.

Potassium is a metal which, when molten out of contact with the air, has a silvery appearance and may crystallise in octahedra on solidifying. At the ordinary temperature it is soft and is easily cut with a knife. It has a specific gravity of 0·87, melts at 62° and evaporates at about 720°, forming greenish vapours. It combines actively with oxygen, forming the oxide, which forms a hydroxide with water, and for this reason it readily decomposes many oxygen compounds. It is almost unaffected by perfectly dry oxygen, but a trace of water suffices to cause energetic reaction ; in this case the water exercises a catalytic influence.

When a piece of potassium is placed in water the liquid is immediately decomposed with evolution of hydrogen, and so much heat is also formed that the potassium melts on the surface of the water and catches fire, together with the hydrogen.

It readily combines with the halogens, and metallic potassium on dissociating into ions evolves 259 Kj., which fact explains why it is possible to abstract chlorine from boron chloride and silicon chloride in the preparation of free boron and silicon. Potassium salts in general give a pale violet-blue colour to the Bunsen flame.

There is no large demand for metallic potassium, and it is to-day placed on the market in small balls under petroleum at a price of £2 16*s.* per kilo, whilst in 1865 it cost £10.

POTASSIUM HYDRIDE : KH. This compound is one of the few hydrogen compounds of metals. It is a solid of silvery appearance and is obtained by passing a current of hydrogen over molten potassium at 300° to 400°. It is decomposed by water with evolution of hydrogen, catches fire spontaneously in the air, and when heated *in vacuo* first melts and then gradually dissociates above 200° as the temperature is raised.

If heated *in vacuo* in a closed vessel so that the evolution of hydrogen is hindered, this exercises a pressure which reaches 45 mm. at 330°, and prevents further dissociation. If the pressure is increased the reverse reaction occurs, that is, the free hydrogen acts on the potassium which has already been liberated and KH is again formed. Exothermic compounds generally behave in this manner, whilst in the case of endothermic compounds the products of decomposition or dissociation do not recombine under pressure.

POTASSIUM OXIDE : K_2O. This compound has only recently been prepared by heating a mixture of potassium nitrate and potassium in the proper proportions :

$$KNO_3 + 5K = 3K_2O + N.$$

It forms a grey crystalline mass which becomes yellowish in the air through formation of **Potassium Peroxide**, K_2O_2. It reacts energetically with water, with which it catches fire.

POTASSIUM HYDROXIDE: KOH (CAUSTIC POTASH)

This compound is prepared on the large scale by adding calcium hydroxide (milk of lime) to a boiling dilute solution of potassium carbonate, K_2CO_3, of 12° to 13° Bé.; $K_2CO_3 + Ca(OH)_2 = CO_3Ca + 2KOH$. The reaction is, however, reversible, and therefore in order to obtain a good yield the concentration and temperature must be maintained between certain limits. The solution of KOH is decanted from the insoluble calcium carbonate and concentrated in iron pans, rejecting the salts which are first deposited and which mainly consist of potassium carbonate and sulphate.

The electrolytic preparation of this compound from potassium chloride in an analogous manner to the process which we will describe for sodium hydroxide, has to-day been greatly developed.

In Germany in 1903, 12,000 h.p. were employed for the production of 28,000 tons of electrolytic potassium hydroxide, and 48,000 tons of chloride of lime; 5000 tons of electrolytic sodium hydroxide and 12,000 tons of the corresponding chloride of lime were also produced.

PROPERTIES. Pure potassium hydroxide is a white crystalline solid which melts fairly easily at a dull red heat and evaporates unaltered at much higher temperatures. It absorbs water very energetically and is deliquescent in the air. It very readily absorbs carbon dioxide from the air forming potassium carbonate. In aqueous solution it has a strongly alkaline reaction, and readily saponifies fats. It attacks the skin and many organic substances energetically, dissolving them. From a concentrated solution, a solid hydrate $KOH.2H_2O$ separates in the cold.

Potassium hydroxide readily reacts with the halogens:

$$6KOH + 6I = 5KI + IO_3K + 3H_2O.$$

On passing chlorine into a cold solution of KOH, potassium hypochlorite, KClO, is formed; if the solution is hot, potassium chlorate, $KClO_3$, is formed.

Potassium hydroxide is easily dissociated in aqueous solution into the ions $K^{\cdot}$ and OH'. On pouring this solution into that of a neutral salt, such as $ZnSO_4$, which is dissociated into $Zn^{\cdot\cdot}$ and SO_4'', a zinc cation unites with the OH' anions and separates as the hydroxide $Zn(OH)_2$, because this is only slightly soluble. This reaction is general for all soluble salts of those metals which form only slightly soluble hydroxides. These general reactions of KOH are due to the OH' anion, and not to the cation $K^{\cdot}$, because on employing NaOH or RbOH, &c., the identical reactions due to the OH' anion are always obtained, and are common to all the hydroxides of the various alkali metals.

On evaporating solutions of KOH a solid mass is obtained, which melts easily and may then be formed into solid sticks if the fused mass is poured into cylinders of well-polished iron or into silver moulds (*see* NaOH).

APPLICATIONS AND PRICES. Potassium hydroxide is used in large quantities for the manufacture of soft-soap and of the more refined soaps, which cannot be obtained with sodium hydroxide alone. It is also used in the preparation of oxalic acid and for preparing caustic lyes, although to-day it is replaced wherever possible by sodium hydroxide, which is cheaper.

Vessels in which KOH is kept must be closed hermetically so that it may not absorb H_2O and CO_2.

The fused commercial product containing 80 per cent. of hydroxide costs

about £26 to £28 per ton, and that containing 90 per cent. of hydroxide £30 to £32. The pure product in sticks costs about £5 4*s*. per 100 kilos, and when purified with alcohol as much as £10. Solutions containing 50 per cent. of KOH are sold at £20 per ton.

In 1908 Germany exported 22,245 tons of potassium hydroxide valued at £389,280, and in 1909 27,477 tons. In 1907 Italy imported 758·3 tons and in 1908 795·9 tons valued at £63,680.

POTASSIUM CHLORIDE : KCl

This compound is found abundantly in the Stassfurt deposits as *sylvine*, or mixed with magnesium chloride as *carnallite*, $MgCl_2.KCl + 6H_2O$, which is ordinarily treated for the extraction of the chloride at a comparatively cheap cost, because it is more abundant. By treating it with a little hot water or with mother liquors already saturated with $MgCl_2$, it is possible to separate the KCl, because the $MgCl_2$ is more soluble. Also by melting carnallite at 176° 75 per cent. of the potassium chloride may be obtained almost pure in the solid form on cooling.

The potassium chloride is purified by recrystallisation from water and forms glassy, cubic crystals of sp. gr. 1·98 ; it melts at 800° and evaporates on prolonged heating to redness. At 0° 100 parts of water dissolve 28 parts of KCl ; at 100° they dissolve 57 parts. It is almost insoluble in alcohol.

KCl is used for the preparation of many other salts, and the crude material is used in agriculture as a fertiliser. In 1905 Italy produced 5000 tons of crude chloride ; in 1904 it imported 3460 tons of the value of £32,900, in 1906 4035·6 tons, and in 1908 5811·8 tons of the value of £56,960.

In 1905 Germany exported 157,100 tons of potassium salts, especially of the chloride, of the value of £1,106,000, and in 1909 the exports increased to 220,000 tons, the total production being about 300,000 tons.

Considerable quantities of potassium chloride are used for the preparation of potassium nitrate from sodium nitrate. The commercial product containing 80 to 90 per cent. of KCl costs about £10 per ton at Genoa. When chemically pure it costs £28 per ton.

POTASSIUM BROMIDE : KBr. This compound is obtained by treating a hot solution of potassium hydroxide with bromine : $6KOH + 3Br_2 = 5BrK + 3H_2O + BrO_3K$. The solution is evaporated to dryness, mixed with carbon, and then heated to redness ; all the bromate is thus transformed into potassium bromide : $BrO_3K + 3C = 3CO + BrK$. It is more economically prepared from a solution of iron bromide, Fe_3Br_8, by heating it with a solution of potassium carbonate. The precipitated iron, consisting of carbonate, oxide, &c., is separated by a filter press, and the solution is then concentrated. The solution is purified by recrystallisation from water.

This bromide is a white salt of sp. gr. 2·4, easily soluble in water, but less soluble in alcohol, and melts at 740° ; it has a very salty taste and is used in photography, and in medicine as a soporific. It costs 4*s*. per kilo retail, or £8 per 100 kilos in large quantities.

In 1905 Germany exported 634·1 tons of KBr and other bromides of the value of £69,760. In 1905 Italy imported 19·8 tons of the bromide and in 1909 32·7 tons of the value of £2616.

POTASSIUM IODIDE: KI. This compound is obtained in the same manner as the bromide, but the potassium iodate which is produced may be reduced with hydrogen peroxide : $IO_3K + 3H_2O_2 = IK + 3H_2O + 3O_2$.

It is prepared pharmaceutically by first preparing an iron iodate, $FeI_2.Fe_2I_6$, by the interaction of iron on iodine, and then decomposing this with a hot solution of potassium carbonate : $Fe_3I_8 + 4K_2CO_3 = 8KI + 4CO_2 + Fe_3O_4$.

Considerable quantities are to-day prepared from the cuprous iodide which is obtained in the treatment of Chili nitrate, the copper being separated with H_2S.

It forms white cubic crystals of sp. gr. 3 ; it melts at 720° and then easily evaporates. 10 parts of KI dissolve in 7 parts of water or 25 parts of alcohol. Various metallic

iodides which are insoluble in water dissolve in aqueous solutions of KI, forming double salts, such as $HgI_2.2KI$.

Solutions of KI also dissolve considerable quantities of iodine, as an I_3 ion (from KI_3) is formed in solution, which is only partially dissociated into I_2 and I.

KI is much used in medicine because it accelerates the metabolism of the blood and is of use after mercurial treatment. It is also employed in photography. It costs about £1 per kilo.

In 1905 Germany alone exported 170·4 tons of KI and other iodine preparations, valued at £263,960. In 1904 Italy imported 37·9 tons of bromides and iodides at an average price of 5*s.* 7*d.* per kilo, in 1906 it imported 53·5 tons of iodides, and in 1908 20·6 tons, valued at £18,128.

POTASSIUM FLUORIDE : KF. This compound is obtained by saturating hydrofluoric acid with potassium carbonate. It is a salt which dissolves in water and attacks glass. It easily forms double salts with other salts of less electropositive metals, and with HF it forms potassium hydrogen fluoride, KF.2HF and also KF.3HF.

With fluosilicic acid, SiF_6H_2, solutions of potassium salts form a gelatinous precipitate of *potassium fluosilicate* SiF_6K_2, which is only very slightly soluble in water.

POTASSIUM HYPOCHLORITE : ClOK. This compound is obtained from KOH and Cl, but if excess of chlorine is present, potassium chlorate is formed, especially on heating :

$$2KOH + Cl_2 = KCl + ClOK + H_2O.$$

It is only known in aqueous solution and was much used for bleaching vegetable fibres under the name of "eau de Javelle"; for this purpose, sodium hypochlorite is used by preference to-day (*see below*). On evaporating this solution to dryness it decomposes :

$$3ClOK = 2KCl + ClO_3K.$$

POTASSIUM CHLORATE : $KClO_3$

Whilst the hypochlorite is formed with a limited quantity of chlorine, the chlorate is obtained by passing an excess of chlorine into a solution of potassium hydroxide, even in the cold, but preferably at 90° :

$$6KOH + 3Cl_2 = 5KCl + 3H_2O + KClO_3;$$

it is also obtained by heating the solution of the hypochlorite :

$$3ClOK = KClO_3 + 2KCl.$$

Until a few years ago the chlorate was prepared on the large scale by the old process of Liebig (1842) by passing chlorine into milk of lime, contained in cast-iron cylinders provided with stirrers, at 40°. A solution of calcium chlorate was thus obtained and was decomposed after filtration with the calculated quantity of potassium chloride. The liquid was partially evaporated, and crystals of potassium chlorate, which is not very soluble, were then obtained and were purified by recrystallisation from water :

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2ClO_3K.$$

In this process some chlorine is lost in the form of $CaCl_2$, which is of no value. To-day it has been replaced by the electrolytic method, since Oettel has shown that on electrolysing concentrated alkaline solutions of potassium chloride in the heat, potassium chlorate is readily obtained. The process of Galle and Montlaur, who used diaphragms, was first used, but to-day diaphragms are largely dispensed with.

The electrolysis is conducted in lead-lined wooden vessels of a capacity of 5 cu. metres, which are insulated below by a vessel of oil. The anodes are formed of iridio-platinum plates containing 10 per cent. of iridium, 1 mm. thick. The cathodes are formed of an alloy of iron and nickel coated with asbestos in order to discharge hydrogen more readily. On working with a current of 465 amps. at an E.M.F. of 5 volts, the temperature of the electrolyte is raised to 45°, and then the transformation of the hypochlorite, which

is first formed, into potassium chlorate occurs. This crystallises and separates, whilst the bath is gradually replenished with more potassium chloride. One horse-power is consumed per 24 hours in order to obtain 1 kilo of potassium chlorate.

C. Kellner electrolyses a concentrated solution of potassium chloride, saturated in the cold, without diaphragms with the addition of about 3 per cent. of potassium hydroxide, which is not all dissolved, and suspends a little calcium hydroxide in the solution which absorbs the small amount of chlorine which remains free at the anode.

The electrolytic manufacture of chlorates was started in 1891 in Switzerland. It then spread to England, France, and Germany in 1894, but the industry can only be profitably developed in countries where large water powers are available at a cheap rate. These works are to-day found specially in Switzerland, France, Finland, Sweden, Norway and Italy.

In the Italian works at Legnano the electrolysis is carried out in large stoneware vessels of about 1000 litres capacity with a 25 per cent. solution of potassium chloride to which 1 per cent. of pure potassium dichromate is added, and which has been freed from sulphates or sulphuric acid by means of $BaCl_2$; a current of 3·5 to 4 volts is used and in about 2 hours the temperature rises to 65° to 70°, when the current is suddenly cut off, so that the chlorate may separate on cooling. The mother liquors are strengthened by more potassium chloride and a little dichromate, and are then pumped into fresh electrolytic baths. The chlorate is purified by two successive recrystallisations from hot water, the mother liquors being separated by decantation, and then finally by a hydro-extractor. The resulting product is very white and of a purity of 98 to 99 per cent. With 700 kw.-hours, 100 kilos of potassium chlorate are produced from 61 kilos of chloride. Special electrodes are used which are more resistant and economical than those of Acheson graphite. In the works at Bussi sodium chlorate is formed as a secondary product in the manufacture of electrolytic sodium hydroxide.

Potassium chlorate crystallises in monoclinic tables which are only slightly soluble in cold water (5 per cent.). It produces a cooling and slightly sharp effect on the palate. It melts at 300°, and on further raising the temperature immediately evolves oxygen, forming KCl and potassium perchlorate, $KClO_4$, which forms O and KCl at still higher temperatures.

With HCl, $KClO_3$ evolves chlorine:

$$KClO_3 + 6HCl = KCl + 3Cl_2 + 3H_2O.$$

It is an oxidising agent and when mixed with 3 parts of sulphur and 1 part of well-dried wood charcoal, it forms a black gunpowder. By replacing the carbon by potassium ferrocyanide a white gunpowder is obtained. On cautiously mixing potassium chlorate with antimony sulphide with a feather a mixture is obtained which easily explodes by friction or shock.

During the transformation of the chlorate into chloride and oxygen—which occurs by heating up to the melting-point—33·4 Kj. (7960 cals.) are evolved.

Potassium chlorate is employed in match factories, especially for Swedish matches, and also in firework factories, for percussion caps and in certain explosive powders. It is also used in dyeing, for oxidising various substances which produce aniline black, and this oxidising action, which does not occur at ordinary temperatures, is accelerated by the addition of minimal quantities of catalytic substances, such as copper and vanadium salts. To-day, however, potassium chlorate has been partially replaced by sodium chlorate which costs less and produces the same effects as the potassium salt.

Crystallised potassium chlorate costs £34 per ton, whilst before the electrolytic process was introduced it cost £60. The chemically pure product costs £40 per ton.

Whilst in 1887 the world's production of potassium chlorate was 6750 tons, of which 5500 were produced in England, the position is completely changed to-day, and the "Société d'Electrochimie" alone produces 1800 tons at St. Michel and at Vallorbe in Switzerland, by the use of 3000 h.p. at £8 per h.p.-year.

In Europe 7 works were in operation in 1900, using 28,000 h.p. altogether, and with a total production of 9000 tons of chlorate.

The world's production of chlorate in 1900 was estimated at 17,500 tons, of which two-thirds was prepared electrolytically. In Italy there is a sodium chlorate works at Bussi belonging to the "Società elettrochimica" of Rome, which produced 217 tons in 1908 of the value of £7024, and a potassium chlorate works at Legnano ("Società elettrochimica," of Dr. Rossi), which was in full work in 1909 and is capable of turning out 350 tons per annum. Italy imported 195 tons of chlorates and perchlorates of sodium and potassium in 1906, about 652 tons in 1907, and about 365 tons in 1908, of the value of £11,658. The protective tariff in Italy is £8 per ton, and moreover all the European works are members of a syndicate.

In 1905 Germany imported 2054·2 tons of chlorate of the value of £54,400, and exported 1069·9 tons of the value of £29,400, that is, at £27 10*s.* per ton. In 1909 it imported 1300 tons and exported 1200 tons.

POTASSIUM PERCHLORATE: $KClO_4$, is obtained mixed with KCl when potassium chlorate is heated till fused, after the first phase of the evolution of oxygen: $2KClO_3 = KClO_4 + KCl + O_2$; the perchlorate may then be separated from the chloride because the latter is much more soluble in water. The electrolytic preparation is the same as that of sodium perchlorate. It starts from sodium chloride, by first preparing the chlorate, and this is again subjected to electrolysis in a concentrated cold solution, cooling the mass with water in serpentine coils. The dissolved sodium perchlorate is then treated with a concentrated solution of potassium chloride, when crystalline potassium perchlorate separates, being less soluble than sodium perchlorate: $NaClO_4 + KCl = KClO_4 + NaCl$. Apparently the presence of a little dichromate increases the yield.

Its oxygen is not as active as that of the chlorate and its oxidising power is only exerted in the undissolved condition at high temperatures.

It is used industrially for fireworks, instead of a portion of the chlorate, because it is more stable, and is also used in the explosive industry on account of the large amount of oxygen which it contains.

The crude perchlorate costs £20 per ton; when refined it costs £48 per ton.

POTASSIUM BROMATE and **IODATE** are similar to the chlorate.

A compound, KHI_2O_6, **Acid Potassium Iodate**, and also **Potassium Periodate**, KIO_4, are known; so are the potassium salts corresponding to the following hydroxides: $I(OH)_7$, $IO(OH)_5$, &c.

POTASSIUM NITRATE: KNO_3 (NITRE, SALTPETRE)

This compound is one of those salts which have been known and used since ancient times. It is found abundantly in the East Indies, in Bengal and Bombay, and in the caves of Ceylon, which were once inhabited by animals and by men, but are to-day only tenanted by bats; it is found as an efflorescence in many soils and especially in hot countries, such as Peru, Bolivia, South Africa, and Egypt. It is obtained by making mounds of earth, potassium salts such as plant ashes and decomposing nitrogenous organic matter such as stable manure, after which the mound is moistened from time to time; the whole is then abandoned to the action of nitrifying bacteria for one or more years. It first forms calcium nitrate with the lime which is always present in the soil, which then forms potassium nitrate in contact with the potassium carbonate; this is then finally extracted with water:

$$(NO_3)_2Ca + CO_3K_2 = 2NO_3K + CO_3Ca.$$

The saltpetre which abounds in the soil of British India and especially in that of Ceylon has been produced in this way. Considerable quantities of this saltpetre have even been extracted to supply Europe, for the manufacture of explosives, for which purpose it is preferred, owing to the absence of perchlorates. After 1855 (the Crimean War) potassium nitrate for gunpowder became a product which was largely consumed, and the so-called conversion

nitrate was then prepared in Germany by evaporating a saturated solution of sodium nitrate (Chili saltpetre) with potassium chloride from Stassfurt, in molecular proportions. When the solution acquires a density of 1·5 almost all the excess of sodium chloride, which is less soluble on heating, separates, and when the solution has cleared, helped by the addition of a little glue, and after repeated decantation of the clear hot liquid, it is allowed to crystallise in vats with stirrers in order to obtain the potassium nitrate as a crystalline powder. The separation on cooling is copious and almost complete, because potassium nitrate is very slightly soluble in cold water, though very soluble in hot (*see* Fig. 174), whilst the remaining sodium chloride remains in solution as its solubility in the cold and on heating is almost equal :

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

The crystalline mass is then separated from the mother liquors by decantation and passed into a hydro-extractor, the cage of which is made of fine metallic netting, and is there washed with a gentle spray of cold water whilst the hydro-extractor is in motion.

The product is then completely dried in copper pans in a current of hot air. If the nitrate is to be used for the manufacture of black gunpowder, it should not contain more than 0·0003 per cent. of chlorides, which are deliquescent.

The conversion of sodium into potassium nitrate is easily understood on considering the solubility of these salts. Four different ions are present in solution, $K^{\cdot}$, $Na^{\cdot}$, Cl', NO_3', and on concentration those ions which form the less soluble salt, namely, NaCl, separate during cooling.

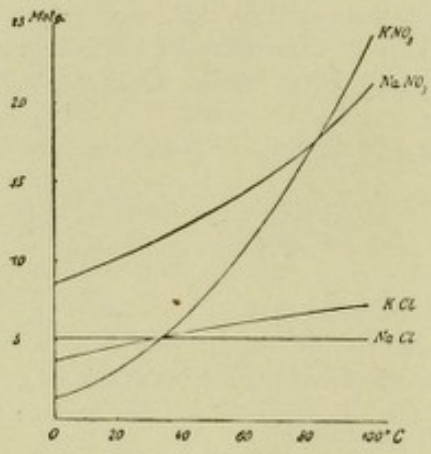


FIG. 174.

The diagram of solubilities (Fig. 174) shows the solubility of these four salts at various temperatures very satisfactorily, and is expressed in molecular weights. We thus see that at 0° 5 mols. (that is, 290 grms.) of NaCl, 1·2 mols. of KNO_3, 3·5 mols. of KCl and 9 mols. of $NaNO_3$ dissolve in the same quantity of water ; at 100° the ratio of the solubilities is completely changed. The solubility of NaCl is maintained at almost the same figure, that is, the curve representing NaCl in the diagram is almost horizontal ; on the other hand, 15 mols. of potassium nitrate are dissolved at 100°, that is, about 2500 grms., about 21 mols. of sodium nitrate and about 7 mols. of KCl, and the *solubility curves* vary greatly. Thus, on cooling the saturated solution at 100°, the KNO_3, which is very soluble on heating and much less soluble in the cold, will separate, whilst the NaCl which changes its solubility very little with change of temperature will remain in solution.

To a *saturated* aqueous solution of a given salt, a certain quantity of another salt, which has no ions corresponding to those of the first salt, may be added. On the other hand, a second salt, one of the ions of which is the same as one of those of the first salt, if added in minimal quantity immediately causes supersaturation and ready separation of the first salt. Thus sodium chloride or magnesium sulphate may be added to a saturated solution of potassium perchlorate without separation of the perchlorate, but if a minimal quantity of potassium chloride, which has the same $K^{\cdot}$ cation as the perchlorate, or of sodium perchlorate, which has the same ClO_4' anion, is added, potassium perchlorate separates immediately, being the less soluble salt. In general, therefore, a salt solution may also be saturated by the concentration of one only of the ions of the salt itself, thus causing the separation of ions of the less soluble salt. This rule may be employed for the separation of various salts from solutions of their mixtures ; for example, to eliminate gypsum from strong solutions of sodium chloride, as this accumulates in such quantities in the vacuum pans that it produces thick incrustations which render concentration more difficult (*see below*).

KNO_3 crystallises in hexagonal rhombic prisms without water of crystallisation. 100 parts of water at 100° dissolve 247 parts of the nitrate and only 13 parts at 0°.

It has a sharp taste, melts at 339°, and decomposes at a higher temperature into potassium nitrite, KNO_2, and oxygen. When heated with carbon to redness it deflagrates and forms potassium carbonate, with evolution of nitrogen and CO_2:

$$4KNO_3 + 5C = 3CO_2 + 2N_2 + 2K_2CO_3.$$

APPLICATIONS. Potassium nitrate is used in the manufacture of *common black gunpowder*, which contains 75 per cent. of potassium nitrate, 12 per cent. of sulphur, and 13 per cent. of wood charcoal. On ignition there is complete interaction, mainly according to the following equation:

$$2KNO_3 + S + 2C = K_2SO_4 + N_2 + 2CO.$$

The proportions of the constituents vary, however, somewhat in the various types of powder, for cannons, fuses, mines, &c., and, as we see, all the oxygen for the combustion of the carbon and the sulphur is furnished by the nitrate.

The power of gunpowder is due to the abundant formation of various gases, especially N, CO, and CO_2, which occupy a volume 1000 times larger than the solid powder. The potassium nitrate is to-day largely replaced by ammonium nitrate which burns without leaving any residue. Potassium nitrate is also used for the preservation of meat (pickled beef, &c.), and as a rapidly acting manure.

Refined potassium nitrate costs about £22 per ton, and when chemically pure up to £34.

1200 tons were produced in Italy in 1904, 2000 tons in 1907, and 1900 tons in 1908, of the value of £41,800; 375·8 tons valued at £7800 were imported in 1904; in 1906 the imports were 228·4 tons, in 1907 580 tons, and in 1908 381·5 tons.

Germany exported 10,465 tons in 1905 valued at £225,000, and 12,474·5 tons in 1909, and imported 2853 tons in the same year.

POTASSIUM NITRITE: KNO_2

This compound is obtained in the same manner as sodium nitrite, for instance, by reducing 1 part of potassium nitrate with 2 parts of lead (or with Fe or Cu); lead oxide is formed which is insoluble in water, whilst the nitrite dissolves and may be then separated and crystallised. It is also prepared industrially to-day from a mixture of CaO and a concentrated solution of potassium nitrate, into which soluble sulphur dioxide, free from air, is passed in the heat: $KNO_3 + CaO + SO_2 = SO_4Ca + KNO_2$. The yield is excellent and the insoluble calcium sulphate is easily separated. A good yield is also obtained by melting together KNO_3 and KOH and reducing at about 350° with a sulphite.

It forms white crystals which melt easily and are deliquescent in the air, because they are very soluble in water. On the other hand they are insoluble in alcohol. It is used in the preparation of organic azo-compounds and costs £76 per ton. When chemically pure in sticks, it costs 4*s.* per kilo.

POTASSIUM SULPHATE: K_2SO_4

This compound is obtained from KCl with sulphuric acid and from solutions of *kainite* ($K_2SO_4.SO_4Mg + MgCl_2 + 6H_2O$) at Stassfurt. On concentrating solutions of this substance, magnesium and potassium sulphates separate in the form of schönite, $K_2SO_4.MgSO_4.6H_2O$, which forms potassium sulphate and $MgCl_2$ on concentration with excess of potassium chloride; kieserite, $MgSO_4.H_2O$, acts in the same way:

$$K_2SO_4.MgSO_4 + 2KCl = 2K_2SO_4 + MgCl$$

Potassium sulphate, being less soluble than magnesium chloride, is easily separated on concentrating the solution.

It forms small rhombic prisms without water of crystallisation and has a

slightly bitter taste ; at 15° it is dissolved by water to the extent of 19 per cent. ; it melts at 1070°.

It is used as a potassium manure at £11 4*s*. per ton, and in alum and glass works, and also in works producing potassium carbonate by the Leblanc process. When very pure it costs up to £30 per ton. In Germany the use, as a fertiliser, of the calcined sulphate of magnesium and potassium is preferred, being more economical.

In 1902 Italy imported 1566 tons of potassium sulphate, 1663 tons in 1904, 3866 tons in 1907, and 4910 tons in 1908 of the value of £56,736. In 1905 Germany exported 6745·5 tons worth about £440,000, and produced 47,994 tons, not including other sulphates, such as kainite, &c. ; in 1909 Germany exported 63,107 tons of potassium sulphate.

POTASSIUM HYDROGEN SULPHATE, POTASSIUM DISULPHATE : $KHSO_4$. This compound is obtained from the neutral sulphate with H_2SO_4 or directly from KCl and H_2SO_4 at a moderate heat. It forms rhombic tablets very soluble in water. It melts at 200°, with loss of water, and is then transformed into potassium pyrosulphate, $K_2S_2O_7$, which forms SO_3 and K_2SO_4 at 600°.

It shows an acid reaction because its anion, HSO_4', is partially decomposed in aqueous solution into $H^{\cdot}$ and SO_4''.

POTASSIUM PERSULPHATE : $K_2S_2O_8$. This is obtained in crystals at the positive pole (anode) in the electrolysis of a concentrated solution of $KHSO_4$, the hydrogen being evolved at the cathode : $2KHSO_4 = H_2 + K_2S_2O_8$ (*see* p. 286).

This aqueous solution has a very saline taste. It is an oxidising agent and the solid salt evolves oxygen even at 100°, forming potassium pyrosulphate.

POTASSIUM SULPHITE and **DISULPHITE : K_2SO_3** and **$KHSO_3$**, are obtained by passing SO_2 through a hot solution of K_2CO_3, until no more CO_2 is evolved (*see below*, Sodium Sulphite). On heating potassium disulphite a molecule of water is liberated and **Potassium Pyrosulphite, $K_2S_2O_5$**, is formed.

In 1907 Italy produced 5 tons of potassium sulphite of the value of £22 8*s*. per ton.

POTASSIUM SULPHIDE : K_2S. This compound is prepared by heating a mixture of potassium sulphate and carbon in well-closed crucibles to a moderate temperature :

$$K_2SO_4 + 2C = K_2S + 2CO_2.$$

The fused mass then forms a red, crystalline substance soluble in water. On concentrating the aqueous solution, $K_2S.5H_2O$ crystallises in colourless prisms which are deliquescent in the air. The solution readily absorbs oxygen from the air with formation of **Potassium Thiosulphate :**

$$2K_2S + H_2O + 2O_2 = 2KOH + K_2S_2O_3.$$

Many solutions of metallic salts separate insoluble metallic sulphides on treatment with K_2S. It evolves H_2S with acids. It has a strongly alkaline reaction in aqueous solution because it is not dissociated into the ions $2K^{\cdot}$ and S'', as this latter combines with water forming SH' and OH', so that the OH' ions give the alkaline reaction. In 1905 Germany imported 6573 tons of potassium and sodium sulphides of the value of £46,754. For the Italian imports and production, *see* Sodium Sulphide.

POTASSIUM HYDROSULPHIDE : KSH. This compound is obtained in aqueous solution by passing a current of H_2S into a solution of potassium hydroxide until this is saturated : $KOH + H_2S = H_2O + KSH$. On concentrating the liquid *in vacuo*, the hydrosulphide separates as crystals containing $2H_2O$, forming colourless rhombohedra which lose water at 200° ; at higher temperatures it melts and then forms a red mass on cooling.

It shows an alkaline reaction and forms potassium sulphide with an equimolecular quantity of KOH : $KOH + KSH = H_2O + K_2S$.

POTASSIUM POLYSULPHIDES : K_2S_3, K_2S_4, K_2S_5. These compounds are easily formed by boiling a solution of K_2S, with liberation of sulphur.

LIVER OF SULPHUR, which is employed medicinally, is obtained as a greenish-yellow

mass by melting 2 parts of potassium carbonate with 1 part of sulphur, and consists of a mixture of K_2S_3, K_2SO_4, and $K_2S_2O_3$.

Certain metallic sulphides are soluble in potassium or sodium sulphide because they form sulpho-salts (double sulphides).

POTASSIUM CARBONATE : K_2CO_3 (POTASH)

This compound is found in abundance in wood ashes and ashes of plants, because these organisms contain potassium salts which are transformed into potassium carbonate at the expense of the organically combined carbon during combustion and incineration. The ashes, which contain from 10 to 20 per cent. of potassium salts, are lixiviated two or three times with water, and the clear solution, of 20° Bé., is concentrated in open iron pans and the residue calcined in furnaces ; *crude potash* is thus obtained which is lixiviated and in turn forms pure potash, which, however, contains a little soda, KCl, and K_2SO_4.

To-day very little vegetable ash is used for the production of potash, except in Russia with its immense forests, because it can be obtained more economically by other means.

Another abundant supply of potash has been known since 1840 in the residues of beet-sugar manufacture. The sugar-beets abstract very large quantities of potassium salts from the soil, which accumulate in the molasses from the sugar. These molasses, containing 45 to 50 per cent. of sugar and 3 to 4 per cent. of potash, are diluted with water and fermented in order to obtain alcohol, which is then distilled. The aqueous residue, of 4° Bé., which contains potassium salts, is concentrated in open pans or *in vacuo* up to 40° Bé. ; the residue is then calcined in a furnace, or preferably in retorts, in order to utilise the products of distillation which contain NH_3, trimethylamine, &c. It is still better to pass these hot gases into red-hot furnaces where ammonia and hydrocyanic acid are formed. The former is absorbed by passing the gases through concentrated sulphuric acid ; the hydrocyanic acid is absorbed by solutions of sodium hydroxide. In this way a single works at Hildesheim in Germany produces 3·5 to 4 tons of sodium cyanide daily.

The solid carbonaceous residue from the calcination of the molasses contains 30 to 60 per cent. of K_2CO_3 which is extracted with water and the solution concentrated, gradually separating the following salts which crystallise out : K_2SO_4 and KCl ; when the concentration has reached 55° Bé., sodium carbonate also separates. The residue is dried in a furnace.

This method was first proposed by Dubrunfaut in 1838, and is still much used in France.

In Italy certain sugar refiners carbonise the molasses with hot furnace gases and then export the resulting crude potassium carbonate, almost entirely to Austria.

Considerable quantities of potassium carbonate may be obtained from the water which has been used for washing crude wool, as was already suggested in 1860. The raw Australian wool contains up to 50 per cent. of perspiration, and this substance is largely composed of fatty substances partially combined with potassium in the form of soaps, &c. The fat is first separated from the wool by extracting it with benzine, and on then evaporating the water in which the wool is washed and calcining the residue potassium carbonate remains, and is purified by redissolving it in water. This potassium carbonate contains less sodium salts than that from molasses.

It is also contained in the ashes of certain marine plants which are treated in order to extract iodine and bromine.

Much potassium carbonate is prepared in Germany from the potassium chloride and sulphate of Stassfurt by the Leblanc process (*see below*, Soda). Lately, however, experiments have again been successfully undertaken on a vast scale, using the Engel-Precht process which was already patented in 1880, but had not yielded satisfactory results. This process consists in mixing a solution of KCl with magnesium carbonate, then passing in a current of CO_2 and stirring the mass continuously ; a double salt is first obtained :

$$3MgCO_3 + 2KCl + CO_2 + 9H_2O = 2(MgCO_3, CO_3KH, 4H_2O) + MgCl_2.$$

This is washed with a solution of magnesium dicarbonate in order to separate $MgCl_2$ without decomposing the double salt. This is then decomposed by

water under pressure at 120°. Basic insoluble magnesium carbonate is precipitated, CO_2 is evolved, and the filtered solution of K_2CO_3 is evaporated and then calcined. By this means potassium carbonate free from sodium salts is obtained, as NaCl does not react with magnesium carbonate. Solvay has further improved this process (Ger. Pat. 159,870).

Chemically pure potassium carbonate is obtained by heating pure potassium tartrate or oxalate to redness, or better still by heating potassium dicarbonate.

PROPERTIES. Pure potassium carbonate forms a white granular powder which becomes deliquescent, because 100 parts of water dissolve 83 parts at 0° and 205 parts at 135°. From concentrated solutions it sometimes crystallises with water of crystallisation, $2K_2CO_3 + H_2O$, and when hot $K_2CO_3 + H_2O$; at 135° it remains anhydrous.

It melts at 890° and evaporates at a white heat. The aqueous solution has a strongly alkaline reaction because the CO_3'' anions in solution react with a part of the water itself : $CO_3'' + H_2O = CO_3H' + OH'$, and we thus have alkaline OH' anions (*see* Hydrolysis, p. 239).

Potassium carbonate has the property of being easily decomposed by acids with evolution of CO_2. In presence of soluble salts of the heavy metals it readily combines with these to form insoluble carbonates which separate, whilst a new soluble potassium salt remains in solution, containing the acid residue which was combined with the heavy metal.

A table of density of potassium carbonate solutions is given under the heading Sodium Carbonate.

Potassium carbonate is largely employed in the manufacture of soft soaps ; still larger quantities are used in the manufacture of Bohemian glass, in dyeing, and in wool washing. When commercially pure it costs £24 per ton, and £38 when chemically pure, whilst the crude product costs from £12 to £16.

The internal consumption in Germany in 1901 was 16,000 tons of potassium carbonate, and 15,000 tons were exported, of the value of about £280,000. In 1905 11,963 tons were exported and in 1907 about 13,300 tons, valued at £240,000. Italy imported 913 tons of potassium carbonate in 1903 ; 604·2 in 1904 ; 838·4 in 1906, and 825·3 in 1908, valued at £14,856. On the other hand, Italy exported the following quantities of crude potassium carbonate, produced from certain sugar residues, obtained by calcining molasses : 56·8 tons in 1906 ; 483·7 tons in 1907 ; and 741·3 tons in 1908, valued at £13,344. Russia, which at one time exported potassium carbonate, now imports several thousand tons.

POTASSIUM DICARBONATE : $KHCO_3$ (Primary potassium carbonate). This compound is obtained in crystals by passing carbon dioxide into a saturated solution of K_2CO_3 ; in a solution of the carbonate a large part of the CO_3'' ions are unaltered, and by means of a current of CO_2 in presence of water these are completely transformed into CO_3H' ions, thus : $CO_3'' + CO_2 + H_2O = 2CO_3H'$; on the other hand, there are also K' cations in the solution and consequently all the carbonate is transformed into the dicarbonate, $CO_3K_2 + CO_2 + H_2O = 2CO_3HK$. The dicarbonate, being less soluble in water than the carbonate, readily separates in monoclinic crystals free from water. Water only dissolves about 20 to 25 per cent. of this substance, and solutions which are not very dilute show a neutral reaction, whilst when very dilute they show a weakly alkaline reaction, because a small part of the CO_3H' anions hydrolyse and form H_2CO_3 and OH' with water.

On simple evaporation the solution is decomposed into $CO_3K_2 + CO_2 + H_2O$, whilst the dry salt only decomposes at 110°.

The dicarbonate is used especially for the preparation of pure potassium carbonate, and costs £32 to £40 per ton, according to its purity.

POTASSIUM PERCARBONATE : $K_2C_2O_6$. On electrolysing a potassium carbonate solution at a very low temperature (− 15°) a bluish deliquescent powder separates at the anode which is potassium percarbonate formed by the union of two carbonate ions : $\begin{matrix} CO_3K \\ \vdots \\ CO_3K \end{matrix}$. At 200° to 300° it is decomposed, forming $CO_3K_2 + CO_2 + O$, and the aqueous

solution already evolves oxygen at 45°, so that it is a useful oxidising agent and also bleaches various substances. With dilute acids or alkali hydroxides it forms hydrogen peroxide :

$$C_2O_6K_2 + 2HCl = 2KCl + 2CO_2 + H_2O_2$$
$$C_2O_6K_2 + 2KOH = 2CO_3K_2 + H_2O_2.$$

Certain metallic oxides such as Ag_2O, MnO_2, PbO_2, &c. are reduced by it with strong evolution of oxygen : $Ag_2O + C_2O_6K_2 = Ag + CO_3K_2 + CO_2 + O_2$.

Solutions of the percarbonate are titrated with permanganate in acid solution (1 c.c. of normal permanganate = 0·099 grm. of $K_2C_2O_6$).

POTASSIUM SILICATE or **SOLUBLE POTASH GLASS.** Van Helmont obtained this substance as far back as 1610 by melting sand with much potassium carbonate. In 1648 Glauber described a method of preparing it, with full details, and in 1815 Fuchs prepared a compound of silicic acid and potash, which contained an excess of silica and was not deliquescent. It is not known in the crystalline condition and is formed by dissolving silicic acid in solutions of potassium hydroxide. It is obtained industrially by melting 45 parts of quartz sand with 30 parts of potassium carbonate and 25 parts of powdered coal in a furnace. The product is broken up and dissolved in hot water under pressure, forming a heavy liquid which is used for various industrial purposes.

On drying the concentrated solution in the air a solid crust is formed on the surface, which becomes white and opaque and may be redissolved in hot water after pulverisation. The composition of the silicate varies considerably, but usually it corresponds approximately to the formula, $K_2O.4SiO_2$, though the number of molecules of SiO_2 may vary.

Solutions of potassium silicate separate silica under the action of the CO_2 of the air.

It is used in the same way as soluble soda glass in cotton printing, for fixing the colours in stereochrome work, for rendering fabrics resistant to fire, for making varnishes, &c. Commercial solutions of 30° to 33° Bé. cost £8 per ton, and sodium silicate in lumps costs £20 per ton (for statistics, *see* Sodium Silicate *below*).

POTASSIUM TRITHIOCARBONATE : K_2CS_3. This is used instead of carbon disulphide against phylloxera (*see* p. 397). It has the advantage over carbon disulphide of not being volatile, therefore causing less loss in the soil. The use of sodium or calcium thiocarbonates is more economical, but the potassium salt also acts indirectly as a potash fertiliser. It is prepared in solution (corresponding to 15 per cent. of CS_2) by the action of potassium sulphide on carbon disulphide : $K_2S + CS_2 = K_2CS_3$.

It is slowly decomposed in the soil by moisture and by carbon dioxide with continuous production of carbon disulphide : $CS_3K_2 + CO_2 + H_2O = H_2S + CS_2 + K_2CO_3$.

The commercial value of the yellow liquid is proportional to the percentage of CS_2 which it is capable of yielding. This is determined by heating the thiocarbonate solution and condensing the CS_2 which distils. There are various other more exact analytical methods which we cannot describe here.

POTASSIUM CYANIDE : KCN. This compound was formerly obtained by heating the following mixture in large covered iron crucibles to redness : 8 parts of dry potassium ferrocyanide with 3 parts of dry potassium carbonate and a little carbon, or preferably with a little sodium in order to avoid the formation of potassium cyanate. It is obtained pure by heating potassium ferrocyanide alone in covered iron crucibles :

$$K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2 ;$$

the fused potassium cyanide is decanted from the iron carbide and extracted with alcohol ; after evaporating the solvent the pure salt is melted. It is prepared on the large scale by Siepermann's process, by heating K_2CO_3 with carbon in presence of a current of ammonia. The Castner process is also important, but is more especially suited to the preparation of sodium cyanide ; in this process a mixture of metallic sodium, coal and sodium cyanide is treated with ammonia at a temperature slightly higher than the melting-point of the sodium cyanide. KCN is also manufactured to-day by the Frank-Erlwein process from calcium carbide and nitrogen (*see* p. 309), and 10,000 tons were prepared in this manner in 1905.

It forms a white crystalline mass of alkaline taste [**Don't taste ! It is extremely poisonous.**—*Translator*] ; it smells of bitter almonds, hydrocyanic acid being already set free by the CO_2 of the air. It is very soluble in water and slightly so in

alcohol ; it is very poisonous although certain animals such as horses, mules, and pigs resist fairly strong doses. It is much used in large quantities for the extraction of gold (*see* Gold). (*Translator's note.*—Sodium cyanide is to-day exclusively used for this purpose.)

In 1909 Germany exported 6282 tons of potassium and sodium cyanides.

Potassium Cyanide is also obtained to-day from beetroot residues (*see* page 435).

The commercial product containing 30 per cent. costs £44 per ton. When of 60 per cent. purity it costs £74, and of about 98 per cent. purity £86. The carbide process has greatly reduced the price : pure, for laboratory purposes, it costs 17*s.* 7*d.* per kilo.

POTASSIUM PHOSPHATES. Three phosphates are known, K_3PO_4, K_2HPO_4, and KH_2PO_4, and are obtained by the action of phosphoric acid on potassium carbonate. They are of little practical importance ; they are not obtained in a well-crystallised condition, and the corresponding sodium salts are usually preferred for practical purposes.

POTASSIUM AMIDE : KNH_2. This compound is obtained by passing a current of dry ammonia over molten potassium and forms a blue liquid which yields a white crystalline mass on cooling. It sublimes at 400° and then dissociates into its elements. With water it forms NH_3 and KOH.

GENERAL CHARACTERISTIC REACTIONS OF POTASSIUM SALTS

The potassium salts are almost all soluble in water although their solutions give white crystalline, only slightly soluble, precipitates of potassium hydrogen tartrate with tartaric acid. Chloroplatinic acid, H_2PtCl_6, gives a yellow crystalline precipitate of potassium chloroplatinate, K_2PtCl_6. This compound is only slightly soluble in water and still less in alcohol.

Potassium fluosilicate and potassium perchlorate are also only slightly soluble and may be sued for separating potassium from other metals. All potassium salts give a pale violet coloration to the Bunsen flame and a spectrum containing two characteristic lines, red and violet, showing that at high temperatures all salts of potassium dissociate, forming potassium ions which give this general reaction.

RUBIDIUM : Rb, 85.45, and CAESIUM : Cs, 132.81

These metals are not abundant but fairly widely diffused in nature, and often accompany potassium in saline waters and in the ashes of plants.

Rubidium is found as an impurity (0·5 per cent.) in the mineral *lepidolite :*

$$K_4Li_4(AlF_2)_3Al_4(Si_3O_8)(SiO_4)_3,$$

and also in the *carnallite* of Stassfurt ; caesium is found in a very rare sulphate of aluminium and caesium called *pollucite* : $H_2Cs_4Al_4(SiO_3)_9$. These metals were discovered as elements by Bunsen and Kirchhoff in 1860 by means of the spectroscope. Rubidium and caesium salts are more insoluble than those of potassium, so that they may be separated from the latter.

These elements are obtained in the free metallic state on electrolysing their respective fused chlorides. They are also obtained from the corresponding hydroxides by heating them in an iron tube, together with magnesium or aluminium, in a current of dry hydrogen :

$$2RbOH + 2Mg = 2Rb + 2MgO + H_2.$$

The metals distil and are collected in petroleum.

Rubidium and caesium have a silvery appearance, but are easily oxidised by the air, Rb forming a *peroxide*, Rb_2O_4. Rubidium has a specific gravity of 1·52 and melts at 38·5° ; when thrown into water it catches fire with a violet flame. Caesium has a specific gravity of 1·85, melts at 27·5°, and readily catches fire in the air ; it boils at 270°.

Rubidium iodide is now sometimes used in medicine instead of potassium iodide.

In contradistinction to potassium, rubidium and caesium form many halogen derivatives in which they act as polyvalent elements : $RbClBr_2$, $RbBr_3$, $CsBr_3$, CsI_5. The compound, $RbICl_4$, is a yellow solid obtained by treating a solution of rubidium iodide with chlorine,

and is slightly soluble in water ; the solution is a powerful oxidising agent, and dissolves gold and platinum.

Caesium chloroplatinate is very insoluble in water and may thus be separated from the potassium salt.

Rubidium and caesium cost about £1 per gramme.

SODIUM : Na, 23

Sodium is not found in the free state in nature on account of its great reactivity, but is widely diffused in the combined state in numerous minerals such as *cryolite*, *borax*, *glauberite*, &c. It is still more abundant in the form of sodium chloride which is found in important geological strata in the form of *rock salt ;* it is very abundant in sea water which contains up to 3 per cent. of sodium chloride. It is also found in large quantities in the form of nitrate as *Chili saltpetre*. In vegetable organisms potassium salts ordinarily predominate, whilst in animal organisms there is a predominance of sodium salts.

It was obtained free for the first time by Davy in 1807 by the electrolysis of fused sodium hydroxide. After 1855 it was prepared industrially by heating a mixture of sodium carbonate, coal, and a little limestone in iron retorts by Deville's method :

$$CO_3Na_2 + 2C = 3CO + Na_2.$$

In 1886 Castner obtained it by a greatly improved method, employing sodium hydroxide and coal mixed with iron carbide, the latter being used to decompose the water which is formed. The reduction of the sodium hydroxide needs a much lower temperature than that of the carbonate, so that there is an economy of fuel, and the apparatus is less attacked. Before 1850 1 kilo of sodium cost about £80 ; after the introduction of Castner's process the price was lowered to less than 8*s*., and it then became possible to use sodium industrially for the preparation of aluminium ; but great improvements have now been made in that industry, rendering it independent of the use of sodium which was always very dear.

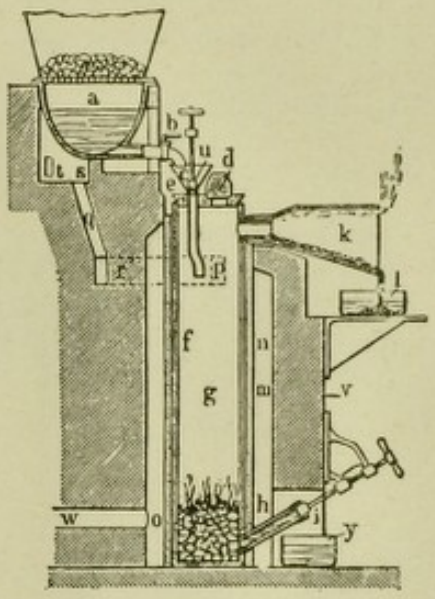


FIG. 175.

In 1898 Netto obtained better results by dropping molten sodium hydroxide contained in *a* (Fig. 175) over red-hot coal contained in a cylindrical vertical retort, *g*. Vapours of sodium are continuously evolved at the top and condensed in the iron vessel, *k*, the molten sodium being collected under petroleum in the vessel, *l*. In the lower part of the retort, at *I*, molten sodium carbonate continuously escapes :

$$4NaOH + 2C = CO_3Na_2 + Na_2 + CO + 2H_2.$$

Sodium is mainly prepared to-day by the electrolysis of molten sodium chloride, employing a cathode of molten lead, with which the free sodium forms an amalgam ; this is passed into a second compartment in which molten sodium hydroxide is present as an electrolyte. The amalgam then acts as an anode, and the sodium is deposited at the cathode without any consumption of NaOH. This process is a happy combination of that of Acker (*see below* under Electrolytic Caustic Soda) with that patented by J. Castner in 1891. By the latter process sodium is obtained by the electrolysis of fused sodium hydroxide (this process is still used in England and in France). At Niagara the combination of the two processes gives excellent results and the sodium costs less than 1*s*. 2*d*. per kilo.

According to an American patent of 1901 electrical energy is greatly economised by melting a mixture of equal parts of NaOH and sodium sulphide ; a low voltage then suffices for the decomposition of the Na_2S alone, which yields sodium, whilst the nascent sulphur immediately forms Na_2S at the cost of the NaOH. In this process it is only necessary to continuously add NaOH in order to obtain as much free sodium as is contained in the hydroxide.

In the *laboratory* it is prepared by heating sodium peroxide with wood charcoal or with calcium carbide :

$$3Na_2O_2 + 2C = 2Na_2CO_3 + 2Na.$$

PROPERTIES. Metallic sodium has a silvery appearance similar to that of potassium ; it melts at 97·6° and boils at 742°, forming colourless vapours which burn with a yellow flame. It oxidises in the air, and on throwing a piece of sodium on to water it travels over the surface and decomposes without catching fire, because it evolves less heat than potassium ; if, however, its movement over the water is hindered by enclosing it in a piece of paper it catches fire because the kinetic energy is then also transformed into thermal energy. It is soluble in absolute alcohol with evolution of hydrogen, forming sodium alcoholate.

Sodium is used for the preparation of silicon, magnesium, sodium peroxide, and certain dyestuffs. Until the year 1880 large quantities of sodium were used for the preparation of aluminium, although it is no longer used for this purpose to-day. A certain amount is used for desulphurising petroleum.

In 1865 sodium cost £2 8*s*. per kilo, but at present it costs less than 4*s*.

The world's production, which is divided between England, Germany, and the United States, was estimated at 350,000 tons in 1905, and the sale price at the works for large quantities sank to less than 2*s*. per kilo. Perhaps the price will become still lower in the future if its direct preparation from sodium chloride by Acker's process is successful.

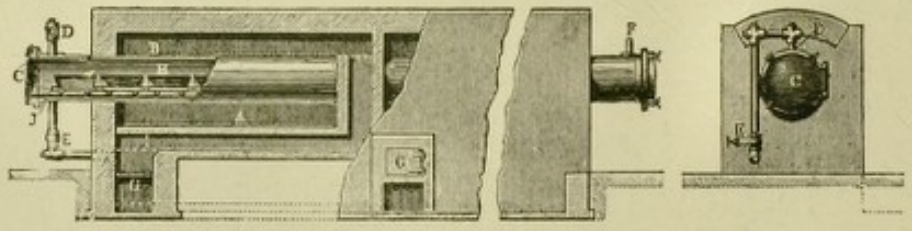


Fig. 176.

SODIUM MONOXIDE : Na_2O. This compound was not known until a short time ago ; it is now prepared from sodium and sodium nitrate in the manner already explained in the case of potassium oxide. Barium nitrate or nitrite may also be used (Ger. Pat. 144,243 of 1903).

SODIUM PEROXIDE : Na_2O_2. This is prepared in Castner's apparatus (1891) by heating sodium to 300° in aluminium trays (Fig. 176) contained in an iron retort, *B*, and passing a current of dry air free from CO_2 over it.

Na_2O_2 is also formed by heating a mixture of 100 parts of the nitrate, $NaNO_3$, and 80 parts of magnesia, MgO, or lime, CaO.

Nitrous vapours are first evolved, and oxygen and nitrogen are then evolved at a red heat ; the remaining mass is heated further to about 400° in a current of dry air free from CO_2. On pouring the mass into cold water a solution of sodium peroxide is obtained which may be employed as such, whilst the magnesia or lime separates partially.

It forms a slightly yellowish white mass which only gives off oxygen at high temperatures, whilst it dissolves in water with evolution of heat, forming oxygen which is liberated by the heating. It forms a hydrate, $Na_2O_2.8H_2O$, with water.

It is an energetic oxidising agent, which, on heating, carbonises many organic substances in the absence of water ; at red heat it has an oxidising power superior to that of all other oxidising agents.

It is advantageously used in aqueous solution for bleaching textile fibres ; in the case of animal fibres which are affected by alkalis (silk and wool) it is necessary to remember that NaOH is also formed which must be gradually neutralised as it is formed with the corresponding quantities of sulphuric or acetic acids :

$$Na_2O_2 + H_2O = 2NaOH + O.$$

When it is poured into water the reaction is sometimes so violent that flame is produced, and Gruner (1910) avoids this difficulty by first mixing the sodium peroxide with a little carbon tetrachloride, which also renders the evolution of oxygen more regular.

It may be used in diving-bells and generally in close inhabited spaces in order to obtain pure air; since a man consumes 25 litres of oxygen per hour he can be kept alive with 1 kilo of Na_2O_2 for more than five hours.

Sodium peroxide costs 2*s.* 4*d.* to 2*s.* 10*d.* per kilo, and is placed on the market under the name of "oxone."

ANALYSIS OF Na_2O_2: The commercial value depends on the quantity of active oxygen which it is capable of yielding. Its strength cannot be determined by titrating with permanganate. The best results are obtained by Archbutt's method; he decomposes 1 grm. of sodium peroxide in Lunge's nitrometer with 15 c.c. of water and two drops of a strong solution of cobalt nitrate; the oxygen which is liberated is then measured. A sample gave 136·6 cu. metres of oxygen = 0·1895 grm.

SODIUM HYDROXIDE: NaOH (CAUSTIC SODA)

PROPERTIES. Fused sodium hydroxide forms a white mass of radiating crystals on cooling, of sp. gr. 2.

It melts at a red heat, and decomposes at about 1200° to 1250° into Na, H and O. In order to obtain pure sodium hydroxide it is melted in vessels of silver and not of other metals which are easily attacked (even Pt).

It is decomposed by electrolysis, separating sodium at the negative pole (cathode). It is very soluble in water with evolution of heat, and is deliquescent in the air, from which it rapidly absorbs carbon dioxide.

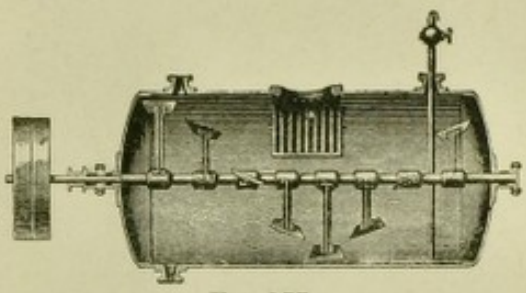


Fig. 177.

Concentrated solutions deposit various hydrates in the cold: from $NaOH.H_2O$ to $NaOH.7H_2O$. Sodium hydroxide is sold according to its strength expressed as sodium oxide, Na_2O. Theoretically the pure compound contains 77·5 per cent. of Na_2O (= 100 per cent. NaOH); in practice it is prepared at strengths of 75 and 77 per cent. Na_2O, more often from 72 to 74 per cent.

PREPARATION BY CHEMICAL METHODS. Since 1853, especially in England, sodium hydroxide is prepared by Gassage's method, from dilute (10 per cent.) boiling solutions of crude sodium carbonate, by immersing in them boxes containing quicklime, and stirring the boiling liquid continuously. If the sodium carbonate solution is more concentrated the yield is lower, because the reaction is reversible. Thus, with solutions of 5 per cent. Na_2CO_3 (5° Bé.), more than 99 per cent. of the carbonate is transformed into the hydroxide, whilst on starting from a solution of 20 per cent. (23° Bé.) only 90 per cent. of the carbonate is so transformed. The reaction occurs even in the cold, but is then slower and less complete. It is preferable to work in the heat, although about 2 per cent. is then lost in the form of *gaylussite* ($Na_2CO_3.CaCO_3.5H_2O$), which is insoluble, and is not decomposed by water. The most favourable equilibrium for the production of NaOH is at 80°, and it is slightly less favourable at 106° to 110°. Theoretically 53 kilos of CaO correspond to 100 kilos of Na_2CO_3; practically a little more lime is used which is slaked directly in the solution of the sodium carbonate.

The reaction occurs more easily with Na_2CO_3 than with K_2CO_3.

The operation is carried out in vertical iron cylinders (Lunge), or in horizontal cylinders (Solvay) as shown in Fig. 177:

$$CaO + H_2O + Na_2CO_3 = CO_3Ca + 2NaOH.$$

A stirrer or an air injector prevents the lime from depositing. The liquid is filtered from the insoluble calcium carbonate when it is found by means of HCl that the clear solution no longer contains sodium carbonate (evolution of CO_2).

The solution is evaporated in well-polished iron pans, to a density of 38° Bé.; the impurities, consisting of Na_2SO_4 and Na_2CO_3, then settle. The decanted liquid is evaporated at 360°, and when almost all the water has thus been driven off small portions of nitrate are added or air is passed through in order to oxidise the cyanogen compounds and sodium sulphide which are present as impurities.

The pure molten sodium hydroxide is then poured into iron or nickel drums, which are hermetically sealed, and after cooling are ready for transport. Each drum contains 150 to 200 kilos of NaOH.

In order to economise fuel and to finally obtain the sodium hydroxide in a cooler condition so that it attacks the metal drums in which it is packed

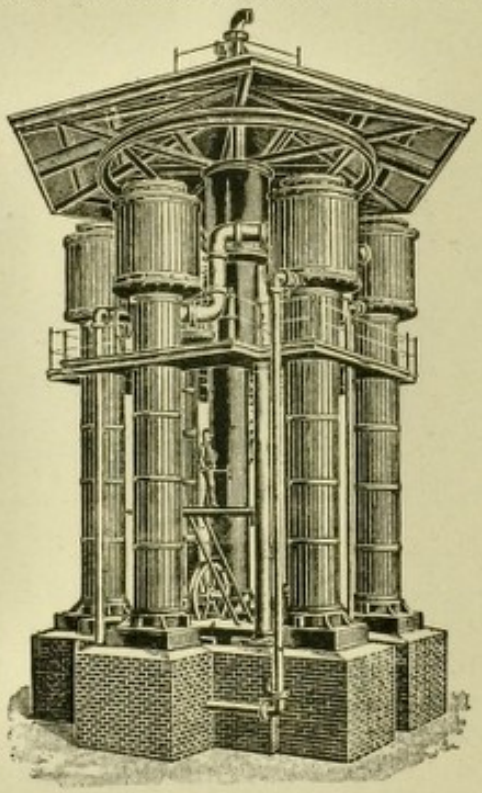


Fig. 178.

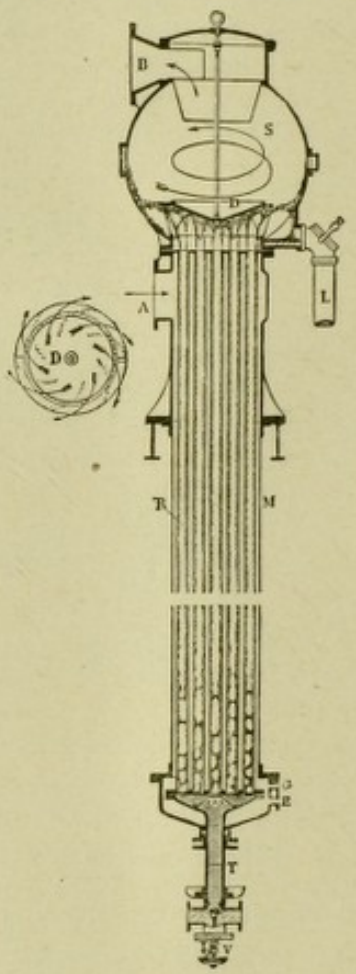


Fig. 179.

less rapidly, ingenious vacuum evaporating plants have been introduced industrially; these are also extremely suitable for the economical concentration of saline solutions, even of such very dilute solutions of 2° to 3° Bé. as are obtained on washing mercerised cotton fabrics in order to remove the concentrated NaOH solution. It is thus possible to advantageously recover sodium hydroxide which would otherwise be lost.

These forms of apparatus were at first especially applied in the sugar industry, but their use has now spread to many other industries. They are based on the principle that liquids boil at lower temperatures when exposed to less than atmospheric pressure.

The simple vacuum plants have now almost ceased to exist, and are replaced by multiple-effect evaporators, in which the steam, which is developed in a first closed evacuated boiler, enters a coil immersed in the liquor in a second boiler which is maintained at a lower pressure than the first, so that the vapour from the first boiler causes the liquid in the second to boil, and the steam evolved in the second boiler causes the liquid in a third boiler at still lower pressure to boil, and so on. In vol. ii, "Organic Chemistry," in the section on Sugar, the theory of vacuum concentrating pans is explained and illustrated by various practical forms of plant.

Later, in the section on Sodium Chloride, we illustrate a triple-effect evaporator,

and we will here describe a new form of plant of a high degree of perfection, and with a sextuple effect, the Kestner plant (Fig. 178).

The six tubes which are seen in the figure act as evaporating boilers. They are 7 metres high, and are fitted with a spherical chamber which acts as a steam separator. When in work the apparatus contains 500 litres of moving liquid in place of 15,000 litres contained in an ordinary quadruple-effect evaporator. The saline solution is concentrated in one passage through the apparatus which only lasts a few minutes. The influx of the liquor into the first boiler regulates the concentration at the exit of the apparatus.

Fig. 179 shows a section of an element of the plant shown in the preceding figure ; each element consists essentially of a bundle of evaporating tubes and of a spherical steam separator.

(*a*) The bundle of evaporating tubes is formed of long tubes, *R*, of 5 to 7 or more metres in length ; these tubes are placed in a steam chamber, *M*. All the tubes communicate below with a chamber fed by a single tube, *T*, which enters the base of the steam chamber through a stuffing-box. All the tubes are screwed into a perforated plate on which the separator is mounted. This arrangement allows the bundle of tubes to expand absolutely freely. The steam passes in at *A*, the condensed water is discharged at *E*, and the steam and air pass off at *G*.

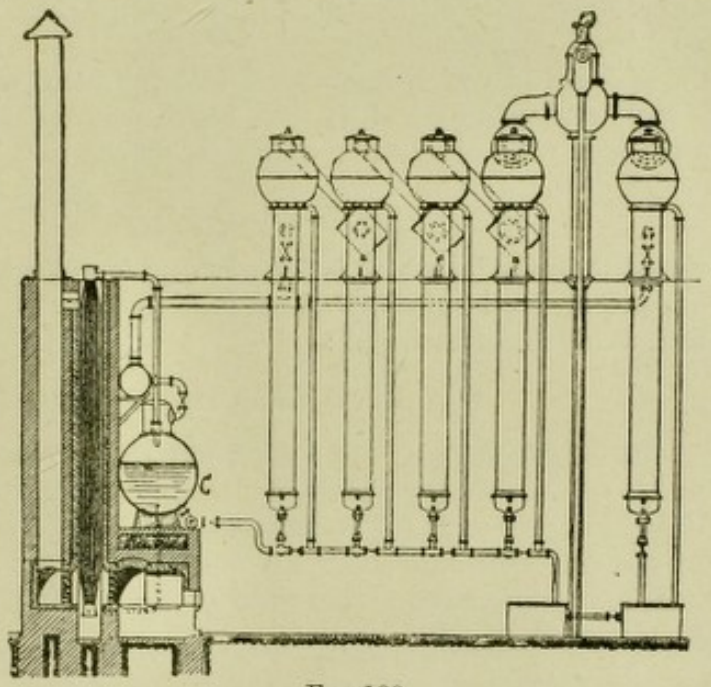


Fig. 180.

(*b*) The separator, *S*, is of spherical shape and comparatively small volume ; it encloses an apparatus, *D*, which carries wings similar to those of a centrifugal pump. The apparatus, *D*, is closed, and the form of its wings is such that the vapours which collide with them acquire a rotary movement in the separator indicated by the arrow. This rotary movement causes the liquid carried over with the vapour to separate from it, through the action of centrifugal force. The condensed liquid is discharged at *L* and the vapour formed in the bundle of tubes escapes at *B*.

The liquid to be concentrated is fed in continuously through the tube, *T*, and enters all the tubes which form the bundle equally. The ebullition due to the steam in the chamber surrounding the tubes produces first bubbles and then steam in each tube, increasing in volume and in velocity. This carries the liquid up to form a thin layer which adheres to the wall of the tube, causing a phenomenon which Kestner calls "*grimpage*," and which is indicated graphically in Fig. 179, inside the tubes. At the top of the tubes the liquid has a velocity of 20 to 25 metres per second, and is thrown against the throttle, *D*, which causes the mixed steam and liquid to acquire a rotary movement, so that dry steam escapes through *B* and passes to the next unit of the apparatus or to the condenser.

When these Kestner plants are applied for the concentration of very dilute solutions, such as the liquids which are recovered in the mercerisation of cotton fibres and tissues (*see* vol. ii, "Organic Chemistry," section on Textile Fabrics), which have a concentration of about 2° Bé., they are usually concentrated up to 12° Bé. in the first elements of the apparatus ; the solution is then passed into the boiler, *C*, as is seen in the general diagram in Fig. 180, and milk of lime is here added in order to causticise the sodium carbonate formed by continuous contact with air during the process. After boiling for one hour the hot solution is then passed through a filter press in which the milk of lime and calcium carbonate are retained by close cotton fabrics, and the clear solution is then concentrated in the final elements to the required density of 32° to 38° Bé.

In order to show the very great economy of fuel which is attained by such plant, we give a few comparative figures.

In order to concentrate 1 cu. metre of NaOH lyes from 10° to 48° Bé., that is, in order to evaporate about 850 litres of water, there are required by direct firing 222 kilos of coal

By indirect heating with steam without vacuum .	.	.	.	.	181	,,
,,	,,	,,	with vacuum and simple effect	.	.	117	,,
,,	,,	,,	,,	,,	double ,,	.	.	59	,,
,,	,,	,,	,,	,,	triple ,,	.	.	41	,,
,,	,,	,,	(Kestner) with sextuple ,,	.	.	22	,,

In plant with quadruple effect each kilo of coal evaporates up to 35 kilos of water.

For a long time sodium hydroxide was almost exclusively prepared by the Leblanc process starting from NaCl (*see* Soda); to-day, however, the electrolytic process has gradually extended in localities where hydro-electric energy is cheap.

A method which has also found practical application, because it is fairly simple and economical, is that based on heating sodium carbonate to redness with iron oxide in rotary cylinders placed in a suitable furnace:

$$CO_3Na_2 + Fe_2O_3 = CO_2 + 2FeO_2Na\,;$$

the sodium ferrite which is thus formed is thrown into hot water, and in this way a concentrated solution of sodium hydroxide is obtained and the insoluble iron oxide is regenerated:

$$2FeO_2Na + H_2O = 2NaOH + Fe_2O_3.$$

ELECTROLYTIC PREPARATION. Considerable quantities of sodium hydroxide are to-day obtained electrolytically, starting from solutions of sodium chloride or from fused sodium chloride. The sodium is obtained in the form of sodium hydroxide, and all the chlorine is absorbed by slaked lime and goes into commerce as chloride of lime (bleaching powder) containing 35 to 37 per cent. of Cl.

It was once believed that in the electrolytic decomposition of an aqueous solution of sodium chloride, only the following reactions occur:

$$NaCl = Na + Cl\,;\quad Na + H_2O = NaOH + H,$$

so that hydrogen should be obtained at the negative pole (cathode) and chlorine only at the positive pole (anode). It is found, however, that in practice oxygen is developed at the anode and that hypochlorite and chlorate, and even sodium perchlorate, are formed in solution. Forster and Müller in 1903 studied all the conditions under which the secondary reactions occur, and it only then became possible to regulate and more or less to eliminate this difficulty. The difficulties are always serious and numerous, but the process is too important not to continually claim the attention of students and of technologists who are concerned in increasing the value of the chloride by transforming it into the alkali hydroxide by means of the simple action of the electric current.

Theoretically one ampère-hour should produce 1·322 grms. of chlorine and 1·491 grms. of NaOH. It should be noted that the same quantity of electrical energy produces a greater weight of potassium hydroxide of molecular weight 56 than of sodium hydroxide of molecular weight 40, although the quantities of chlorine remain the same in both cases. The electrolytic process is thus of greater advantage in potassium hydroxide manufacture.

The electrolytic processes may be divided into three groups: the electrolysis of aqueous solutions of sodium chloride, with and without diaphragms, and electrolytic decomposition of molten sodium chloride.

TABLE OF SPECIFIC GRAVITIES AND STRENGTHS OF SOLUTIONS OF SODIUM AND POTASSIUM HYDROXIDES

Sp. gr. at 15°	Degrees Baumé	Per cent. by weight of NaOH	Per cent. by weight of KOH	Sp. gr. at 15°	Degrees Baumé	Per cent. by weight of NaOH	Per cent. by weight of KOH
1·007	1	0·61	0·9	1·252	29	22·64	27·0
1·014	2	1·20	1·7	1·263	30	23·67	28·0
1·022	3	2·00	2·6	1·274	31	24·81	28·8
1·029	4	2·71	3·5	1·285	32	25·80	29·8
1·036	5	3·35	4·5	1·297	33	26·83	30·7
1·045	6	4·00	5·6	1·308	34	27·80	31·8
1·052	7	4·64	6·4	1·320	35	28·83	32·7
1·060	8	5·29	7·4	1·332	36	29·93	33·7
1·067	9	5·87	8·2	1·345	37	31·22	34·9
1·075	10	6·55	9·2	1·357	38	32·47	35·9
1·083	11	7·31	10·1	1·370	39	33·69	36·9
1·091	12	8·00	10·9	1·383	40	34·96	37·8
1·100	13	8·68	12·0	1·397	41	36·25	38·9
1·108	14	9·42	12·9	1·410	42	37·47	39·9
1·116	15	10·06	13·8	1·424	43	38·80	40·9
1·125	16	10·97	14·8	1·438	44	39·99	42·1
1·134	17	11·84	15·7	1·453	45	41·41	43·4
1·142	18	12·64	16·5	1·468	46	42·83	44·6
1·152	19	13·55	17·6	1·483	47	44·38	45·8
1·162	20	14·37	18·6	1·498	48	46·15	47·1
1·171	21	15·13	19·5	1·514	49	47·60	48·3
1·180	22	15·91	20·5	1·530	50	49·02	49·4
1·190	23	16·77	21·4	1·546	51		50·6
1·200	24	17·67	22·4	1·563	52		51·9
1·210	25	18·58	23·3	1·580	53		53·2
1·220	26	19·58	24·2	1·597	54		54·5
1·231	27	20·59	25·1	1·615	55		55·9
1·241	28	21·42	26·1	1·634	56		57·5

The material of which the electrodes are constructed is of great importance in the electrolytic processes because it has to resist the action of the alkali and of the nascent chlorine. Those formed of compact retort graphite serve very well, although the large consumption of electrodes does not depend on the action of the reagents only, but largely on the intensity of the electric current. Electrodes of powdered and sheet platinum have yielded good results, but a net of platinum wire which costs relatively little has given still better results. To-day, however, the electrodes which are generally used are made of artificial graphite produced by the firm of Acheson at Niagara (*see* Graphite, p. 360). When carbon electrodes are used there is evolution of carbon dioxide at the anode which causes loss of sodium hydroxide, and it is therefore necessary to interrupt the electrolysis when the solution contains 8 per cent. of sodium hydroxide. In order to avoid the formation of carbon dioxide anodes of ferroso-ferric oxide are prepared which, however, melt with difficulty at 2000° to 3000°, and need to be carefully cooled in order to avoid the formation of cracks. These anodes are not attacked by oxygen, and thus cause the oxidation of the chloride to chlorate, which latter is so obtained gratuitously. The sodium hydroxide solution obtained by this process by the Elektron Company of Griesheim (*see below*) is concentrated up to 50 per cent. At this point, however, it acquires a yellow colour from the presence of iron; the elimination of this latter substance is easily carried out by an osmotic process without the use of a

membrane, by allowing the solution to diffuse into water running in the opposite direction in long channels.

Diaphragms, which are constructed of porous earthenware (*see below*), are used to keep the products of the electrolytic decomposition separate. Otherwise hypochlorites or chlorates would be formed by the interaction of the sodium hydroxide and the chlorine. The spaces in which the anodes and the cathodes are disposed are thus separated without prevention of the passage of the current. It was not, however, an easy matter to prepare such diaphragms, which must be resistant to the action of the current, of the chlorine and of the alkali.

To these technical difficulties a grave commercial difficulty was added, which consisted in the excessive quantities of chloride of lime which were obtained compared with the quantity of sodium hydroxide, these being in the proportions of about 2·5 to 1. There was not a sufficient demand for the former product, and the price therefore descended in recent years from £8 to £3 12*s*. per ton. Thus, the commercial basis of the whole industry was endangered. To-day, however, the price has risen (in Italy) to £5 12*s*. per ton, through an arrangement between the producers and through the protective tariffs.

In many quarters a suggestion has been made to utilise the chlorine for the production of hydrochloric acid, thus reversing the process used until now of obtaining chlorine from hydrochloric acid. The transformation of sodium hydroxide into carbonate has also been proposed because there is a greater demand for the latter. These projects, however, although technically possible, have not been applied, because they collide with the thermochemical balance of their manufacture; thus more energy is required in order to transform sodium chloride into sodium hydroxide and chlorine than to transform it into carbonate and hydrochloric acid; there would therefore be a waste of energy in passing from the hydroxide to the carbonate and from chlorine to HCl, which can, on the other hand, be obtained by simple chemical processes with less consumption of energy. The chlorine is now used to some extent for the manufacture of carbon tetrachloride (*which see*), and a portion of the chlorine is placed on the market in the liquid state. The electrolytic process should only be used to satisfy the demand for chlorine and sodium hydroxide. To-day, after the great growth of aeronautic enterprise, the collection of the hydrogen which is evolved at the negative pole in large quantities has also been taken in hand. The potassium hydroxide works of Griesheim alone produce 60 cu. metres of hydrogen daily.

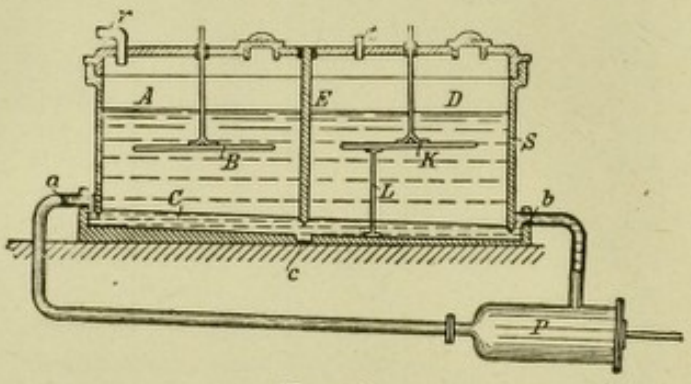


FIG. 181.

I. PROCESSES WITHOUT DIAPHRAGMS. The great difficulties which were first encountered in applying electrolytic processes with diaphragms led Castner in America, Kellner in Austria, and Sinding-Larsen in Norway almost simultaneously to devise processes without diaphragms, based on the employment of metallic mercury as a cathode and conducting the electrolysis of the salt solution in such a manner that the sodium cation is immediately dissolved by mercury at the instant of its formation, forming an amalgam. This is then passed into water below the apparatus, where a somewhat concentrated solution of pure sodium hydroxide is obtained, and thus pure somewhat concentrated sodium hydroxide solution, almost free from chlorides, is obtained with evolution of hydrogen and regeneration of mercury, which is then again pumped into the apparatus.[1]

[1] Patents for the various modifications of this process are numerous, and it will suffice to mention here those

A simple diagram of one of these forms of apparatus, the first one used by Kellner, is shown in Fig. 181. The stoneware vessel, *S*, with a slightly inclined bottom, is divided into two cells by the partition, *E*. In the cell, *A*, we have the anode, *B*, formed of an iridio-platinum plate immersed in a concentrated solution of sodium chloride. The mercury, *C*, at the bottom acts as a cathode and combines with the sodium to form an amalgam ; this sodium is then utilised and the mercury regenerated in the cell, *D*, where there is a cathode, *K*, of iridio-platinum immersed in water. This decomposes the amalgam, forming NaOH and hydrogen, which is evolved at the cathode, *K*, whilst the mercury which is liberated acts as an anode and is pumped into the first cell, *A*, by the pump, *P*. Since a small part of the amalgam is already decomposed in the cell, *A*, the anodic oxygen in *D* is formed in presence of less alkali than corresponds to the evolved hydrogen, so that a small portion of the mercury in *D* is oxidised. Kellner overcame this difficulty by introducing between the cathode, *K*, and the anode (amalgam) a secondary electrode, *L*, formed of a metallic spiral, thus establishing a short circuit in such a manner that external work was avoided, but sufficient current remained to accelerate the solution of the sodium in the mercury, thus removing it more easily and more rapidly from the action of the aqueous solution of the salt.

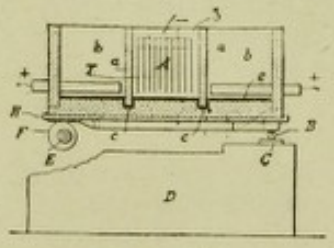


Fig. 182.

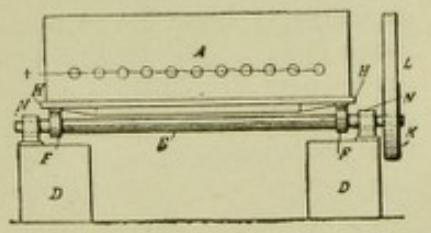


Fig. 183.

In England, and in America at Niagara, the Castner process was applied and unites those of Kellner and Solvay into a single process. There are three parallel cells (Figs. 182 and 183) separated by a hydraulic seal of mercury ; at the bottom of the cells the depth of the mercury is a few millimetres. In the lateral cells, *b*, the solution of sodium chloride is contained together with the anodes ; the amalgam from each lateral cell in turn is treated in the central cell, which contains water, by means of the gentle raising and lowering produced at one extremity of the apparatus by means of an eccentric, *E*.

A similar plant is working at Niagara Falls with a current efficiency of 90 per cent. and consuming 6000 h.p. ; 50 tons of salt are treated daily producing 36 tons of sodium hydroxide of 97 to 99 per cent., and about 90 tons of chloride of lime containing 36 per cent. of chlorine.

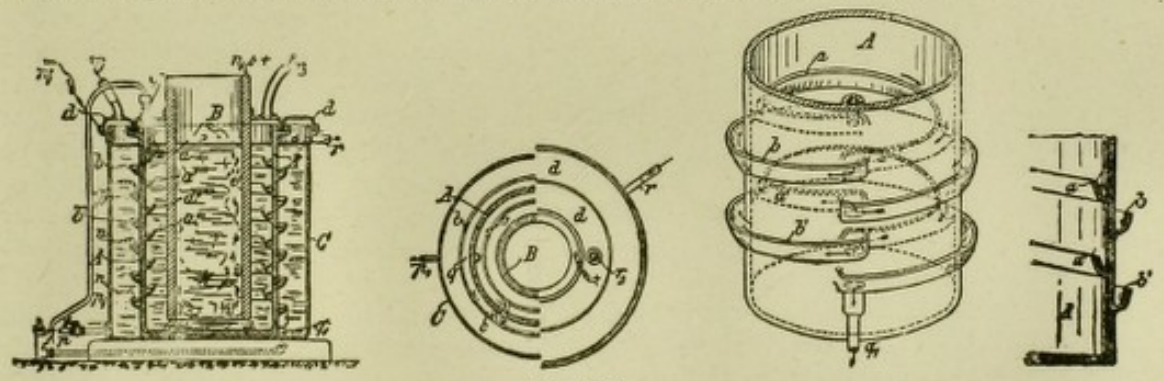


Fig. 184.

In 1899 Solvay (Ger. Pat. 100,560) discovered a means of working with less mercury by making use of the lower specific gravity of the amalgam, which floats at the top and is continuously discharged as a fine coating only, which is formed at the surface, without circulating large masses of mercury. The electrolysis is conducted in two parallel vats in communication with one another and so arranged that a bucket-wheel raises the mercury and keeps it in continuous circulation. The batteries of this plant are suitable for currents of 10,000 to 15,000 amps. The factories at Jemappes in Belgium, at Ljubimoff in Russia, and of the Società del Caffaro at Brescia work by this process.

Kellner further improved his process by a most ingenious apparatus (Fig. 184), in which the mercury circulates round a cylinder immersed in the bath through channels which form spirals on the inside and outside of the cylinder alternately.

of Atkins, 1892 ; Hermite, 1893 ; Vautin, 1894 ; Kellner, 1893 and 1896, &c. ; Castner, 1894, 1896, &c. ; Störmer, 1897 ; Rhodin, 1899 ; Solvay, 1899, &c. In these processes good yields are obtained with great current density.

A porcelain or stoneware cylinder, A, closed below, is provided with a channel which forms a spiral, first passing round once at the top along the internal wall, and then continuing through a hole, c, and forming a second spiral round the external wall of the same cylinder; it then re-enters and takes a third turn round the inside, a fourth round the outside, &c., until it arrives at the lower part of the cylinder. Inside the cylinder, A, there is a bottomless cylinder which acts as an anode, and is filled with solid sodium chloride. The space between the cylinders, A and B, is filled with a concentrated solution of sodium chloride, whilst the cylinder, A, is surrounded by water contained in an iron cylinder, C; the mercury passes in through the tube, q, from which it passes into the channel, a, and is in contact at several points with the negative pole (cathode) as it flows slowly round the spiral. Inside the cylinder, A, the mercury becomes covered with sodium amalgam, which is produced by the electrolytic decomposition of the NaCl, but when, on continuing its course, it enters the channel which passes along the external wall of A, it immediately forms sodium hydroxide in contact with the water, and the mercury is regenerated and again enters the interior of A in order to form further sodium amalgam, which is decomposed outside, and so on. In the interior of A chlorine is continuously developed and escapes from the tube, r_2, whilst outside A a solution of sodium hydroxide is formed which gradually increases in concentration and is discharged by a cock; the hydrogen escapes by the tube, r_1. The apparatus is closed above by the cover, d, which carries the tubes for the escaping gases, &c. This apparatus is not suitable for a very large output, for which the Solvay process is preferable.

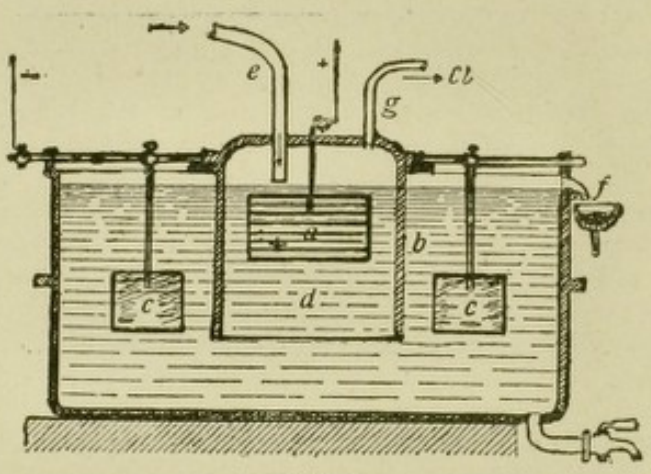


FIG. 185.

The Chemico-Metallurgical Company of Aussig (Austria) keeps the products of the electrolytic dissociation separate, by making use of the different densities of the liquids in the two chambers containing the electrodes. The apparatus may be considered in principle as a type intermediate between those with diaphragms and those without diaphragms, and is shown in Fig. 185. The anode, a (positive pole), is formed of a bundle or disc of carbon which is placed in a bell, b, non-conductive and resistant to chlorine, which is immersed in the NaCl solution. The cathodes (negative pole), c, are formed of two iron plates. The exact adjustment of the distance of the anode, a, from the lower level of the bell is of the highest importance, because the separation of the chlorine from the sodium hydroxide which is formed in the vat and which escapes from f depends on this adjustment. The electrolyte, which is a concentrated solution of NaCl, enters slowly and continuously through the tube, e, whilst the chlorine gas escapes through the tube, g; apparently 85 to 90 per cent. of the current is utilised by this process.

The solution which is obtained contains about 10 per cent. of sodium hydroxide and much sodium chloride. On evaporating the liquid almost the whole of the sodium chloride first separates in the solid state, and the concentrated solution of sodium hydroxide is then evaporated separately to dryness and then contains only 2 to 3 per cent. of chlorides.

In 1896 Kellner proposed to treat the alkaline solution of NaOH directly with carbon dioxide (chimney gases) in order to thus cause sodium carbonate to crystallise.

The engineer Rambaldini has lately devised a continuous electrolytic process for the preparation of sodium hydroxide without diaphragms, based on the difference in density between the electrolyte and the resulting hydroxide solution, as these solutions may be superposed without mixing. In spite of repeated experiments on a small industrial scale this process has not yet been accepted by the large caustic soda works as possessing any advantages (Ger. Pat. 183,853 of 1902, granted in 1907).

II. PROCESSES WITH DIAPHRAGMS. Various German works now united under the single name of Chemische Fabrik Griesheim-Elektron already started experiments on the production of electrolytic soda in 1884, starting from a patent of C. Höpfner, and in 1890 the first European works was erected at Griesheim, using 400 h.p., which was already

doubled in 1892 and was later increased to 2000 h.p. Since cheap water-power is scarce in Germany, a new plant using 3000 h.p. was erected at Bitterfeld in Saxony in 1893, as cheap lignite is found abundantly in this locality almost on the surface. In 1895 the Bitterfeld establishment was doubled in size and in 1898 it was absorbed by the Elektron Company. They work with a system of diaphragms, but the details of the process are kept secret. The difficulties encountered in obtaining resistant diaphragms were very great: diaphragms of soap, albumen, parchment-paper, collodium, hard rubber, porous earthenware, limestone, asbestos fabrics, &c., were tried, but all proved useless. These materials were destroyed in a few days. The Elektron Company finally succeeded in preparing resistant diaphragms from porous plates of Portland cement; and lately good diaphragms have also been prepared in America from asbestos fabrics coated with cement or sodium silicate. The preparation of the anodes for this process has already been described.

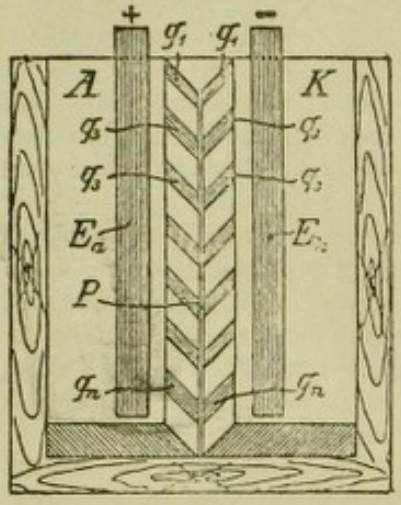


Fig. 186.

The Badische Anilin und Soda Fabrik of Ludwigshafen, and certain other important works in Europe and America, to-day use diaphragms very successfully. To-day 33,000 horse-power are used altogether in such works in various countries, with a total production of 70,000 tons of sodium hydroxide and 120,000 tons of bleaching powder.

Of the numerous methods and forms of apparatus for decomposing sodium chloride solutions electrolytically with the employment of diaphragms, we will only record the most important. Ordinarily the solution of the chloride is electrolysed at a temperature of 80° to 90° with a current of 100 to 200 amps. per square metre of electrode surface and at a tension of 3·5 to 4 volts.

After the greater number of difficulties encountered in the manufacture of resistant diaphragms had been overcome, these methods, which were those first attempted for the preparation of electrolytic caustic soda, regained the upper hand, and the consumption of electrodes and of diaphragms does not form such a serious item in this industry as in the past, when it prevented its development.

The greater number of these diaphragms, which act as osmotic membranes, offer great resistance to the passage of the current and do not even separate the products of the electrolytic dissociation very well.

The firm of Meister Lucius und Brüning of Höchst has partly overcome this difficulty by applying to the two sides of the diaphragm, *P* (Fig. 186), a series of non-porous bands, *q*, arranged in the same manner as a Venetian blind, and inclined upwards, as shown in the figure, in such a manner that the bubbles of gas are forced to rise. In America diaphragms of sheet asbestos coated with cement have been used since 1905; these offer much less resistance to the current than other diaphragms.

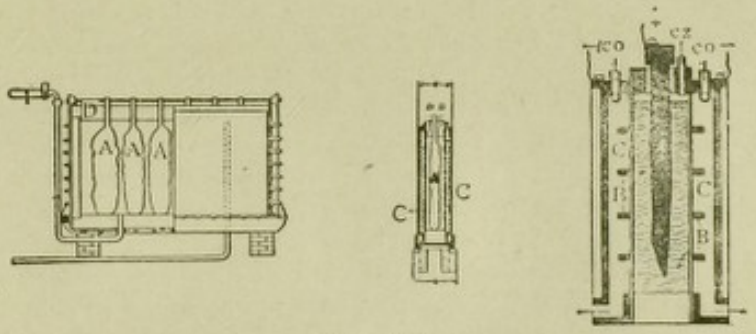


Fig. 187.

A process which has enjoyed much success during recent years and has been applied on a vast scale by an English company for the production of sodium carbonate and chloride of lime is that of Hargreaves in its latest modification (1898). The electrolytic cell is constructed with a diaphragm about 6 mm. thick, formed of an asbestos fabric impregnated with sodium silicate, and compressed into sheets, which allows osmotic phenomena, but not filtration of the liquid to occur. The external face of the diaphragm, *D* (Fig. 187), is connected with the cathode, *C*, formed of a close net of copper wire, or of a perforated plate. The internal portion between the two diaphragms forms the chamber in which the salt solution is placed, and the carbon anodes, *A*, dip into this solution. The chamber containing the cathode does not contain any liquid, but a jet of steam or a spray of water is introduced in order

to dissolve the sodium as fast as it is formed when the system is working. The sodium hydroxide solution collects at the base of this chamber, and if direct production of sodium carbonate is desired it is only necessary to pass in a current of moist carbon dioxide. The chlorine escapes from the anode chamber through a tube at the top. Through special circumstances this process has acquired a certain importance in England. Each cell has a surface of 10 sq. metres of diaphragms and of cathodes, and decomposes 106 kilos of NaCl per twenty-four hours, producing 177 kilos of chloride of lime, containing 37 per cent. of active chlorine, and 95 kilos of calcined soda, containing 98 per cent. of Na_2CO_3 ; an electric current of 2300 amps. at 3·9 volts is required, and the current efficiency is 97 per cent. The diaphragms are 3 metres long and 1·5 metres wide, last more than a month, and cost about 5*s*. 10*d*. each. A plant composed of 250 of these electrolytic cells occupies a space of about 3500 sq. metres.

Another process which has been applied practically is that of Le Sueur (1898). The apparatus consists of an iron tank containing the bath, and anodes formed of nets of iridio-platinum wire ; the diaphragms are horizontal and corrugated ; the cathode is formed of an iron net.

The *Outhenin-Chalandre* process is employed in various works, especially in those of the Swiss and Lyonese Company, "La Volta," at Chèvres, near Geneva, at Montiers in Savoy, and those of the Società elettrochimica of Rome at Bussi.

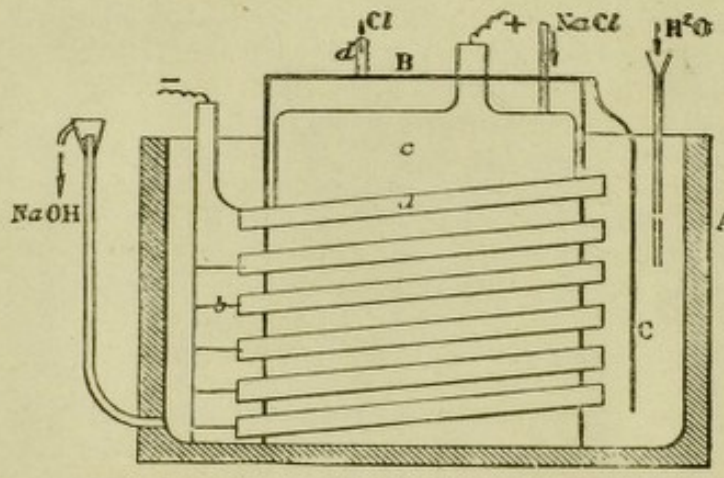


Fig. 188.

The apparatus is shown diagrammatically in Fig. 188. The box, *B*, is constructed of ebonite or cement and contains the anode, *c* ; one side of it is furnished with a double wall, *C*, which does not reach to the bottom ; the two opposite walls of this box are perforated by long, porous, inclined tubes open at the two ends, which serve as diaphragms, and contain the cathodes, *b*, formed of metallic plates united to the negative pole. The anode is placed between two series of these tubes ; the whole is placed in a large tank, *A*, which contains a solution of alkali hydroxide and the NaCl solution is passed into the ebonite tank through the upper tube. When the current passes chlorine is evolved through the tube, *b*, whilst the sodium separated at the cathode inside the tubes is transformed into sodium hydroxide, a solution of which passes out through a syphon tube, whilst fresh water continuously passes in. The hydrogen which is evolved in the inclined tubes passes up these and collects in the chamber formed by the double walls from which it passes into gasometers in order to be utilised.

III. ELECTROLYSIS OF THE FUSED CHLORIDE. Lyte (1892–1895) endeavoured to decompose the fused lead chloride obtained as a by-product in various industries by means of the electric current. The idea of a process of decomposing molten chlorides by a dry method was thus started. In the electrochemical works at Bitterfeld electrolytic soda is also prepared by a dry method, but the details are kept secret. In France the *Hulin* process was tried, but was abandoned because various difficulties were met with and a large quantity of electrical energy was required, the current efficiency being low. The process is based on the decomposition of molten sodium chloride, contained in a large crucible, by the current. The crucible was placed in a furnace and large carbon anodes were used, molten lead being employed as the cathode. The latter combined with the sodium as it was formed, producing an alloy of lead with 25 per cent. of sodium, which was collected in the liquid state and decomposed with steam in separate vessels under proper precautions.

A current of 7500 amps. per square metre was used at a tension of 7 volts ; 81 grms. of chlorine and 54 grms. of sodium were obtained per electrical h.p.-hour.

In Savoy, near Modano, the *Vautin* method was tried which is a slight modification of

the preceding one, but it was also abandoned. An E.M.F. of 6 volts was required and a current of 7500 amps. per square metre ; each horse-power produced 1·24 kilos of sodium and 1·85 kilos of chlorine daily.

In order to show the inferiority of this method compared with the wet methods, it is sufficient to note that in order to obtain 9 tons of sodium hydroxide of 70 per cent. of Na_2O the following amounts of electrical energy are required :

By the Hargreaves-Bird process . . .	2609	kw.-hours
,, Castner-Kellner ,, . . .	2694	,,
,, Hulin (dry-method) ,, . . .	6106	,,

In order to work by the dry process it is therefore necessary to have at disposal large quantities of cheap electrical energy. This condition is realised at Niagara Falls, where the *Acker* process (1900), which is an improvement of the preceding process, is used. By this process the heat of combination of the sodium with steam is also utilised by employing the hydrogen so formed for heating purposes. This process still consumes much energy compared with the other methods, but a ten times larger production of soda is attained and the sodium hydroxide thus obtained at high temperatures is free from water. The consumption of electrodes, especially of the cathodes, is however very large, although these are constructed of Acheson graphite and last one hundred times longer than those of amorphous carbon ; the latter are destroyed in a few minutes.

APPLICATIONS, PRICES, AND STATISTICS.[1] Caustic soda is used in large quantities in the manufacture of soap, which consists of the potassium or sodium salts of fatty acids. Caustic soda is also used in paper mills, cotton mills, aniline dyestuff factories (for the preparation of alizarine, resorcin, naphthol, &c.), for mercerising cotton (*see* vol. ii, "Organic Chemistry," section on Textile Fibres), for purifying petroleum, mineral oils, &c. The production of sodium hydroxide is carried out more especially in England and in Germany ; the latter country produced 70,000 tons of caustic soda in 1901, of which only 5000 tons were electrolytic, and 35,000 tons of potassium hydroxide, of which 30,000 tons were manufactured by the electrolytic process. Germany exported about 6000 tons of caustic soda in 1905 of the value of £60,760 and 8340 tons in 1909 ; in France the production of electrolytic caustic soda does not reach 5000 tons. England exported 80,000 tons in 1909. In Russia the consumption of caustic soda in 1897 was 23,500 tons, of which 7770 tons were imported from Germany and from England ; in 1907 the consumption rose to 38,336 tons, and the imports fell to 208 tons.

In 1902 Italy imported 17,000 tons of caustic soda of the value of £182,280 ; but in 1905 the Società elettrochimica of Rome commenced to produce 2500 tons in their works at Bussi, and the imports then decreased to 16,540 tons, and in 1904 to 14,150 tons at £10 4*s.* per ton. In 1908 the works at Bussi produced 2715 tons of the value of £28,240. The imports have now decreased further because in 1906 other works were established by the Società elettrica ed elettrochimica at Caffaro in Brescia, who place on the market by preference concentrated solutions of very pure caustic soda of 38° Bé., which are more convenient for practical use, as the disadvantage of preparing the solution is saved to the consumer and a portion of the expense of concentration is saved by the manufacturer. These works produced 4100 tons of caustic soda of 38° Bé. in 1908 of the value of £16,400. In the works at Bussi a further 8 tons of fused caustic soda are produced per day together with 0·8 to 1·0 ton of potassium chlorate, as the temperature in the anodic cell rises to 60° to 70°. Concentrated solutions of caustic soda are despatched in iron drums and in tank-waggons.

It is interesting to note that in spite of this national production imports still remain rather high, being 15,750 tons in 1906 ; 14,420 tons in 1907 ; and 14,350 tons in 1908, of

[1] A works for the daily production of 3·15 tons of sodium hydroxide and 7·5 tons of chloride of lime would cost about £12,000 for plant, exclusive of plant for motive power and steam production. The complete daily cost of working would be £54 and the gross daily profit would be about £69. We give in detail the expenses which would be incurred in England, but they would have to be considerably altered to suit Italian conditions.

The daily expenses in an English works may be estimated as follows : 5·85 tons of salt, £3 8*s.* ; 4·53 tons of lime for absorbing the chlorine, £5 5*s.* 7*d.* ; 0·9 ton of hydrochloric acid, £4 4*s.* ; 0·7 ton of coal for evaporating sodium hydroxide solutions and producing a portion of the power (250 h.p.), £4 8*s.* ; the wages of 45 people at a mean daily wage of 6*s.* 9*d.* = £15 4*s.* ; administration expenses, £1 12*s.* ; packing, £3 4*s.* ; lubricants, various stores, and losses, £2 2*s.* 5*d.* ; rates and taxes and insurance, £1 1*s.* 8*d.* ; repairs and amortisation, £5 5*s.* 7*d.* various expenses, £1 1*s.* 7*d.* ; daily charge for 1000 electric h.p. at £2 11*s.* per h.p.-year, £7. The gross daily profits from 7·5 tons of chloride of lime at £5 per ton would be £37 10*s.*, and for 3·15 tons of sodium hydroxide at £10 per ton, £31 10*s.*, from which one must deduct £11 12*s.* for freight.

the value of £160,000. This is due to two circumstances, namely, the increased consumption in the country, and the fact that the Italian works are not able to further increase their production of caustic soda until they have found an outlet for the chloride of lime which is produced in quantities almost 2½ times greater than the soda.

The price of fused caustic soda is £10 to £12 16*s.* per ton, according to its strength and purity; solutions of 38° Bé. (32 per cent. of NaOH) are sold at £4 to £4 8*s.* per ton.[1]

SODIUM CHLORIDE : NaCl (Common Salt)

This salt is the raw material for the preparation of almost all the other artificial sodium salts. It is widely diffused in nature, and is found abundantly in sea water (about 3 per cent.), from which it is extracted industrially in France, Italy, and other countries. It is found in very important tertiary deposits as *rock-salt*, and abounds in Wielezka in Poland, in Austria, Spain, England, and Roumania, but more especially at Stassfurt, where there are immense deposits which extend over kilometres of surface and have a thickness at certain points of 500, 900, and even 1500 metres. It is also found in moderate quantities in Sicily.

We have discussed the manner in which these immense deposits were formed, in connection with Stassfurt salts (*see* p. 424), and we still see similar deposits being continuously formed to-day in the regions south of the Dead Sea, which contains up to 8 per cent. of NaCl (*see* Analysis, p. 209).

When these are pure it is obtained directly from the large rock-salt deposits by the ordinary methods of mineral mining, that is, by excavating galleries and carrying the salt to the surface in blocks.

If the rock-salt deposits are at a great depth (1000 to 2000 metres) or if the salt is impure, that is, mixed with earth, gypsum, &c., the sodium chloride is extracted by water, by drilling wells and removing the saturated solution, which is then evaporated in order to recover the crystallised salt.

In the hot countries of the Mediterranean basin, salt is extracted from sea water which is evaporated by means of the sun's heat, in a series of flat and very large basins excavated in the earth and communicating with one another, the so-called *salt-pans*. The water enters into the first basins at high tide, and in these the less soluble impurities and suspended matter (gypsum, clay, calcium carbonate, iron, &c.) are deposited. It then passes into the

[1] **Analysis of sodium hydroxide.** In order to determine the commercial value of a consignment of caustic soda it is necessary to take great care in the selection of the sample by removing several pieces from various parts of the molten block immediately after the vessel containing it has been opened and the block broken up. The pieces, amounting altogether to at least a kilo, are immediately placed in a dry glass vessel closed with a good stopper of glass or of paraffin-coated cork, so that they may not absorb moisture and carbon dioxide from the air.

The larger pieces are rapidly broken up before analysis and about 20 grms. are placed in a weighing-bottle with a ground-glass stopper. This is carefully weighed and the contents are poured into a graduated litre flask and the caustic soda dissolved in freshly boiled distilled water, the weighing-bottle being reweighed; from this solution various portions are taken for the determination of impurities (sulphates, chloride, &c.) and of the strength in sodium hydroxide and sodium carbonate, exactly as is indicated below for the analysis of sodium carbonate; thus 20 c.c. of the solution may be titrated almost at the boil with $\frac{N}{2}$ hydrochloric acid in presence of itmus as an indicator; 1 c.c. of $\frac{N}{2}$ acid corresponds to 0·02 grm. of NaOH or 0·0265 grm. of Na_2CO_3. This first result gives the total alkalinity which for the moment may be calculated into Na_2CO_3; 20 c.c. of the solution of caustic soda are then treated with an excess of barium chloride solution (5 c.c. of 10 per cent. solution) and the volume made up to 100 c.c. with water; the carbonate which is always present in more or less amount in caustic soda is thus precipitated and sodium hydroxide alone remains in solution; 50 c.c. of the clear solution are removed and titrated with $\frac{N}{2}$ acid in presence of methyl orange or phenolphthalein; by calculating this second result as NaOH we have the contents of true sodium hydroxide. By calculating this into sodium carbonate and subtracting it from the total alkalinity found by the preceding test, the quantity of sodium carbonate contained in the sample is found.

The quantities found in 20 c.c. of solution are re-calculated into weights per 100 grms. of the sample under examination.

The strength is ordinarily expressed in English degrees, that is, in percentages of Na_2O; the German degrees and the Descroizilles degrees will be explained below in connection with the analysis of sodium carbonate.

The water is determined by difference, because direct determinations by heating in an oven are not exact, and it is more accurate to determine the carbonate, hydroxide, iron, alumina, sulphates and chlorides, the rest being water. The composition of a commercial caustic soda manufactured by the firm of Solvay of 76° to 77° strength was as follows: Na_2O = 76·1 per cent. (= 95·203 per cent. of NaOH), Na_2CO_3 = 1·82 per cent., Al_2O_3 + Fe_2O = 0·017 per cent., NaCl = 1·93 per cent., SO_4Na_2 = 0·48 per cent., water 0·55 per cent.

so-called concentrating pans, where it is partially evaporated up to 25° Bé., and separates pure crystallised salt. The remaining solution is concentrated in successive basins where a mixture of sodium chloride and magnesium sulphate is deposited, and finally from the last mother liquors a further mixture of potassium chloride, magnesium chloride, and varying quantities of potassium bromide and iodide is obtained. These salt-pans sometimes occupy a surface of hundreds of acres. The salt pans of Comacchio in Ferrara produced about 16,000 tons of salt in 1909, and those of Cervia in Ravenna 15,000 tons, those of Margherita di Savoia 45,000 tons, and those of Corneto Tarquinia from 3000 to 5000 tons. The salt-pans of Sicily yield 140,000 tons and more. The Sicilian salt-pans yield three to five complete crystallisations per annum, and produce 220,000 tons in all, without including 20 rock-salt mines.

In cold countries sea water is allowed to freeze in winter, by which means ice almost free from salt is separated, and this operation is repeated until a concentrated solution is obtained which is then evaporated over direct flame in large pans, or, as in Stassfurt, it is evaporated in Pick triple-effect vacuum pans, based on the principle of Rillieux and

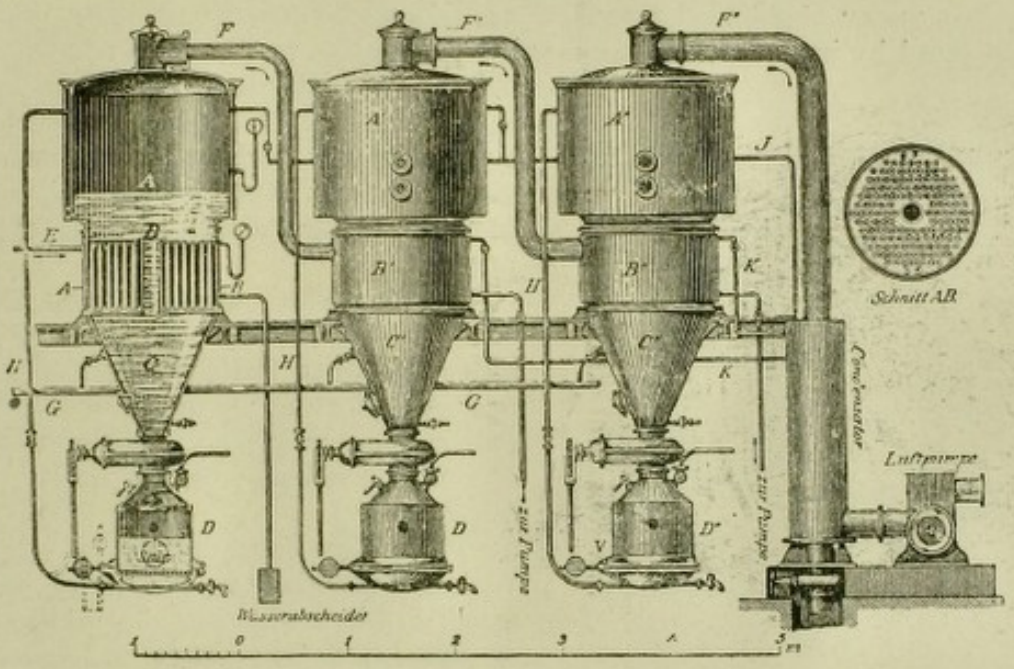


FIG. 189.

of Robert (*see also* Sextuple-Effect Apparatus, p. 443, *and* vol. ii, "Organic Chemistry," section on Sugar): the salt solution enters the first boiler (Fig. 189), where its boiling-point is lowered by diminishing the pressure by means of a pump, and on then heating by a bundle of tubes, *B*, in which steam circulates, which proceeds from the boiler through the tube, *E*, evaporation takes place; the steam which escapes from the first boiler, *A*, has a temperature below 100°, and, passing through the tube, *F*, it heats the solution contained in the second boiler, *A'*, where the pressure is still less than in *A*, and thus this liquid boils at a still lower temperature; the vapours which escape from *F'* and which have again a still lower temperature serve to boil the salt solution in the third boiler, *A''*, in which a still higher vacuum is produced by the pump and by condensing the vapours from *F''* by means of a jet of water. The solution enters the boilers through the tube, *G*, and as the salt gradually crystallises it passes into vessels, *D*, which are provided with a perforated false bottom which retains the salt whilst the mother liquor returns to the boiler through the tube, *H*. Every two or three hours the salt is discharged from the chamber, *D*. A small Pick apparatus produces one ton of salt per twenty-four hours. It must, however, be noted that in these and other forms of apparatus for concentrating saline solutions, serious trouble is caused by the incrustations of calcium sulphate produced by the gypsum dissolved in the salt water. In 1898 Vis patented a process for avoiding this difficulty by effecting separation of the gypsum from the brine by the addition of $CaCl_2$ or Na_2SO_4, **that is, of two very soluble salts which cause a concentration of Ca or SO_4 ions, and therefore separation of the calcium sulphate (pp. 99 and 432).**

In certain parts of Germany saline solutions are concentrated by so-called gradation, which consists in repeatedly pumping the salt water to the top of a framework 10 metres or more high (Fig. 190), filled with bundles of thin twigs. The solution falls from the top in a finely divided shower, passing over a large evaporating surface formed by the wooden twigs. Evaporation is helped by the sun and wind, but much salt (20 to 30 per cent.) is lost by passing away into the air. When the liquid has acquired a certain concentration it is finally evaporated in boilers or preferably in Pick vacuum pans.

In 1895 Hirsel proposed the separation of salt from concentrated solutions by cooling them to $-10°$ or $-20°$, so causing almost complete crystallisation of the salt, as $NaCl.2H_2O$, which is then dehydrated.

PROPERTIES. Sodium chloride crystallises in transparent cubes of sp. gr. 2·13, which sometimes form hollow quadratic pyramids formed of little steps. Its solubility is almost the same in hot or cold water; thus at ordinary temperatures 26 per cent. are dissolved, and 28 per cent. at 100°. The saturated solution separates large monoclinic tablets of $NaCl + 2H_2O$ at $-10°$, which lose water at 0°, and are then transformed into cubes. The degrees Bé. indicated by hydrometers immersed in salt solutions also indicate the percentage of salt directly. It melts at 815°, boils at 1750°, and evaporates at a white heat. On heating, salt decrepitates, because the interstitial water inclosed by the small crystals evaporates.

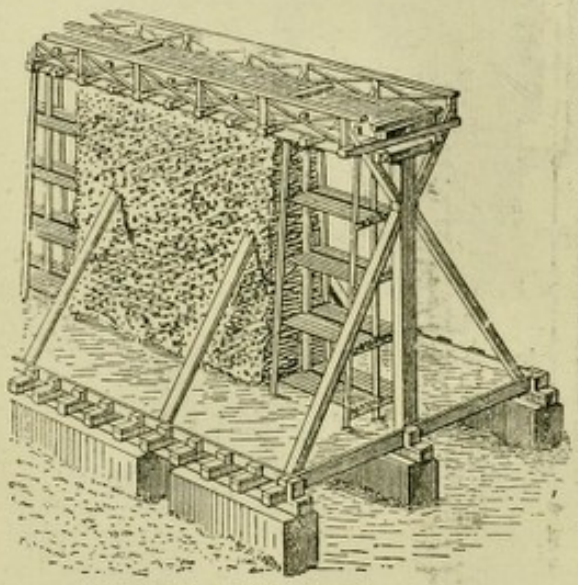


Fig. 190.

Cooking salt contains from 2 per cent. to 5 per cent. of moisture and also sometimes 0·5 per cent. of magnesium chloride, magnesium sulphate, and calcium sulphate; the magnesium chloride renders cooking salt deliquescent.

From the consumption of salt in various countries the degree of industrial development and of civilisation of the inhabitants may be deduced; thus the more civilised nations have greatly reduced or abolished the State monopoly of this product, which is a prime necessity for the people.

The Table on the opposite page shows the production and consumption of salt in various countries, the difference between the consumption and production being due to the increase of industries, to exportation or to importation. A further column shows the mean annual consumption per inhabitant, including the salt used for both industrial and alimentary purposes. The figures refer to 1896.

These figures are disconcerting from the Italian point of view, because they place Italy almost at the tail of civilised nations, salt being not only a condiment for the gourmet but a substance which is indispensable for the proper assimilation of food, because it is necessary for the production of the hydrochloric acid of the gastric juice; each healthy individual therefore requires at least 8 kilos of salt per annum merely for the performance of normal physiological functions.

It must also be remembered that the pre-eminently carnivorous populations of England, Belgium, and France already obtain a portion of the salt which they require in the meat which they eat, whilst the Italians, and especially the inhabitants of the open country, are mainly vegetarians, and therefore require larger quantities of salt than the inhabitants of other countries. And since the exact opposite is the case, that which could reasonably be expected happens, and explains the sad pre-eminence of Italy in those who suffer from pellagra.

In Italy, rock-salt, which costs less than 8*s*. per ton at the mine, actually costs £1 4*s*.

	Total production in tons	Total consumption in tons	Annual consumption per inhabitant in kilos			Sale price of edible salt per kilo
			Total	For industrial purposes	For alimentary purposes	
	1896	1896	1896	1896	1896	Pence
England and Ireland .	2,146,850	1,656,500	43·7	31·2	12·5	1·06
Belgium . . .	100,000	202,700	34·0	—	—	—
United States of America .	1,261,600	1,497,700	23·8	8·8	15·0	
France . . .	842,500	809,500	21·5	16·3	5·2	2·40
Germany . . .	1,049,640	871,140	17·6	9·9	7·7	2·40
Switzerland . .	40,000	48,000	16·4	—	—	1·92
Russia . . .	1,392,000	1,392,000	12·3	4·0	8·3	0·96
Austria-Hungary .	467,240	478,600	11·5	3·7	7·8	
Italy . . .	451,800	192,412	7·1	0·7	6·4	3·84
Spain . . .	320,900	158,100	9·0			2·11
China . . .	1,648,000	1,800,000	5·0			
Total for the whole earth	13,241,800	13,241,800	8·9	—	—	—

for certain industries, £4 16*s.* for agricultural use, and £16 (or £28 if refined) for human consumption, on account of the Government tax.[1]

In 1904 Germany produced 1,080,000 tons of rock-salt valued at £250,000 and 621,800 tons of sea-salt of the value of £760,000. In 1908 Germany produced 1,332,000 tons of rock-salt valued at £280,000 and 665,600 tons of cooking salt of the value of £880,000 obtained from solutions or saline springs.[2] France possesses rock-salt deposits 10 to 70 metres thick, which occupy an area of 400 sq. kilometres. In 1908 France produced 143,000 tons of rock-salt and 593,000 tons of salt from saline springs. In 1904 Spain exported 350,000 tons of salt at 5*s.* 5*d.* per ton, of which 300,000 tons were sea-salt, three-quarters of which were produced at Cadiz.

A very large quantity of salt is consumed industrially and for agricultural purposes (cattle salt).

APPLICATIONS. Salt is used for many industrial purposes; for the manufacture of sodium carbonate and hydroxide, dyestuffs, soaps, glassware, chlorates, hypochlorites, coal-tar dyestuffs, &c. In certain cases the Government assist the consumption by diminishing the price after denaturation of the salt in such a manner that it cannot be used for human consumption (this, of course, does not apply to England). According to the various industrial purposes to which it is applied various denaturating substances are added

[1] The total production of salt in Italy in 1871 was 267,000 tons and 458,497 tons in 1902, of which only 35,000 tons were rock-salt; in 1908 473,857 tons of sea-salt were produced, and in 1907 18,638 tons of salt from the springs at Volterra and 600 tons from Salsomaggiore; whilst in Sicily 31,540 tons of rock-salt were mined in 1907 of the value of £21,120, and 27,100 tons in 1908. The total exports of salt from Italy in 1908 were 85,500 tons, and the imports were 26,100 tons; in 1902 Sicily and Sardinia exported 145,000 tons at a price of 6*s.* per ton.

The industrial consumption in Italy in 1904 has been estimated at 16,514 tons in the alkali industry and for the smelting of metals (produced in Sicily and denaturated and thus freed from tax, so that it costs about £1 per ton), 6114 tons denaturated for various industries at £4 16*s.* per ton, 7708 tons for agricultural use at £4 16*s.* per ton, 3631 tons for cold storage at £8 per ton, 470 tons for salting fish at £6 per ton, and about 5000 tons denaturated for the soap industry at £4 16*s.* per ton. The price of edible salt in Italy in 1848 was 3*d.* per kilo, after 1869 it was 5½*d.*, after 1884 3½*d.*, and since 1894 4*d.*

[2] In Germany 956,436 tons of industrial salt were consumed in 1908, of which 800,000 tons were rock-salt, and 15,000,000 hectolitres of brine (680,000 gals.) were used in various industries. The solid industrial salt was used for the following purposes: 115,418 tons for cattle; 530,000 tons for the production of soda and Glauber salt (sodium sulphate); 123,650 tons in the manufacture of dyestuffs and chemical products; 14,720 tons in soap works and in the refining of oil; 14,200 tons in tanneries; 45,200 tons for salting fresh hides; 22,100 tons for metallurgical purposes; 9100 tons in the manufacture of earthenware; 76 tons in glassworks; 1830 tons in paper mills; 4637 tons in wool-combing and in textile factories; 11,000 tons for ice manufacture and cold storage 8110 tons for the removal of ice from tramways during frost.

(abroad), such as colouring matters, sodium disulphate, iron oxide, coal, petroleum, evil-smelling substances, &c.

SODIUM BROMIDE and **IODIDE**: **NaBr** and **NaI**. The former melts at 760° and the latter at 690°. The bromide is slightly soluble in alcohol, the iodide very soluble. At temperatures below 30° they both crystallise with $2H_2O$. They are used in medicine and have a similar action to the potassium salts.

SODIUM CHLORATE: $NaClO_3$, which is now obtained electrolytically, and sodium perchlorate, $NaClO_4$, are more soluble in water than the corresponding potassium salts, and may be economically substituted for them for certain industrial purposes. The methods of preparation are similar to those of the corresponding potassium salts (*which see*). In 1908 Italy produced 220 tons at £32 to £36 per ton at Bussi (Società elettrochimica of Rome), by electrolysing sodium chloride in the preparation of NaOH and Cl from hot solutions of NaCl.

SODIUM IODATE: $NaIO_3$, which also exists with $3H_2O$. This compound is found in Chili saltpetre, from which it is now removed because it appears to be harmful to vegetation when the nitrate is used as a manure. A periodate, $NaIO_4.3H_2O$, and superiodate, $IO\begin{matrix}(ONa)_2\\(OH)_3\end{matrix}$ are also known; they have no practical importance, but confirm the variable valency of the halogens.

ALKALI HYPOCHLORITES (BLEACHING SALTS)

Hypochlorites of the alkali metals are formed, together with the chlorides, by passing Cl into a cold solution of sodium hydroxide, but it should be observed that excess of chlorine must not be added because hypochlorous acid is then formed, which is less stable, and on heating chlorates are produced:

$$2NaOH + 2Cl = NaCl + H_2O + NaOCl.$$

The hypochlorites have a sweetish, disagreeable smell; they are caustic and already decompose under the influence of sunlight, and more easily on heating, forming oxygen, chlorides, and chlorates, as is shown in the following equations:

(1) $3ClONa = 2NaCl + ClO_3Na$. (2) $2ClONa = 2NaCl + O_2$.

In presence of an excess of alkali hydroxide, the hypochlorites are stable even at a temperature of 50°.

The hypochlorites slowly oxidise and destroy organic dyestuffs; the action is much more rapid and energetic if hypochlorous acid is liberated by means of other very weak acids, such as carbon dioxide. If an excess of a strong acid is employed then the oxidising hypochlorous acid is not liberated, but chlorine is formed instead, as was stated above:

$$NaOCl + 2HCl = H_2O + NaCl + Cl_2.$$

POTASSIUM and **SODIUM HYPOCHLORITES**: **KOCl** and **NaOCl**, are employed for bleaching vegetable fibres (cotton, linen, &c.), under the name of *Eau de Javelle* for the former and *Eau de Labarraque* for the latter.[1] The latter is more economical and is also prepared by the double decomposition of dissolved calcium hypochlorite and sodium carbonate or sulphate; insoluble calcium carbonate or sulphate is formed and sodium hypochlorite remains in solution. It is now obtained by direct electrolysis in the cold of dilute solutions of sodium chloride without employing diaphragms, allowing the products of the electrolysis (Cl + NaOH) to mix, so that dilute solutions of sodium hypochlorite result directly with evolution of hydrogen: $NaCl + H_2O + \text{electric current} = NaOCl + H_2$.

[1] After Scheele had discovered chlorine in 1774 Berthelot immediately noted the bleaching properties of this gas and tried to employ it practically in aqueous solution. In 1789 at Javelle, near Paris, another liquid for bleaching purposes was prepared by passing chlorine into a solution of potassium hydroxide. In 1798 Tennant, in England, obtained a liquid for bleaching purposes by passing chlorine into milk of lime. In 1799 Tennant further found that by the action of chlorine on solid calcium hydroxide a solid product was obtained which was much more stable and easier to transport. The industrial importance of chloride of lime or bleaching powder dates from that time.

For this purpose various small forms of apparatus are constructed which are adapted for the use of individual bleaching works. The first plant was the Hermite plant (1883), with cathodes formed of zinc discs alternating with anodes of platinum gauze and a bath of magnesium chloride and hydroxide. This had many drawbacks and was gradually replaced by more practical forms of plant, amongst which the best is that which has been devised of recent years by Kellner and is illustrated in Fig. 191. Alternate positive and negative electrodes are placed parallel to one another in an earthenware vessel, *a b*: they consist of a series of ten to twenty glass plates surrounded by iridio-platinum wire. The first and last electrodes where the current enters and escapes are entirely constructed of iridio-platinum gauze. By means of a pump, *g*, the solution of NaCl is forced in from the vessel, *h*, through the apertures, *e* and *f*, into the interspace between the individual plates of the electrodes which form so many individual baths, and on passing the current electrolytic dissociation occurs in each chamber with an E.M.F. of 5 volts; and, therefore, if there are 10 chambers in the battery a total E.M.F. of 50 volts will be required. By means of the pump, *g*, the solution is continually circulated, passing from the upper receiver to the lower through a tube which is not shown in the figure. In the lower vessel a coil is placed through which cold water circulates in order to prevent the temperature from rising above 20° to 25°. The formation of chlorate, which has no bleaching action, is thus avoided. In an ordinary apparatus, using a solution of 110 kilos of salt in 1 cu. metre of water, a current of 120 amps. is required. The electrodes finally become covered with a little gypsum contained in the salt, and then increase the internal resistance considerably so that the liquid becomes heated. This trouble is overcome by reversing the direction of the current now and again by changing the poles; the deposit then passes into solution.

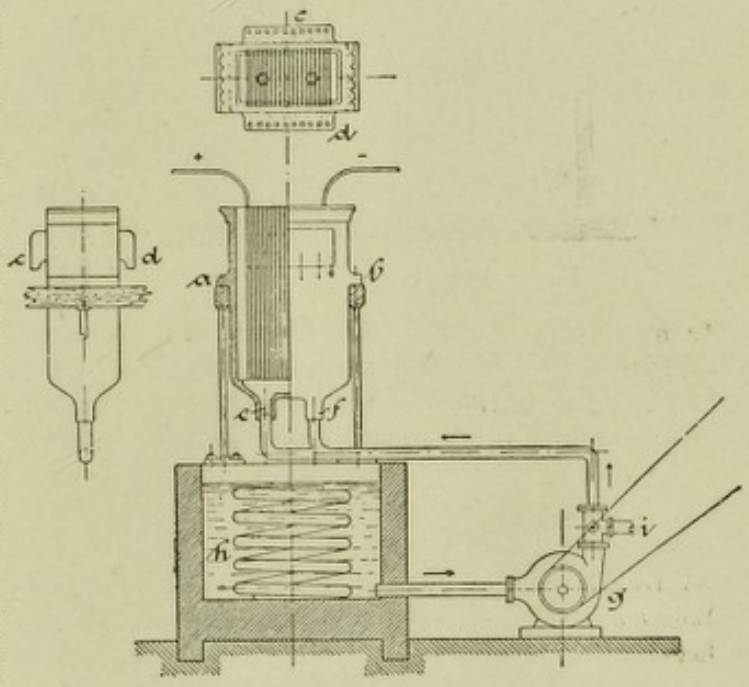


FIG. 191.

Another form of apparatus brought out by Haas and Oettel in 1900 gives good results. A dilute solution (10 per cent.) of sodium chloride is ordinarily employed, because a solution of hypochlorite containing 1·3 grms. of chlorine per 100 c.c. is sufficiently strong, as solutions containing only 0·2 per cent. of active chlorine are effective for bleaching; these solutions are more stable in the dark than when exposed to the light.

Electrolytically produced solutions of sodium hypochlorite are more active than solutions of bleaching powder, even for equal strengths of active chlorine, because a portion of the hypochlorous acid in the electrolytic solutions is present in the free state, and is much more energetic; on electrolysing solutions of calcium chloride, $CaCl_2$, solutions containing much free HOCl are also obtained. In order to determine the quantity of this free acid, and, therefore, the quality of the bleaching liquid, it is treated with carefully neutralised hydrogen peroxide and the hydrochloric acid so formed is titrated. HCl is formed by the hypochlorous acid and not by sodium hypochlorite, as is seen by the following equations:

$$NaOCl + H_2O_2 = NaCl + H_2O + O_2.$$
$$HOCl + H_2O_2 = HCl + H_2O + O_2.$$

Kellner has also constructed apparatus for bleaching textiles continuously and directly in an electrolytic bath (Fig. 192) by passing the fabric continuously between alternating electrodes, *c* and *c'*, supported by glass rods. The fabric passes continuously over rollers, *F*, and is alternately immersed in the bath and withdrawn.

A plant for electrical bleaching with sodium hypochlorite corresponding to a bleaching works which uses 900 kilos of bleaching powder per twenty-four hours would require 100 h.p., and the daily expenses would be about £3 8*s*. including labour, power, amortisation, interest, and one ton of salt at £1 per ton. The relative advantage compared with the use of bleaching powder varies with the price of the latter, but it is necessary to remember that the sodium hypochlorite solution is more effective.

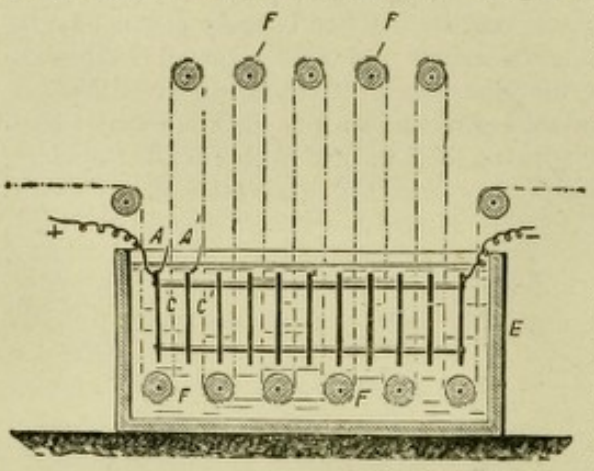


FIG. 192.

SODIUM NITRATE: $NaNO_3$ (CHILI SALTPETRE)

This is found in great abundance in that part of Chili which is adjacent to Peru (Province of Tarapacà), and in Bolivia, mixed with soil and covered by layers of clay, gypsum, and sodium chloride 1 to 3 metres in depth. The earthy mass from which it is extracted is called *caliche*; it contains from 15 to 55 per cent. of the nitrate and ordinarily 40 per cent. over a distance of 200 to 300 kilometres, and of a thickness of 1 to 5 metres. The *caliche* also contains as impurities sodium perchlorate, sodium iodate (up to $\frac{1}{2}$ per cent.), a little potassium nitrate, and much sodium chloride (up to 20 per cent.).

The origin of these important deposits must be sought in the decomposition of enormous accumulations of nitrogenous organic matter in the presence of strong bases (lime, magnesia, soda, &c.), and also in the action of nitrifying bacteria (p. 301). The organic matter must have been of vegetable origin, because in these nitrate deposits phosphates are never found. The nitrate layers remain unaltered in these regions because rain is very rare and sometimes does not occur for two or three successive years.

The *caliche* is ground and lixiviated with hot water and the solution is then concentrated in large iron pans heated by steam coils and the nitrate crystallises on cooling in numerous vessels exposed to the open air. A crude commercial product is thus obtained for fertilising purposes, &c., which contains 95 per cent. of $NaNO_3$ and 1 to 2 per cent. of NaCl. Sometimes it contains up to 1 per cent. of sodium perchlorate, which is injurious to vegetation. The mother liquors are utilised for the preparation of iodine (*see* p. 153). At one time only *caliche* containing more than 25 per cent. of nitrate was treated. To-day, with improved modern plant, a 15 per cent. raw material is treated.

In order to remove the chlorate which it sometimes contains from the crude Chili nitrate, the nitrate is dissolved in the cold with the exact quantity of water corresponding to its solubility, and the chlorate thus remains undissolved because it is less soluble.

We have already recorded on p. 303 *et seq.* the processes which are now used for the utilisation of atmospheric nitrogen and preparation of nitrogenous substances capable of replacing nitrate for agricultural purposes.

According to Fr. Pat. 398,738 of 1909, the nitrites which are always formed in the process of electrolytic fixation of nitrogen may be completely transformed into nitrates by heating them to about 300° in presence of NO_2, thus:

$$Ca(NO_2)_2 + 2NO_2 = Ca(NO_3)_2 + 2NO,$$

and the latter regenerates NO_2 with the oxygen of the air.

Sodium nitrate crystallises in rhombohedra closely resembling cubes, hence the name of *cubic nitre* in contradistinction to *prismatic nitre*, under which name potassium nitrate is known.

It melts at 318°, is a little more soluble in cold water than potassium nitrate, 80 per cent. being dissolved by water at 0°, 90 per cent. at 20°, 111 per cent. at 50°, 168 per cent. at 100°, and 225 per cent. at 120°. It is somewhat hygroscopic and cannot, therefore, be used in gunpowder. It has a specific gravity of 2·20 and specific heat of 0·278.

STATISTICS, APPLICATIONS, AND PRICES. In 1860 225,000 tons were exported from Chili; in 1890 the exports were 1,000,000 tons; in 1900, 1,453,000 tons, of the value of £13,000,000; in 1904 the Chilian exports were more than 1,470,000, out of a total production of 1,550,000 tons, of which one-third was consumed in Germany, which in turn used one-fifth of the product for industrial purposes and four-fifths for agriculture. In 1908 the Chilian production was 1,800,000 tons, of which 350,000 tons were used in the United States, 650,000 were imported by Germany, 300,000 by France, 220,000 by Belgium, 130,000 by Holland, 145,000 by England, 60,000 by Austria-Hungary, and 60,700 by Italy, valued at about £640,000, and about 8000 tons by Spain. In 1890 Italy only imported 8506 tons and in 1906 about 32,500 tons. In view of this enormous consumption, which exceeded 2,000,000 tons in 1909, doubts arose as to whether the Chilian deposits might not soon be exhausted; various inquiries were made by private companies and by the Chilian Government, which resulted in artificially discordant figures, covering more or less dishonest speculations, and whilst, on the one hand, it was said that the still unexploited deposits could only yield a maximum of 100,000,000 tons of nitre, so that they would be exhausted in thirty to forty years, on the other hand the results of the inquiry which was made by the engineer Bertrand showed that up to June 1909 the presence of at least 250,000,000 tons of nitrate in deposits containing more than 15 per cent. had been proved. It is also supposed that in the regions which have not yet been definitely explored by the commission of inquiry, double or three times the quantities of nitrate exist, so that there can be no question of exhaustion for 100 or 150 years, even supposing that the annual consumption reaches 4,000,000 tons. We may add that nitrate deposits have been discovered in California containing about 20,000,000 tons of sodium nitrate; and other very important deposits have been found in the Argentine, but in localities which are not easily accessible.

In any case agriculture will sooner or later have to face the grave problem of a substitute for Chili saltpetre, although good practical results have already been obtained in the direction of the utilisation of atmospheric nitrogen (*see* p. 303 *et seq.*).

Sodium nitrate is mainly used for agricultural purposes, but also for the manufacture of sulphuric and nitric acids, the preparation of potassium nitrate, &c.

The effects produced by nitrate in agriculture are truly enormous, especially if the fertilisation is completed with superphosphates and potassium salts; in some localities the production is trebled. It is spread over the ground a little at a time to the amount of 100 to 130 kilos per hectare in all, as it is very soluble and is easily carried away by rain. The plants appear to assimilate the nitrate when it has been transformed into calcium nitrate in the soil (Grandeau).

Crude nitrate (95 per cent.) costs £8 16*s.* to £10 16*s.* per ton at the Port of Genoa; when refined by recrystallisation and powdered it costs double the amount; and chemically pure nitrate, three times the amount. When it is refined in Chili by simple clarification of the original hot solution it is whiter and contains 96 per cent. of nitrate; this quality is used industrially and only costs 8*s.* to 16*s.* more per ton than the crude product.

The price of nitrate has oscillated somewhat of late years on account of the trust formed by the producers, and of the export tax of £2 11*s.* 2*d.* per ton levied by the Chilian Government. At the port of Dunkirk nitrate cost £7 per ton in 1898; £8 4*s.* in 1901, £8 16*s.* in 1903, £10 in 1905, £10 16*s.* in 1908, £9 4*s.* in 1909, and £8 8*s.* in 1910; the trust ceased to exist in August 1909. The freight for nitrate from Chilian to European ports in sailing vessels is 12*s.* per ton, which is less than the freight from Genoa to Brescia.

ANALYSIS OF NITRATE. The moisture is determined by heating 50 grms. to 130° until the weight no longer decreases. The dry product is dissolved in water, filtered, the filter washed and dried and the quantity insoluble in water deduced from the residue remaining on the filter. The solution is diluted to one litre and the chlorine

of the chlorides determined in one portion by titrating it with a normal solution of silver nitrate. The sulphates are precipitated with barium chloride and the separated barium sulphate washed, ignited, and weighed. The perchlorates are determined in 10 grms. of nitrate in which the chlorides have already been determined. The sample is melted in a covered porcelain crucible with soda free from chlorine ; after 10 to 15 minutes no further bubbles of gas are evolved, and the mass is dissolved in nitric acid diluted, and the additional quantity of chlorine formed from the chlorates then determined with titrated silver nitrate solution ; the remaining matter is considered to be nitrate. Commonly, however, the strength of nitrate is determined with Lunge's nitrometer, of which we give an illustration in Fig. 193. 0·35 grm. of the nitrate is weighed and placed in the little open cup at the top of the Figure to the left ; the tube, *A*, has been previously filled with mercury by suitably raising the tube, *C*, which is also filled with mercury, and allowing the air to escape from *A* by means of the cock, *O*. As much air is allowed to enter *B* as corresponds to 100 c.c. of air at 0° and 760 mm. under the conditions obtaining at the time ; this will necessarily be more than 100 c.c., and is found from tables. By this means the necessity of reducing the volumes of the gas to 0° and 760 mm. afterwards is avoided. The nitrate is dissolved in a very small quantity of water, and by then lowering the tube, *C*, and opening the cock, *O*, the solution, but no air, is allowed to enter *A* ; 3 to 4 c.c. of strong sulphuric acid are poured in small portions into the small cup and allowed to enter *A* each time. The nitrate solution, acid, and mercury are then shaken strongly together, causing the nitrogen in the nitrate in the presence of concentrated sulphuric acid and mercury to be evolved in the form of NO gas. In order to read the volume of gas so formed the tube, *C*, is raised until the mercury in *B* reaches the 100 c.c. mark. *B* and *C* are then lowered simultaneously, until the mercury in *B* at the 100 c.c. mark is at the same level as the mercury in *A*, which contains the NO, and the volume which these occupy is read off, as it is now corrected to 0° and 760 mm. Each cubic centimetre of NO corresponds to 0·003789 grm. of $NaNO_3$. In the Figure a small bottle is also seen at the left-hand top corner which is connected with the nitrometer and is used when it is necessary to evolve gas outside the instrument, for example, in the analysis of H_2O_2 which evolves a definite volume of oxygen in contact with MnO_2.

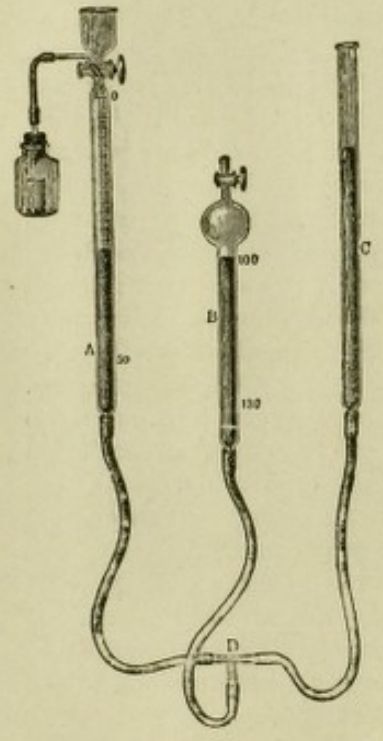


FIG. 193.

SODIUM NITRITE : $NaNO_2$. This compound is obtained by melting sodium nitrate in iron pans and adding portions of lead a little at a time, keeping the temperature between 450° and 500°, as otherwise the iron pan is destroyed. The molten lead should all be transformed into oxide. The fused mass is poured into water, neutralised with dilute sulphuric acid or nitric acid, as a little NaOH, &c., is formed, and the lead separates in the form of oxide. The aqueous solution of the nitrite is concentrated in open pans to 40° Bé., and is then poured into vessels in which it crystallises. In this way it is possible to transform as much as 93 per cent. of the nitrate into nitrite which is obtained fairly pure (up to 98 per cent.) by a further crystallisation.

A better yield is now obtained by mixing a concentrated solution of sodium nitrate with quicklime ; the solution is heated until it is saturated and a current of SO_2 free from air is then passed through :

$$NaNO_3 + CaO + SO_2 = SO_4Ca + NaNO_2.$$

Dittrich, on the other hand (Ger. Pat. 212,203 of 1908), reduces nitrate by mixing it to a paste with sawdust (charcoal and graphite produce a violent and irregular reaction) ; it is then melted in open pans, extracted with water, and the solution concentrated to 45° Bé. and allowed to crystallise.

A molten mixture of sodium nitrate and sodium hydroxide has also been used and heated to 300° to 400°, anhydrous sulphite being then added (*see* Potassium Nitrite).

During the manufacture of synthetic nitric acid by the electric process (p. 303) nitrite is obtained, and at Notodden in Norway 2700 tons were produced in 1904.

Sodium nitrite crystallises more easily than potassium nitrite and is not deliquescent.

Nitrites may be distinguished from nitrates by adding them to a hot concentrated solution of sodium hydrosulphite; nitrites evolve ammonia whilst nitrates remain unaltered.

Nitrates may be determined quantitatively, even in presence of nitrites and organic matter, by heating the mixture with a solution of ammonium chloride of known strength; the whole is then concentrated down to a few cubic centimetres, taken up with water and distilled in the presence of magnesia, the ammonia formed from the residual ammonium chloride which is not decomposed by the nitrite being collected in titrated sulphuric acid. The loss of ammonia, compared with that originally present in the ammonium chloride which was added, allows the quantity of nitrite to be calculated; nitrates do not react.

Sodium nitrite may also be determined when mixed with nitrates by the method of W. M. Fischer and Steinbach (1910), by adding methyl alcohol and then dropping in a known volume of titrated sulphuric acid, and passing a current of air through the mixture which carries over the methyl ether of nitrous acid which is instantaneously and quantitatively formed and boils at $-11°$.

Maderna and Coffetti (1908) measure the quantity of nitrogen dioxide which is formed on treating the mixture with potassium ferrocyanide in presence of acetic acid in Lunge's nitrometer; this is formed from the alkali nitrite, while the nitrates remain unchanged. In order to avoid errors in reading the volume of gas, due to the vapour tension of acetic acid, they have replaced this latter by a concentrated solution of citric acid.

The strength of nitrites in general is determined with a titrated solution of potassium permanganate according to Lunge, the estimation being based on the reaction recorded on p. 336. It is much used in azo dyestuff works, and in dyeing for the diazotisation of various colours on the fibre—cotton, silk, &c. (*see* vol. ii, "Organic Chemistry").

Commercial sodium nitrite costs about £34 per ton; the chemically pure fused product in sticks costs 3*s*. 3*d*. per kilo.

Germany is the largest consumer of sodium nitrite, on account of the great importance of its aniline dyestuff factories, and has to supplement its own production by considerable imports, which were 1617 tons in 1908 and 2634 tons in 1909, the exports being 754 tons.

SODIUM SULPHATE: Na_2SO_4

This compound is found ready formed in large saline deposits in Spain (Toledo), at Tiflis, in Siberia, in Sicily, both with and without water of crystallisation and in many mineral waters. It is found crystallised without water in the form of *thenardite*, Na_2SO_4, and with water as *mirabilite* or *Glauber salt*, $Na_2SO_4.10H_2O$. It is found at Stassfurt in monoclinic crystals as *glauberite*, $Na_2SO_4.CaSO_4$. There are important Glauber salt deposits in Italy in the Province of Caltanisetta. An American company has proposed the utilisation of natural sodium sulphate from the Caspian Sea by the manufacture of sodium carbonate and hydroxide on the spot, as is already done with the Glauber salt deposits in Eastern Siberia.

It is also obtained from the mother liquors of sea-salt, which contain

magnesium sulphate and NaCl; this solution separates sodium sulphate by double decomposition on evaporation and cooling.

At Stassfurt it is produced in a regular industrial manner by utilising the mother liquors from the treatment of carnallite or kieserite, which still contain about 25 per cent. of magnesium sulphate and 50 per cent. of sodium chloride. These solutions are evaporated to a concentration of 34° Bé., at a temperature of 33°; they are then allowed to crystallise during the cold winter nights in large tanks (28 metres × 22 metres × 21 cm. deep):

$$MgSO_4 + 2NaCl = Na_2SO_4 + MgCl_2.$$

The crystals which separate contain 10 mols. of water. On starting directly from solutions of magnesium sulphate, instead of using the theoretical proportions, $MgSO_4$ and 2NaCl (that is, about 100 to 100), the double quantity of NaCl is used, namely, 100 kilos of $MgSO_4$ and about 200 kilos of NaCl; in this way a more complete separation of sodium sulphate is obtained although only about half of the magnesium sulphate is transformed into the sodium salt.

The greater part of commercial sodium sulphate is produced in the Leblanc soda works or hydrochloric acid works by heating sodium chloride with sulphuric acid in furnaces (*see* p. 160). It is also obtained by the Hargreaves-Robinson process (*see* p. 164).

When pure sodium sulphate is required crude sulphate is dissolved in boiling water to saturation; the acid which is present is then neutralised with milk of lime, and a solution of chloride of lime is added with vigorous stirring until all the iron is precipitated. The hot solution is poured into lead-lined wooden vats. Crystals of $Na_2SO_4.10\,H_2O$, containing 56 per cent. of water of crystallisation, are thus obtained in large or in small pure crystals according to whether the solution has been cooled slowly and quietly or rapidly with stirring.

The anhydrous sulphate is easily obtained by Pechiney's method, by heating the crystallised salt to 40° to 50°, when it melts in its water of crystallisation to a supersaturated solution, and then adding $MgSO_4$ or NaCl or a mixture of these two salts. On stirring, the anhydrous sulphate then separates because the concentration of the SO_4'' anions or Na' cations has been increased (*see* p. 99). By the action of 16 parts of NaCl on 100 parts of Glauber salt 90 per cent. of the latter is separated as the anhydrous sulphate; in certain cases this operation is carried out in order to economise cost of transport. A partial dehydration may also be obtained by letting the finely crystallised or powdered Glauber salt stand in the air for some time, stirring it up repeatedly. The phenomenon of efflorescence then allows the anhydrous salt to be obtained because the tension of the water vapour of the crystallised salt is larger than the mean vapour tension of the moisture in the air and thus the water of crystallisation evaporates; anhydrous sulphate obtained in this way is lighter and very voluminous. This very economical process can be carried out with advantage in hot climates such as that of Sicily, so that the sulphate may become lighter and may be carried a long distance with small expense.

Sodium sulphate crystallises from cold aqueous solutions at temperatures below 30° in large monoclinic, colourless, and transparent crystals, $Na_2SO_4 + 10H_2O$, containing 56 per cent. of water, which become covered with a white powder of anhydrous sodium sulphate by efflorescence in the air. At 34° this Glauber salt melts in its own water of crystallisation and a portion of the anhydrous sulphate separates. This melts at about 886°. The varying solubility of this salt with alteration of the temperature, which acquires a maximum at 34°, is of interest.

100 parts of water at		0°	dissolve	12	parts of	$Na_2SO_4 + 10H_2O$	
,,	,,	18°	,,	48	,,	,,	,,
,,	,,	25°	,,	100	,,	,,	,,
,,	,,	30°	,,	200	,,	,,	,,
,,	,,	34°	,,	354	,,	,,	,,
,,	,,	50°	,,	263	,,	,,	,,
,,	,,	100°	,,	238	,,	,,	,,

Since the solubility diminishes above 34° we must suppose that above this temperature the molecules of $Na_2SO_4.10H_2O$ are decomposed with separation of the anhydrous sulphate, and that the solubilities above 34° therefore refer to anhydrous sodium sulphate, Na_2SO_4. This phenomenon has not yet, however, been satisfactorily explained theoretically.

The fact is also interesting that a saturated solution of sodium sulphate at 34° may be cooled down to the ordinary temperature without the smallest trace of separation of the crystals, even on shaking the solution strongly, in spite of the fact that its solubility at that temperature is much less. The solution is, therefore, extraordinarily supersaturated and in a metastable condition.

If, however, to this supersaturated solution, which must be kept in flasks which are closed with a stopper or with a plug of cotton-wool, a trace of atmospheric dust or any body which has been in contact with the air, such as a glass rod, is introduced, the solution immediately becomes solid forming a compact crystalline mass (labile phase of the supersaturated solution), and a certain quantity of heat is developed because in general substances in the liquid state or in solution have a higher latent heat than when in the solid state. Crystals of $Na_2SO_4 + 6H_2O$ sometimes separate from the supersaturated solution at 10° ; they easily decompose in the air, forming anhydrous Na_2SO_4.

APPLICATIONS. The greater portion of the sodium sulphate which is produced is employed in the manufacture of sodium carbonate by the Leblanc process. It is used in the manufacture of glass, ultramarine, and also to a considerable extent in dyeing with coal-tar dyestuffs, also in freezing mixtures, and in order to transform organic calcium salts into sodium salts. It is used in medicine and for animals as a purgative.

The commercial price of crystallised sodium sulphate containing 56 per cent. of water of crystallisation is from £1 12*s.* to £2 per ton.

In 1905 Germany produced 68,455 tons and exported 4847 tons of sodium sulphate at £1 10*s.* per ton ; in 1909 it exported 9023 tons and imported 7453 tons ; in 1909 Russia produced 70,000 tons ; in 1893 Italy produced 4900 tons of the anhydrous sulphate and 1000 tons of crystals ; in 1902 it produced 5300 tons of the anhydrous sulphate and 2820 tons of crystals (Glauber salt) ; the former was used for glass-making, the latter for dyeing ; in 1908 the production was 11,500 tons of anhydrous sulphate valued at £22,732, and 6542 tons of Glauber salt valued at £11,858 ; in 1904 Italy imported 9790 tons of anhydrous sulphate at £1 12*s.*, which was mainly supplied by Marseilles for use in the glassworks of the East Italian coast. In 1908 the imports rose to 17,836 tons, of which four-fifths were supplied by France and one-fifth by England.

SODIUM DISULPHATE : $NaHSO_4$ (Acid Sodium Sulphate, Primary Sodium Sulphate, Sodium Hydrogen Sulphate, Sodium Disulphate). This compound is formed by the action of sulphuric acid on NaCl or on the neutral sulphate at moderate temperatures.

It is formed industrially during the first phase of the decomposition of NaCl by H_2SO_4 in the manufacture of HCl, but it is more especially obtained in the manufacture of nitric acid (p. 339) from sodium nitrate and sulphuric acid, but always retains a little sulphuric acid :

$$NO_3Na + H_2SO_4 = NO_3H + SO_4HNa.$$

It crystallises from aqueous solutions at the ordinary temperature with one molecule of H_2O. Its chemical behaviour is analogous to that of potassium disulphate. Its solution has a strongly acid reaction because the SO_4H' anion is dissociated in turn into SO_4'' and $H^{\cdot}$.

It is used as an acid flux at high temperatures and often replaces sulphuric acid in dyeing, so that the acid action of the dye-bath may take effect gradually, as this is more advantageous in certain cases in order to obtain uniform shades on wool.

Nitric acid works are often embarrassed by the large quantities of sodium disulphate which cannot be utilised, in spite of the fact that every 100 kilos corresponds to 60 kilos of sodium sulphate or 35 kilos of sulphuric acid ; in

Germany this bisulphate is valued at 10*s*. per ton. Certain works situated near the coast get rid of it by dropping it into the sea. It might, however, be profitable to mix it with the required quantity of sodium chloride and heat it in the usual hydrochloric acid pans or in cast-iron cylinders in order to obtain sodium sulphate and hydrochloric acid. It is sometimes mixed with sand and the mixture heated in furnaces in order to obtain concentrated sulphuric acid and sodium sulphate (*see also* Note, p. 343).

In 1908 Italy produced 1600 tons of sodium disulphate of the value of £2560.

SODIUM SULPHITE : Na_2SO_3. This compound is prepared as follows : A measured quantity of aqueous sodium hydroxide solution is saturated with SO_2 and acid sodium sulphite is thus formed. A quantity of sodium hydroxide solution equal to that already taken is then added, which transforms the disulphite into neutral sulphite, Na_2SO_3, which crystallises out on cooling as $Na_2SO_3 + 7H_2O$. Instead of the sodium hydroxide solution sodium carbonate solution may be employed. In this case dicarbonate is first formed which then evolves CO_2.

Sodium sulphite is a *reducing agent*, as it easily abstracts oxygen from other substances forming sodium sulphate. The presence of traces of certain substances (negative catalysts, p. 68) sometimes suffices, however, to prevent the oxidation of the sulphite ; traces of mannite act in this way.

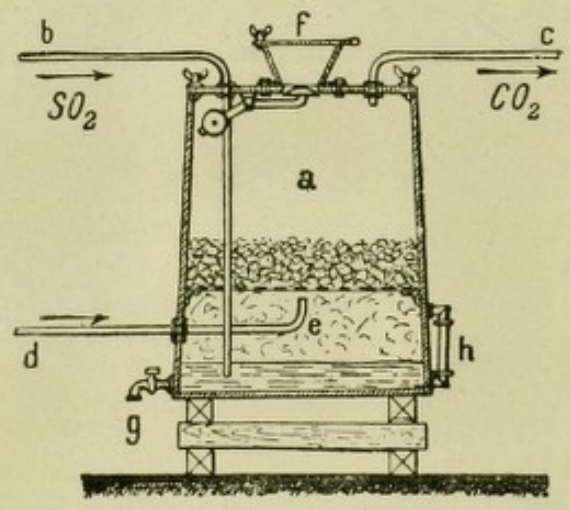


Fig. 194.

On a large scale the process of Basse and Faure is used. Large crystals of sodium carbonate, $Na_2CO_3 + 10H_2O$, are placed in a lead-lined wooden vat with a perforated false bottom. The current of SO_2 is introduced below and transforms the sodium carbonate into sodium disulphite which dissolves in the water of crystallisation of the soda and collects at the bottom of the vat. At the top of the vat carbon dioxide alone escapes. The solution of the disulphite obtained has a density of 34° Bé. ; it is saturated with the necessary quantity of crystallised soda, concentrated in shallow iron or leaden pans up to 40° Bé., and then allowed to crystallise n cast-iron vats.

APPLICATIONS. Sodium sulphite is used industrially as an *antichlor* instead of thiosulphates which were once used in order to eliminate chlorine from paper or cotton which had been bleached with chlorine, because chlorine yields oxygen with water and this transforms the sulphite into sulphate. It is used as a weak bleaching agent for delicate fibres, such as silk and wool. It is also added to sugar juices which are to be concentrated in open pans in order to prevent the sugar from turning brown. Solutions of sulphite and thiosulphate dissolve silver salts and are therefore used in photography. Sulphites may be detected in presence of sulphates and thiosulphates by precipitating the three products with lead nitrate from 5 c.c. of a 1 per cent. solution ; 5 to 6 c.c. of a 12 per cent. solution of sodium thiosulphate are then added with stirring, and the whole is filtered. Lead sulphite, $PbSO_3$, alone remains on the filter and is well washed and the residue treated on the filter with dilute sulphuric acid, which forms SO_2 recognisable by its smell, and the acid filtrate decolorises potassium permanganate solution. Crystallised commercial sodium sulphite, in trucks, costs £8 per ton, and the purer commercial powder £10 per ton.

Italy produced 1028 tons of sodium sulphite in 1907 and 470 tons in 1908, valued at £4206 ; it imported 158·4 tons of sulphites, disulphites, and thiosulphates in 1908, valued at £3168. In 1908 Germany exported 2387 tons of sulphite and 3047 tons in 1909.

SODIUM DISULPHITE : $NaHSO_3$. This compound is obtained by the method described above and is used as a very energetic antichlor for vegetable

textile fibres, in paper manufacture, &c., when a chlorine bleach has been applied.

It is used in dyestuff factories, as an energetic bleaching agent for wool and silk, and also in tanneries and for preserving wine, beer, &c.

Concentrated solutions of sodium disulphite at 38° to 40° Bé. cost about £4 per ton, but the crude crystalline product costs £10 per ton, and the pure anhydrous salt three times that amount.

Italy produced 182 tons of sodium disulphite in 1904 and 310 tons in 1905 of the value of £1064 ; and in 1908 809 tons of the value of £2356.

SODIUM THIOSULPHATE : $Na_2S_2O_3 + 5H_2O$. This compound is also incorrectly called sodium hyposulphite. It is obtained in large quantities from the sulphurised residues which are obtained in the manufacture of Leblanc soda. These residues are allowed to oxidise in the air and then form calcium thiosulphate which is soluble in water. On boiling the solution with sodium sulphate insoluble calcium sulphate is deposited, and a solution of sodium thiosulphate remains, which can be concentrated.

It is also formed by boiling an aqueous solution of sodium sulphite with sulphur : $SO_3Na_2 + S = S_2O_3Na_2$, and also by passing a current of air at 150° into a solution of sodium hydrosulphide :

$$2NaHS + 2O_2 = H_2O + Na_2S_2O_3.$$

It is very soluble in water (1 : 1 at 15°), showing a feebly alkaline reaction. It crystallises with $5H_2O$ and melts at 56° in its water of crystallisation which it loses on heating to 100° ; at higher temperatures it is decomposed into Na_2SO_4 and Na_2S_5.

The aqueous solution is decomposed by acids with evolution of SO_2 and separation of sulphur. It easily forms supersaturated solutions, which crystallise instantaneously with evolution of heat immediately a crystal of the thiosulphate is added. It acts as a strong reducing agent. It transforms Cl, Br, and I into the respective halides, NaCl, NaBr, and NaI, and is therefore used as an antichlor in the bleaching of cotton and paper, because it eliminates the last traces of chlorine remaining in the fibre after bleaching. With iodine it forms sodium tetrathionate,

$$2Na_2S_2O_3 + I_2 = 2INa + S_4O_6Na_2,$$

and this reaction is used in analytical chemistry for the quantitative determination of iodine. It is used in photography as a fixing agent because it dissolves silver salts at those points of the plate which have not been influenced by light, forming a soluble double salt. It is also used in dyeing.

In order to detect a small quantity of thiosulphate even in presence of sulphite, for instance, in foodstuffs, the mixture is heated with water and excess of sodium carbonate ; after boiling and cooling, a few drops of a 10 per cent. solution of potassium cyanide are added and the whole is concentrated on the water-bath, taken up with water and alcohol, acidified with HCl and filtered. To the filtrate a few drops of ferric chloride are added ; if the red coloration of the sulphocyanide is produced thiosulphates were certainly present, because these form potassium sulphocyanide with KCN.

$$Na_2S_2O_3 + KCN = Na_2SO_3 + KCNS.$$

The crystalline commercial product costs £6 8*s*. to £7 4*s*. per ton ; the less impure product costs £8 per ton, and when chemically pure £20. In Italy 10 tons were produced in 1905 and 215 tons in 1908 of the value of £1742.

SODIUM HYDROSULPHITE, $Na_2S_2O_4$. This is an energetic reducing agent which is easily oxidised by the air and precipitates various metals from their solutions (Ag, Cu, Hg, &c.). It is used in dyeing, for bleaching textile fibres, and as a special reducing agent in indigo vats as it reduces indigo blue to

indigo white; in the printing of fabrics it is used as a discharge for the colours. It is also used for bleaching soaps, oils, sugar syrups, &c. (*see* vol. ii, section on Cane Sugar). Freshly prepared solutions have the greatest reducing power; after an hour three-fourths of the hydrosulphite (which has a neutral reaction) is transformed into sodium disulphite with an acid reaction:

$$S_2O_4Na_2 + O + H_2O = 2NaHSO_3.$$

The hydrosulphites are used to distinguish nitrates from nitrites (p. 461); they are obtained by dissolving zinc in solutions of sodium disulphite with which it does not evolve hydrogen, and by then precipitating the dissolved zinc with milk of lime or soda solution.

It is also formed on mixing a solution of a disulphite with titanous chloride (Ti_2Cl_6), and then immediately pouring the whole into a solution of sodium hydroxide, thus precipitating titanium hydroxide, which can be recovered.

It is obtained electrolytically by using neutralised disulphite as the cathodic liquid and a solution of sodium chloride as the anodic liquid, thus avoiding current losses due to secondary reactions.

A very promising new process which leads directly to dry sodium hydrosulphite consists in treating metallic sodium with liquid or gaseous SO_2 in presence of petroleum ether, from which it is easily separated: $Na_2 + 2SO_2 = Na_2S_2O_4$. The following constitution is now attributed to sodium hydrosulphite: $NaSO_2.O.SONa$ (Binz, 1909).

In order to separate sodium hydrosulphite from its solutions these are treated with salts (NaCl or $CaCl_2$ or $MgCl_2$, &c.), and the hydrosulphite is then pressed and washed with alcohol in order to eliminate all the water, and finally dried in a vacuum desiccator in the cold. It can be dried and rendered stable more economically and without much oss by placing it in ovens on hollow iron plates in which superheated steam circulates.

Stable compounds of hydrosulphites have been successfully prepared by combining them with formaldehyde, as a new crystallised stable compound separates from the solution which is extremely stable and very useful as a discharging agent in various operations connected with the printing of textiles. The reducing power of these *hydrosulphite formaldehyde compounds* is increased by the addition of zinc oxide or magnesium carbonate, or by reducing them with zinc, &c.

Hydrosulphites are also rendered more stable by mixing them with salts of weak acids such as borates, basic phosphates, &c. (*see* Ger. Pats. 141,452, 162,875, 125,207, 129,861, 148,125, 162,912, 171,363, 144,632, 133,040, 144,281, 213,586; Fr. Pat. 341,718 and additions and Eng. Pat. 20,580).

Solid sodium hydrosulphite now costs 4*s.* per kilo.

About twenty various hydrosulphite preparations for use in dyeing are on the market containing aldehydes, zinc compounds, tin compounds, &c. (*rongalite*, *blanchite*, *hyraldite*, *decroline*, &c.).

SODIUM PERSULPHATE: $Na_2S_2O_8$. This is prepared, as has been described in the section on Persulphuric Acid (p. 286), by electrolysing a solution of sodium sulphate in H_2SO_4 (Ger. Pat. 81,404) and gradually adding solid sodium carbonate to the cooled anodic chamber in order to neutralise the persulphuric acid that is formed.

POTASSIUM PERSULPHATE is also known, and is obtained by electrolysing a saturated solution of potassium disulphate.

But **AMMONIUM PERSULPHATE, $(NH_4)_2S_2O_8$**, is of more importance, and is formed by electrolysing a saturated solution of ammonium sulphate at 7°, when it separates as a solid. In general the current density per unit surface of the electrodes should be rather high. According to the patents (Ger. Pats. 155,805, 170,311, and 173,977) good results are obtained by the electrolysis of sulphates even without diaphragms, by adding small quantities of fluorides. Ammonium persulphate dissolves in twice its own weight of water. When dissolved in sulphuric acid it forms *Caro's reagent* (*see* p. 286). Pure crystallised ammonium persulphate costs about 2*s.* 10*d.* per kilo.

Another patent on the preparation of persulphates is Ger. Pat. 205,069.

SODIUM SULPHIDE: Na_2S, and SODIUM HYDROSULPHIDE: NaSH. These compounds are similar to the potassium compounds and are used in place of them as they are cheaper. Sodium sulphide is used, for instance,

in dyeing cotton with sulphide dyestuffs, in the manufacture of dyestuffs, for tanning hides, for denitrating artificial silk (*see* vol. ii, "Organic Chemistry"), for cleaning cotton, silk, &c., and, containing much dissolved sulphur, as an insecticide, especially against locusts.

Sodium sulphide is prepared on a large scale by heating sodium disulphate with sodium chloride and coal to above 950° :

$$NaHSO_4 + NaCl + 2C = Na_2S + HCl + 2CO_2.$$

The disulphate, which is an almost valueless by-product in the manufacture of nitric acid, can thus be utilised.

The pure sulphide is prepared from the aqueous solution in octahedra : $Na_2S + 9H_2O$. It is also sold in the fused anhydrous condition as in this form it costs less to transport and also keeps better. The aqueous solution has a strongly alkaline reaction (p. 239). The crystallised sulphide for industrial use costs £8 per ton, the anhydrous product £12, and the fused product often costs £26. Germany exported 6600 tons of sodium sulphide in 1905 at £6 16*s*. per ton ; in 1908 it exported 6536 tons, and in 1909 7600 tons.

Italy produced 140 tons in 1905, 450 tons in 1906, 486 tons in 1907 and also imported 669·4 tons of the fused product in 1907, 666·5 tons in 1908, and 1344 tons in 1909 of the value of £2151.

Analysis of Sodium Sulphide. The strength is determined with a tenth normal solution of iodine after first acidifying with acetic acid, in presence of starch paste (1 c.c. of $\frac{N}{10}$ iodine corresponds to 0·0039 grm. of Na_2S).

The titration may also be carried out very exactly, even in presence of hydrosulphites or other impurities, by first acidifying the solution of Na_2S slightly with acetic acid and then titrating it with a titrated solution of zinc sulphate ; the end of the precipitation of zinc sulphide is found by spotting it on to paper containing cadmium sulphate, until this no longer gives a yellow spot.

The *hydrosulphide* is obtained from calcium sulphide from Leblanc soda residues, by treating it in the cold with sodium disulphate :

$$CaS + NaHSO_4 = CaSO_4 + NaSH.$$

The hydrosulphide is decomposed on boiling in the following manner :

$$2NaSH = Na_2S + SH_2.$$

Various *polysulphides*, N_2S_2, Na_2S_3, Na_2S_4, and Na_2S_5, are also known ; the last is obtained by adding sodium to pure sulphur.

SODIUM CARBONATE : Na_2CO_3 (SODA)

This is certainly the most important of the salts of the alkali metals from an industrial standpoint, on account of its wide application.

It is found in nature in certain rocks and is dissolved from them by rain water, which carries it into alkaline mineral springs (Vichy, Carlsbad, &c.). Certain supplies of such water collect in basins forming lakes in Egypt, America, &c., which by slow and spontaneous evaporation deposit a salt of the formula : $Na_2CO_3.CO_3HNa + 3H_2O$, which is called *Urao* in Colombia and *Tro-na* in Egypt. From the lakes of California and especially of Inyo County large quantities of soda are obtained by simple crystallisation. The natural soda of Lake Magadé near Kiù in Uganda is profitably sold in China and Japan.

Before the invention of the Leblanc process soda was extracted from the ashes of marine plants (Chenopodium, Salicornia, Atriplex, Salsola, &c.) ; in Southern France and Spain such plants are still specially cultivated in order to obtain soda and other products from their ash. Almost all soda is, however, to-day prepared by chemical means, starting from sodium chloride, which is treated according to one of the two methods described below.

PROPERTIES. Soda is a white substance of varying crystalline character according to the quantity of water of crystallisation which it contains. On slowly cooling an almost saturated solution of soda of 32° Bé, large crystals with 10 mols. of water, $NaCO_3 + 10H_2O$, that is, 63 per cent. of water, are obtained, forming monoclinic prisms of common *soda crystals*; these effloresce in the air forming a white powder of $Na_2CO_3 + H_2O$.

Soda crystals melt in their water of crystallisation at 32·5°, forming a saturated solution of this hydrate, but at a more elevated temperature another hydrate, $Na_2CO_3 + 2H_2O$, separates as a powder which loses a further molecule of water in the air, forming another fairly stable hydrate, $Na_2CO_3 + H_2O$, which only loses the final molecule of water at 100°, forming anhydrous soda.

Other hydrates are also known and they all have their own solubility curves. The anhydrous carbonate easily absorbs moisture from the air, up to 15 per cent. without becoming deliquescent, differing in this way from potassium carbonate. It melts at 850°, losing a small quantity of CO_2, and volatilises at very high temperatures. 100 parts of water at 20° dissolve 7 parts of anhydrous soda, at 37·5° 59·5 parts, and at 100° only 45·1 parts; thus we see that soda behaves in a similar manner to sodium sulphate.

In aqueous solution it has a strongly alkaline reaction, for the same reasons as were explained in the case of potash. The acids all evolve carbon dioxide with soda.

We give a Table on the opposite page showing the densities and concentrations of solutions of sodium and potassium carbonate. We will now explain in some detail the various industrial processes used for the preparation of soda, which constitutes one of the most important products supplied by modern chemical industry.

I. **LEBLANC PROCESS.** This is the older process,[1] and is based on the transformation of sodium chloride into sodium sulphate in the manner which we have already described in connection with the manufacture of hydrochloric acid (p. 160).

The crude sulphate is then mixed with an excess of coal and calcium carbonate and the whole was formerly heated to redness in reverberatory furnaces somewhat different from those shown on p. 161. Now, however, revolving furnaces, consisting of large cylinders revolving on their axes and continuously traversed by the flame from a neighbouring hearth, are used. Rotary furnaces for the

[1] The origin of the soda industry may be traced back to the eighteenth century. In 1736 Duhamel showed that sodium chloride and natural soda contain the same base, and indicated that it should therefore be possible to transform salt into soda. In 1776 Scheele showed that on heating a solution of sodium chloride with lead oxide and then passing carbon dioxide into the filtered liquid, soda was obtained. This process was patented by Turner in 1787. In 1775 the French Academy awarded a prize to the work of Malherbe and De la Metherie, who succeeded in preparing soda in the laboratory by heating Glauber salt (sodium sulphate) with carbon. Attempts to manufacture soda on a large scale by this process failed completely. Nicola Leblanc (1742–1806) first devised a complete process for transforming sodium chloride into the carbonate by way of sodium sulphate. In laboratory experiments he transformed sodium sulphate easily and directly into the carbonate by heating it with carbon and calcium carbonate, and in 1783 he obtained a prize from the Academy for his process. Leblanc, who was the medical man of the Duke of Orleans, obtained from him £8000 in order to construct the first soda works at St. Denis in 1781; but in 1793, when the Duke of Orleans was guillotined, the St. Denis works were also closed, and the Committee of Public Safety obliged Leblanc to make his secret public in order to replace potash by soda for the national requirements, as this could not be obtained on account of the commercial isolation of France. As a compensation they then made over the works of the Duke of Orleans to Leblanc; but he no longer had the means to work a factory on such a large scale, and became extremely poor. In 1806 he retired into an almshouse, where, as a last resource in his great misery, he committed suicide. In France he was only recognised much later, after hundreds of millions of tons of alkali had been industrially prepared in England and Germany by the Leblanc process, and it is only of late years that his countrymen thought of erecting a monument to their unfortunate fellow-citizen. The manufacture of soda had already been attempted by Losh in England, who could not obtain a footing until the enormous taxes which were levied on salt were reduced. The large works of Muspratt in England (1824) almost presented the soda to their customers in order to show that it had a value at least equal to natural soda. From that time this industry extended, especially in England, and underwent great improvements in mechanical directions, whilst, on the other hand, from a chemical standpoint the prescriptions of Leblanc were almost exactly followed. The more important improvements were those of Gossage, who in 1836 introduced the coke tower for absorbing HCl (*see* Note on p. 161); that of Stevenson and Williamson, who devised rotary soda furnaces, and then the systematic lixiviation and the mechanical calcining furnace. Later, through the assiduous work and repeated experiments of Schaffner, Mond, and Chance, it became possible to utilise the enormous quantities of sulphur which were formerly lost, and are still in large part lost to-day, in the alkali waste.

SPECIFIC GRAVITIES AND STRENGTHS OF SOLUTIONS OF SODIUM AND POTASSIUM CARBONATE

Sp. gr. at 15°	Degrees Baumé	Per cent. by weight of K_2CO_3	Per cent. by weight of Na_2CO_3	Sp. gr. at 15°	Degrees Baumé	Per cent. by weight of $K_2CO_3 \frac{5}{2}$	Per cent. by weight of Na_2CO_3 at temp. of 30°
1·007	1	0·7	0·67	1·231	27	23·5	21·42
1·014	2	1·5	1·33	1·241	28	24·5	22·29
1·022	3	2·3	2·09	1·252	29	25·5	23·25
1·029	4	3·1	2·76	1·263	30	26·6	24·18
1·037	5	4·0	3·43	1·274	31	27·5	25·11
1·045	6	4·9	4·29	1·285	32	28·5	26·04
1·052	7	5·7	4·94	1·297	33	29·6	27·06
1·060	8	6·5	5·71	1·303	34	30·7	27·97
1·067	9	7·3	6·37	1·320	35	31·6	(59·5 per cent. at temp. of 37·5°)
1·075	10	8·1	7·12	1·332	36	32·7	
1·083	11	9·0	7·88	1·345	37	33·8	41·1 at 100°
1·091	12	9·8	8·62	1·357	38	34·8	
1·100	13	10·7	9·43	1·370	39	35·9	
1·108	14	11·6	10·19	1·383	40	37·0	
1·116	15	12·4	10·95	1·397	41	38·2	
1·125	16	13·3	11·81	1·410	42	39·3	
1·134	17	14·2	12·43	1·424	43	40·5	
1·142	18	15·0	13·16 at temp. of 30°	1·438	44	41·7	
1·152	19	16·0	14·64	1·453	45	42·8	
1·162	20	17·0	14·49	1·468	46	44·0	
1·172	21	18·0	16·27	1·483	47	45·2	
1·180	22	18·8	17·04	1·498	48	46·5	
1·190	23	19·7	17·90	1·514	49	47·7	
1·200	24	20·7	18·76	1·530	50	49·9	
1·210	25	21·6	19·61	1·546	51	50·1	
1·220	26	22·5	20·47	1·563	52	51·3	

production of large quantities, which give good results, are constructed, for instance, by the works of Carrick and Wardale in Gateshead (Fig. 195).

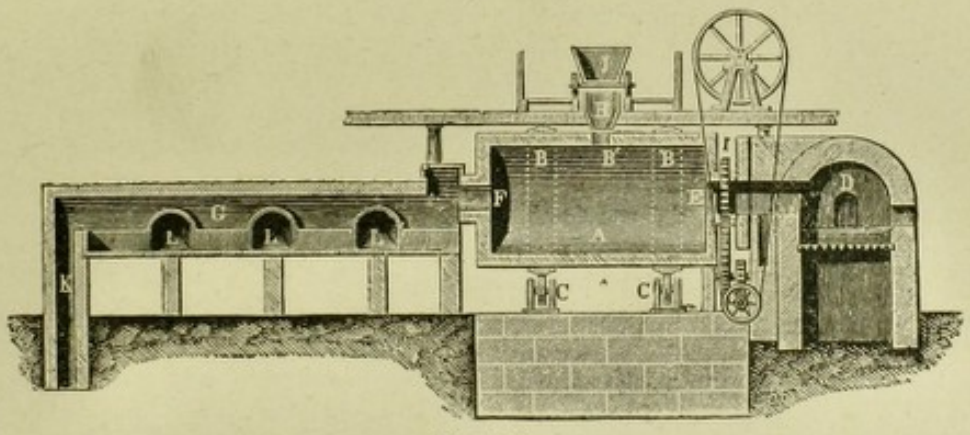


FIG. 195.

The mixture of sulphate, limestone, and coal is introduced into the rotary cylinder, *B'*, which consists of a large wrought-iron cylinder lined with refractory bricks, 6 to 8 metres long and 2½ to 3½ metres in diameter, holding 15 to 20 tons of the mixture, four charges of which are treated per day. The cylinder revolves on four wheels, *C*, through the action of the cog-wheel, *I*. The flames and hot gases from the furnace, *D*, enter through the

mouth, E, which is joined to the cylinder by means of a ring, affording a sufficiently closed joint, although it allows the cylinder to revolve. The very hot gases which escape at the outlet, F, pass over the surface of soda solution obtained by previous operations, and contained in the pan, G, which is thus evaporated.

In practice 100 kilos of sodium sulphate from the pan, which should not be melted to a compact mass but should be porous, is used in lumps as they are obtained from the salt-cake pans and mixed coarsely by hand with shovels, or by rapid mechanical mixers, with 80 to 90 kilos of crushed limestone or chalk containing little magnesia, iron and silica, and 40 to 50 kilos of coal in small pieces. The coal should contain a little ash, always less than 10 per cent., and more especially very little silica, as this causes loss of soda in the form of soluble silicates or may even form other insoluble mixed silicates ; if it contains much nitrogen the coal forms cyanides and sulphocyanides which render the soda impure.

When the operation is almost finished 6 to 7 per cent. of further sulphate and a little powdered limestone are added ; the mass then becomes more liquid and is easily discharged through the opening, B', when this is turned downwards, into suitable cars which are arranged under the furnace. The fused mass solidifies, and becomes spongy and friable after some days under the influence of atmospheric moisture.

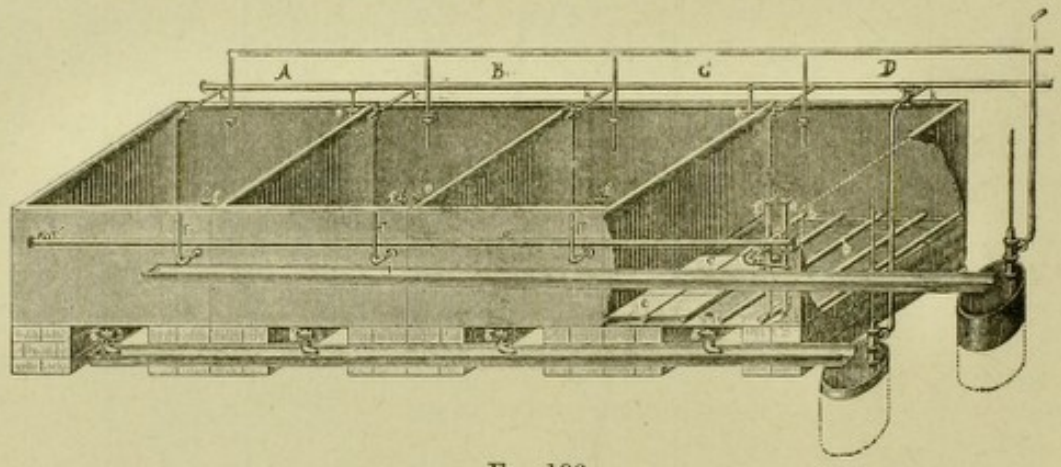


Fig. 196.

In the furnaces the two following reactions occur:

(a) $SO_4Na_2 + 2C = Na_2S + 2CO_2$ and $SO_4Na_2 + 4C = Na_2S + 4CO$

(b) $Na_2S + CaCO_3 = CaS + CO_3Na_2$.

The end of the reaction is indicated by the appearance of bluish flames of CO as a portion of the $CaCO_3$ is decomposed into $CaO + CO_2$, and the CO_2 in presence of carbon is in turn converted at that temperature into $CO : CO_2 + C = 2CO$.

The *black ash* thus obtained consists of a mixture of sodium carbonate, excess of calcium carbonate, sodium sulphide, excess of coal, calcium oxide, and other impurities. After cooling, the black ash is systematically lixiviated with cold water in a suitable plant, and since the liquid becomes hot the temperature is lowered as far as possible to 40° or 50°, as in this way less highly coloured solutions are obtained and the formation of sodium hydroxide is avoided (*see below*).

For this purpose several iron tanks with a perforated double bottom are used, arranged in series (Fig. 196). The bottom is covered with a thin layer of cinders, and then each vat is filled with lumps of black ash, and water is passed into the vat, A. A pipe dips down to the bottom of this vat which carries the solution into the upper part of the vat, B, and in the same way the solution passes from B to C and from C to D ; the solution in D should be of 28° to 30° Bé. ; if it is more concentrated it dissolves more sulphide and iron salts which colour the solution deeply. On then lowering the tube, f, into the vat, D, the solution is discharged into channels, i, which carry it into a tank from which it is pumped into the evaporating pans. The soda in A will be the first to dissolve completely ; the muddy residue is then discharged from the cock, g, at the base, and then after thoroughly rinsing with water, this vat is filled with fresh crude soda. At this point the solution which passes into the last vat, D, instead of being discharged is passed through the tube, e, into the first vat, A, where it becomes saturated and is then discharged through the tube, f ;

the vat, *B*, which remains empty is then filled as was done for *A*, and then *B* becomes the last vat to be discharged, and so on in such manner as to obtain a rational, systematic, and continuous lixiviation.

The whole of the impurities, consisting of calcium sulphide, calcium carbonate, coal, and a certain quantity of other impurities, form the so-called *alkali waste*. It must be borne in mind that during lixiviation the calcium oxide reacts with the soda, forming insoluble calcium carbonate and soluble sodium hydroxide :

$$CaO + H_2O + CO_3Na_2 = CaCO_3 + 2NaOH.$$

For this reason amongst others, a works manufacturing sodium carbonate always manufactures sodium hydroxide as well. In fact, if an excess of coal is added in the black-

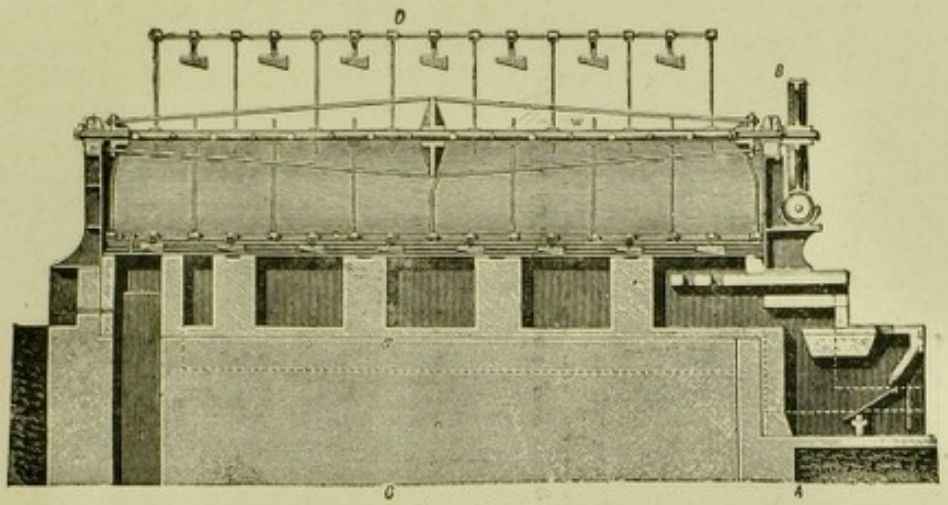


Fig. 197.

ash furnace, and this is heated to higher temperatures and the crude soda lixiviated with hot water, more sodium hydroxide than sodium carbonate may be formed.

When the production of carbonate alone is required, the small amount of hydroxide which is present in the solution obtained on lixiviation must be transformed into carbonate by passing a current of air and carbon dioxide through the solution. This process is called *carbonating*, and chimney gases are commonly used ; by this means the small amounts of dissolved calcium sulphide and sodium sulphide which are present are oxidised, forming sulphates, and the alumina, iron, and silica which are present as impurities in the solution are precipitated at the same time. The completion of this reaction is recognised by the fact that lead acetate paper is no longer blackened.

On standing, a clear solution of sodium carbonate is obtained, which is decanted and evaporated. When a certain concentration has been acquired, crystals of sodium carbonate, $Na_2CO_3 + H_2O$ (*black salt*), already separate from the hot liquor, and are gradually removed, whilst new solution is added to the liquor in the pans; and thus the process becomes continuous.

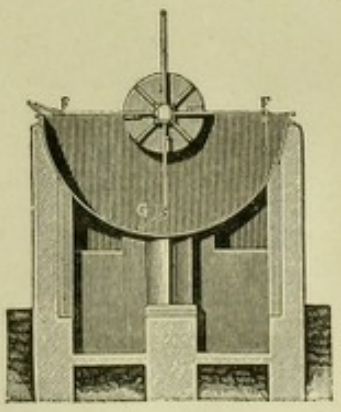


Fig. 198.

For this purpose long, narrow, round-bottomed pans are used, heated by direct flame, and so arranged that the lower part of the bottom rests on the brickwork of the hearth, and is not directly heated by the flame, so that the salt which separates is not burnt.

To-day, however, Thelen's open pans, heated by direct flame, are generally employed ; these are provided with an automatic stirrer, and the pure carbonate which separates on evaporation is automatically discharged.

Fig. 197 represents a longitudinal section, and we see how the inclination of the scrapers on the stirrer causes all the crystals to pass to one extremity of the pan from whence they may be removed by a suitable elevator. Fig. 198 shows a transverse section of the same pan, and shows still more clearly the movement of the scrapers which are partially movable.

The highly concentrated mother liquors are discharged at intervals and contain sodium

ferrocyanide and other impurities together with soda. These mother liquors are finally concentrated apart and the residue calcined, impure soda ash being thus obtained.

The black salt which is first obtained is separated from the mother liquors in a hydro-extractor ; if the soda has been previously carbonated it is then calcined in ordinary reverberatory furnaces and not in cylindrical rotary furnaces, because it would then melt, in which case it would be necessary to work it up again. If carbonisation and oxidation have not been performed the soda is mixed with sawdust and charged into reverberatory furnaces for calcination. It is important to regulate the temperature in such a manner that the soda does not melt, as otherwise it becomes unserviceable, and it must also be kept continually moving so that all the sawdust may be converted into carbon dioxide which forms carbonate with the NaOH.

For this purpose rotary calcining furnaces are constructed ; a much used form is that of Mactear, which is able to produce 100 tons of calcined soda ash per week.

An iron platform (Fig. 199) 6 to 7 metres in diameter (2) is mounted on wheels (3) and is covered by refractory material (1); its extreme rim is provided with a small channel all round (51) in which molten soda forms a hydraulic seal with the vault of the furnace (6, 7, and 23), which is supported by a suitable iron framework. Under the circumference of the platform there is a cogwheel which enables the whole platform to be revolved by means

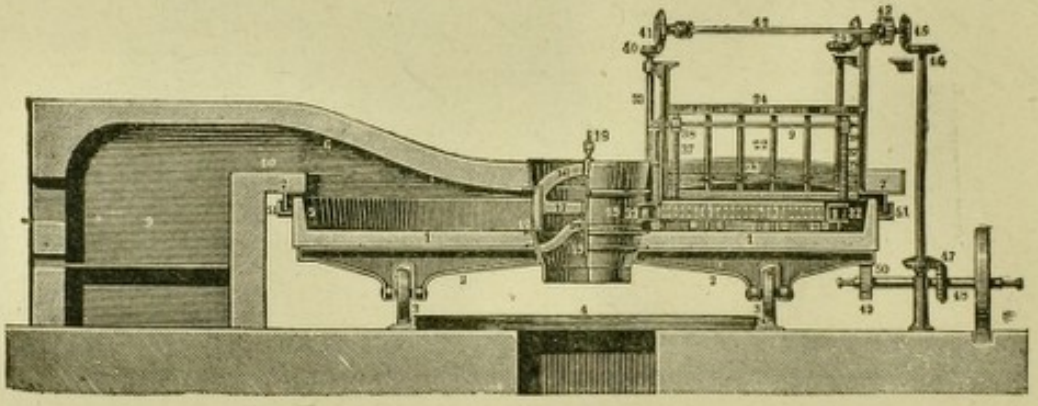


Fig. 199.

of the spur-wheels (50). The soda to be calcined is charged through the central aperture (18), and is finally discharged through the central opening (19). During the circular movement hot gases and flame pass in from the hearth (9), and the mass of soda is continuously stirred up by a system of agitators (22) fixed in the roof of the furnace and actuated by cogwheels. The soda which is obtained from these furnaces is already sufficiently pure for many industrial purposes. If a purer crystalline soda is required it is dissolved in suitable vats and a little chloride of lime is then added in order to oxidise and precipitate the various impurities, iron, alumina, &c. The clear, decanted, or filtered solution is evaporated in ordinary pans, for example, Thelen pans (*see above*).

The refined soda crystals which are thus obtained are calcined in an ordinary very clean furnace, after which they are ready for sale, and are ordinarily placed in sacks on which their strength in soda is marked.

If large transparent soda crystals are required the concentrated hot solution is allowed to cool slowly in suitable vats ; the soda crystals of commerce are thus obtained, of the composition $NaCO_3 + 10H_2O$; these are still wrongly preferred in some quarters to calcined soda, although they contain 63 per cent. of water.

In order to be able to meet the competition of the Solvay process (Ammonia Process, *see below*), it is necessary in using the Leblanc process to utilise all the by-products as far as possible ; thus the HCl formed in the manufacture of the sodium sulphate must be used for the preparation of chlorine or bleaching powder, and the sulphur contained in the alkali waste (consisting of about 40 per cent. of CaS, 22 per cent. of $CaCO_3$, 3 per cent. of iron sulphide, 15 per cent. of sand and silicates, 4 per cent. of soda, 10 per cent. of lime, &c.), must also be utilised as far as possible.

Until a few years ago (1900) this alkali waste, apart from being a source of much loss of

capital, as it contained 20 or 25 per cent. of sulphur, constituted a regular calamity for the industry and for the inhabitants of the neighbourhood of the works. A truly enormous bulk of material was thus obtained, because each ton of soda which was produced supplied 1½ tons of dry waste, and thus all this material collected in regular mountains which developed a smell of hydrogen sulphide through the action of the air, which was thus polluted, and water dissolved coloured and evil-smelling sulphides which passed into the soil and defiled the water of wells and rivers.

The treatment of alkali waste thus constituted a problem of capital importance both from the hygienic and financial standpoints : all the sulphur was lost in quantities which corresponded to about one-third of the weight of soda produced ; and England alone lost more than 150,000 tons of sulphur annually of the value of about £400,000.

Numerous experiments were made and very important work was undertaken on this question, and after repeated failures, and after the hopes aroused by Schaffner in 1880 (he obtained calcium thiosulphate, CaS_2O_3, after many operations and then decomposed this with HCl, thus recovering sulphur and SO_2), the process had to be abandoned through the increased price of HCl, and from the fact that only 50 per cent. of the sulphur was recovered. Mond then attempted to solve the question, and finally the Schaffner-Helbig process arose, which reduced the sulphur losses to a minimum, at the same time recovering calcium carbonate.

According to this system calcium sulphide was decomposed with magnesium chloride in solutions of 24° Bé. in closed iron cylinders provided with stirrers, and heated by direct steam, $CaS + MgCl_2 + H_2O = MgO + CaCl_2 + H_2S$; the hydrogen sulphide which was evolved was partially burnt and SO_2 was thus obtained which was passed together with the remaining H_2S into a solution of $CaCl_2$ and then immediately separated all the sulphur, $SO_2 + 2H_2S = 2H_2O + S_3$, always under the condition that exactly the right proportions of H_2S and SO_2 were present. In presence of $CaCl_2$ the sulphur separated in lumps and was thus easily filtered.

On then passing a current of carbon dioxide into the mixture of $CaCl_2$ and MgO resulting from the first reaction, magnesium chloride and calcium carbonate were formed ; the latter was then again used in the manufacture of soda : $MgO + CaCl_2 + CO_2 = CO_3Ca + MgCl_2$.

In 1888 Chance rendered the process more economical by perfecting the process of Gossage (1838) by which CaS was decomposed with CO_2 and H_2O, and the H_2S which was formed completely burnt, forming SO_2, which was used for the manufacture of sulphuric acid. Chance found it more remunerative to partially burn the hydrogen sulphide in such a manner that the H only was transformed into H_2O, and all the sulphur was separated as such : $H_2S + O = H_2O + S$ (*see* p. 199).

The important point in this process is to employ exactly the right proportions by volume of H_2S and air. The process is remunerative, but requires very costly plant.

To-day the method of Chance, modified by Claus, is everywhere employed. A current of carbon dioxide (chimney gases) is passed into the residues in aqueous suspension : $CaS + CO_2 + H_2O = CaCO_3 + H_2S$, and the hydrogen sulphide evolved is collected in large gasometers and then burnt with an insufficient quantity of air ; the sulphur is then separated (regenerated sulphur) or is burnt with excess of air ; it then forms SO_2 which is utilised in lead chambers for the manufacture of sulphuric acid.

It is estimated that by this process about 80,000 tons of sulphur are annually obtained in Europe. Since 1904 the United Alkali Company in Liverpool has transformed H_2S and SO_2 into sulphuric acid with a yield of 90 per cent. by passing these gases over platinum catalysers at 538°.

II. AMMONIA-SODA PROCESS (or SOLVAY PROCESS). This process was already proposed by Dyar and Hemming in 1838, but was rendered industrially effective after many failures by the brothers Solvay in 1865.[1]

This is based on the reaction which occurs at ordinary temperatures between a solution of sodium chloride and one of ammonium dicarbonate, with formation of sodium dicarbonate :

$$CO_3HNH_4 + NaCl = NH_4Cl + CO_3HNa.$$

[1] It appears that Vogel in 1822 was already aware of the reaction by which soda is obtained by the ammonia process, and it is said that J. Thom in 1836 manufactured 100 kilos per day ; but the first patent is that of Dyar and Hemming, of June 30, 1838. However, Dr. V. Ravizza showed by documents at a meeting of the Chemical Society of Milan in February 1910 that the Milanese pharmacist Gerolamo Forni on March 6, 1836, offered a project to the Austrian Government for the manufacture of 250 tons of soda annually by the ammonia process.

At high temperatures the reverse reaction may also occur. If the solution is concentrated the sodium dicarbonate, which is only slightly soluble, separates in the crystalline condition, whilst the ammonium chloride remains in solution. On then heating a solution of the dicarbonate, sodium carbonate is easily obtained :

$$2CO_3HNa = CO_3Na_2 + CO_2 + H_2O.$$

The ammonia process cannot be employed for the preparation of potassium carbonate because the corresponding potassium dicarbonate is more soluble and does not separate in crystals.

Industrially the process starts from a cold saturated solution of NaCl ; this is saturated with moist gaseous NH_3 in such a way that each litre of the solution contains 268 grms. of NaCl and 78 grms. of NH_3.

It is found in practice that in order to obtain a good yield it is necessary to employ about double the quantity of sodium chloride that is theoretically required ; thus for 100 kilos of soda of 99 per cent. 210 to 220 kilos of salt are required, a part of which is lost (about 20 per cent.). (*Translator's note.*—This should be 50 per cent.)

The NaCl solution should not contain salts of calcium, magnesium, or iron, and in case these are present it is necessary to separate them with a little ammonium carbonate ; this separation is not easy and is to-day effected economically by first using the saturated salt solution for washing the gases which escape from the apparatus in which the saturation with ammonia occurs ; in this way about 1·2 per cent. of ammonium carbonate is introduced into the solution and complete saturation with ammonia is only carried out after the carbonates of calcium, magnesium, iron, &c., have been separated.

The saturated solution containing about 26 to 27 per cent. of NaCl is obtained by passing a current of water through vessels filled with salt and arranged in series. In a saturated solution of salt *dry* gaseous ammonia would precipitate NaCl because this is less soluble in an ammoniacal solution ; but by employing *moist* NH_3 as it is regenerated from NH_4Cl, NaCl is not precipitated, because this carries with it sufficient moisture to sufficiently dilute the solution, which at the end of this operation should still be saturated with salt. The original salt solution has a density of 23° to 24° Bé., and after saturation with ammonia a density of only 16° Bé., so that the volume is increased and each litre contains 60 to 70 grms. of ammonia. If fresh salt is added to resaturate the solution further impurities in the form of calcium and magnesium are introduced ; and in order to avoid this disadvantage, almost dry ammonia is to-day employed by preference to obtain a saturated salt solution. The saturation of the salt solution (brine) with ammonia may be carried out in any of the usual forms of column apparatus similar to those employed in the manufacture of alcohol, or in the Grüneberg apparatus (p. 324), by allowing the brine to fall into the column from above and passing the current of gaseous ammonia from below. Solvay, however, employs a saturator shown in Fig. 200.

The two vessels, R and R', which contain the saturated salt solution are used alternately and are in communication above and below, through p, p', r, r', with a vertical cylinder, A, into which the ammonia passes through the tube, T, which terminates in a perforated funnel. The ammonia from the rectifying column is first cooled to 70° to 80° in large cast-iron coils cooled by cold water, after which the ammonia passes through the salt solution which is maintained in circulation by the agitator, W, in such a manner that it continuously enters and passes out of the vessel, R or R'. Since the solution tends to become heated it is necessary to cool it by passing cold water through the serpentine coil, S. The excess of ammonia passes out through the tube, T, and is absorbed by a dilute solution of NaCl. When the solution in R is saturated with ammonia it is necessary to add a little powdered salt through the tube, V, in order to also saturate the solution with NaCl ; the stirring is then stopped and the solution is driven over into the conical cylinder, D, by compressed air. Here the impurities are allowed to settle and are separated by means of the valve tube, M, whilst the clear solution passes out through the tube, U, and, together with that remaining in the vessel, R or R', is continuously pumped into the carbonating apparatus which is called the *absorber*.

The absorber used by Solvay consists of a column formed of an iron cylinder 2 metres in diameter and 15 metres high, divided into many portions by means of perforated

plates, *b*. The ammoniacal salt solution passes in through the tube, *f*, which feeds several absorbers, and fills the columns up to a height of 12 metres. Compressed carbon dioxide passes in through the tube, *d*, at the base of the column and saturates the ammoniacal salt solution, forming insoluble sodium bicarbonate ; the excess of CO_2, which carries with it a little ammonia, escapes at the top of the column and is conducted into the saturator containing salt solution (*see above*). The liquid mass, containing sodium bicarbonate in suspension, is filtered on vacuum filters in order to collect the bicarbonate, whilst the liquid, which contains ammonium chloride and free ammonia (60 grms. per litre), is mixed with milk of lime (200 grms. CaO per litre), and heated in the usual apparatus (pp. 324 *et seq.*), for the regeneration of all the ammonia.[1] Inside the Solvay column batteries of tubes in which cold water circulates are placed at various heights so that the whole mass is kept at a temperature below 40°.

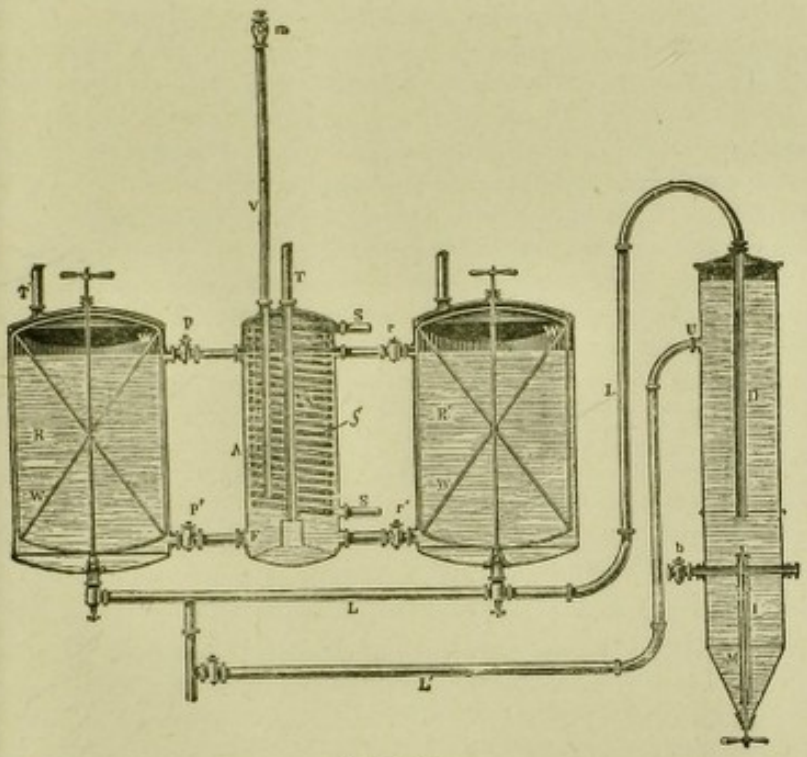


Fig. 200.

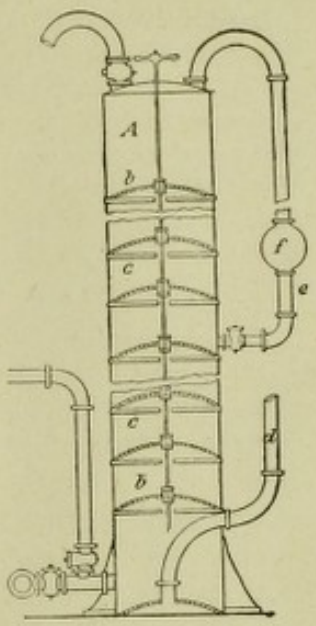


Fig. 201.

A simpler type of absorber is that proposed by Honigmann and consists of several iron cylinders with a conical bottom, united in series.

After these have been filled with ammoniacal salt solution a current of compressed carbon dioxide is passed through them successively, and when the contents of the first cylinder are saturated it is emptied and filled afresh. The CO_2 then enters the second cylinder, which is not yet saturated, first, and passes through the successive cylinders and finally into the original first cylinder containing the fresh solution ; work is continued in a similar manner to that employed in systematic lixiviation (*see* p. 470). During the saturation with CO_2 cold water is passed over the external surface of the cylinders in order to maintain the temperature below 40°. The complete carbonisation lasts from 12 to 15 hours.

The carbon dioxide employed in this process is obtained by heating limestone ($CaCO_3$) in suitable lime-kilns (*see* Lime), arranged in layers alternately with gas coke containing little sulphur and arsenic (100 parts of limestone and 20 parts of coke). The carbon dioxide produced by the kilns is cooled and freed from dust and SO_2 by washing it in one of the usual towers with a counter-current of water.

The lime which remains in the kilns is used in the regeneration of ammonia from the ammonium chloride solutions.

[1] The liquid which is discharged from the apparatus after the recuperation of the ammonia contains, per 100 c.c. of liquid, 1·4 grms. of CaO, 2 grms. of $CaCl_2$, 15 grms. of calcium and sodium chlorides, and 0·003 grm. of NH_3 ; this liquid is allowed to stand in order to recover the lime which separates.

The sodium bicarbonate which collects in compact cakes on the vacuum filters is sprinkled with a fine spray of water in order to free it from the last traces of mother liquor. In order to transform it into carbonate it is calcined in reverberatory furnaces, or preferably in rotary furnaces or in pans with agitators similar to the Thelen pans (*see above*), but closed so that all the carbon dioxide which is developed during the heating may be recovered. These gases, containing 50 per cent. of CO_2, are cooled and washed and led through suitable pipes to the absorbers in order to be directly utilised in the formation of sodium dicarbonate. The soda ash which remains is dry, white and bulky, and contains 98 to 99 per cent. of Na_2CO_3.

As a by-product in the production of Solvay soda a solution of calcium chloride is obtained which Solvay has endeavoured to utilise by heating the solid residue of $CaCl_2$ obtained on evaporation with silica at a high temperature in a current of air. Free chlorine is thus obtained : $CaCl + SiO_2 + O = CaSiO_3 + Cl_2$; since, however, this chlorine cannot compete with electrolytic chlorine the liquid is now only used as brine in ice factories.

This process of treatment of the magnesium chloride is of no practical importance because electrolytic chlorine is now obtained at a very low price. Some works have found it profitable to treat the solution of $CaCl_2$ with sulphuric acid or sodium disulphate ; precipitated gypsum is thus obtained which can be used in various ways ; after filtration a very dilute solution of HCl remains which may also be utilised in certain cases.

III. CRYOLITE PROCESS. Much soda is to-day obtained in North America and Denmark from a mineral which is very abundant in those countries and especially also in Greenland, namely *cryolite*, which is a double fluoride of aluminium and sodium, $AlF_3.3NaF$. The finely powdered mineral is mixed with lime and heated in suitable furnaces. It forms insoluble calcium fluoride which is utilised in glass and porcelain factories, and the double oxide of aluminium and sodium (sodium aluminate) which is soluble :

$$2(AlF_3.3NaF) + 6CaO = 6CaF_2 + Al_2O_3.3Na_2O \text{ (soluble)}.$$

The mass is lixiviated with water and a current of carbon dioxide is passed through the solution which precipitates aluminium hydroxide which is utilised for the preparation of alum, aluminium sulphate, or metallic aluminium, whilst a solution of sodium carbonate remains, which is concentrated in order to obtain solid soda.

$$Al_2O_3.3Na_2O + 3H_2O + 3CO_2 = 3CO_3Na_2 + Al_2(OH)_6.$$

IV. ELECTROLYTIC PROCESS. When the principal difficulties in the preparation of electrolytic caustic soda had been overcome, the direct preparation of the carbonate from electrolytic soda by passing carbon dioxide into the cathodic zone, so obtaining crystallised sodium bicarbonate, was thought of ; this could then be finally treated in the same way as that obtained in the Solvay process. The results of these attempts were kept secret, but many consider that this process could not be practical because the thermal balance of the chemical reactions passed through in order to obtain sodium carbonate in the ordinary way is more satisfactory than by the electrolytic process (*see above*), and in fact the commercial price of these products already expresses the difference in the thermochemical balance, and except in special cases it would not pay to transform electrolytic chlorine into HCl and electrolytic caustic soda into sodium carbonate.

APPLICATIONS. Soda is used in large quantities in the manufacture of soap and glass, in laundries, in the preparation and washing of textile fibres, in the manufacture of paper, in dyeing, and generally for the preparation of many sodium salts such as silicates, phosphates, the dichromate, borax, &c.

In glass factories the replacement of sodium sulphate by sodium carbonate can be predicted when it is sufficiently cheap, as 3 kilos of soda produce the same effect as 4 kilos of the sulphate. It will have the advantage that the air of the neighbourhood will not be polluted with sulphur dioxide. It will also effect an economy in fuel and an increase in the output of the furnaces, which will also be less attacked and will produce glass of better quality.

STATISTICS AND TRADE IN SODA. For a long period England was the mistress of the world's trade in soda products in virtue of her powerful mercantile marine and large quantities of cheap fuel, and it was only much later that the soda industry was able to develop on the continent of Europe, especially after the introduction of the ammonia-soda

process. The fight between the two systems was severe, and the Leblanc process has only been able to continue its existence by thorough utilisation of the by-products, hydrochloric acid and sulphur.

In England, where the Leblanc process was most widely used, Mond established the first ammonia-soda works in 1875.

To-day more than 60 per cent. of the output of soda in England is produced by the Solvay process, and on the Continent 80 per cent. is now so produced. The entire quantity of sodium chloride used in England in the various alkali works was 670,000 tons in 1880, 850,000 tons in 1890 and 700,000 tons in 1894, 35,000 tons of sulphur being re-utilised in the Leblanc works.

The Leblanc process is steadily decreasing in importance, and would perhaps have already been completely abandoned if enormous quantities of capital were not invested in those works which originally adopted it. Its entire extinction cannot be far off, because the glass factories, which consumed much sodium sulphate from the Leblanc works, will certainly replace it by sodium carbonate, because the actual price of soda no longer justifies the use of the sulphate which yields less satisfactory results. When this occurs the Leblanc process will no longer have any justification for its existence.

The strength of soda is commercially indicated by degrees which have various values in different countries. *German degrees* indicate the percentage of Na_2CO_3; *Gay-Lussac degrees* the percentage of Na_2O; *Descroizilles degrees* (French) the quantity of H_2SO_4 which is neutralised by 100 parts of soda; and *Newcastle degrees* (English) differ very little from Gay-Lussac degrees: actually 1° Gay-Lussac = 1·71° German = 1·58° Descroizilles = 1·01° Newcastle.

The world's consumption of soda in 1882 was 700,000 tons, of which only 160,000 tons were ammonia soda, and has increased rapidly up to the present time, being about 1,760,000 tons in 1902, of which only 250,000 tons were prepared by the Leblanc process. England is the country which produces the largest quantity, and in 1876 more than £7,000,000 was already invested in this industry, which employed 22,000 workpeople. The English production in 1880 was 430,000 tons and exceeded 800,000 tons in 1896; in 1909 95,000 tons were exported. North America only produced 1100 tons in 1886, but in 1898 the production had risen to 300,000 tons. Germany, which produced 42,000 tons of soda in 1878, raised its production to 300,000 tons in 1901 of the value of more than £1,520,000; but in 1905 this fell to 250,000 tons. In 1904 Germany exported 46,768 tons of soda ash, and 4133 tons of crystals; in 1905 it exported 56,093 tons altogether, and in 1907 the exports fell to 37,000 tons of soda ash and 2700 tons of soda crystals; the internal consumption in Germany is between 240,000 and 280,000 tons. The Deutsche Solvay-Werke, with a capital of £2,000,000, showed a net profit of £360,000 in 1904, and the same profit is still maintained.

Brunner, Mond & Co., in England, with a capital of £3,000,000, paid a dividend of 100 per cent. for several years continuously and still pay 30 per cent.

Before 1897 Russia imported almost all its soda from abroad; in 1897 the consumption was 43,143 tons, of which 13,000 were imported; in 1907 the consumption rose to 63,500 tons and the imports fell to 352 tons.

Italy does not produce sodium carbonate, and imported 26,000 tons in 1902; 27,750 tons in 1904 at £5 per ton; 35,538 tons in 1907, and 38,351 tons in 1909, of the value of £191,260. One-half of this comes from France, one-fifth from Germany, one-fifth from England, and one-tenth from Belgium. In 1873 France produced 57,000 tons of soda, and in 1900 the production had risen to 225,000 tons, of which 20,000 were produced by the Leblanc process.

The continuous fall in the price has greatly contributed to the large increase in the consumption of soda; thus in England, where crystallised soda containing 63 per cent. of water was sold at £10 per ton in 1840, the price had fallen in 1860 to £5 12*s.*, in 1870 to £4, in 1880 to £3 9*s.* 6*d.*, and in 1890 to £2. In Italy to-day it is sold at £2 16*s.* per ton and calcined ammonia soda at £5 4*s.*[1]

This continuous fall in prices has enabled soda to be used in very many industries in which its use would not formerly have been thought possible; for instance, in building operations, by adding it to the mortar in order to be able to work in winter without fearing the action of the frost. A large palace at Brussels was actually constructed during a severe

[1] The approximate cost of production per ton of 100 per cent. soda by the two processes may be deduced

winter by avoiding freezing of the mortar by the addition of soda. This fall in price has rendered it difficult, if not impossible, to start new works in various countries in competition with those which already exist, and which are being continually perfected.

In America only 1100 tons of soda were produced in 1886 and about 300,000 tons in 1898, all by the ammonia process.

The German production of soda in 1878 was 42,000 tons (100 per cent.), and in 1890 was 195,000 tons, three-fourths of which was ammonia soda ; in 1894 the production rose to 250,000 tons, and in 1891 it reached 300,000 tons of the value of £1,520,000. The firm of Solvay in its various works in different countries produced 940 tons of soda altogether in 1870 and about 400,000 tons in 1889. There are also other works in Europe which produce ammonia soda with plants erected by Honigmann. In 1891 an English syndicate was formed comprising 45 large works and called the United Alkali Company, Limited, with a capital of about £8,800,000, which paid fabulous dividends in certain years (*see above*).

ANALYSIS OF SODA. The strength of pure soda solutions may be found from the Table of Specific Gravities, p. 469. In the case of soda ash it is necessary to heat it to gentle redness before analysis. The strength, or alkalinity, is determined with a normal solution of HCl, using methyl orange in the cold, or litmus with heating, as an indicator. The amount of insoluble matter is determined by dissolving 50 grms. of soda in hot water and collecting the residue on a tared filter. The iron in this insoluble portion may be determined by the usual analytical methods. Sodium chloride is determined by titration with silver nitrate in a definite quantity of the solution which is first exactly neutralised whilst hot with nitric acid ; a few drops of potassium chromate solution are used as indicator. The sulphates are precipitated with $BaCl_2$ in a solution of the soda which has been acidified with HCl, and heated, and the barium sulphate then weighed. Free sodium hydroxide, which may be present in certain qualities of the carbonate, is determined in 2 grms. of the material by dissolving it in water and then adding 10 c.c. of barium chloride solution (1 : 10) ; the whole is then diluted with hot water to 100 c.c., shaken, and allowed to settle in a closed bottle : 50 c.c. of the clear solution are then withdrawn and titrated with a normal solution of HCl in presence of methyl orange, and the alkalinity thus found is calculated as NaOH and deducted from the total alkalinity first found in order to obtain the true contents of sodium carbonate.

SODIUM DICARBONATE : $NaHCO_3$ (Sodium Hydrogen Carbonate, Primary Sodium Carbonate, Sodium Bicarbonate)

This substance is formed on passing a current of CO_2 and steam over soda maintained at a temperature of 80° : $CO_3Na_2 + CO_2 + H_2O = 2CO_3HNa$; or by passing CO_2 into a concentrated soda solution.

It is obtained industrially in the manner already described as the first product in the manufacture of ammonia soda, but in this case it always retains small quantities of ammoniacal salts, and must therefore be recrystallised from water for certain purposes. It crystallises without water of crystallisation in small monoclinic tablets soluble in 10 parts of water in the cold, and the solution has a weakly alkaline reaction. The dry salt decomposes even below 100°, forming CO_2. On boiling the solution a portion only of the CO_2 is first evolved, forming sodium sesquicarbonate, $CO_3Na + CO_3HNa + 2H_2O$, which is identical with the *Tro-na* of the Egyptian lakes, and on continuing the evaporation further CO_2 is evolved and the carbonate alone remains : $2NaHCO_3 = CO_2 + H_2O + CO_3Na_2$.

from the following table, where the mean prices of the prime materials at the localities where it is manufactured are taken:

	Leblanc Soda			Solvay Soda		
	Tons	*s.*	*d.*	Tons	*s.*	*d.*
Coal at 8*s.* per ton	0·4	3	2·5	0·210	1	8·2
Limestone at 2*s.* per ton	0·175		4·2	0·166		4·03
Salt (NaCl) at 14*s.* 5*d.* per ton	0·150	2	1·9	0·220	3	2·0
Pyrites and nitrate for H_2SO_4		2	7·7			
Ammonium chloride (loss)				0·005	1	5·8
Labour and staff		2	2·9		1	1·4
Interest and amortisation		1	2·5		1	0
		11	9·7			
Recovery of hydrochloric acid and sulphur		2	6·1			
Cost price		9	3·6			9·

Sodium bicarbonate is used for the washing of silk and wool of fine quality; also in medicine and in the preparation of effervescing drinks. The crude commercial product costs about £8 per ton and when refined £10 per ton, whilst the chemically pure product costs £16 16*s*. Italy imported 1530·2 tons in 1904 of the value of £12,240, and 1308·4 in 1908, which came from England. England exported 23,000 tons in 1909 and Germany 1227 tons.

SODIUM PHOSPHATES

These are less soluble, and crystallise better than the potassium phosphates:

(*a*) **TRISODIUM PHOSPHATE: Na_3PO_4 (Basic or Tertiary Phosphate).** This is formed on saturating 1 mol. of phosphoric acid with 3 mols. of sodium hydroxide and crystallises in six-sided prisms with 12 mols. of water. The aqueous solution has a weakly alkaline reaction and absorbs carbon dioxide from the air because it is largely dissociated hydrolytically into disodium phosphate and NaOH.

(*b*) **DISODIUM PHOSPHATE: Na_2HPO_4 (Neutral Phosphate, Secondary Phosphate, or Common Sodium Phosphate).** This compound is ordinarily employed for various chemical reactions because it is the most stable phosphate. It is obtained from dicalcium phosphate on precipitating the calcium with sodium carbonate:

$$PO_4HCa + CO_3Na_2 = CO_3Ca + PO_4HNa_2.$$

It is prepared on the large scale directly from bone ash or phosphorite by digesting it for several days with dilute H_2SO_4, by which means a solution of phosphoric acid and monocalcium phosphate is formed; this is then concentrated in order to separate the gypsum completely, filtered, diluted, and neutralised with Na_2CO_3, in order to separate all the remaining calcium. On concentrating the filtered solution the neutral phosphate crystallises out.

It crystallises from cold aqueous solutions with $12H_2O$ in large monoclinic prisms which easily effloresce in the air; from solutions of a temperature higher than 30° it crystallises with $7H_2O$ and does not then effloresce in the air. It dissolves in 4 parts of water and the aqueous solution has a weakly alkaline reaction. On passing a little carbon dioxide through the solution it acquires an amphoteric reaction, that is, it simultaneously shows both acid and alkaline reaction, reddening blue litmus paper and turning red litmus paper blue in the same manner as milk.

It melts at about 300° after losing its water of crystallisation, and is then transformed into sodium pyrophosphate, $Na_4P_2O_7$, which crystallises with $10H_2O$, and is converted into monosodium phosphate on boiling it with HNO_3.

Crystallised commercial disodium phosphate costs £8 per ton, whilst the refined product costs £14 and the anhydrous product about four times as much. It is used in the preparation of enamels, in tinning and soldering, and also as a weighting material in the dyeing of textile fibres; it is also used in medicine. Italy produced 250 tons in 1905 and 600 tons in 1907 of the value of £5640.

(*c*) **MONOSODIUM PHOSPHATE: NaH_2PO_4 (Primary Phosphate or Acid Phosphate).** This product is obtained as stated above, and crystallises with one molecule of water which it loses at 100°. The aqueous solution has a weakly acid reaction. At 200° it is transformed into disodium pyrophosphate, $Na_2H_2P_2O_7$, and this at 240° forms sodium metaphosphate: $P_2O_7H_2Na_2 = H_2O + 2PO_3Na$; but other compounds are also formed according to the conditions of heating by condensation of one or more molecules of sodium metaphosphate, for example, $Na_2P_2O_6$, &c.

The molten metaphosphate dissolves metallic oxides forming orthophosphates: $PO_3Na + CuO = PO_4NaCu$. According to the nature of the metallic oxide variously coloured phosphates are so formed and are characteristic of the individual metals (*phosphate beads*, which are used in chemical analysis).

SODIUM BORATE. The most stable of the borates is **Sodium Tetraborate**, called **Borax**, $Na_2B_4O_7 + 10H_2O$, which has already been mentioned in connection with **Boric Acid**. It is found ready formed in certain lakes in India China, Persia, and Thibet, from where it is sent to Europe under the name of *tinkal*. The minerals containing boron were mentioned on p. 404; common borax is known in prismatic crystals, $Na_2B_4O_7 + 10H_2O$, and in octahedra containing only 5 mols. of water of crystallisation. The prismatic product is prepared by adding boric acid to a boiling solution of sodium carbonate

(1 : 1) and allowing it to crystallise. Much borax is now prepared from **Boronatrocalcite** (Tiza), $Na_2B_4O_7 + 2CaB_4O_7 + 18H_2O$, which is found in Chili, by boiling it with soda or by first preparing boric acid and then saturating it with soda. Octahedral borax is obtained by cooling a solution of common borax of sp. gr. 1·26 (30° Bé.) to 70°, and collecting that portion of the crystals which separates above a temperature of 56° ; the mother liquors then yield ordinary borax. Its solubility in water is as follows : at 0° 2·83 per cent., at 20° 7·88 per cent., at 40° 17·90 per cent., at 60° 40·43 per cent., at 80° 76·19 per cent., and at 100° 201·4 per cent.

According to U.S. Pat. 911,695 (1909) by Bayley, borax is obtained much more economically by mixing borates in molecular proportions with sodium sulphate and heating to redness, but not to fusion, in suitable rotary furnaces similar to those used for Leblanc soda (p. 469) ; after cooling, the borax is dissolved in water and allowed to crystallise : $2Ca_2B_6O_{11}$ (colemanite) + $3Na_2SO_4 = 3CaSO_4 + CaO + 3Na_2B_4O_7$.

In 1906 and 1908 M. G. Levi proposed the preparation of borax by electrolysing two tepid solutions of boric acid (cathodic) and of sodium chloride (anodic) separated by a porous diaphragm ; sodium borate is then formed at the cathode. The cathodes are formed of lead and the anodes of carbon ; on replacing the sodium chloride by sodium sulphate smaller yields are obtained. A good crystallisation of borax is obtained with a very small excess of soda. The process may be profitable where electric energy is cheap. Borax is used to facilitate the brazing of metals ; these are joined in the heat in presence of borax by an alloy formed of from 2 to 3 parts of copper and 1 part of zinc. Molten borax dissolves the metallic oxides and keeps the surfaces clean, preventing further oxidation, and the alloy thus comes into direct contact with the polished surfaces of the metals and brazes them firmly together. When brazing is unnecessary the metals are soldered with an alloy of tin and lead, in which case lower temperatures are used, and zinc chloride, ammonium chloride, colophonium, or stearine are used as cleaning agents instead of borax. Borax is used for glazing earthenware, though borocalcite is now preferred. It is also used in the manufacture of anthracene dyestuffs.

Refined borax costs £18 per ton, and the chemically pure product £28 16*s.* per ton (*see* Boric Acid, p. 405). In Italy the borax industry has undergone many fluctuations in the output ; from 1100 tons in 1893 it fell to 375 tons in 1902 ; shortly afterwards the conditions appear to have improved, and in 1905 the production rose to 1007 tons, and in 1906 to 1061 tons ; in 1907 it was 881 tons, and in 1908 it returned to 1025 tons of the value of £15,200 ; in 1904 the imports fell to 228 tons (which was half of that of the previous year), in 1906 to 149 tons, in 1908 they rose to 259 tons, and in 1909 they were 320 tons of the value of £4740. It should be noted that this product is favoured by a protective tariff of £1 12*s.* per ton. The exports rose to 164 tons in 1904 and 607 in 1906, and fell to 30 in 1908, rising again to 182 tons in 1909 of the value of £2686.

The United States have become large producers of borax, almost all of which comes from California, and in 1904 the production was 45,747 tons and in 1905 46,334 tons of the value of £220,000.

SODIUM PERBORATE : $Na_2B_4O_8.10H_2O$ (or $NaBO_3.4H_2O$, which is more stable in the air). This product is used for the preparation of very pure hydrogen peroxide, and its aqueous solution already behaves as H_2O_2, evolves oxygen at 40°, and is used as a very effective antiseptic for the cure of sores. Jaubert (Ger. Pats. 193,559 and 207,580) prepares the perborate by mixing 248 grms. of boric acid with 78 grms. of sodium peroxide, and pouring the mixture slowly into two litres of cold water acidified with H_2SO_4 ; the crystals which separate are washed with alcohol and dried at 50° ; the solubility in water is about 2 per cent.

According to Ger. Pat. 218,569, the perborate is prevented from decomposing easily during its formation by replacing the sulphuric acid or hydrochloric acid by carbon dioxide, which does no harm even if present in excess. 150 kilos of sodium peroxide are added to 200 kilos of water, avoiding any rise of temperature by the addition of ice. 150 kilos of boric acid are then added and chimney gases freed from dust are passed through the liquid until 50 c.c. of the filtered solution only decolorise 5 to 10 c.c. of an $\frac{N}{5}$ solution of permanganate which has been acidified with sulphuric acid.

In order that the perborate may be capable of storage it is necessary to use pure prime materials and thus to obtain a well-crystallised product as is effected by Girsewald (Ger. Pat. 204,279) by working with a not too concentrated alkaline solution and finally completing the reaction by saturating the mother liquors with sodium chloride. It is also necessary to maintain a low temperature during the entire operation.

It is now used for bleaching in common with magnesium perborate.

It costs from 2*s*. 5*d*. to 3*s*. 2½*d*. per kilo (p. 237); it preserves its activity well when crystallised, and is very much used in works to-day as a cleaning and bleaching agent, instead of sodium peroxide, &c. It is also mixed with soap.

SODIUM SILICATE (Soluble Glass, Soluble Soda Glass, Water Glass). This compound was discovered in the Middle Ages by Van Helmont, but its preparation was precisely described by J. V. Fuchs in 1825. It was first employed, however, in the first half of the past century. It is similar to potassium silicate, and is obtained by melting 45 parts of powdered quartz with 23 parts of calcined soda and 25 parts of powdered coal in reverberatory furnaces or in crucibles. After the molten mass has cooled it is powdered and dissolved in 56 vols. of water with the aid of steam in autoclaves provided with stirrers, at high temperatures and under pressure. A heavy solution is thus obtained which is ready for sale. It is also prepared from 100 parts of siliceous sand, 60 parts of sodium sulphate, and 15 to 20 parts of powdered wood charcoal; whilst in the primitive furnaces with direct flame 1·5 kilos of coal were used for every kilo of silicate produced, to-day with the Siemens regenerative furnace (*which see*) the consumption of coal is only 0·29 kilo. A double silicate of sodium and potassium is also known and used; this is more fusible than simple silicates of sodium or potassium.

When the resulting molten sodium silicate has a brown colour due to the formation of Na_2S this may be eliminated by passing a current of air through the molten mass or by adding copper or lead oxide to the solution.

Soluble glass must be kept in closed vessels because the carbon dioxide of the air decomposes it with separation of gelatinous silicic acid.

In the solid state its composition varies between $Na_2O.4SiO_2$ and $Na_2O.2SiO_2$, and its solubility increases with diminution of the silica. Its greenish colour is due to impurities containing iron. Solid sodium silicate does not keep in the air so well as potassium silicate.

It slowly dissolves in cold water and the solution contains more alkali than the part which is still undissolved.

Soluble glass is used to render objects which have been impregnated with it more resistant to fire. It is used as an adhesive for glass, porcelain, stone, &c. It is much employed for adulterating (weighting) soap and in stereochromy as a medium for mineral pigments (zinc white and yellow, chrome green, &c.). It is also used in dyeing as a weak alkali.

Sodium silicate is placed on the market in solutions of 38° to 40° Bé. at a price of £2 16*s*. to £3 12*s*. per ton; of 50° to 55° Bé. at £3 4*s*. to £4 per ton, and the solid at £4 to £4 16*s*. per ton. A commercial silicate of 33° Bé. yielded on analysis 23·3 per cent. of SiO_2, 6·7 per cent. of Na_2O, 1·7 per cent. of chlorides and sulphates, and 67·6 per cent. of water. A sample of 40° Bé. contained 26·1 per cent. of SiO_2, 9·8 per cent. of Na_2O, 1·7 per cent. of impurities, and 62·4 per cent. of water.

In Italy 2100 tons of liquid sodium silicate were produced in 1893, more than 7000 tons in 1900, 3720 tons in 1905, and 5270 tons in 1908, of the value of £16,890. In 1904 1523·3 tons of liquid sodium silicate were imported at £2 16*s*. per ton and 2325·4 tons of the solid silicate at £4 8*s*. In 1908 the imports were 2700 tons of liquid silicate of the value of £6480 and 3650 tons of solid silicate of the value of £14,600; in 1909 they were 2650 tons of liquid and 2250 tons of solid.

In 1893 Germany exported 4400 tons of silicate, and in 1905 11,600 tons.

SODIUM AZIDE : NaN_3. This substance is obtained from organic compounds or preferably by heating sodium amide in a current of nitrous oxide at 200° :

$$NH_2Na + N_2O = N_3Na + H_2O.$$

Its aqueous solution has a weakly alkaline reaction (*see* pp. 327–328).

CHARACTERISTIC REACTIONS OF SODIUM SALTS. All sodium salts colour the Bunsen flame yellow and give a brilliant yellow line composed of two lines very close to each other in the spectrum. With potassium pyrantimonite the neutral salts of sodium give a white crystalline precipitate of acid sodium pyrantimonate in the cold.

This reaction is one of the very few which permit sodium salts to be distinguished and separated from potassium salts.

LITHIUM : Li, 7

This is a somewhat rare element, but is widely diffused in small quantities. It is found in various mineral waters, for example, in those of Salsomaggiore, which are the richest known in lithium and strontium ; also in the ashes of many plants, especially in those of beetroot, tobacco, and tea. It is also found in animal organisms. As silicate, combined with other metals, it forms certain minerals such as *lithiferous mica* (*lepidolite*), $K_4Li_4(AlF_2)_3Al_4(Si_3O_8)(SiO_4)_3$; as phosphate in *triphyllite* and *lithiophyllite*, $Li(FeMn)PO_4$, and is also found more abundantly in *ambligonite*, $Li(AlF)PO_4$.

It is a soft metal with a silvery lustre and was obtained by Bunsen and Matthiessen in 1855 by the electrolysis of lithium chloride or preferably of a mixture of LiCl and KCl. It melts at 108°, and has a specific gravity of 0·59 (water = 1) ; it is thus the lightest metal and floats even on petroleum in which it is preserved in order to protect it from ready oxidation. It decomposes water more slowly than sodium ; it burns at 200° with an intense white light which differs from that of lithium salts, which colour the flame crimson red and give a characteristic brilliant red line in the spectrum together with a less brilliant orange line (*see* Spectroscopic Plate at the commencement of this volume). Metallic lithium costs 3*s*. 2*d*. per gramme, and when chemically pure 9*s*. 7*d*.

Lithium salts are similar to sodium salts and also have certain resemblances to those of magnesium.

Lithium burns intensely in an atmosphere of hydrogen forming **LITHIUM HYDRIDE, LiH**, which is a fairly stable white powder.

LITHIUM CHLORIDE, LiCl, crystallises in octahedra and is deliquescent in the air.

Lithium may be separated from its soluble salts by means of sodium phosphate or sodium carbonate because it forms a phosphate, Li_3PO_4 (+ $\frac{1}{2}H_2O$), and a carbonate, Li_2CO_3, which are almost insoluble in water, and in this respect it resembles the metals of the second group.

Certain salts of lithium, especially the carbonate, and the salicylate to an even greater extent, and also mineral waters containing lithium are used in medicine as a remedy for arthritis, renal calculi, stone in the bladder, &c. Pure lithium carbonate costs about 16*s*. per kilo. In the United States 1150 tons of lithium minerals were treated in 1903 of the value of £4800 and 575 tons in 1904 of the value of £1000.

AMMONIUM

When treating of ammonia we already noted that in aqueous solution it may be considered to partially consist of a hydrate of ammonia, $NH_4.OH'$, resulting from the combination of one of its molecules with one molecule of water, and that this substance must be supposed to be partially dissociated into two ions, the cation NH_4' called ammonium, which behaves in all reactions as though it were an alkaline metal, and the anion OH', which is the cause of the alkaline reaction of aqueous ammonia. Dilute ammonia solutions conduct the electric

current less than similar solutions of KOH, thus showing that a portion only of the ammonia is present as a hydrate, which is confirmed by the fact that the tensions of ammonia solutions follow Henry's law fairly closely, and thus the greater part of the NH_3 is not combined with H_2O. The monovalent ammonium ion forms numerous salts just as though it were a metallic element, and these salts have very great chemical and physical resemblances to potassium salts with which they are ordinarily isomorphous. This ammonium group may even be separated by absorption by mercury, with which it forms an amalgam (a property characteristic of metallic elements only and not of their compounds). When, however, attempts are made to isolate this "ammonium metal" it is decomposed into NH_3 and H.

Ammonia in aqueous solution, being less dissociated than sodium and potassium hydroxides, forms an alkali or base which is much less energetic, and is therefore easily displaced by other bases from its salts. Its basic action is diminished in presence of ammoniacal salts, because these increase the number of $NH_4^{\cdot}$ ions in solution, thus displacing the previous ratio between the ammonium $NH_4^{\cdot}$ and OH' ions, a ratio on which the basic power depends (p. 98).

Ammoniacal salts are solid, and are unstable on heating.

AMMONIUM CHLORIDE : NH_4Cl (SAL AMMONIAC)

This compound was obtained by burning camel's dung. It is prepared to-day in the same way as ammonium sulphate from the ammoniacal liquor of gasworks (*see* Ammonia, p. 323), and attempts have also been made to obtain it by decomposing ammonium sulphate with KCl. It forms a white crystalline substance of fibrous structure which sublimes without melting. It dissociates at 350° into two gases, NH_3 and HCl, which reunite again on cooling (*see* p. 40). This dissociation only occurs in presence of small traces of moisture which act catalytically, and since all catalysts which cause a certain reaction are also capable of producing the reverse reaction when external temperature conditions are suitably changed, in harmony with the law of mass and of chemical equilibrium, on mixing completely dry ammonia and hydrochloric acid no combination occurs ; whilst if water vapour is present it immediately takes place at temperatures below that of dissociation.

Ammonium chloride is very soluble in water and the solution has a weakly acid reaction because the $NH_4^{\cdot}$ ion hydrolyses with the minimal quantities of dissociated hydroxyl groups of the water forming NH_3 and H_2O and leaving unaltered $H^{\cdot}$ acid ions of the water. On heating, the solution loses part of the hydrolised ammonia, and thus its acid reaction is increased because new quantities of ammonium cations $NH_4^{\cdot}$ hydrolyse forming further free acid $H^{\cdot}$ ions.

Ammonium chloride is used in soldering because on heating it liberates HCl which dissolves the oxides on the surface of the metals (*see* Borax, p. 480) ; it is used in dyestuff factories and in calico printing.

The crude commercial product costs about £26 per ton, and when purified £32.

AMMONIUM FLUORIDE : NH_4F. This compound is obtained by the interaction of HF and NH_3, or also by subliming a mixture of NH_4Cl + NaF. It forms deliquescent crystals which readily attack glass. On heating a solution of this salt a portion of the NH_3 is evolved and an acid ammonium fluoride, $NH_4F.HF$, remains, which is commonly used for etching glass. Pure ammonium fluoride costs £80 per ton ; the doubly refined product costs £140 per ton and when chemically pure 6*s.* 5*d.* per kilo.

It is used as a disinfectant in the manufacture of spirits, beer, &c., and does not attack metallic objects very much. It is now more economically obtained in solution by utilising the silicon fluoride formed in superphosphate manufacture (*which see*).

AMMONIUM SULPHATE : $(NH_4)_2.SO_4$

The preparation of this salt has been already described when discussing ammonia (p. 323) ; it forms a white mass of crystals which are isomorphous with those of potassium sulphate. It melts at 140° and then decomposes in the same manner as all ammonium salts of polybasic acids, forming ammonia and acid ammonium sulphate, NH_4HSO_4. It is very soluble in water (in an equal weight at 100°), and the solution is slightly hydrolysed in the same manner as ammonium chloride solutions. The process of Addie and Mond for absorbing ammonia in the distillation of coal, peat, &c. (p. 326), by washing the gas with sulphuric acid was improved according to Eng. Pat. 20,870 of 1904, U.S. Pat. 845,332, and Ger. Pat. 181,846 of 1909. According to these patents the gas is cooled to the condensation point of the tar, which is then condensed ; the gas is then passed through a separator, reheated, and the ammonia absorbed by sulphuric acid. Collet and Eckardt (1910) proposed the preparation of ammonium sulphate by passing a stream of $SO_2 + NH_3 +$ air into water. The ammonium sulphite which is thus formed is transformed into ammonium sulphate by the action of the air ; similarly by treating calcium cyanamide in the heat with SO_2 and steam soluble ammonium sulphite is obtained which is then oxidised, and insoluble calcium sulphite remains :

$$CaCN_2 + 2SO_2 + 4H_2O = CaSO_3 + CO_2 + SO_3(NH_4)_2.$$

It is used in artificial manure at a price of £14 per ton, and is obtained almost exclusively in gas manufacture. In 1860 the world's production was only 10,000 tons, but this rose to 493,000 tons in 1900 of the value of £5,200,000 ; and in 1903 it exceeded 576,000 tons of the value of £6,000,000 ; in 1906 it was 759,000 tons, in 1907 850,000 tons, in 1908 800,000 tons, and in 1909 more than 900,000 tons. The production of the various countries is seen in the following Table :

	1903 tons	1906 tons	1907 tons	1908 tons
England . . .	234,000	283,000	316,000	325,000
Germany . . .	140,000	267,000	287,000	313,000
United States . .	—	75,000	—	82,000
France . . .	44,000	49,000	52,700	57,600
Belgium . . .	35,000	26,000 ?	—	20,000 ?
Holland . . .	—	40,000 ?	—	20,000 ?
Austria-Hungary .	—	30,000	—	55,000
Italy . . .	3,685	4,820	5,058	5,346
Spain . . .	—	10,000	—	20,000

Italy is continuously increasing her imports of ammonium sulphate for agricultural purposes. In 1904 they were 5370 tons, in 1904 6975 tons, in 1906 9738 tons, in 1907 14,940 tons, in 1908 16,700 tons, and in 1909 18,915 tons, of the value of £246,896. In 1907 100 tons of ammonium sulphate were produced from the boric *soffioni*.

England exported 145,000 tons in 1900, 162,000 tons in 1903, 201,400 tons in 1906, 235,000 tons in 1908, and 264,000 tons in 1909.

The exports in 1908 were distributed as follows : 24,000 tons to France, 24,500 tons to Germany, 9000 tons to Belgium, 51,600 to Spain and Portugal, 7300 to Italy, 7400 to Holland, 39,000 to Japan, 29,000 to the United States, &c.

Of the ammonium sulphate produced in England in 1908 168,000 tons were produced n gasworks, 20,000 tons in blast furnaces, 52,000 tons from the distillation of shales, and 85,000 tons from coke-ovens and producers (in 1898 only 11,000 tons were produced from coke-ovens and producers).

In 1905 Germany imported 48,000 tons of ammonium sulphate and exported 27,559 tons at £12 10*s.* per ton ; in 1908 it imported 47,000 tons and exported 73,000 tons ; in 1900 it imported 58,000 tons and exported 58,000 tons.

On electrolysing ammonium sulphate, Ammonium Persulphate $(NH_4)_2S_2O_8$, is obtained and is now employed commercially as an oxidising agent, because on heating in aqueous

solution it forms ammonium sulphate, sulphuric acid, and oxygen (*see* Persulphuric Acid, pp. 286 and 466). It is used for the preparation of other persulphates.

AMMONIUM NITRATE : NO_3NH_4, is very deliquescent, melts at 159°, has a bitter taste, and decomposes above 170° into $2H_2O$ and N_2O. This is not a simple dissociation, because on cooling this mixture the original product is not regenerated as in the case of ammonium chloride.

It is obtained by saturating nitric acid with gaseous ammonia or ammonium carbonate and on evaporating the solution large crystals are thus formed which absorb heat when dissolved in water. According to Ger. Pat. 178,620 and Norwegian Pat. 19,410 of 1908, it may be prepared by mixing a solution of calcium nitrate with excess of ammonia and passing carbon dioxide through the liquid :

$$Ca(NO_3)_2 + 2NH_4OH + CO_2 = CaCO_3 + 2NH_4NO_3 + H_2O.$$

It may also be obtained, according to Ger. Pat. 184,144, from ammonium sulphate and excess of sodium nitrate, either in solution or by fusion.

It is used in freezing mixtures and for the preparation of explosives, which may be handled without danger because they do not easily catch fire. It costs £40 per ton.

AMMONIUM NITRITE : NH_4NO_2. This compound is formed by the action of an electric discharge on moist air. It forms a crystalline deliquescent mass which decomposes on heating or even in hot concentrated solution into $2H_2O + N_2$, with evolution of heat, so that it is not possible to recombine the products of the decomposition by pressure, as the reaction is exothermic. In this case also the phenomenon is not one of dissociation as is the case in the formation of sodium hydride.

AMMONIUM HYPONITRITE : $\begin{matrix} N—O—NH_4 \\ \| \\ N—O—NH_4 \end{matrix}$ is obtained from gaseous NH_3 and an ethereal solution of hyponitrous acid ; it melts at 64° with decomposition.

AMMONIUM CARBONATE : $CO_3(NH_4)_2$. This compound forms a transparent crystalline mass which sublimes at 60°, is rather unstable, and is obtained together with ammonia from **AMMONIUM BICARBONATE : CO_3HNH_4**, or acid ammonium carbonate, which is more stable and is formed from aqueous ammonia and CO_2 or also from gaseous ammonia with CO_2 and steam. It is commonly prepared by the sublimation of a mixture of equal parts of calcium carbonate and ammonium sulphate with addition of one-eighth part of powdered wood charcoal. It is easily found already formed in the commercial **sesquicarbonate**, which is a mixture of one part of ammonium carbonate with two parts of the bicarbonate and a little *ammonium carbamate*, $NH_2.CO_2.NH_4$.

It is used in the manufacture of dyestuffs, for the degreasing of fabrics and in medicine.

It costs £40 per ton. It is mainly manufactured in England and Germany and in 1908 673·2 tons were imported into Italy. The sesquicarbonate is obtained by heating a mixture of ammonium sulphate or chloride with calcium carbonate.

AMMONIUM PHOSPHATES. Normal triammonium phosphate is not known because it is not stable, although phosphoric acid is tribasic ; mono- and di-ammonium phosphates of little importance are however known.

SODIUM AMMONIUM PHOSPHATE (Secondary Phosphate) : $PO_4NaH.NH_4$ (Phosphorus Salt or Microcosmic Salt). This is the most important of the various ammonium phosphates and is found in guano and in fermented urine. It is obtained by crystallising a mixture of disodium phosphate and ammonium chloride :

$$Na_2HPO_4 + NH_4Cl = NaHNH_4.PO_4 + NaCl.$$

On melting, it loses water and ammonia, forming a vitreous mass of sodium metaphosphate, which when fused dissolves various metallic oxides forming metallic orthophosphates which are variously coloured according to the nature of the metal (phosphate bead).

AMMONIUM SULPHIDE : $(NH_4)_2S$. This compound is obtained from H_2S and NH_3 at − 18°, but at ordinary temperatures even in aqueous solution it decomposes to form $NH_3 + NH_4SH$ (ammonium hydrosulphide). At 45° it dissociates into 2 vols. of NH_3 and 1 vol. of H_2S. On passing hydrogen sulphide into a concentrated solution of ammonia until this is completely saturated,[1] a solution of ammonium hydrosulphide, NH_4SH, is

[1] In order to easily determine whether a liquid is saturated with a gas 8 to 10 c.c. are placed in a test-tube and the liquid is then shaken strongly after closing the mouth of the test-tube with the thumb. If pressure is

obtained and if the same volume of ammonia as was first employed is added to this a solution of normal ammonium sulphide, $(NH_4)_2S$, is obtained.

AMMONIUM HYDROSULPHIDE : $(NH_4)SH$. This compound is obtained in a crystalline condition by passing a current of H_2S into an alcoholic solution of ammonia. The aqueous solution obtained as described above becomes yellow on standing in the air, because the hydrogen sulphide which is formed by hydrolysis oxidises in the air with separation of sulphur, and this dissolves in the ammonium hydrosulphide, forming *ammonium polysulphides*, $(NH_4)_2S_x$, which are also obtained directly by heating ammonium hydrosulphide with sulphur. The pure solid hydrosulphide dissociates at 45° into 1 vol. of NH_3 + 1 vol. of H_2S.

The solution of the hydrosulphide is used in the laboratory in analysis for the precipitation of metallic sulphides which cannot be separated otherwise because they are soluble in acids. The yellow hydrosulphide is used for dissolving those metallic sulphides which are capable of forming thionic acids which form soluble ammonium salts. Ammonium sulphide is used in organic chemistry as a reducing agent.

GENERAL REACTIONS OF AMMONIUM SALTS. They are all volatile and decompose on heating ; the other bases (alkalis or alkali earths) drive off ammonia from solutions of ammonium salts on heating.

Chloroplatinic acid gives a yellow crystalline precipitate of ammonium chloroplatinate, $(NH_4)_2PtCl_6$, only slightly soluble in water, with ammonium salts. Excess of tartaric acid also forms a slightly soluble acid ammonium tartrate.

SECOND GROUP OF THE METALS

These are all *divalent*, and are divided into three sub-groups, in accordance with certain analogies in their chemical and physical properties :

(*a*) **Calcium, Strontium, Barium** ; (*b*) **Glucinum, Magnesium** ; (*c*) **Zinc, Cadmium,** and **Mercury.**

ALKALI EARTH METALS

Ca, 40.09 ; Sr, 87.6 ; Ba, 137.37

These metals are thus called because on the one hand their oxides are similar to those of the alkali metals, and present, on the other hand, certain similarities to the earths (alumina, &c.).

With increase of the atomic weight and atomic volume their basicity ncreases ; thus the derivatives of barium are more stable than those of calcium, which is also in harmony with their heats of formation. They also combine directly with nitrogen, forming nitrides, in common with lithium and magnesium.

They are easily distinguished from the alkali metals because they form insoluble carbonates, sulphates, and phosphates. They have no great affinity for oxygen, although they cannot be obtained in the free state by reducing their oxides with carbon because these oxides only melt at extremely high temperatures in the electric furnace, and at such temperatures the alkali earth metals which are liberated immediately react with carbon to form carbides.

CALCIUM : Ca, 40.09

This compound is very abundant and widely diffused in nature, especially as calcium carbonate in the form of *marble*, *chalk*, *calcspar*, &c. ; as phosphate in *phosphorite* ; as sulphate in *gypsum*, *anhydrite* and *alabaster* ; as fluoride in *fluorspar* ; as a pure silicate, $CaSiO_3$, in *wollastonite*, &c., and also abounds

produced in the tube, which is easily observed on lifting the thumb, it is a sign that the liquid was saturated, but suction is produced, this was not the case.

as a component of various other rocks ; it is also found in all vegetable and animal organisms, in egg-shells, sea-shells, &c.

Calcium was discovered by Davy in 1808, and was prepared in the pure state by Bunsen in 1855. Moissan obtained it later by heating calcium iodide to a dark red heat with an excess of sodium, which also served to dissolve the metallic calcium as it was formed. After cooling, the sodium was separated and dissolved in absolute alcohol, and calcium thus remained in the form of a lustrous crystalline powder. Metallic calcium is now obtained by the process of Ruff and Plato (Ger. Pat. 153,731) by electrolysing at 800° a mixture of 100 parts of $CaCl_2$ and 16 parts of CaF_2, which melts at 660° ; graphite is used as the anode and an iron wire as the cathode, pure calcium of 99·3 per cent. being deposited on the latter. Other electrolytic processes are given in Ger. Pats. 144,667 and 155,453.

In dry air metallic calcium keeps fairly well, but in moist air it becomes covered with a layer of hydroxide. Calcium decomposes water in the cold with considerable evolution of energy. It has a silvery lustre, which is slightly yellowish in shade. Its specific gravity is 1·83, and it is harder than tin. It has a great absorbent power for gases and can be used for the production of a vacuum in various media. It melts at a red heat (760°) and burns with an orange-red flame. Its vapours combine readily with oxygen and nitrogen. One gramme of calcium once cost 17*s*. 6*d*. ; it is now prepared industrially at 9*s*. 7*d*. to 12*s*. per kilo, and is employed in metallurgy for removing the last traces of carbon from alloys and metals by melting them with a little calcium. It serves as a good reducing agent in organic chemistry and is used instead of magnesium in Grignard's reaction. Certain metallic alloys containing calcium are of special interest.

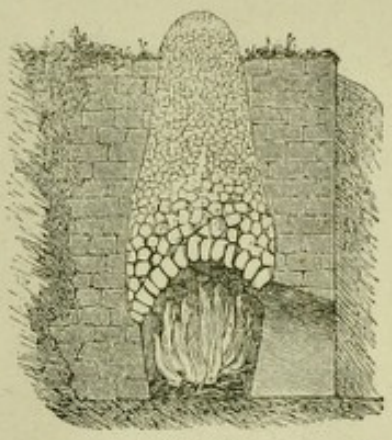


Fig. 202.

CALCIUM NITRIDE : Ca_3N_2. This is a brown substance which is obtained by heating calcium to a red heat in a current of nitrogen ; it is decomposed by water, forming calcium hydroxide and ammonia.

CALCIUM HYDRIDE : CaH_2. This compound is formed in the cold, but the reaction proceeds more rapidly on heating by the direct interaction of Ca and H_2. It is a grey powder which decomposes water energetically with evolution of hydrogen, and it has therefore been proposed for filling balloons.

CALCIUM OXIDE : CaO (QUICKLIME)

The practical importance of this substance is universally known. The chemically pure product is obtained in the laboratory by heating pure calcium nitrate or carbonate to redness. Industrially limestone is used ; this forms large deposits and is often found as pebbles in river beds. On heating this limestone in intermittent or continuous kilns to about 1000° all the CO_2 of the carbonate escapes and CaO remains. In order to dissociate 1 kilo of $CaCO_3$, 425 Cals. are required, and since 1 kilo of coal produces 8000 Cals. $\frac{100 \times 425}{8000}$, *i.e.* 5·3 kilos of coal will be theoretically required in order to decompose 100 kilos of calcium carbonate into $CaO + CO_2$. But in practice the best lime-kilns (those of Hoffmann, Dietzsch, &c.) use about 10 to 12 kilos of coal.

The type of kiln which was mostly used in the past was distinguished by its simple construction, and consisted of an open channel formed of brickwork which was filled from above (Fig. 202). Large pieces of limestone were first arranged to form an arch, which was temporarily supported by wood, on which smaller pieces were heated. The fuel was

burnt at the lower part of the furnace, but the heat was not well utilised, and 500 to 600 kilos of wood were used per cubic metre of lime, which weighed 1400 to 1600 kilos ; each operation producing 10 to 20 cu. metres of lime takes from 40 to 45 hours. It is finished when the limestone blocks have become white hot, and have somewhat decreased in volume (about one-sixth). The kiln is then allowed to cool for twelve hours, is discharged at the lower part which has served as a hearth, and is again recharged.

A furnace for continuous work in which the heat is better utilised and the carbon dioxide recovered is illustrated in section and perspective in Fig. 203, in which the heating is produced by three lateral hearths with a grate, *F*, which alternate with three discharging openings, *S*. The limestone is charged in above from cars by means of inclined planes or elevators, through the mouth, *B*, which is immediately closed so that the carbon dioxide may be collected in the upper tubes, *C* ; the progress of the burning of the lime is watched by observing the red-hot limestone through the windows, *g*, and the temperature and the draught are regulated by means of the damper, *D*.

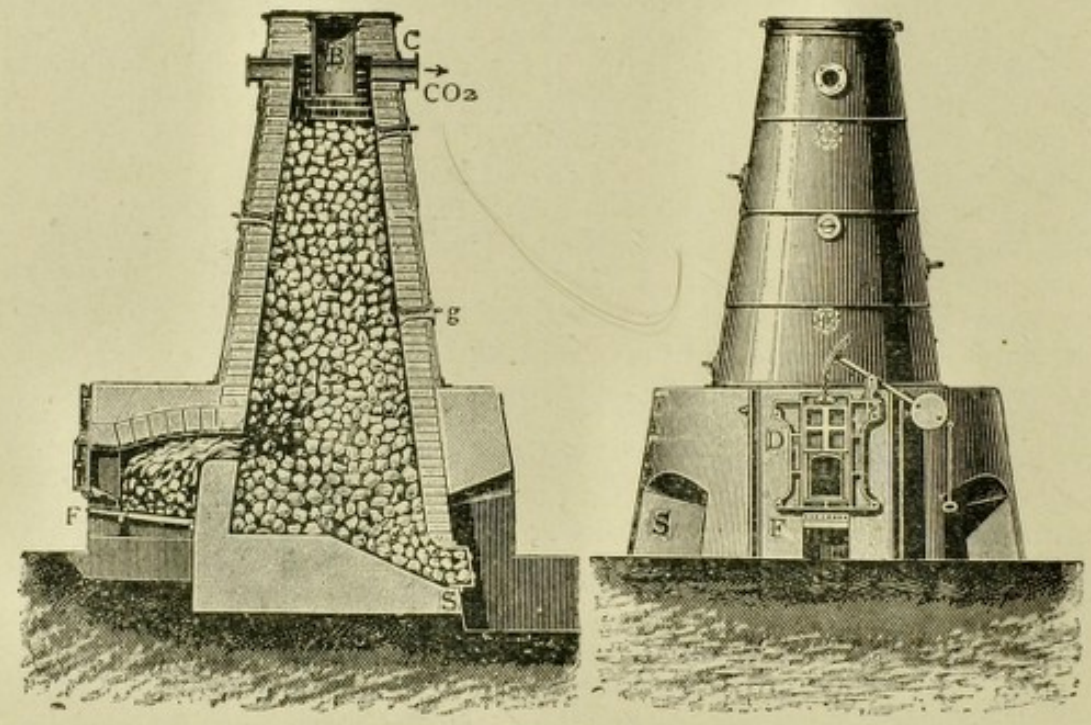


Fig. 203.

Another form of continuous kiln, much used in sugar factories, where both the lime and the carbon dioxide are utilised, is shown in Fig. 204. In this there are no lateral hearths, but it is charged from above with a mixture of limestone and coke which is raised in cars, *V*, by the elevator, *E* ; the kiln, *F*, is formed of a sheet-iron shell of conical form constricted below and lined internally by a layer of firebrick. The whole of the furnace is raised above the ground, and supported by cast-iron columns, *K*. The whole weight of the limestone and carbon with which it is charged is supported by the conically raised floor, *T* ; the interval which separates the lower mouth of the kiln from the floor allows the quicklime to be gradually removed and allows sufficient air for the combustion to enter. The small side-windows, *g*, allow the progress of the burning to be observed. The carbon dioxide which collects above is led by the tube, *C*, to a washing apparatus, *P*, and then passes through the tube, *L*, into the exhaust pump.

In certain cases the circular Hoffmann furnace which is generally adopted in the ceramic industry is used (*see* Porcelain), and economises fuel very considerably. There are also somewhat complex gas-fired kilns which we will not describe here ; it is said that in America rotary furnaces have been employed, similar to those used for cement, which require about 8·5 kilos of coal per 100 kilos of limestone.

The proportions of limestone, coal, and air in the lime-kilns of the Solvay Soda Works are adjusted in such a manner that the gas which is collected above contains about 32 per cent. of CO_2, but less than 28 per cent. if the charges are only introduced every three

hours and not more frequently. When the CO_2 is to be utilised coke is used instead of coal in order to obtain it in a purer state.

Commercial quicklime always contains a little silica, alumina, and iron oxide, which sometimes gives it a slightly yellow or grey colour.

The limestone used for the production of quicklime should not contain much magnesia, because 6 to 8 per cent. of this ingredient already causes the formation of poor lime (of poor quality), and when 20 per cent. is present the lime is useless; those quicklimes which contain little magnesia are called *fat* (or *rich*) limes.[1]

When pure, calcium oxide forms a whitish mass which only melts at about 3000° and then volatilises. When heated in the oxy-hydrogen flame it emits an intense white light (Limelight, p. 175).

Calcium oxide absorbs water very actively combining with it with evolution of much heat and transformation into a voluminous amorphous mass of **calcium hydroxide**, $Ca(OH)_2$ (**slaked lime**). On standing in the air it absorbs CO_2 and H_2O vigorously and may be used as a dehydrating or drying agent.

Quicklime is used for the preparation of slaked lime and therefore of mortar, and also for the manufacture of crucibles which resist high temperatures (for melting platinum in the oxy-hydrogen flame); it is also used in glass manufacture and in the smelting of metals. Italy produced 28,000 tons in 1907 for this latter purpose, of the value of £11,200.

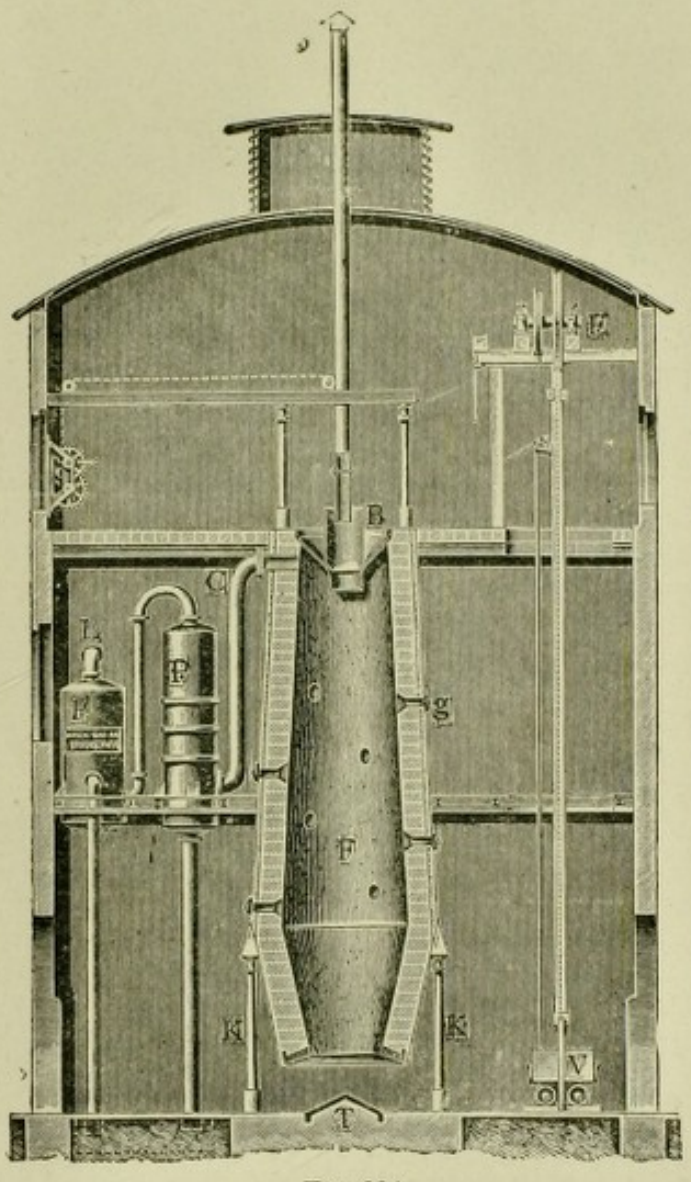


FIG. 204.

ANALYSIS OF QUICKLIME AND SLAKED LIME. It is ordinarily necessary to note how much CaO and how much $CaCO_3$ it contains. In order to determine the first, 100 grms. of the lime are slaked with water in a half-litre flask, and made up to half a litre. The whole is then stirred and a 100 c.c. sample immediately taken before it settles, placed in another half-litre flask and again made up to half a litre with water; 25 c.c., corresponding to 1 grm. of the original lime, are removed after shaking and are titrated with a normal solution of HCl, using phenolphthalein as an indicator. As soon as the red colour of the solution disappears the CaO has all been neutralised and $CaCO_3$ only remains. The determination of CaO + $CaCO_3$ is then made by dissolving a given quantity of the lime in excess of normal HCl and titrating back the excess of HCl with a normal solution

[1] But in Lombardy lime obtained from calcareous dolomite is often used and contains magnesia; although when magnesia is present in small quantities it weakens the lime and is an inert component, if present in large quantity it gives equally good lime; thus the following limestone, $CaCO_3$ = 54·80 per cent., $MgCO_3$ = 44·8 per cent., SiO_2 = 0·1 per cent., iron oxide and alumina = 0·2 per cent., gives a fat strong (*i.e.* weakly hydraulic) lime.

of NaOH. One cubic centimetre of normal HCl corresponds to 0·028 grm. of CaO, and by deducting from this total the quantity of HCl corresponding to the CaO, the quantity of CaO combined with CO_2 as carbonate is found.

CALCIUM HYDROXIDE : $Ca(OH)_2$ (SLAKED LIME)

When quicklime is moistened with about one-third its weight of water heat is developed [$CaO + H_2O = Ca(OH)_2 + 15{\cdot}5$ Cals.], and the temperature rises up to 160°. A white powdery swollen mass of slaked lime results, which when mixed with a further three or four parts of water forms a soft homogeneous paste which is kept in a trench dug out of the ground, where it loses the excess of water together with soluble alkali salts which spoil the mortar as they would produce efflorescence in the brickwork.

Calcium hydroxide is a white mass, only slightly soluble in cold and less in hot water, so that the cold solution (lime water) becomes turbid on heating. One part of lime dissolves in 760 parts of water at 0° ; in 776 parts at 15°, in 813 parts at 20°, in 885 parts at 30°, in 962 parts at 40°, in 1044 parts at 50°, in 1158 parts at 60°, in 1330 parts at 70°, and in 1482 parts at 80°. The aqueous solution has a strongly alkaline reaction because the hydroxide is partly dissociated into $Ca^{\cdot\cdot}$ and $2OH'$. Slaked lime does not lose all its water even at 300°, and only regenerates the oxide at a red heat. It absorbs CO_2 from the air, being slowly transformed into carbonate.

The solubility of calcium hydroxide in water does not vary much with the temperature, and a saturated clear solution at the ordinary temperature contains 1·3 grms. of $Ca(OH)_2$ per litre.

USES OF LIME. Lime is used in the preparation of sodium and potassium hydroxides from the carbonates. It is also used in the manufacture of chloride of lime by absorbing chlorine and in the recovery of ammonia from gas water, and largely in sugar refineries, candle works, &c.

The largest quantity is, however, used for the preparation of common mortar for building purposes by mixing it with water and sand ; this mortar hardens slowly in the air (not under water) because a large portion of the lime absorbs CO_2 from the atmosphere and is thus transformed into carbonate which then becomes crystalline and very hard.

For each cubic metre of fat slaked lime 3 to 5 cu. metres of sand are required, whilst with weak lime not more than 2 cu. metres can be used.

In 1903 Italy produced 830,850 tons of fat lime of the value of £510,640, 842,000 tons in 1906, and 858,000 tons in 1908.

CALCIUM PEROXIDE : CaO_2. On mixing hydrogen peroxide with lime-water calcium peroxide separates in crystals containing $8H_2O$. It loses water at 130° and parts with its oxygen at a red heat. It is to-day prepared with sodium peroxide which reacts with a calcium salt. Attempts were made to use it for bleaching textile fibres, but its cost is too high (£2 per kilo).

SODA-LIME. This product is obtained by heating a mixture of equal parts of powdered sodium hydroxide and calcium hydroxide to redness. It is obtained pure and of homogeneous composition in small quantities by quenching, for example, 80 grms. of pure powdered calcium oxide from marble with a hot solution of 20 grms. of NaOH in 60 grms. of water in a porcelain crucible. The mixture is immediately and rapidly stirred and then heated directly over a flame in order to drive off all the water. When it is cooled the mass detaches itself from the crucible and is crushed in a mortar, and the granulated soda-lime so obtained is kept in well-closed glass vessels. It is used as a drying agent and for absorbing CO_2. It costs 7*d.* per kilo.

CALCIUM CARBONATE : $CaCO_3$

Calcium carbonate is found abundantly in nature in the form of *limestone* as the principal component of entire mountain chains, forming compact masses of very fine grain, generally amorphous, mixed with clay and with other minerals. When pure, however, and of granular crystalline structure it forms

large deposits as *marble*. Dolomitic mountains are composed of a mixture of magnesium and calcium carbonates in which the latter preponderates.

The important deposits of true *chalk* consist of pure amorphous carbonate formed of microscopic remains of small marine animals. Many stalactites are also formed of calcium carbonate.

Calcium carbonate is widely diffused throughout the vegetable and animal kingdoms ; egg-shells, corals, and pearls contain large quantities of calcium carbonate, as do also the bones of vertebrate animals.

It crystallises in two systems, that is, it is dimorphous and thus forms *arragonite* in rhombic prisms of sp. gr. 3, and *calcite* in hexagonal rhombohedra of sp. gr. 2·7, and when this latter is sufficiently pure and transparent it goes by the name of *Iceland spar*, which is used in optical instruments ; it is isomorphous with $MgCO_3$, $ZnCO_3$, $FeCO_3$, and $MnCO_3$, whilst arragonite is isomorphous with $BaCO_3$, $SrCO_3$, and $PbCO_3$.

On heating to redness calcium carbonate loses 44 per cent. of CO_2, and calcium oxide, CaO, remains in the form of a white porous mass. The evolution of CO_2 is more rapid and complete if it is carried away by a current of air or steam as fast as it is formed. The temperature of decomposition of the carbonate varies with the pressure and thus at 56 mm. pressure dissociation occurs at 625° ; at 255 mm. at 740° ; at 678 mm. at 810° ; at 763 mm. (or at the ordinary pressure) at 812°, and at 1333 mm. at 865°. Practically, however, at ordinary pressure and with rapid heating dissociation does not occur at 812°, but only towards 925°, although even at ordinary pressures it may fall to 800° if the heating of the carbonate is not rapid and the CO_2 is immediately removed as fast as it is formed by a current of air or preferably by a current of superheated steam. This fact is explained by remembering that the temperatures indicated above at which the dissociation of the carbonate occurs also depend on the *partial pressure* due to the CO_2 which is evolved ; we have thus a behaviour analogous to that explained on p. 277, in connection with the catalytic formation of sulphur trioxide.

On heating CaO in a vessel containing CO_2, recombination occurs in the proportions indicated by the dissociation pressures. On the other hand on heating calcium carbonate in closed vessels at a high temperature (about 1200°) no dissociation occurs, because at these temperatures the pressure is so great that the carbonate melts (artificial marble).

One kilo of calcium carbonate requires 425 Cals. for its dissociation.

Calcium carbonate is almost insoluble in pure water and its extremely small solubility may be determined (in common with that of other very slightly soluble substances) by a determination of the electric conductivity of the solution. The carbonate is more soluble in water containing CO_2, because the primary carbonate or calcium dicarbonate, $Ca(CO_3H)_2$, is formed, which is soluble in water in the proportion of 0·385 grm. per 1000 grms. of water. This fact explains why all natural waters contain more or less calcium dicarbonate, which readily loses CO_2 again, and thus becomes insoluble ; one is thus also able to understand how the so-called scale is formed in boilers, how stalactites are formed, &c.

Calcium carbonate is decomposed by acids with evolution of all the CO_2 which it contains.

If a soluble carbonate such as Na_2CO_3 is added to a soluble calcium salt, insoluble calcium carbonate separates ; the precipitate is at first amorphous, but rapidly becomes crystalline. In the heat these crystals take the form of arragonite which is slowly transformed into crystals of calcspar. Arragonite is less stable than calcspar, and that which is now found in nature is undergoing slow transformation into calcspar, which takes thousands of years, although at 300° the transformation occurs very quickly.

When limestone has a very fine compact grain and shows parallel stratification, it is used for the preparation of *lithographic stones*, which have a yellowish homogeneous appearance, are of hardness 3 in Mohr's scale, and can be perfectly polished by suitable machinery, in which condition they are able to receive the finest imprints.

The lithographic stones of Pappenheim and of Solenhofen in Germany are world-famed. For some years good lithographic stones have been obtained from Sardinia (Bannei) and Cagli (Pesaro); this latter quarry yielded 200 tons of stone in 1908 of the value of £480.

Calcium carbonate in the form of *marble* is of great industrial importance and abounds in Italy, the most valuable coming from the Apuan Alps. Commercially two forms of marble are distinguished, namely, that of compact structure called *oriental alabaster*, and that with a crystalline or saccharoid structure (*statuary marble*), that of Carrara being renowned for its whiteness and clearness. There are also the most varied coloured marbles of varying value. In 1903 the production of Apuan marble was about 300,000 tons, of which about 220,000 tons, crude, worked, and sawn, were exported. In 1908 the Italian production was 425,000 tons of which 155,400 were exported. Unshaped marble is sold at £1 16*s*. per ton. In 1907 2500 tons of powdered marble were also produced of the value of £500. One cubic metre of limestone weighs about 2 tons. In 1905 a single block of red statuary granite was obtained by suitable means from the quarry at Baveno of a volume of 15,000 cu. metres.

CALCIUM CHLORIDE : $CaCl_2$

In general the halogen salts of metals are obtained by treating the metallic oxide or carbonate with a halogen hydracid (HCl, HBr, &c.).

Calcium chloride is obtained as a by-product in various industrial processes, such as the manufacture of ammonia soda. It is also obtained by dissolving the pure carbonate in HCl and evaporating to dryness; it then forms a porous mass.

It is very soluble in water (100 parts of water dissolve 37 parts of $CaCl_2$ at 0°; about 41 parts at 14°; 45·5 parts at 25°; and 50·67 parts of $CaCl_2$, or 99·97 parts of crystallised $CaCl_2.6H_2O$ at 29·5°). On dissolving the crystalline product a strong cooling effect is produced, whilst on dissolving the anhydrous product the reverse is the case; by mixing with snow the temperature may be lowered to − 48°. This substance crystallises with $6H_2O$ in transparent hexagonal prisms which are deliquescent in the air, melt at 29°, and then readily lose 4 mols. of water, whilst the last 2 mols. are only removed above 200°, leaving a white, porous, very hygroscopic mass which only melts at 806°. On then melting the $CaCl_2$ and allowing it to solidify it forms a compact crystalline mass which readily absorbs water and is employed as a good dehydrating agent for drying gases and removing water or moisture from other liquids such as ether, &c. It is most efficacious for drying gases when in a spongy condition. It cannot be used for drying gaseous NH_3 because it combines with this gas forming $CaCl_2.8NH_3$. The crude product is also used in 5 to 10 per cent. solutions for watering roads as its use prevents the formation of dust.

When the anhydrous chloride is melted in presence of moist air it partially decomposes, forming CaO and HCl.

The crude fused product which is obtained in Solvay soda works (p. 476) is generally used in artificial ice factories, in the form of a 6 to 10 per cent. solution of $CaCl_2$ as the cooling brine, as this solution does not freeze even at 8° to 9° below zero. This crude chloride contains 70 to 75 per cent. of $CaCl_2$ and costs £1 12*s*. to £2 16*s*. per ton. In Italy 3700 tons were produced in 1906 of the value of £13,320; in 1904 1035 tons were imported; 1740 tons in 1908 of the value of £5560, and 1406 tons in 1909 of the value of £4501. The pure product costs up to £20 per ton, and if it is anhydrous and chemically pure it costs more than £40 per ton.

In 1905 Germany exported 2825 tons of the value of £5680.

CALCIUM BROMIDE AND IODIDE : $CaBr_2$ and CaI_2. These salts are similar to the chloride but more deliquescent. By the action of the carbon dioxide of the air on the iodide HI is first separated, and this yields free iodine with the oxygen.

CALCIUM FLUORIDE : CaF_2. This compound is found in nature in colourless cubes or octahedra as *fluorite* or *fluorspar* and is sometimes variously coloured. It is also found in compact amorphous masses. It is also present in small quantities in the bones and teeth. It is formed as a voluminous precipitate from solutions of $CaCl_2$ with solutions of soluble fluorides, or by heating cryolite ($Al_2F_6.6NaF$) to redness with calcium carbonate, or by boiling cryolite with milk of lime (*see* p. 476).

It is only decomposed by strong acids such as H_2SO_4; it is insoluble in water, and

melts easily at a red heat and is therefore used metallurgically as a flux in the treatment of ores. It becomes phosphorescent on heating and by the action of direct sunlight.

The crude natural product is sold at £2 16*s.* to £4 per ton ; the chemically pure precipitated compound costs more than 5*s.* 7*d.* per kilo. The United States produced about 57,000 tons of fluorspar of the value of £72,000 in 1905.

CALCIUM HYPOCHLORITE (CHLORIDE OF LIME, BLEACHING POWDER)

This salt has not yet been obtained in the pure state, but chloride of lime, which must not be confused with calcium chloride, contains calcium hypochlorite as its active ingredient and probably has the following formula : $Ca<^{Cl}_{OCl}.H_2O$ mixed with $CaO.Ca<^{Cl}_{OCl}.H_2O$; it was first prepared by Tennant in England in 1798 by saturating lime with gaseous chlorine :

$$2Ca(OH)_2 + 2Cl_2 = 2H_2O + Ca(OCl)_2 + CaCl_2.$$

It is maintained by many that the true composition of chloride of lime is $Ca<^{Cl}_{OCl}$.

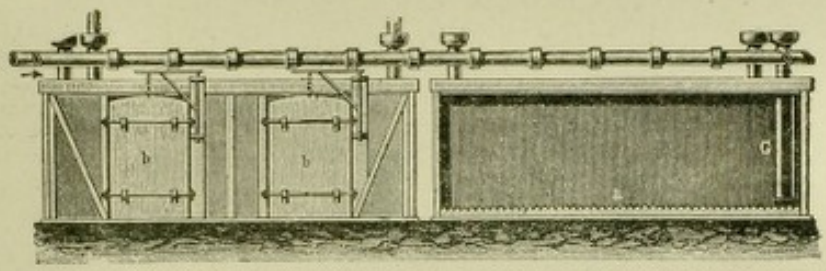


Fig. 205.

INDUSTRIAL MANUFACTURE OF BLEACHING POWDER. The calcium hydroxide employed for the absorption of the chlorine must be pure and not very moist.[1]

The chlorine should not contain HCl as otherwise $CaCl_2$ is formed and renders the bleaching powder deliquescent. The fact must be taken into account that in winter chlorine is dryer than in summer, because a good deal of moisture is deposited in the pipes. The lime is exposed in lead chambers (Fig. 205) 20 to 30 metres long, about 10 metres wide, and 2 metres high, supported by a wooden framework. The floor of the chambers is of asphalt and 10 kilos of bleaching powder can be produced daily per square metre of surface. These chambers are also constructed of metal, sometimes even of iron, but not in brickwork, as it is necessary to rapidly dispel the heat which is formed in the chamber during the reaction. Two or three of these chambers are arranged in series in order to enable work to be carried on continuously.

The layer of slaked lime, 80 to 100 cm. in thickness, should be loosely heaped, and the chlorine which passes in at the top of the chamber rapidly penetrates throughout the mass to the bottom. By watching the process through a few small windows it is possible to tell by the more or less greenish colour of the gas whether the lime is still absorbing chlorine. Generally saturation is complete in 24 hours. Before opening the chamber it is connected for twelve hours with the works chimney, and air is thus carried through it in order to remove all excess of chlorine. If the product has not a strength of 35 to 36 per cent. of active chlorine the mass is remixed with shovels and treated with chlorine once more.

[1] This calcium hydroxide is only prepared from very pure limestone, which leaves no residue on treatment with acids, and contains no Mn and Fe ; the presence of organic matter is of no consequence because, on burning the limestone to quicklime in the usual kilns this is destroyed. Rich limes, which are slaked more easily, absorb chlorine more easily than poor limes. The slaked lime is sieved with great care and allowed to cool in the barrels for some days. Theoretically calcium hydroxide, $CaO + H_2O$, contains 24·3 per cent. of water, the rest being CaO ; practically bleaching powder of good strength is obtained by the employment of a quicklime containing about 2 per cent. to 4 per cent. more than the theoretical quantity of water. Although the maximum strength is obtained by passing very dry chlorine over very dry slaked lime, in practice it is not easy to work under such conditions. A larger quantity of free water in the slaked lime enables it to absorb chlorine very rapidly, but lumps are formed in the mass with which chlorine is unable to react

In order to accelerate the absorption of the chlorine and to avoid serious injury to workmen on discharging the bleaching powder from the chamber various forms of plant have been proposed, of which the most practical and efficacious is that of Hasenclever (1891), Fig. 206. This consists of four superposed leaden cylinders 2 to 3 metres long, furnished with stirrers, *A*, which continuously transport the lime which falls into a hopper, *E*, successively from one cylinder to the next below it.

At the same time chlorine enters through a wide lower tube, *Cl*, and traverses the cylinders in the opposite direction to the lime. The chlorine is completely absorbed in the upper cylinder where the fresh lime enters, and very little passes up the exit flue, *o*. In the lower part of the plant there is a discharge outlet for the saturated bleaching powder, which is at once collected in barrels. The workmen who handle bleaching powder smear their bodies with fat and wear a mask which protects their respiratory organs and eyes.

The Società elettrochimica of Rome are using ten of these plants in their works at Bussi.

The greater portion of bleaching powder is to-day produced in electrolytic alkali works in order to utilise the large quantities of chlorine which they obtain. In 1907 (Fr. Pat. 370,873) the Elektron works at Griesheim produced bleaching powder containing 80 to 90 per cent. of active chlorine, by almost completely saturating milk of lime with chlorine and continuing to stir it ; after filtration the liquid is slowly evaporated *in vacuo* and thus a solid chloride of lime is obtained which is more stable and purer than the ordinary product and is soluble in water.

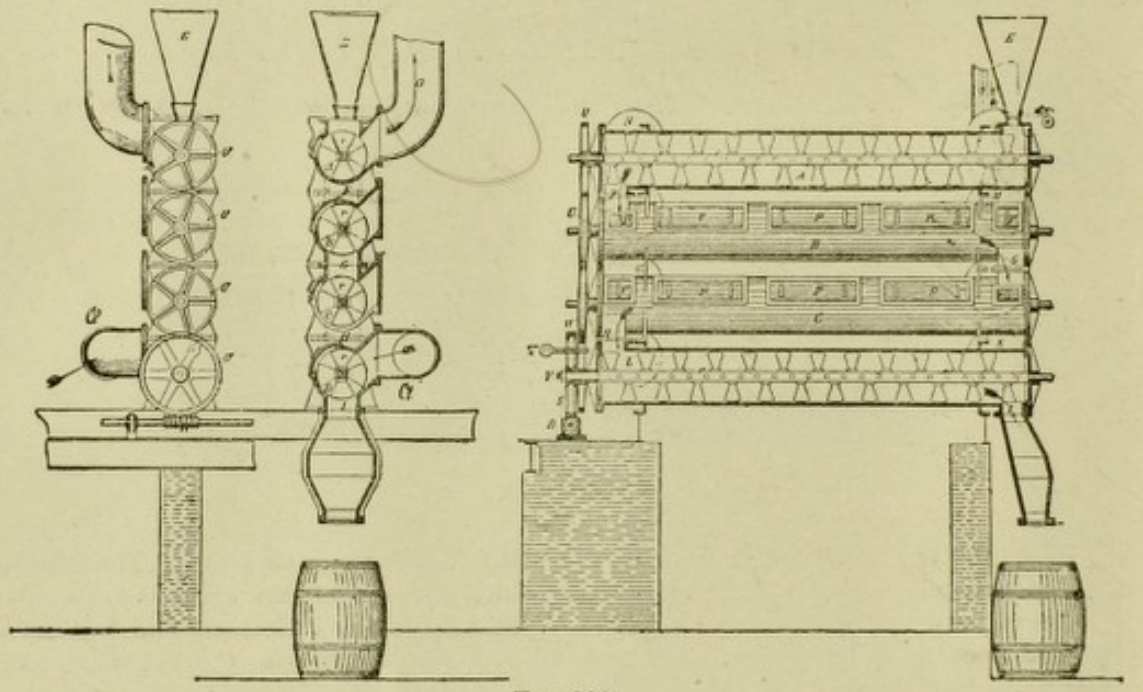


Fig. 206.

Commercial bleaching powder is a soft white powder with an odour of chlorine, and its aqueous solution has an alkaline reaction and is a strong bleaching agent. It is decomposed by the air through the action of the carbon dioxide.

It also decomposes slowly in closed vessels with formation of oxygen, and this change is more rapid under the influence of sunlight and of heat. In some cases closed vessels in which it is contained may even explode. In order to store bleaching powder without danger it is kept in wooden vats in the dark for some time after it has been prepared. Barrels containing bleaching powder should not be sealed hermetically, and should be kept in well-ventilated dark store-rooms.

On treating bleaching powder with dilute hydrochloric or sulphuric acid, twice as much chlorine is evolved as is apparently active, that is, united to oxygen :

$$CaCl.OCl + 2HCl = CaCl_2 + H_2O + Cl_2$$

$$Ca\begin{matrix}Cl\\OCl\end{matrix} + H_2SO_4 = SO_4Ca + H_2O + Cl_2$$

The value of bleaching powder is proportional to the amount of this active chlorine which is evolved with acids.[1]

On heating bleaching powder with NH_3 nitrogen is evolved:

$$3Ca\begin{matrix}Cl\\OCl\end{matrix} + 2NH_3 = 3CaCl_2 + 3H_2O + N_2.$$

USES AND PRICES. Chloride of lime is used for the preparation of chlorine, chloroform and oxygen (*see* Oxygen), as a disinfectant, as an oxidising agent, and more especially for bleaching cotton fabrics, and in printing on wool, because it more readily absorbs the dyestuffs after such treatment. The price of bleaching powder varies with its strength, and for a strength of 35 per cent. chlorine may reach £8 per ton. In 1906, when the European syndicate which fixed the prices ceased to exist, the price fell to £1 4*s.* per ton, and in Italy, where the two existing works enjoy the advantage of a protective tariff of £1 16*s.* per ton, the price rose again to £5 12*s.* and £6, and it is gradually rising in other countries.

The world's production of bleaching powder in 1904 was 260,000 tons and now exceeds 300,000 tons, of which about 60,000 tons are produced in France and 100,000 tons in Germany, of which more than 60,000 tons were produced in the manufacture of electrolytic alkali, and 27,300 tons were exported in 1909. England produces more than 190,000 tons and exported 37,000 tons in 1909. The United States imported 50,000 tons from Europe in 1907, 36,000 tons in 1908, and 45,000 tons in 1909. Russia consumed 10,000 tons of bleaching powder in 1895 and about 12,000 in 1908, and now only imports 300 tons from other countries. Italy consumed about 10,000 tons of bleaching powder in 1902, almost all of which was imported; in 1903 the Italian production at Bussi started and already exceeded 4000 tons in 1905; in 1907 it was also produced at Caffaro (Brescia), and amounted to 5700 tons altogether, increasing to more than 9000 tons in 1908. Meanwhile the imports diminished to 5200 tons in 1906, 3000 tons in 1907, 2941 tons in 1908, and 2993 tons in 1909 of the value of £13,170. On the other hand, the exports increased, being 110 tons in 1906, 344 tons in 1907, 1190 tons in 1908 of the value of £4993, and 853 tons in 1909.

CALCIUM NITRATE: $Ca(NO_3)_2$ (crystallising with $4H_2O$). On treating of potassium nitrate we already mentioned that the nitrogen of putrefied organic matter was oxidised in presence of lime by certain nitrifying bacteria which transformed it into calcium nitrate; this is often found as an efflorescence on the walls of stables.

It is very soluble in water and in alcohol and is readily transformed into potassium nitrate by potassium salts. It is abundant, naturally formed, in Venezuela and is an excellent manure. When purified it is used for incandescent mantles.

The crude product, used as a manure, costs £40 per ton, but it is now also obtained electrolytically from atmospheric nitrogen (p. 303), and is sold at less than £8. The chemically pure product, as used in connection with incandescent lighting, costs 1*s.* 7*d.* per kilo; in 1909 12,000 tons were produced by the Birkeland-Eyde process at Notodden.

BASIC CALCIUM NITRATE is less deliquescent (*see* p. 304), and contains about 13 per cent. of nitrogen, 26 per cent. of lime, and 24 per cent. of water, together with very small amounts of nitrites (which are sometimes harmful to vegetation).

CALCIUM NITRITE: $Ca(NO_2)_2$, is produced together with calcium nitrate in the electric processes for the utilisation of atmospheric nitrogen (*see* p. 303); in order to separate it the solution is concentrated until on cooling to 30° to 35° crystals of the nitrite are deposited, whilst the nitrate remains in solution.

[1] In commerce the strength is also often given in Gay-Lussac degrees which indicate the number of litres of active chlorine which can be evolved from 1 kilo of bleaching powder; thus, for example, a bleaching powder which contains 25 per cent. by weight of active chlorine is called 79° Gay-Lussac; if it contains 40 per cent. of active chlorine it is of 126° Gay-Lussac, because 1 kilo of this bleaching powder would evolve 400 grms. of chlorine and a litre of this gas weighs 3·16 grms., and $\frac{400}{3{\cdot}16} = 126°$.

The strength of bleaching powder is determined with $\frac{N}{10}$ solution of sodium arsenite obtained by dissolving 4·950 grms. of pure As_2O_3 in 200 c.c. of water, and 20 grms. of pure sodium dicarbonate; the whole is boiled with stirring, allowed to cool, and made up to 1 litre; 1 c.c. of this solution corresponds to 0·00355 grm. of active chlorine. The titration is carried out by stirring up to 7·1 grms. of the well-mixed bleaching powder to a paste with water, diluting with water to 1 litre, shaking well, and immediately removing 50 c.c. (= 0·355 grm.) of the sample; this is titrated in a beaker with the solution of the arsenite, the end of the operation being detected by spotting the liquid on to filter paper impregnated with starch and potassium iodide solution until the blue spot produced by iodine liberated by the chlorine is no longer obtained.

According to Ger. Pat. 220,539 of 1909, the nitrite may be transformed into nitrate by heating it to over 300° in presence of NO_2: $Ca(NO_2)_2 + 2NO_2 = Ca(NO_3)_2 + 2NO$; the nitric oxide is mixed with the necessary quantity of air to retransform it into NO_2 and then re-enters the cycle. In a similar manner nitric acid may be obtained from the mixture of nitrates and nitrites.

CALCIUM SULPHIDE. This is a yellowish mass which is obtained on heating calcium sulphate with charcoal; on dissolving in water it forms calcium hydrosulphide, $Ca(SH)_2$. When it is very pure and dry it is not phosphorescent, but becomes so in presence of traces of other salts.

CALCIUM SULPHITE and DISULPHITE: $CaSO_3$ and $Ca(SO_3H)_2$. These compounds are obtained by the action of SO_2 on slaked lime and on milk of lime in wooden chambers or boxes.

The SO_2 fumes are passed in at the bottom of a tower which contains limestone (calcium carbonate) and down which a shower of water falls from above. A solution of calcium sulphite is so formed, which collects at the bottom of the tower, and carbon dioxide only escapes at the top.

Calcium sulphite is solid and forms a readily transportable source of SO_2 which can be regenerated from it by the action of acids. It is insoluble in water, but readily soluble in aqueous SO_2 forming calcium disulphite.

The disulphite is used in large quantities in cellulose works and paper mills, also in sugar factories, spirit distilleries, and breweries, as a disinfectant, &c. U.S. Pats. 84,698 of 1907 and 945,426 of 1908 describe two forms of industrial plant for the manufacture of calcium disulphite.

Neutral commercial calcium sulphite costs £18 per ton and the purified product £26 per ton. The bisulphite in solutions of 13° to 14° Bé. costs £6 per ton.

CALCIUM SULPHATE: $CaSO_4$

This compound is found abundantly in nature without water of crystallisation as *anhydrite*, or crystallised with 2 mols. of water in large monoclinic prisms or as a granular crystalline mass known as *gypsum*. In the natural state, in the form of a pellucid mass which cleaves to form sheets, it is known as *selenite* and is used for optical instruments.

When natural gypsum is heated to 110° to 120° it loses a considerable part of its water, probably forming $CaSO_4 \cdot \frac{1}{4}H_2O$, and this product has the valuable property, when worked to a paste with water, of recombining with the whole of its water of crystallisation, and immediately becoming very hard with separation of the excess of water; for this reason it is used for very varied industrial and artistic purposes under the name of *plaster of Paris*. But if it is heated to 170° it loses all its water of crystallisation, and also its property of hardening when mixed with water, and is then known as *dead* or *over-burnt* plaster. In order to increase the rapidity with which plaster of Paris sets and hardens it may be mixed with 0·1 to 0·5 per cent. of sodium phosphate.

On a small scale plaster of Paris is prepared by gradually heating the natural powdered gypsum in iron pans with continuous stirring until water is no longer condensed on the cover of the pan.

On a large scale it is heated in large ovens similar to those used for baking bread, out of contact with the products of combustion. The furnace is heated with wood and coal up to a suitable temperature and the fuel is removed before the gypsum is introduced. Gas-fired furnaces are also used, and at present metallic drums heated by a current of hot air are coming into use.

The burning of crude gypsum takes from 12 to 24 hours; 60 to 70 kilos of coke are used for heating per cubic metre of plaster of Paris which is produced. In modern furnaces, for example, of the Perin type, 27·5 kilos of coke are used per 1000 kilos of gypsum, starting from crude gypsum with 22 per cent. of water and finally obtaining plaster of Paris containing 7·70 per cent. of water.

A method of manufacture which is often adopted is the following: The natural gypsum, in large lumps as it is quarried, is first crushed and then ground in the usual form of mill with horizontal stones.

After grinding in this way the crude gypsum is heated in open iron pans furnished with stirrers and holding about 60 to 70 kilos. These pans are arranged over a hearth heated with coal and lined with refractory bricks in order to avoid direct contact with the flame or with the hot gases ; in this way heat is transmitted through the refractory lining and the temperature of the mass of gypsum does not exceed 120° to 130° ; 18 to 20 kilos of coal are used per 100 kilos of gypsum.

During heating the stirrer is always kept in slow motion and the end of the process is recognised by the fact that the mass ceases to " boil," because no more steam is evolved in the form of vapour jets which rise through the powdered gypsum.

" *Scagliola* " is thus obtained ; in order to obtain ordinary plaster of Paris the gypsum is heated in small pieces in furnaces without stirrers, but a poorer quality is thus obtained ; this process takes a few hours.

Dead burnt plaster may apparently be partially regenerated by the addition of about 4 per cent. of sodium disulphate.

It appears that when the gypsum is removed from the ovens it contains no water and only absorbs 7 to 8 per cent. on standing in the air ; it has then the power of setting in the well-known manner.

The gypsum which is obtained on precipitating a soluble calcium salt with sulphuric acid crystallises with $2H_2O$; it is very slightly soluble in water (1 part in 450 parts both at 0° and 100°), and acquires its greatest solubility at 35°, namely, 2·5 grms. per litre. Natural anhydrite behaves like gypsum freed from water, that is, it does not set with water.

Gypsum is used for making models of artistic figures by using a paste of 1 part of gypsum and $2\frac{1}{2}$ parts of water, because it reproduces even the finest details ; it is used for modelling, &c.

It is used as a corrective for certain soils. When it is moistened with a solution of glue and a little zinc sulphate *stucco* is obtained which is used for ornamentation and sets very slowly, but more strongly than pure gypsum.

In Italy 264,843 tons of gypsum were produced in 1890 of the value of £97,160 and in 1902 the production was 341,883 tons ; in 1908 it exceeded 361,000 tons, of the value of £120,000 ; 270 tons of calcium sulphate were also produced as a chemical product. The works of the Sindacate della Valle Camonica are alone capable of producing 80,000 tons of gypsum. In 1903 390,000 cu. metres were used in Paris. The imports into Italy in 1907 were 20,000 tons, 15,000 tons in 1908, and 21,000 tons in 1909, of the value of £25,240. In 1909 Germany imported 11,285 tons of gypsum and exported 63,220 tons.

CALCIUM SILICATE : $CaSiO_3$

This compound is found pure and crystalline as *wollastonite*, $CaSiO_3$, a mineral which is not very abundant. Calcium silicate is an important constituent of natural silicates which abound in many minerals and geological formations. Since a remote epoch it has been used as a constituent of glass and it is specially in connection with this substance that calcium silicate is of great importance to us.

GLASS [1] consists of an amorphous transparent mixture of alkali silicates

[1] Glass is of very ancient origin : the Egyptians were well acquainted with its production and working 1800 B.C., and perhaps the Chinese manufactured glass at a still earlier date. The art of melting and blowing glass passed from the Egyptians to the Phœnicians and then to the Ancient Romans (200 B.C.),who used it for artistic objects. The glass industry then developed at Byzantium and later in Venice where it acquired great importance. Glass mirrors have been manufactured since 1400 ; before that time metallic mirrors were used. In Bohemia the glass industry developed in the Middle Ages, then declined, and reacquired great importance during the past century. In the tenth century stained glass for windows, especially in churches, already occurs. In France and in England the glass industry became important towards the end of the Middle Ages, and in1800 the large works at the Faubourg St. Antoine in Paris were founded and were then removed to St. Gobain. In Germany the industry received a great impetus through the introduction of the Siemens furnaces. The mirror industry developed in Austria in 1700 and in Germany only after 1850. Various attempts to revive this industry in Venice at the beginning of the nineteenth century were unsuccessful and the actual revival of glass-working at Murano (near Venice) is largely due to Dr. Salviati, who, by investigating with an enlightened mind the good points of the old processes and bringing them into harmony with modern science and industry in the middle of the nineteenth century, was able to revitalise the new works, which once more gained the admiration of foreigners for the intelligent work of the men who are able to shape in a thousand fashions and with exquisite artistic taste the soft formless paste which is incessantly drawn from the red-hot furnaces.

The Venetian renaissance was completed in its most highly artistic forms by the remarkable ability of Luigi

with calcium and lead silicates, obtained by fusion in the heat. Glasses are divided into four principal groups:

I. **Glasses consisting of Calcium and Potassium Silicates.** These are very hard, not very fusible, and very resistant to the action of water and acids. They are completely colourless and are used for the preparation of chemical and physical apparatus. They have a specific gravity of about 2·40.

II. **Glasses consisting of Calcium and Sodium Silicates.** These are more fusible and less resistant than those of the preceding class; they resist the solvent action of water and of acids. They are used for making ordinary sheets and cheap objects, and have always a slight bluish-green colour and a specific gravity of about 2·65. Mirrors are often made of a mixture of glasses of groups I. and II.

III. **Glasses composed of Lead and Potassium Silicates.** These are very soluble and are suitable for many ornamental objects. They have a high specific gravity, possess very marked lustre, and refract light very strongly.

They are used in the preparation of so-called *crystal glass* of sp. gr. 2·9 to 3·25 and also form *flint glass* of sp. gr. 4 to 5, in which considerable quantities of boric acid and bismuth are added to the lead silicate. The *paste* (strass) which is used for the manufacture of artificial gems is very refractive and transparent and belongs to this group.

Lead glasses are used for lenses and optical apparatus, but these are now also prepared with barium because they are then harder although still very refractive.

IV. **Common Bottle Glasses.** These consist of silicates of sodium, potassium, calcium, and aluminium accompanied by iron, manganese, and sometimes by magnesium. They contain less alkali than other glasses and have a yellow or dark green colour. White, opaque, or translucent glasses are obtained by the addition of barium sulphate, &c.

Glass is amorphous and transparent, and is a bad conductor of heat and electricity.

The composition of glasses ordinarily varies within the following limits:

$$K_2O.CaO.6SiO_2 \text{ and } 5K_2O.7CaO.36SiO_2;$$

the K may be replaced by Na and the Ca by Pb.

Good glasses for chemical purposes ordinarily contain so much silica that a trisilicate is formed, and the following proportions give good results: $1{\cdot}34K_2O + 1CaO + 7SiO_2$. Zulkowski maintained in 1899 that glass is a true chemical compound, which he supposes to be a double silicate of the general formula $Si_nO_{2n-1}<\begin{matrix}OM'\,M'\,O\\O—MO''\end{matrix}>Si_nO_{2n-1}$, where M′ is the alkali metal and M″ the divalent metal Ca, Pb, &c.[1]

Lobmeyer, born at Vienna in 1829, who succeeded in creating an entirely new art of cutting and polishing glass with such refined taste that in a very short time he claimed the attention of the whole world by the industrial production of beautiful artistic objects.

In the nineteenth century the glass industry acquired a new impetus amongst all civilised nations, when it became possible not only to produce artistic objects for the wealthy but also such as could be produced cheaply and on a large scale.

The large modern glass industry has been enabled to arise through the valuable assistance of chemistry and engineering. By means of the first the composition of the necessary pastes for obtaining the most varied qualities of glass with precision and security was studied; and the second furnished the necessary means for the large-scale mechanical production. The exact relations between the prime materials, quartz, silicates, sodium and potassium carbonates, sodium sulphate, lime, lead oxide, &c., and carefully regulated temperatures allow the various types of glass to be obtained with certainty.

The old glass-melting furnaces yielded a very impure glass, and the heating was not so regular as in modern furnaces using special hearths with suitable draught, aided by powerful fans and fed by fuel of the first quality. The large consumption of fuel and the results which are often unsatisfactory render the success of important enterprises very difficult.

[1] We here give the composition of certain glasses of various qualities and also of various epochs:

	SiO_2 Per cent.	Na_2O Per cent.	CaO Per cent.	$Al_2O_3+Fe_2O_3$ Per cent.	MgO Per cent.	MnO Per cent.
Impure mirror glass from St. Gobain	73	11·5	15·5	0·8		
Window glass	69 to 71	11·17	10 to 13·5	2·7		
Common green bottle glass	63·5	9·5 (+ 1·3 K_2O)	14	5	4·0	3·0
Bohemian glass tubes	74·4	18·5 (K_2O)	7·2	0·5		
Brown glass rods from Ancient Egypt	66·0	22·3	8·4	2·4		0·9

A good glass should be resistant to the action of the atmosphere, of water, carbon dioxide, acids, and dilute alkalis. No quality of glass, however, is absolutely resistant. Even in the air glasses lose their transparency and become dull in time, because alkali is dissolved. A good glass should resist the action of strong HCl vapours for twenty-four hours.

The resistance increases with increasing amounts of SiO_2, though this constituent must not exceed 80 per cent. on account of the infusibility and fragility of the resultant glass. For equal contents of silica, that glass which contains the most lime and the least alkali is most resistant. The coefficient of dilatation increases with increasing amounts of alkali.

The property of Bohemian glass of being very resistant is largely due to its high content of silica, apart from the presence of potassium instead of sodium salts. Bluish-green glass, containing much ferrous oxide, only allows very small quantities of thermal rays to pass.

Apart from its chemical composition the quality of glass depends largely on the mechanical treatment. Rapid cooling renders it fragile but very hard, whilst slower cooling renders it elastic. By cooling molten glass by immersion in oil or resin, as was proposed by De la Bastia in 1874, or by compressing it between very cold iron plates, as proposed by Fr. Siemens, extremely hard glass is obtained which resists the strongest impacts and may be used for pavements or for street lamps. If glass is kept molten for several days it becomes turbid and also forms many small crystals on solidification, and the surface is no longer smooth and lustrous.

PRIME MATERIALS FOR GLASS MANUFACTURE. (1) **Silica.** This is ordinarily employed in the form of quartz, flint pebbles, or siliceous sand. When pure colourless glasses are required, the sand should not contain iron, but if this is present in small amount it sometimes pays to eliminate it by washing or digesting with dilute hydrochloric acid. A very pure sand sent from Australia for use in European glass manufacture gave the following analytical results : SiO_2 = 99·7 per cent. ; CaO = 0·1 per cent. ; MgO = 0·06 per cent. ; $Al_2O_3 + Fe_2O_3$ = 0·09 per cent. The quartz and flints are first heated to redness in furnaces in order to render them brittle, and are then powdered. For ordinary glass common sand is employed, even if it contains clay, because the mass then melts more easily.

(2) **Alkali.** In past days potassium carbonate or plant ashes were almost exclusively employed, and then anhydrous sodium carbonate (Leblanc soda ash) was introduced and became general. Since 1840, however, through the initiative of Baader di Monaco, the use of sodium sulphate obtained directly in the Leblanc process has become very extended of late years. This product is lower in price than soda and can replace it very well if 6 to 7 per cent. of coal is mixed with it (in spite of the fact that sodium sulphide is then formed in the furnace which colours the glass brown and which must be corrected with an oxidising agent), and at high temperatures it is decomposed by the silica. All the sulphur of the sulphate escapes as sulphur dioxide, which is lost because it is mixed with large quantities of furnace gases.[1] The replacement of sodium sulphate by the carbonate has been prophesied by many now that the price of the latter is so low :

$$2Na_2SO_4 + 6SiO_2 + C = 2Si\begin{array}{l}\diagup ONa\\ =O\\ \diagdown O\\ \diagup O\\ =O\\ \diagdown O\\ \diagup O\\ =O\\ \diagdown ONa\end{array} + 2SO_2 + CO_2$$

Sodium chloride cannot be employed because it is too volatile and is not decomposed by SiO_2 except in presence of air and of steam, with loss of chlorine and HCl. For ordinary potash glass, wood ashes are employed, and for the best glasses pure potassium carbonate. Potassium sulphate is not employed because it is too difficult to decompose.

(3) **Lime.** This is used in the form of carbonate ; for glass of high quality, marble

[1] The German law of 1895 forbids glassworks from allowing gases containing more than 0·01 per cent. by volume of SO_2 to escape from their chimneys, and this renders the use of sulphate difficult. In any case it is necessary to pass the chimney gases through cylinders or towers filled with lumps of limestone kept moist with a spray of water. A solution of calcium sulphite and bi-sulphite is thus obtained which can be utilised in various industries, whilst CO_2 escapes.

is employed. In Bohemia wollastonite or calcium silicate is used, while slaked lime is rarely employed. The limestone should be as free from iron as possible and 20 parts are often used per 100 parts of silica. In order to facilitate fusion, a little calcium fluoride is sometimes added.

(4) **Lead Oxide.** This is used in the form of minim Pb_3O_4, which is then converted into lead peroxide, and should not contain copper or tin.

(5) **Certain Natural Silicates.** Felspar, pumice, basalt, lava, &c., are of similar composition to glass, and may be used in glass manufacture with the addition of a few other ingredients.

(6) **Broken Glass.** The mixture of materials for the production of common glass is made with about one-third of broken glass which is present in the works or is acquired.

(7) **Decolorising Materials.** These act in two ways: by oxidising the impurities which colour the glass or by producing supplementary colours which destroy the colours due to the impurities. Manganese dioxide, which has been used for this purpose since ancient times, acts partially by oxidising the green ferrous oxide, producing a yellow oxide which has a less intense colour, and partially forms manganic silicate which is violet and eliminates the greenish-yellow colour, forming colourless manganous silicate. Nickel oxide is sometimes used instead of manganese dioxide.

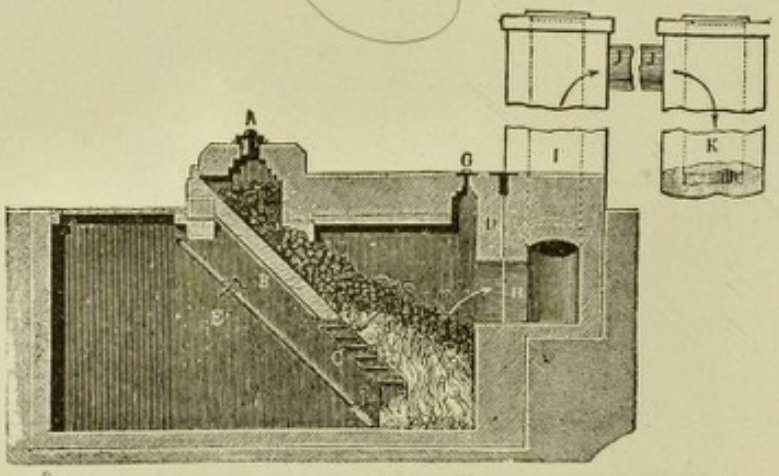


Fig. 207.

Pure arsenious oxide is used and so is potassium nitrate, and the addition of a little antimony sulphide or oxide increases the lustre of the glass.

According to Ger. Pat. 217,422 of 1907, colourless optical glass is obtained by melting in an electric induction current and instead of the ordinary gas furnace.

Hardened Glasses which resist fluctuations of temperature from 200° to 100°, &c., are obtained by adding MgO and ZnO to a lead glass prepared with 75 parts of sand, 13 parts of sodium bicarbonate, 9 parts of manganese carbonate, 6 parts of zinc oxide, and 50 parts of minim; the coefficient of dilatation is high and it may be used for lamp glasses (*Cristalleries de Baccarat*). In Germany the same and even better results were obtained at an earlier date with borosilicate glass which is the best for the manufacture of steam gauges for high pressures.

GLASS MANUFACTURE. The materials, which have been previously analysed, are finely powdered and mixed in the proportions required for the desired quality of glass.[1]

These substances are melted in suitable fireclay pots which are placed in melting furnaces constructed of highly refractory materials.

The gas furnaces of Fr. Siemens are now general in the glass industry, and consist of three perfectly distinct portions, the generator or producer, the true melting furnace, and the regenerator. Siemens' gas producer (1861), which has enabled 30 to 40 per cent. of fuel to be saved, is based on the principle of passing a current of air or steam through the red-hot fuel, consisting of peat, wood residues, or preferably coke, arranged on an inclined plane, *B*, the lower part of which consists of a grate arranged in steps, *C* (Fig. 207); the whole is enclosed in a brickwork chamber. Energetic combustion is only started in the lower portion of the heaped-up fuel, through which air is drawn from within; at the same time a fine spray of water is introduced through the tube, *E*. The products of combustion

[1] Here are, for example, two recipes for window or bottle glass:

	Sand	SO_4Na_2	Soda	$CaCO_3$	Coke	Potassium Nitrate	MnO_2	As_2O	Sb_2S_3
I.	kilos 100	37	5	36	2	—	—	—	—
II.	„ 100	—	39	17	—	2·8	0·400	0·280	0·140

In these recipes the 5 to 6 per cent. of alkali which is lost during treatment is already allowed for.

pass through the remaining fuel producing a kind of distillation with formation of a gas of high calorific power, whilst the CO_2 is reduced to CO and the steam is decomposed by the red-hot carbon with formation of hydrogen. The mean composition of such producer gas (p. 393) is 28 to 33 per cent. CO, 1½ to 4 per cent. H, 0·8 to 4 per cent. CO_2, 62 to 64 per cent. N, with a calorific power of 800 to 1000 cals. per cubic metre.

The hot gases from the producer pass along a flue, *I*, about 4 metres high, through a large, wide, horizontal iron tube, and then descend when somewhat cool down a vertical flue, *K*, at the bottom of which there is a cistern of water where the tarry products of the distillation of the fuel condense. These would otherwise obstruct the succeeding pipes. The gas in *I* is hot, whilst in *K* it is cooler, so that there is a pull from *I* towards *K*, and this causes a strong air draught through the grate of the producer without any necessity for fans or air injectors.

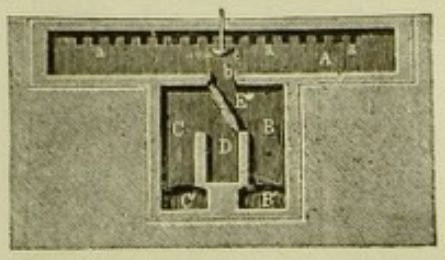


FIG. 208.

The gases from *K* pass through small hot flues, *a* (Fig. 208) or *k'* (Fig. 209), situated below the melting furnace, into a common chamber, *A*, whence they pass through a reversible valve, *E*, for half an hour into the chamber, *C*, from whence they are carried through the flue, *C'*, into a couple of red-hot regenerators described below (Figs. 209 and 210). Meanwhile the gases from the melting furnace, *f'* (Fig. 209), pass through the flue, *B'*, into the chamber, *B*, after having given up their heat to the other pair of regenerators, *d'* (Fig. 209), and then pass to the chimney through the flue, *D*. After half an hour *D'* has cooled somewhat, whilst *d'* has become red hot. The current of gas is then reversed by altering the position of the reversible valve,[1] so that the gases from the generator first pass through *B* and *B'* and then into the red-hot regenerator, *d'*, whilst the gases from the melting furnace then heat the colder regenerator, *D'*, to redness and pass through the flue, *C'*, into the chamber, *C*, and thus to the chimney through *D*.

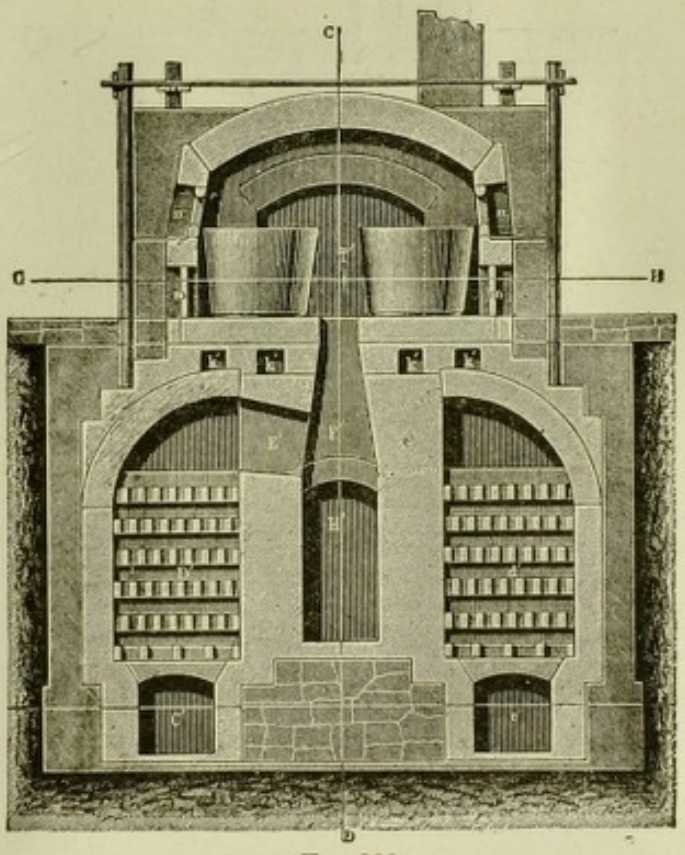


FIG. 209.

The regenerators (Fig. 209) are arranged in two pairs under the melting furnace, and consist of two systems of vertical chambers filled with firebricks which are arranged at equal intervals so that plenty of space is left for the passage of the gas. A pair of regenerators which have been heated to redness and comprise the two halves, *D'* (Fig. 209), serve on the one hand (*D'*) to heat the gas from the producer, and on the other hand, the air which passes to the melting furnace. The red-hot gases and air pass through separate flues into the common chamber, *E'*, and then pass to the furnace through its floor, and between the crucibles where the mixture catches fire producing so much heat, up to 1200°, that the mixture in the crucibles melts. These hot gases then escape through the opening in the floor at the other side of the furnace and heat the other pair of regenerators, *d'*, which are used after half an hour for heating the air and producer gas. On p. 367 we have already seen these generators

[1] Since this valve does not close perfectly, it has been replaced by a similar valve to the Clegg valve used in gasworks (*see* Lighting Gas, vol. ii, " Organic Chemistry ").

applied to coke production. Apart from Siemens' furnaces, similar types evolved by Nehse and Dralle are now employed, and it is estimated that to-day, for completely working 100 kilos of glass, 130 kilos of coal are required. The heat is still incompletely utilised, but three to four times less fuel is used than in the old furnaces. At the surface of the molten glass impurities and the excess of alkali sulphates and chlorides (glass-gall) separate and are removed with an iron ladle, or if present in small quantities are allowed to volatilise.

The glass is not worked at this very high temperature—1000° to 1100°—but is cooled to about 800° by allowing cold gases (air) to circulate in the flues, *k'*, under the furnace floor.

The preparation of glass in pots is accompanied by many difficulties and a considerable expense for pots, which easily wear out.[1] Moreover the work is not continuous because for half a day the glass is melted and the molten glass is then worked during another half day. For these reasons, attempts were made without success by Chance and Donzel to employ tank furnaces, but later Siemens succeeded in solving this problem very completely and advantageously by using the hearth of the furnace itself as a tank, and in Fig. 210 a

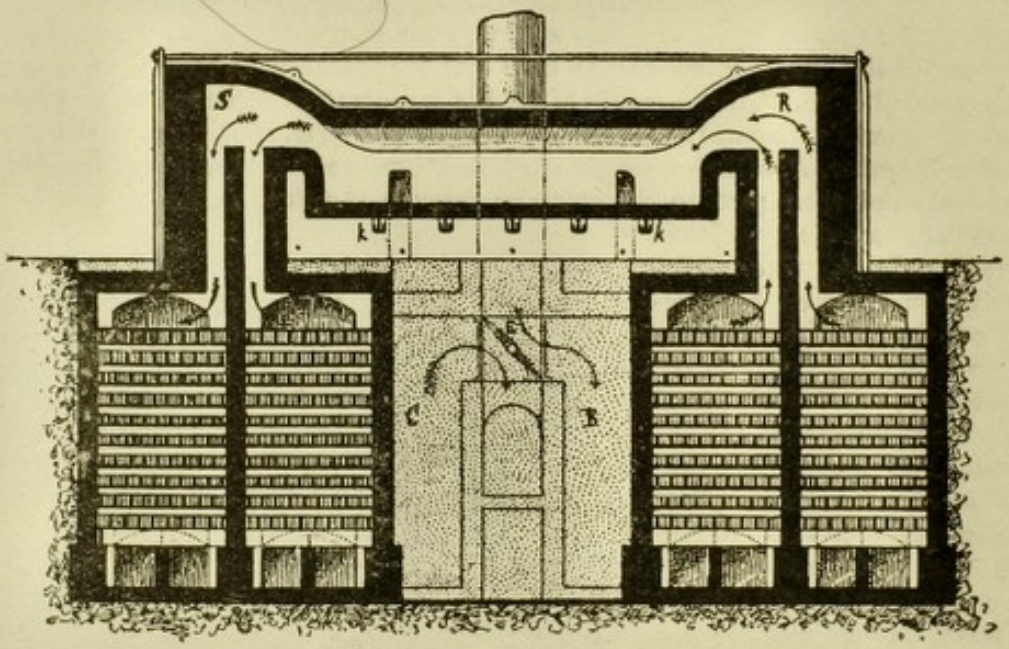


FIG. 210.

section of one of these furnaces is shown together with the course of the gases which enter at *R* and escape at *S*, giving off their heat to the regenerators placed below.

There are other systems of regenerative (but not recuperative) furnaces which it would take too long to describe, and it is also impossible to describe the working of glass in order to obtain sheets, bottles, mirrors, vases, tubes, &c., in this volume.

STATISTICS. The glass industry has to-day acquired a certain importance in Italy, and the supply, even of cheaper articles, is commencing to be almost independent of other countries. In 1903 about 10,000 operatives were employed in Italy in various glassworks, which produced 46,167 tons of various objects of crystal glass of the value of £440,000 (in 1908, 70,515 tons of the value of £671,120); to this must be added 17,100 tons of glass sheets and bell-jars of the value of £258,000 (and 19,650 tons in 1908 of the value of £291,040); furthermore there were produced 143 tons of artistic glass and enamels of the value of £28,600 (1943 tons in 1908 of the value of £156,000), and also 5300 tons of glass beads of the value of £180,000 (4500 tons in 1908 of the value of £157,000), of which four-fifths were exported. Italy still imported 5300 tons of ordinary and flint glass in 1903 (11,766 tons in 1908), 3400 tons of bottles and carboys (3797 tons in 1908), 3000 tons of ordinary and flint glass sheets (6046 tons in 1908), and 169 tons of mirror glass (98 tons in 1908). The

[1] The works now prepare these crucibles from a paste of fireclay with finely ground chamotte treated with a little water and minimal quantities of soda, which are carefully determined in each case. By prolonged mixing a very plastic (colloidal) mass is thus obtained (E. Weber's process, 1905), so that crucibles may be obtained which already set in the mould in a few hours, and may be removed from it in two days.

large glass factories of Belgium import large quantities of glass into Germany (more than 5000 tons in 1890), in spite of an import duty of £1 4*s*. per ton.

In Germany in 1903, 61,000 workpeople were employed in the glass industry, and 156,000 tons of glass were exported, of which 100,000 tons consisted of green bottles of the value of £1,400,000, and 56,000 tons of other articles. On the other hand, Germany imported 15,000 tons of glass of the value of £520,000.

Austria also exports large quantities (47,000 tons in 1887).

The Belgian glass industry employed 10,124 workpeople in 1880, about 23,000 in 1900 and about 31,000 in 1906, in 72 works. In the five years 1891 to 1895 Belgium's average exports were of the value of £1,920,000, and in the five years 1901 to 1905 the mean annual exports were of the value of £3,440,000, of which 50 per cent. was consumed by England and British possessions (India, Australia, and Canada); 50 per cent. of the average exports consist of window glass, and 30 per cent. of mirror glass.

In France the glass industry occupied 37,000 workpeople in 1896 and about 43,000 in 1901, of whom 800 were employed in the manufacture of optical glass, 10,900 in the manufacture of bottles (14,700 in 1906) and 3600 in the manufacture of window glass. The imports amounted to 24,000 tons in 1897 of the value of £600,000, and the exports to 104,000 tons of the value of £1,080,000. In 1906 the imports rose to 30,000 tons of the value of £720,000, and the exports to 132,800 tons of the value of about £1,680,000.

In the United States three Pittsburg works alone have a total capital of £2,480,000, and employ 5000 workpeople. The annual wages of these amount to £600,000, and the production is 466,000 tons. The Rochester Tumbler Company is the most important glass and bottle factory in the world. It produces 1,000,000 articles per week, and covers a surface of six hectares.

Forty per cent. of all the glass manufactured in the United States comes from Pittsburg. The Macbeth Emaux Glass Company is the largest lamp-glass works in the world. In 1905 there were 400 glassworks in the whole of the United States with an invested capital of £18,000,000, employing 64,000 workpeople, paying £7,600,000 yearly in wages, consuming prime materials of the value of £5,200,000, and manufacturing finished products of the value of £16,000,000, including £6,600,000 of various bottles, £4,400,000 of pressed and blown glass, £2,320,000 of window glass, and £1,600,000 of plate glass.

The United States supply half the world's production of flint glass plates as is shown by the following summary for 1905: France, 1,420,000 sq. metres; Belgium, 2,350,000 sq. metres; Germany, 1,410,000 sq. metres; Holland, 80,000 sq. metres; Italy, 80,000 sq. metres; Austria-Hungary, 275,000 sq. metres; Russia, 310,000 sq. metres; England, 739,000 sq. metres; United States, 5,500,000 sq. metres.

CALCIUM CARBIDE: CaC_2

This product has only acquired importance during recent years, but was already obtained by Wöhler in 1862 by heating an alloy of calcium and zinc with carbon. It was obtained in the electric furnace after many attempts by Borchers in 1891, and the first patent was taken by Böhm in the same year. In 1892 it was also obtained accidentally by Wilson, and was then at once prepared in the electric furnace by Moissan, from which time the process became industrial.

When chemically pure, it forms transparent crystals of sp. gr. 2·2, and is obtained by heating calcium oxide, obtained by heating pure marbletor edness, with metallic calcium or with pure carbon (sugar charcoal), $CaO + 3C = CO + CaC_2$. C. A. Hansen showed in 1909 that during this reaction an equilibrium is established by the pressure of the CO and that the reaction starts at 1275°, and only continues at 1450° on condition that the pressure of the CO is kept below the critical limit, otherwise the reaction ceases.

Calcium carbide is very inactive towards most reagents and insoluble in all solvents, but immediately decomposes in contact with water and with acids with production of acetylene gas, $CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$. It is therefore necessary to always keep it in well-closed bottles and thus avoid access of moisture.

Enormous quantities of calcium carbide are to-day produced industrially in electric furnaces of very varied forms, which are described in numerous patents which follow one another incessantly by Siemens and Halske, Heroult, Bullier, Pictet, Regnoli, &c.

We will only describe a single type of furnace, that of Tenner, because it is the least complex (Fig. 211). The furnace is lined internally with refractory materials and has a movable bottom which acts as the negative electrode, and is formed of a car which carries an iron plate covered to a depth of 20 cm. with a compact layer of coke held together by tar. The positive electrode of carbon may be lowered from the top of the furnace. The gases which are formed during the reaction, consisting of carbon monoxide at 2500°, escape through the flue, *d*. When the furnace is ready, connection is established between the poles of a dynamo working with a current of 1500 to 2000 amps. at 65 to 100 volts. The anode is then lowered until an electric arc is produced in the finely powdered mixture of 56 parts of calcium oxide and 36 parts of coal then charged in through the small opening, *c*, so that it covers the anode at the bottom of the furnace to a depth of 30 cm. The mass then becomes heated up to 3000° and higher. Further materials are added during several hours and then, after the molten or crystalline calcium carbide has cooled, it is discharged by removing the car through the door, *D*.

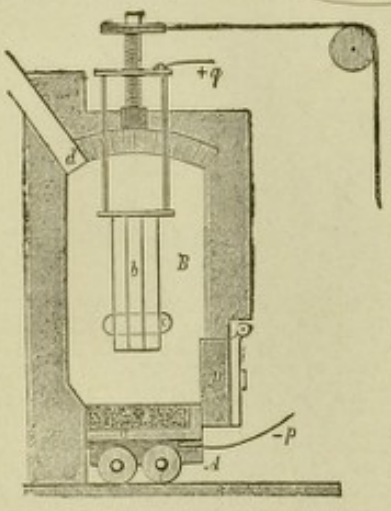


Fig. 211.

Erlwein and Engelhardt (Ger. Pat. 206,175 of 1907) have proposed the use of induction furnaces in which there is less loss of thermal energy. Since the carbide is not produced directly by the electric current, but by the high temperature, it is immaterial whether alternate or continuous current is used. For the production of 1 kilo of calcium carbide 2800 cals. are required, which correspond to 3·24 kw.-hours, that is, to 4·4 h.p.-hours (*see* p. 371), and thus theoretically each horse-power should produce 5·04 kilos of pure carbide per twenty-four hours (which should yield 349 litres of acetylene per kilo of carbide), but in practice less than 4 kilos are obtained even under the most favourable conditions. More exactly, for each effective horse-power measured at the furnace (and not in the transformer) 3·8 kilos of carbide of good quality (300 litres per kilo of carbide) are obtained per twenty-four hours, or 4·3 kilos of a strength which yields 280 litres of gas per kilo, or again 5 kilos of a strength of 250 litres per kilo. The cost of a ton of carbide may be calculated approximately as follows: 1·2 tons of limestone, 10·4*s*. + 0·6 tons of coke, 21·6*s*. + 12·8*s*. for consumption of electrodes + 28·0*s*. for labour + 15·2*s*. for general expenses, amortisation, &c. + 36·8*s*. for electrical energy, calculated at the price of 48*s*. per horse-power-year ; total for one ton of carbide £4 8*s*. (*Translator's note.*—These figures do not add up correctly.) In Italy in the works at Terni and at Bussi the Tofan furnace is used which produces about 1·8 tons of carbide per horse-power-year (almost the theoretical amount) of a strength of 300 litres of acetylene gas per kilo.

Lime for the manufacture of carbide should contain little magnesia (not more than 1 per cent.) and no phosphates, which would cause the acetylene to be contaminated with poisonous hydrogen phosphide.

The practical application of carbide for lighting purposes is known to all, and the contrivances for the preparation of acetylene vary very greatly. It is now used metallurgically as a reducing agent for various metallic oxides, salts, &c., and the metals Cu, Pb, Ag, Ni are thus easily obtained from their corresponding dry chlorides mixed with a little metallic oxide : $4CuO + CuCl_2 + CaC_2 = 5Cu + CaCl_2 + 2CO_2$. It is used for the production of acetylene for the oxy-acetylene blow-pipe, for illuminating purposes, &c. (p. 176). It is also used in large quantities to-day in the manufacture of calcium cyanamide (*see* p. 309).

STATISTICS. This industry, which has rapidly acquired very large proportions and extended to almost every country, has only been able to continue and overcome competition in those places where electrical energy is cheap. Italy is amongst those nations which are most favoured in this respect, as it has various cheap water-powers, but the industry is more especially helped by the protective tariff of £4 per ton which allows Italian manufacturers to sell carbide at low prices abroad and at dear prices in Italy.

The Italian production, imports, and exports are given by the following figures :

	Production Tons			Exports Tons	Imports Tons
1900	2,800				
1903	16,250			5,000	—
1904	27,300	at 22·4*s.* to	24·0*s.*	4,365	—
1905	28,200	17·6*s.*	20·0*s.*	8,955	688
1906	28,350	16·8*s.*	19·2*s.*	10,200	1,660
1907	30,560	16·8*s.*	19·2*s.*	8,587	801
1908	35,750	19·2*s.*	22·4*s.*	4,840	1,760
1909	—	—		1,811	3,132

Up to 1907 there were 4 carbide factories in Italy which together utilised 46,000 h.p., but the most important is that at Terni (Società italiana del carburo), which alone accounts for more than two-thirds of the whole Italian production ; in 1905 it produced more than 23,680 tons, and in 1907 more than 24,800 tons.

The Società dei prodotti azotati (calcium cyanamide) of Bussi now produces its own carbide and in 1908 two new works were erected at Narni in Perugia and at Capostello in Aquila.

The *world's production* of calcium carbide in 1909 is estimated at about 280,000 tons.

In *France* carbide costs £3 12*s.* more per ton than in Sweden, but in 1908 it enjoyed a protective tariff of £2 8*s.* per ton. There are 10 amalgamated works in France capable of producing 40,000 h.p. and 2 independent works commanding 8000 h.p. In 1904 only 18,000 tons of carbide were produced on account of the diminished demand, whilst the ordinary production is about 30,000 tons.

In *Germany*, the carbide industry consumes about 10,000 h.p. ; the production is about 12,000 tons, but it is not increasing because Germany is less satisfactorily placed than other nations in regard to the cost of electrical energy, and there is no protective tariff for carbide. On the other hand, the consumption is increasing and the imports in 1904 were 14,840 tons, 17,256 tons in 1905, 22,727 tons in 1906, 25,834 tons in 1907, 29,000 tons in 1908, and 27,000 tons in 1909. The German exports oscillate between 8000 and 10,000 tons. Of the imports into Germany about one-third come from Norway, about one-half from Switzerland, and about one-sixth from Austria.

At Cordoba in the *Argentine*, a works was erected in 1900 which produced 1 ton of carbide daily and 4 tons daily in 1908.

In *Japan* there is a single carbide works which now utilises 10,000 h.p. Formerly the production was only 90 tons per annum, which covered the consumption.

Switzerland utilises 66,000 h.p. in the manufacture of carbide, although it only produces 30,000 tons of carbide, of which 25,000 tons are exported.

Austria utilises 35,000 h.p. in its carbide factories and the annual production is about 25,000 tons.

The *United States* and *Canada* produce about 45,000 tons of carbide.

Norway has a production of more than 30,000 tons, and *Sweden* of about 15,000 tons.

Spain and *Portugal* together produce about 12,000 tons.

Commercial carbide has a greyish-yellow colour, and each kilo produces about 300 litres of acetylene gas with water.[1] In Italy carbide costs from £10 to £12 per ton ; that which

Analysis of Calcium Carbide. Commercial calcium carbide consists of pieces from the size of a pea to that of a nut and should not contain more than 10 per cent. of dust. Its commercial value depends upon the yield of acetylene. The chemically pure product should theoretically yield 548·7 litres of acetylene gas at 0° and 760 mm. pressure per kilo of carbide when treated with water. A good commercial product yields 300 litres of acetylene, although carbide of poor quality is often found in practice which yields less than 280 litres. The quantitative determination is carried out by weighing about a gramme of calcium carbide in a flask, introducing a test-tube containing two or three times its weight of water, closing with a stopper carrying a tube filled with dry calcium chloride, and then weighing the whole. The apparatus is then inclined so that the water escapes from the test-tube and liberates all the acetylene from the carbide, which is dried by passing through the calcium chloride tube. A current of air is finally drawn through the apparatus in order to displace all the acetylene, and the whole is reweighed, the loss in weight representing the quantity of acetylene by weight evolved from the given weight of carbide, and the volume is found from the fact that one litre of acetylene weighs 1·165 grms.

In the analysis of carbide, the rational preparation of the sample is of the greatest importance, as already described in the case of coal (*see* p. 371) ; one of every five barrels is opened and a kilo removed.

It is always necessary in analysing a sample of carbide to determine how much hydrogen phosphide it produces as this is poisonous. The acetylene should not contain more than 1 grm. of hydrogen phosphide per cubic metre,

was exported or produced by works outside Italy in 1909 was sold at £4 8*s.* to £4 16*s.*, charged into the bins of the consumer.

The carbides of strontium and barium are obtained in a similar manner to calcium carbide.

CALCIUM PHOSPHATE—CHEMICAL MANURES AND SUPERPHOSPHATES

In the section on phosphoric acid (p. 346) we have already seen how this acid may give rise to three series of salts.

TRICALCIUM PHOSPHATE : $Ca_3(PO_4)_2$, or Tertiary Calcium Phosphate, is somewhat scarce in the soil and in rocks, forming various minerals which are described below under Chemical Phosphatic Manures. Plants absorb the phosphate from the soil and accumulate it more especially in the seeds of cereals, vegetables, &c. The phosphates also exercise a very great influence on the development of the animal organism, because they are the fundamental constituent of bone, of which the ash (p. 313) contains up to 82 per cent. of tricalcium phosphate. This phosphate is almost completely insoluble in water and is obtained from soluble salts (alkali phosphates) by the addition of a soluble calcium salt in presence of ammonia. It separates as a gelatinous mass, which after drying forms a white amorphous powder easily soluble in acids (even in acetic acid), and which is attacked by carbon dioxide dissolved in water and may thus be assimilated by plants from the soil.

The **SECONDARY PHOSPHATE, $CaHPO_4 + 2H_2O$,** is also called **Dicalcium Phosphate,** because the calcium has replaced two atoms of hydrogen of the phosphoric acid. It is found already formed in small crystals in guano and is obtained as an amorphous powder by mixing a solution of disodium phosphate with calcium chloride in presence of a little acetic acid. It dissolves in a little water, but is decomposed by much water with production of a turbidity consisting of tricalcium phosphate, whilst the remaining solution acquires an acid reaction. On heating to redness it is transformed into calcium pyrophosphate, $Ca_2P_2O_7$.

The **PRIMARY PHOSPHATE : $Ca(PO_4H_2)_2$ (Monocalcium Phosphate)** is obtained from the other phosphates by treating them with the calculated quantities of sulphuric or hydrochloric acid. It is soluble in much water, whilst when treated with a little water tricalcium phosphate is formed and a very acid liquid remains.

CHEMICAL FERTILISERS

In the course of this work we have become acquainted with numerous salts, chlorides, nitrates, sulphates, carbonates, ammonium salts, phosphates, &c., and as many of these have acquired great agricultural importance, and to-day form the basis of successfu agriculture by maintaining or increasing the fertility of the soil, we will devote some pages to the important industry of artificial manures. In 1840, Liebig disproved the erroneous and traditional conceptions which were then prevalent [1] in connection with substances

and the quantity of this is determined according to Lunge and Cederkreutz by passing the gas produced by 50 grms of the carbide through a fresh solution of sodium hypochlorite (about 75 c.c. containing 2 to 3 per cent. of hypochlorite); phosphoric acid is thus formed which may then be precipitated with magnesia mixture in the form of magnesium ammonium phosphate, $Mg_2P_2O_7$, of which 1 grm. corresponds to 0·8198 grm. of calcium phosphide, Ca_3P_2, contained in the carbide or to 0·307 grm. of hydrogen phosphide, PH_3. W. Hinrichsen showed in 1907 that only half of the phosphorus contained in the carbide is transformed into hydrogen phosphide, and that the rest forms organic phosphorous compounds which are absorbed by the hypochlorite, whilst it is not known whether they are poisonous. In any case, he advises the determination of all the phosphorus by the process of completely burning the acetylene according to the method of Lidholm (1897).

[1] Until the middle of last century, and, if we wish to go backwards in history, also from the remotest antiquity when agriculture itself arose, the only substance which was supposed to supply and replace the nourishment periodically removed from the soil was stable manure and excrements in general. Guano, the excrement of birds, has been used agriculturally in Peru since 1300 (during the rule of the Incas), and the birds which produced it were protected by law.

The action of dung was attributed by Palissy in 1550 to the soluble salts which it contained. In 1780,

which fertilise the soil, by numerous experiments and treatises, especially by his book on agricultural chemistry and his celebrated pamphlet "Die Latrinenfrage," in which he showed that all green plants obtain their most important nourishment in the form of mineral matter, carbon dioxide, ammonia, water, phosphoric and silicic acids, lime, magnesia, potash (and soda), iron, &c. Human and animal excrements are important not on account of the organic matter itself which they contain, but on account of the organic substances which are produced by these on putrefaction, by which the organic carbon is transformed into carbon dioxide and the organic nitrogen into ammonia, nitrates, &c., so that in order to maintain the fertility of the fields it suffices to treat the soil with inorganic salts which are utilised by the plants and which are formed to a large extent during the putrefaction of organic matter, such as stable manure, &c.

The use of artificial chemical manures has only extended and continuously increased since this precise and rational theory was enunciated by Liebig.

In order to determine the absolute value of a chemical manure it is necessary to consider it apart from other agricultural factors, which are also of great importance, such as the character of the soil, the amount of heat and light, &c. Wolff, Sachs, Stohmann, and others made artificial cultures of plants in water only, in which they dissolved various mineral salts. On the other hand, Hellriegel employed quartz sand which had previously been boiled with acid and washed with water, to which he then added the various inorganic chemical manures which he wished to study, and watched the growth of the various plants.

The result of all these experiments was that lime, potash, magnesia, iron, phosphoric and sulphuric acids, nitrates, ammonia, and nitric acid, all in the state of salts, are indispensable to vegetation, whilst the plants absorb the carbon, oxygen, and hydrogen which are necessary to their development from the carbon dioxide of the atmosphere and from water.

Atmospheric nitrogen is not directly assimilated as was shown by Boussingault, although we have already seen, in speaking of nitrogen, that certain micro-organisms may serve as intermediaries, as in the case of leguminosæ, by assimilating free nitrogen (p. 30).

In the case of the ordinary commonly cultivated plants, the addition to the soil of potash, phosphoric acid, and nitrogen is always indispensable, because the soil contains little of these elements, and is easily exhausted.[1] In acid and peaty soils phosphates are almost completely absent and there is a deficiency of calcium carbonate.

In 1906 *Germany* used various artificial manures of the value of £15,000,000, of which £2,880,000 was spent on ammonium sulphate, £6,000,000 on sodium nitrate, and £1,520,000 on potassium salts (200,000 tons at £7 12*s*. per ton). The rest is accounted for by superphosphates, basic slag, guano, &c.

In 1905 *Italy* consumed more than 500,000 tons of various artificial manures, more than two-thirds of which consisted of superphosphates, of a total value of about £1,720,000.

France annually consumes about 2,000,000 tons of various chemical manures.

In 1899 *Japan* imported various chemical manures of the value of £77,600, in 1906 of £3,000,000, and in 1909 the imports rose to a value of £4,000,000.

We have already considered potassium and nitrogenous manures when discussing the potassium salts of Stassfurt, sodium nitrate, and the utilisation of atmospheric nitrogen (pp. 303, 424 and 459). We will now consider the phosphatic manures.

PHOSPHATIC MANURES. Under the best conditions soils contain up to 0·3 per cent. of phosphorus pentoxide, but ordinarily less than 0·1 per cent. Various crops annually remove considerable quantities of this substance. Thus wheat removes about 46·5 kilos of tricalcium phosphate per hectare, hemp 95 kilos, trefoil 111 kilos, sugar-beet 94·5 kilos, &c.

If, therefore, a corresponding quantity of phosphoric acid is not replaced and returned

Leblanc showed the importance of ammonium salts for vegetation, and Sprengel confirmed this idea and added that mineral salts in general play a great part in vegetation. It was, however, through the influence of two agriculturists, Thaer in Germany and Dombasle in France, from 1800 to 1840, that in Europe a theory prevailed that the importance and efficacy of stable manure was not due to mineral salts, but to the organic humus which is formed during its fermentation and putrefaction.

The influence of this erroneous theory has extended to our own days, and we still find it amongst the old farmers who have not yet opened their eyes to the light of modern science.

[1] It has been calculated that in France from 25,000,000 hectares of cultivated soil, about 600,000 tons of nitrogen, 300,000 tons of phosphorus pentoxide and 755,000 tons of potash are annually removed by the various crops.

Powdered blood containing about 16 per cent. of nitrogen, horn powder containing about 14 per cent. of nitrogen, and hide powder with 7 to 10 per cent. of nitrogen are sometimes used as organic nitrogenous manures, but are not very efficient,

to the soil, this will become sterile in a short time. This is what has happened during past centuries in Greece, Sicily, Egypt, and Spain, which once formed the so-called granary of Europe, and to-day their production is enormously diminished because the replacement in adequate amount of the phosphoric acid removed by the corn was not thought of.

Liebig proposed in 1840 to render the fertilising action of bone-meal [1] more effective by first treating it with sulphuric acid in order to obtain soluble phosphates, and in 1857 he proposed to treat mineral phosphates in a similar manner thus converting them into superphosphates. In England about 200,000 tons of superphosphates were already produced in this manner in 1862.

Since this time one of the largest branches of modern chemical industry has arisen which has developed with startling rapidity and caused a true revolution in agricultural methods (*see below*, Statistics).

The most important source of mineral phosphates which was used in the past for the preparation of manures was *guano*, which consists of enormous deposits of excrements and skeletons of birds and other animals, formed during past geological epochs, and according to their geological position and to the action exercised by water they are more or less nitrogenous.

Powdered guano is often used without chemical treatment, although endeavours are now made to render it somewhat assimilable and more soluble by suitable treatment with mineral acids.

Guano is found more especially in Peru, Colombia, Bolivia, Patagonia, &c. In 1902 Peru exported 61,000 tons of guano.

Germany imports variable quantities (2360 tons in 1904, 8030 tons in 1906, and 22,000 tons in 1907).

The most abundantly used phosphatic deposits to-day consist of *phosphorite* which is the prime material for the superphosphate industry. It is an amorphous tricalcium phosphate, entirely of organic origin, being perhaps formed by the fossilisation and mineralisation of ancient deposits of nitrogenous guano. Unaltered teeth of various sizes belonging to various species of animals are often found in phosphorite. The phosphorite which is used for the production of superphosphates throughout the world is mainly furnished by the United States (Florida, Tennessee, South Carolina), by Algeria and Tunis (especially from the deposits of Gafsa), and in minimal quantities by Belgium and France (*see* Statistics *below*).

Recently a deposit of 25,000,000 tons of phosphorite has been discovered in Tennessee and another of 30,000,000 tons in the Society Islands.

Phosphorite is also found together with various other minerals and soils forming deposits of *phosphatic chalk* and *sand*, containing 60 to 75 per cent. of tricalcium phosphate, of which important seams abound in England, Spain, &c. The utilisation of poorer phosphatic deposits has now been also undertaken by concentrating them, that is, by increasing their strength by means of heating in furnaces, sometimes followed by treatment with mineral or organic acids. The concentration of phosphorite is sometimes also effected by levigation with water.

Very numerous deposits of other phosphates are also found in nature distributed in smaller or larger quantities, especially phosphates of aluminium, iron, and the relatively abundant *apatite*, consisting of a calcium fluophosphate, $Ca_3(PO_4)_2.CaF_2$.

Apart from phosphorite and guano, basic slag and unfossilised bones are also used as sources of phosphoric acid.

The bones [2] are first defatted by immersion in boiling water, or preferably by treating

[1] For more than a century already the beneficial action of phosphates on the soil had been known, and they were employed in the form of bone-meal. In 1840 the Duke of Richmond in England showed practically that the fertilising value of bones was not due to the gelatine and fat, but to the calcium phosphate which they contained. In 1841 Flaming in England made the first attempt to treat bones with acids in the manner proposed by Liebig. In 1856 Elie de Beaumont showed the value of finely divided mineral phosphates, but the results would have been more immediate and advantageous if the mineral phosphate (tricalcium phosphate) had been suitably transformed in order to render it more soluble and more easily assimilable.

[2] Bones contain from 55 to 65 per cent. of tricalcium phosphate, from 1 to 3 per cent. of magnesium phosphate, and from 2 to 9 per cent. of calcium carbonate. They also contain certain quantities of fat and of glue (gelatine) and small quantities of fluorides. From an ox or a horse 40 to 50 kilos of tricalcium phosphate may be obtained; from a pig or a calf from 7 to 12 kilos, from a ram from 4 to 5 kilos, and the same quantity from a man. Apart from the bones of all the animals which are slaughtered daily, large quantities have been amassed in the quaternary epoch (that of primitive man) in the caves of Gallenreuth in Franconia, of Lherm in France, and of Suffolk in England &c., and are also formed to-day in the pampas of the Argentine through periodic hetacombs of horses

them with carbon disulphide, petroleum benzine, or carbon tetrachloride. The gelatine is then removed in autoclaves at a pressure of 1½ atmospheres in presence of steam, which transforms the ossein into gelatine and dissolves this latter. Bones which have simply been defatted still contain 3·5 to 4 per cent. of nitrogen ; after the gelatine has been removed, they only contain 0·9 to 2 per cent., and when powdered form *bone-meal* which is an effective phosphatic manure and also contains nitrogenous matter.

These bones are often employed for the preparation of *bone superphosphate*, which contains all the phosphoric acid in a form soluble in water, because there are no substances present which cause reversion as do the alumina and iron in phosphorite. Such bone superphosphate also contains 1 per cent. of nitrogen. The units of nitrogen in bone superphosphate are paid for apart from those of P_2O_5, and these latter units fetch ·5*d.* to ·7*d.* more than when present in mineral superphosphates.

Bones which have simply been defatted and powdered do not keep well because a fermentation occurs which destroys a considerable portion of the nitrogen. This difficulty is avoided by moistening them with dilute sulphuric acid.

Bone black, which is obtained by calcining the defatted bones in closed vessels out of contact with the air, is first employed as a decolorising agent in sugar refineries, after which it scarcely contains any more nitrogen, but is often further employed for the preparation of bone superphosphate, because it contains from 65 to 75 per cent. of tricalcium phosphate.

BASIC SLAG is obtained in steelworks from the dephosphorisation of steel by the basic Thomas-Gilchrist process in presence of much lime (*see* Iron). For each ton of steel, 200 to 300 kilos of slag is obtained, which floats upon the molten steel in the converter, and is easily separated from the surface with suitable ladles, when it sets to a hard spongy mass which is powdered in ball mills. Basic slag is now also obtained in open-hearth furnaces and is equal to Thomas slag. To obtain it in a more brittle condition before powdering, it is poured into water whilst still molten.

The phosphoric acid in the slag is probably present in the form of basic tetracalcium phosphate, $Ca_4P_2O_9$, united with 1 mol. of calcium silicate, $CaSiO_3$, and contains about 75 per cent. of total phosphorus pentoxide which is soluble in ammonium citrate, since it behaves as dicalcium phosphate. It also contains from 10 to 20 per cent. of free lime, from 4 to 30 per cent. of iron oxide (Fe_2O_3 + FeO), and from 2 to 20 per cent. of silica. It usually contains from 14 to 16 per cent. of P_2O_5 or from 16 to 18 per cent. ; and for equal strength in phosphoric acid, that is preferred which contains most SiO_2.

Basic slag is placed on the market for direct consumption in very fine powder, 80 per cent. of which passes through sieve No. 100 (French scale), and its efficiency is proportional to its degree of fineness. It varies in colour from reddish brown to dull yellow (*see* Analysis *below*).

In 1892 Europe produced about 1,000,000 tons of slag ; in 1899 the production rose to 1,650,000 tons, and Italy imported about 70,000 tons in 1902.

The demand for this product is so great that the unit of P_2O_5 fetches almost as high a price as the same unit in the form of superphosphate.

THEORY OF SUPERPHOSPHATE MANUFACTURE. Tricalcium phosphate, however finely divided, being insoluble in water, only comes into contact or is absorbed by the roots of plants very slowly, and it is therefore advantageous to transform it into monocalcium phosphate, $CaH_4(PO_4)_2$ (superphosphate), which is soluble in water, and therefore easily dissolves in the soil and penetrates uniformly throughout all the strata of arable land. In contact with the lime in the soil it is transformed into dicalcium phosphate and also into tricalcium phosphate, insoluble in water, but it is then so uniformly

and cattle. Our descendants in the distant future will find bone deposits in many cemeteries of our present large towns.

Rocky conglomerates formed of bone abound in Algeria, and of these 6000 tons were exported in 1893 and 225,000 tons in 1898.

Germany imported 5600 tons of bones from La Plata and the Levant in 1903 and 1000 tons in 1907 at a price of £4 to £4 16*s.* per ton. It also imported *crushed bone* from Calcutta, Bombay, &c., to the amount of 13,500 tons in 1903 and 8900 tons in 1907 at £4 16*s.* to £5 12*s.* per ton, and also *bone-meal* from India, South America, and Russia to the amount of 6000 to 9000 tons at £4 per ton if degelatinised and at £4 16*s.* to £5 4*s.* per ton when it still contained the gelatine. To these quantities 3450 to 4500 tons of imported *bone ash* must be added at £2 16*s.* to £3 12*s.* per ton.

Defatted bone and bone-meal were exported from India in 1906 to the extent of 17,060 tons, and 9400 tons in 1909. Germany imported 1750 tons of defatted bone in 1908 and 2792 tons in 1909, and exported 2330 tons in 1909.

distributed and so finely divided that it is carried to the root terminals and the juices of these attack and assimilate it rapidly. The solubility of superphosphate is, therefore, of advantage entirely and only because it temporarily facilitates this subdivision and penetration into the soil.

Finely ground tricalcium phosphate may also be employed directly for peaty, marshy, and acid soils, or for other soils when an immediate effect is not required.

Superphosphates are the product resulting from the treatment of natural tricalcium phosphate with strong sulphuric acid in such a manner that the maximum amount of monocalcium phosphate soluble in water is obtained, together with a little dicalcium phosphate soluble in ammonium citrate, mixed with the crystalline gypsum which results from the reaction.[1]

If an excess of sulphuric acid is employed, this remains free and free phosphoric acid is also formed, whilst the resulting superphosphate is moist and forms pasty lumps. If too small a quantity of phosphoric acid is used dicalcium phosphate is mainly formed which is insoluble in water, but soluble in ammonium citrate.[2] Thus also, if unaltered tricalcium phosphate remains this forms dicalcium phosphate in contact with the monocalcium phosphate. The iron in the phosphorite is partially obtained as primary phosphate, but in certain cases if the phosphates must be dried it reacts with the monocalcium phosphate forming insoluble ferric phosphate and thus diminishes the amount of soluble phosphate, that is to say, a *reversion* occurs which it is necessary to avoid by working with phosphorite which contains little iron, and regulating the temperature of drying of the superphosphate. This reversion also occurs in the soil, and in order to retard it the admixture of finely divided stable manure with the superphosphate has been proposed. With regard to yield, the superphosphate works calculate that 2 tons of superphosphate are obtained from 1 ton of phosphorite.

The strength in phosphates is given in percentages of P_2O_5 soluble in water and in ammonium citrate, but 80 per cent. of this should be soluble in water. In the German superphosphate trade the strength is given in phosphorus pentoxide soluble in water, and thus the same superphosphate will be indicated in Germany by a figure somewhat lower than that on which it would be sold in Italy.[3]

[1] The reaction may, in many cases, be thus represented:

$$6Ca_3(PO_4)_2 + 6H_2SO_4 + 12H_2O = 6CaSO_4.2H_2O + 4PO_4H_3.Ca_3(PO_4)_2$$

and this latter slowly transforms, forming $3CaH_4(PO_4)_2.H_2O$ with water. From this the amount of water which must finally be added to the mixture in order that the superphosphate may not be moist may be calculated. By some the reaction is interpreted in the following manner:

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O = CaH_4(PO_4)_2 + 2CaSO_4.2H_2O.$$

In the treatment with sulphuric acid it must be remembered that phosphorite sometimes contains a considerable quantity of calcium carbonate, from 1 to 20 per cent. or more, which facilitates the action of the acid on the phosphate, because apart from heat, carbon dioxide is developed which renders the mass more porous and thus facilitates the reaction and more complete drying. It must be noted, however, that an excessive quantity of calcium carbonate results in loss of sulphuric acid.

Phosphates such as apatite which do not contain much calcium carbonate react with sulphuric acid with more difficulty because the mass does not become heated and a moister and less porous product results. In such cases it is necessary to work with hot acid or to admix phosphorite containing much limestone.

If the phosphorites contain fluorides (from 0·5 to 7 per cent.) or small quantities of chlorides, hydrofluoric or hydrochloric acids are formed by the action of the strong sulphuric acid, and since silicic acid is simultaneously liberated, gaseous silicon fluoride, SiF_4, finally results, which has an irritating smell and is obnoxious. This must therefore be removed by absorption in water as otherwise it would be harmful to the health of the workpeople and the vegetation of the vicinity.

[2] In superphosphate works the exact determination of the quantities of sulphuric acid which must be added to each type of phosphorite, including the amount consumed by the carbonates, fluorides, sesquioxides, &c., is of mportance, and the water necessary to obtain a superphosphate containing 10 per cent. of moisture, and gypsum n the crystalline form, must also be determined. If water is present either in excess or in too small a quantity the superphosphate remains moist.

In German works the quantity of sulphuric acid necessary for the decomposition of phosphorite is determined by Rümpler's method, by weighing out 20 grms. of powdered phosphorite, treating it with an exactly measured excess (for example, 20 c.c.) of sulphuric acid of 45° Bé., which has been accurately titrated, in a graduated 1-litre flask and digesting in a water-bath for two hours. After cooling, the whole is made up to 1 litre with water It is filtered then and 50 c.c. of the filtrate are titrated with a $\frac{N}{10}$ solution of sodium hydroxide until a precipitate commences to form, showing that all the free sulphuric acid is saturated and that the reaction with mono-calcium sulphate has started. By deducting the free sulphuric acid found from the quantity of acid employed, the quantity of acid necessary for treatment of the given phosphorite can be exactly calculated, although in the case of phosphorites rich in sesquioxides a little more than the calculated quantity is employed. Any tricalcium phosphate which may remain unaltered constitutes a loss to the manufacturer, because superphosphates are to-day sold according to the strength of P_2O_5 soluble in water and in ammonium citrate only.

[3] **Analysis of Superphosphate.** *Preparation of the sample.* The preparation of the sample is of great importance. It should be removed from several sacks and at various depths from each sack by means of a sampling tube .

INDUSTRIAL PROCESSES. The natural phosphate in smaller or larger pieces, sometimes as gravel, is loaded loose into vessels and passes from these into trucks in which it is conveyed to the works. When it arrives in a very moist condition, which is rarely the case, it must first be dried in ovens. Ordinarily it contains from 1 to 3 per cent. of moisture, but not more than 5 per cent. can be tolerated because a larger quantity renders the subsequent grinding difficult.

The lumps of phosphorite are first roughly crushed in a Blake crusher (p. 256), which has an output of 3 or more tons per day. The material which has thus been crushed must then be finely powdered and sieved. Among the many systems proposed for this

These portions are then quickly mixed and the whole forms about 1 kilo, which is then divided and introduced into three dry glass bottles, preferably closed with glass stoppers or with a good cork stopper which should finally be paraffined. The stopper is tied down with a string, the ends of which are fastened and fixed to a label with a seal, and the stopper itself is also fixed with the seals of the buyer and the vendor.

On the label the statements referring to the contract and the quality and quantity of the product are stated, and it is also inscribed with the testimony of the two parties who have assisted in removing the sample. The sample is sent to a laboratory selected by common accord for the execution of the analysis. The second sample may be eventually sent to another laboratory for control, and the third is reserved in case of disagreement between the results of the two first laboratories.

In the laboratory the chemist notes if all the seals are in order and enters the details on the label, and then if the superphosphate is dry it is passed through a sieve, breaking up any remaining lumps until the whole sample has passed through. If the sample is very moist, it is necessary to mix it by hand as well as possible.

Usually the determination of the phosphoric acid soluble in water and in ammonium citrate is of most importance, and sometimes also the total phosphate. The results are expressed in phosphorus pentoxide, P_2O_5, and the determination is made in the following manner (official Italian method): For the *determination of the phosphoric acid soluble in water and in citrate*, 5 grms. of the substance are stirred up with 40 to 45 c.c. of water and the liquid decanted through a folded filter. The residue is treated similarly three or four times with water, and finally the whole is poured on to a filter. The filtrate is collected in a 250 c.c. flask, acidified with a few drops of HNO_3, and the residue washed on the filter until the flask is filled. The filter with its contents is placed in a 250 c.c. flask and digested at 30° to 40° for one hour with 100 c.c. of an ammonium citrate solution (prepared by dissolving 400 grms. of citric acid in water, neutralising with ammonia and diluting with water to 1 litre) and frequently stirred; after cooling, it is made up to 250 c.c. with water and filtered.

The first aqueous solution contains the phosphates soluble in water and the second the phosphates soluble in citric acid. The phosphoric acid may be determined separately in these, but more usually, as the amount of P_2O_5 soluble in water and in citrate is required (80 per cent. of which should be soluble in water), 50 c.c. of each solution are mixed together, diluted with 50 c.c. of water and 50 c.c. of ammonia of sp. gr. 0·9, and magnesia mixture then added a little at a time, whilst stirring with a glass rod without touching the walls of the vessel. The magnesia mixture is prepared from 55 grms. of crystalline magnesium chloride, 70 grms. of ammonium chloride and 650 c.c. of water made up to 1 litre with ammonia of sp. gr. 0·96. After adding the magnesia mixture the whole is allowed to stand for five or six hours and then decanted through a filter, the weight of the ash of which is known. The residue is washed several times by decantation with dilute ammonia, and finally poured on to the filter, washing until a few drops of the filtrate no longer give a precipitate with $AgNO_3$ after acidification with HNO_3. The filter is then dried in an oven, heated to redness in a platinum crucible and allowed to cool in a desiccator, the precipitate being weighed as magnesium pyrophosphate, from which the weight of P_2O_5 may be found by multiplying by 0·64.

The *total phosphorus pentoxide*, soluble and insoluble, is determined by treating 5 grms. of superphosphate with 25 grms. of hydrochloric acid + 5 grms. of nitric acid + 70 grms. of water, boiling for half an hour and diluting with water to 250 c.c. To 10 c.c. of this solution 4 c.c. of an ammonium citrate solution (of standard strength) are added; it is neutralised with NH_3, and 5 c.c. of HNO_3 + 15 c.c. of ammonium nitrate + 40 c.c. of a molybdic acid solution are added. The molybdic acid solution is prepared by dissolving 150 grms. of ammonium molybdate in 1 litre of hot water, pouring this solution into a litre of nitric acid of sp. gr. 1·2 and allowing the whole to settle for some days. After adding the molybdic acid solution the liquid is heated to 80° to 90° for ten minutes, allowed to cool, filtered, and the precipitate washed with a solution of ammonium nitrate, containing 150 grms. of ammonium nitrate + 10 c.c. of HNO_3; the filter is then pierced and the contents rinsed into a beaker with 2½ per cent. ammonia solution and precipitated as above with magnesia mixture.

In certain cases, for instance, in bone superphosphate, the determination of the total nitrogen contained in the manure in the form of nitric acid, ammonia, and organic nitrogen is of interest. For this purpose the Kjeldahl-Jodlbauer method is used (*see* description and figure in vol. ii, "Organic Chemistry"), using 1 grm. of the material in a 300 c.c. long-necked, hard glass flask with 30 c.c. of phenolsulphuric acid mixture, prepared by first mixing 200 grms. of sulphuric anhydride with 500 c.c. of strong sulphuric acid and then adding to this solution a solution of 40 grms. of pure phenol in 500 c.c. of strong sulphuric acid; after digesting the substance with 30 c.c. of this mixture for one hour, about 1 grm. of mercury and 2 to 3 grms. of dry zinc dust are added little by little with shaking and cooling.

The whole is digested for a further hour and then heated to boiling for one to three hours until the liquid in the flask has become colourless. After cooling, this is poured into a half-litre flask containing 200 c.c. of water; 100 c.c. of sodium hydroxide solution of sp. gr. 1·29 are added together with about 1 grm. of zinc dust and the whole is then immediately distilled, using a delivery tube with a special bulb which prevents the spray from the soda solution from passing into the distillate. The ammonia which distils is passed into an absorption flask containing 25 c.c. of normal hydrochloric acid coloured with methyl orange.

When the liquid which distils is no longer alkaline, the excess of HCl is titrated with normal soda and the quantity of ammonia or of nitrogen then calculated. One cubic centimetre of normal HCl corresponds to 0·017 grm. of NH_3 or 0·014 grm. of nitrogen.

The *Analysis of Basic Slag* is ordinarily confined to the determination of the degree of fineness and the percentage of total phosphoric acid, but it should be noted that in order to ascertain that the slag has not been adulterated with ordinary ground phosphorite, it is advisable to always determine the amount of phosphoric anhydride soluble in citric acid, which is always from 75 to 80 per cent. of the total anhydride in the pure slag, whilst in phosphorite it is only 10 to 12 per cent.

The fineness is determined by weighing the quantity of powder which remains on a Kahl No. 100 sieve (or French sieve) after sieving 50 grms. of the slag for a quarter of an hour. This weight must be multiplied by 2

purpose the best results are obtained with the ball mills of the firm of Friedrich Krupp. In Figs. 212 and 213, transverse and longitudinal sections and a view of one of these mills are shown. They consist of a rotating drum of 2½ to 3 metres wide and up to 2 metres in length constructed of perforated steel or hardened cast-iron plates. They contain two to three tons of steel balls of varying sizes (from 5 to 12 cm. diameter). The drum is actuated by a motor of 25 to 35 h.p. The plates inside the drum are so arranged that they form steps at their junctions, and thus the balls which are carried round by the movement of the drum continually fall back on to one another below, hitting and pulverising the fragments of phosphorite until they acquire such a degree of fineness that they first pass through the holes in the plates and then partially through a fine sieve by which the plates are surrounded. The coarser portion which does not pass through the sieve is carried up by ledges to the top of the drum during its rotation and then falls back to the bottom through a slit which is suitably placed between one plate and another, so that it is again ground. The fine powder which passes through the sieve gradually collects at a lower aperture closed by a flap. These mills have been greatly improved of recent years by various works (*see below*, Cement Industry). In many works Griffin mills are used with two or four pestles. Since 1905 the Kent mill has been widely used (Fig. 214), and consists of a large free grinding drum, *t*, which contains three revolving cylinders 1, 2, and 3 ; the upper cylinder, 1, rotates at a velocity of 180 revolutions per minute, and since it supports the grinding cylinder it causes this also to revolve at 40 revolutions per minute, and the drum in turn causes

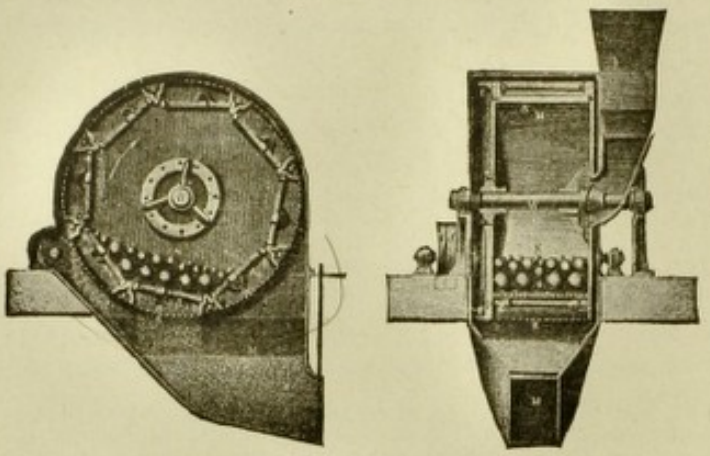


FIG. 212.

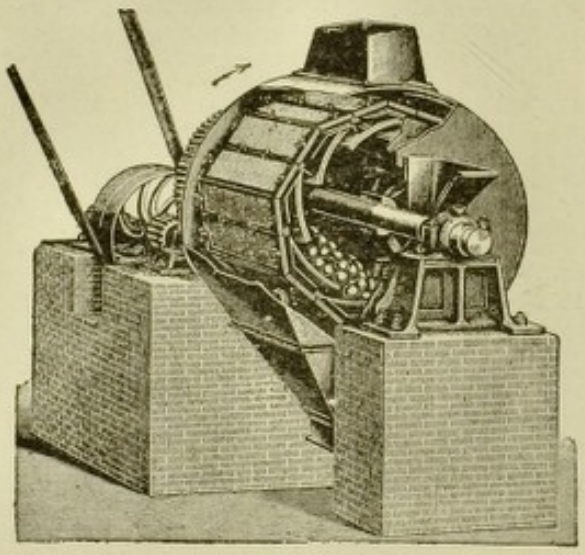


FIG. 213.

and subtracted from 100. A good slag has a degree of fineness of 80. These sieves do not, however, always yield concordant results.

We here give a Table of the French numbers for metallic gauze sieves. These may be transformed into English numbers by using the relationship between the French or Parisian inch (27·1 mm.) and the English inch (25·4 mm.) ; thus, No. 80 French sieve corresponds to No. 75 English.

No. of French sieve	No. of meshes per cm.	No. of meshes per sq. cm.	Thickness of wires in mm.	No. of French sieve	No. of meshes per cm.	No. of meshes per sq. cm.	Thickness of wires in mm.
4	1·4	2	—	60	22·2	493	0·167
6	2·2	5	—	65	24·0	576	0·155
8	2·9	8	—	70	25·9	671	0·143
10	3·7	14	—	75	27·8	773	0·134
15	5·6	31	—	80	29·6	876	0·125
20	7·4	53	—	90	33·3	1109	0·111
25	9·6	93	0·420	100	37·0	1369	0·100
30	11·1	123	0·333	110	40·7	1600	0·090
35	12·9	166	0·280	120	44·4	1970	—
40	14·8	219	0·250	130	48·1	2310	—
45	16·7	280	0·220	140	51·8	2685	—
50	18·5	342	0·200	240	88·6	7840	—
55	20·3	412	0·180				

the cylinders 2 and 3 to revolve by friction. All the cylinders are partially dependent on one another because they are connected with three steel springs, *m*, in such a manner that when one of them is displaced through the passage of an especially large or hard lump of phosphate the energy is recovered by pressure on the other cylinders and is thus not lost. The phosphate which has previously been coarsely ground is introduced into the mill at its two extremities by means of a hopper, *b*, and as it is pulverised it adheres to the internal surface of the grinding drum through centrifugal action, so that it is continuously carried round, and the continual grinding action of the particles on one another causes a very much finer grinding than is the case in ball mills. This machine also uses less power and is less rapidly worn. It has the additional advantage that the large amount of noise characteristic of ball mills is absent. The Kent mill is now also used in cement works.

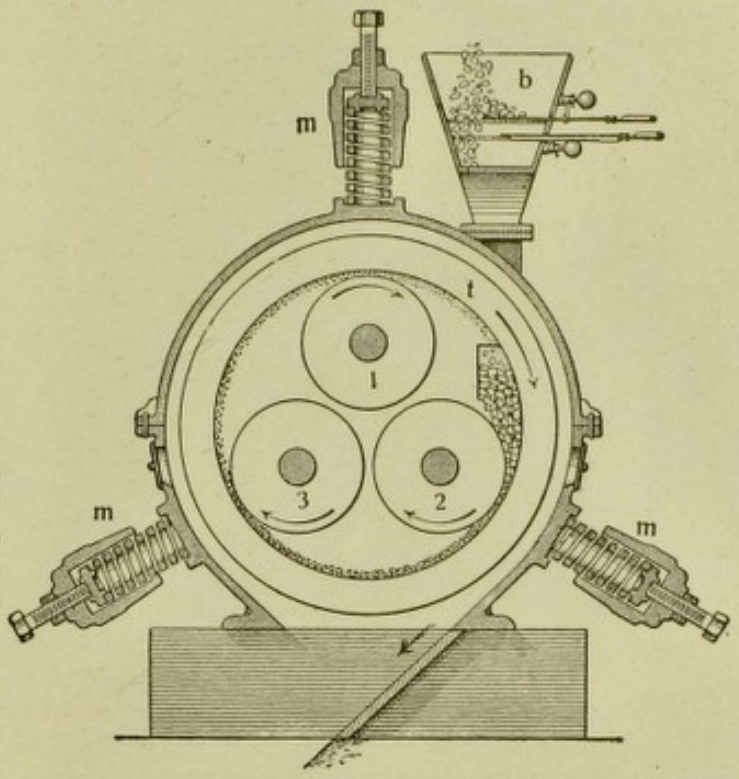


FIG. 214.

The treatment of bone is carried out with somewhat different machinery. The first crushing of the degreased bones is carried out between toothed cylinders such as are seen in plan and in elevation in Fig. 215. A further crushing is carried out in a stamp mill (Fig. 216) which breaks the bones upon a grating which allows the smaller pieces to pass through. Below the grating there is a helical transmitter which carries the product to a grinding mill which powders it, and after sieving it is treated in the same way as phosphorite.

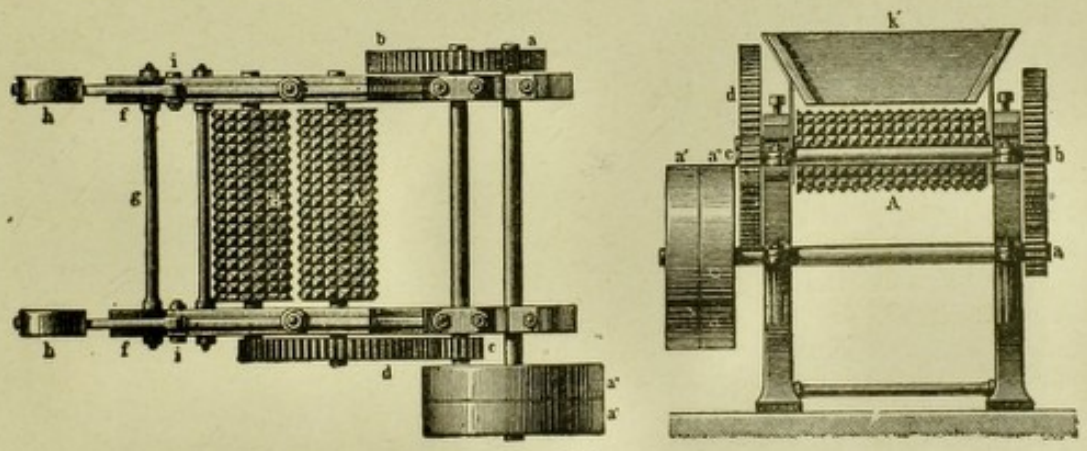


FIG. 215.

After the phosphate has been finely powdered it is treated with sulphuric acid in order to convert it into superphosphate. Superphosphate works ordinarily produce their own sulphuric acid and employ one portion of it at 60° Bé. as obtained in the Glover tower and the rest at 52° Bé. as obtained directly in the lead chambers. It is always necessary to accurately determine the strength of the acid which is employed in order to be able to exactly calculate the quantity which is required for a given weight of the previously analysed phosphorite.

The first reaction between the acid and the phosphate is carried out in a mixer.

The first types of mixing machine consisted of an inclined leaden cylinder (Fig. 217) containing a shaft provided with blades which mixed the powder and the acid which were introduced into a hopper at the upper part and then discharged from the lower part into a chamber beneath ("pit" or "den"). To-day horizontal cast-iron mixers with blade-stirrers are generally used.

Lorenz employs a mixer with a special stirrer similar to the earth-board of a plough, which revolves rapidly so that complete mixing is attained in half a minute. The mixer, *a* (Fig. 218), is supported on a wall which separates the two pits which receive the superphosphate; it has two discharging openings, each of which communicates with one of these pits, *g*. Up to 8 tons of superphosphate can be produced per day with a motive force of 2 h.p. Since the reaction occurs to a considerable extent in the mixer, in which the mass becomes hot and evaporates a little water, drier superphosphates are obtained by these methods. The acid passes in directly from the lead chamber and the Glover tower and is brought to the required strength in the vat, *k*. A smaller vat, *h*, measures off the necessary quantity of acid corresponding to the charge for each operation.

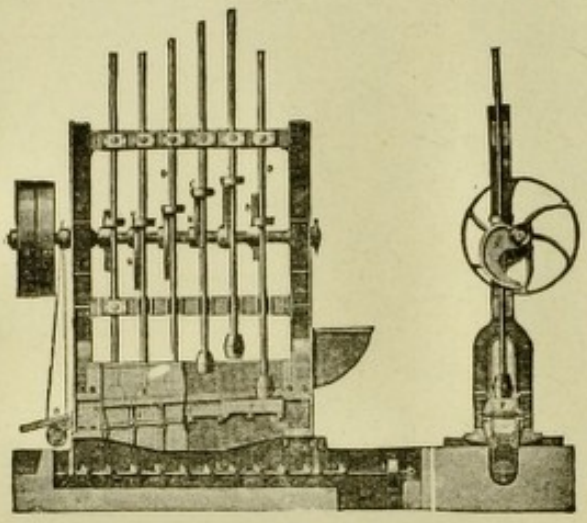


Fig. 216.

The superphosphate passes out of the mixer in an almost liquid condition and collects in the pits in horizontal layers until these are half filled, after which they are completely closed. In these pits the reaction between the sulphuric acid and the tricalcium phosphate is completed. The temperature rises considerably and much gas is evolved consisting of carbon dioxide, silicon fluoride, hydrofluoric acid and hydrochloric acid. These gases escape through the outlet, *b*, and pass through it into the absorption tower.

There are several adjoining pits divided by walls and thus whilst one chamber is being filled the contents of a second are standing and a third is emptied, after which it is allowed to cool slightly. Each pit is capable of holding 50 to 100 tons of superphosphate. After 2 to 4 days the windows and discharging doors of the pits are opened. These apertures are closed before filling with bricks or with wooden boards which fit tightly and are plastered over with clay in order to prevent the gas from escaping. In some works the superphosphate is already discharged after twenty-four or thirty-six hours in order to powder and sieve it whilst still hot, and dry it by means of a current of air drawn over it with a fan in order to remove steam. The chambers are usually discharged by hand with pickaxes, and since the temperature of the mass is high and noxious gases are evolved a fan should be employed during discharging in order to draw the gases away into the flue leading to the absorption towers. The workmen wear clogs and are provided with "Hard" masks (safety masks) containing a sponge moistened with a dilute soda solution in order to preserve their lungs and eyes from the action of the poisonous gases. In better appointed works there are various mechanical appliances for the extraction of superphosphates from the chambers (*see* Fig. 219), thus avoiding any injury to the workmen (*see also* Ger. Pats. 189,245, 193,916, and 196,938). Since 1908 the simple apparatus of the engineer Allegri has also been employed in certain Italian works. It acts like a

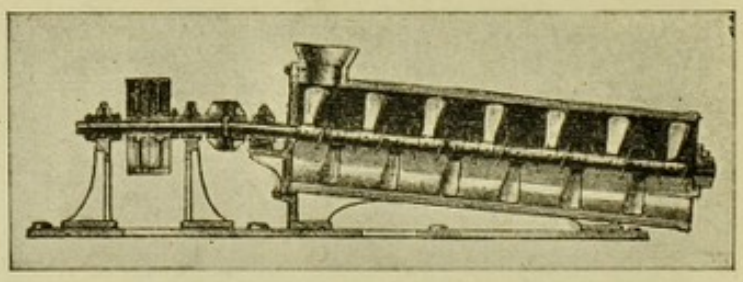


Fig. 217.

plough which gradually removes a small layer from the chamber on to a continuous band which carries it to the storehouse. One of these machines using 4 h.p. discharges 20 tons or more of superphosphate per hour, and apart from the rapidity with which it works it

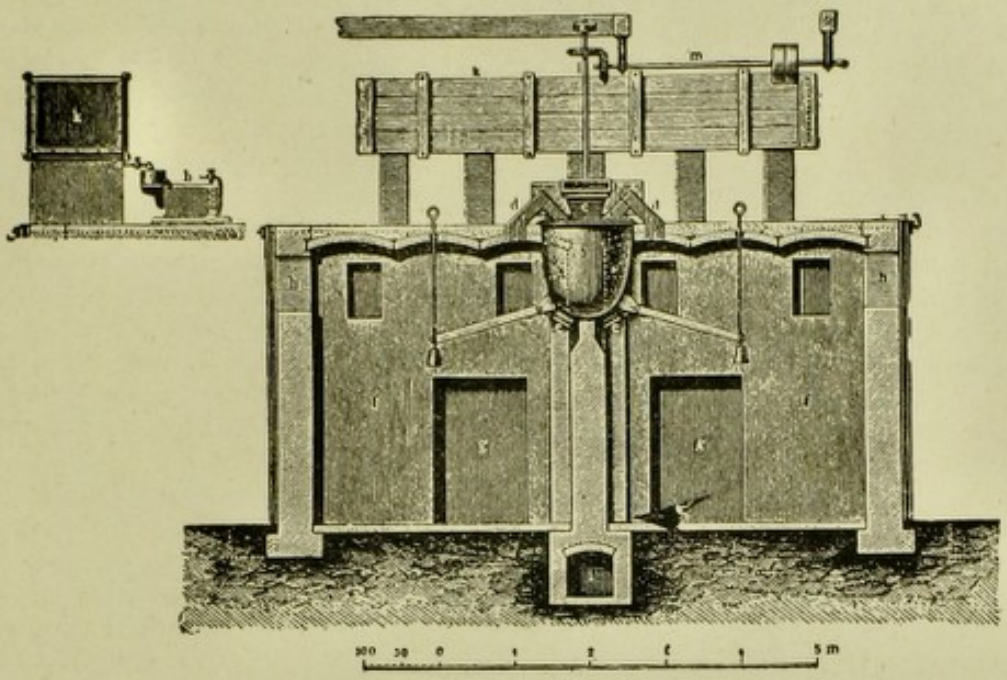


FIG. 218.

effects a considerable saving in labour. We illustrate Milch's apparatus, which is somewhat widely used in Europe, in Fig. 219. The maturing chamber which collects the superphosphate paste consists of a very large horizontal cast-iron cylinder, *i*, which may contain up to 30 tons of superphosphate and runs on wheels. The upper longitudinal portion

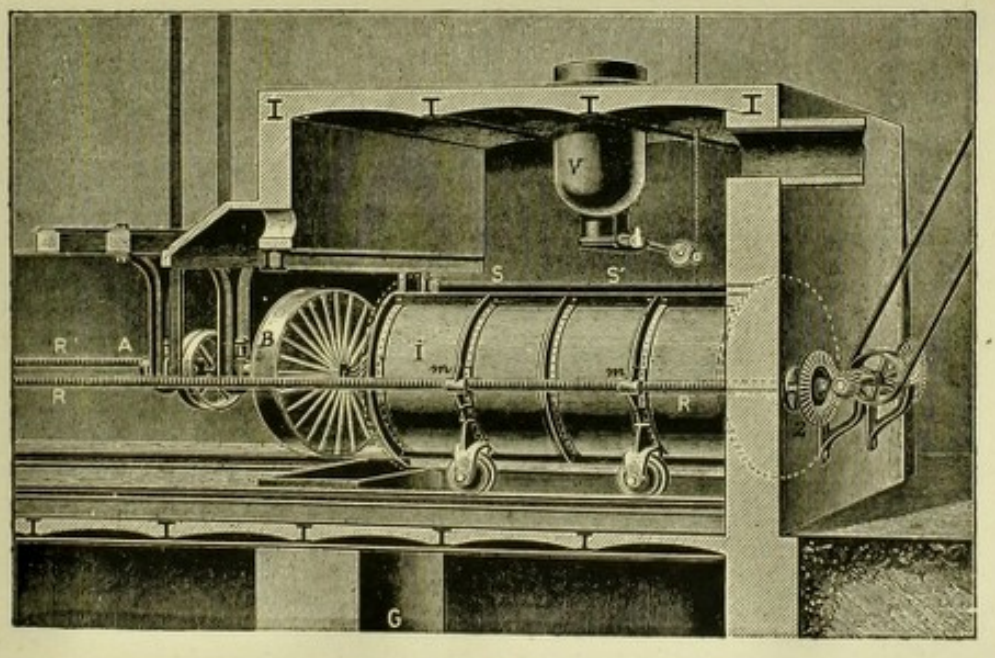


FIG. 219.

of the cylinder, *S* and *S'*, and the diametrically opposite portion, consist of long slits which are closed by plates during filling ; a single plate at the top is opened whilst the superphosphate paste is passed in from the mixer, *V*. When the whole mass contained in the cylinder has hardened (after three to four hours) it is removed from the inside of the chamber by causing two long horizontal screws, *R*, which carry sleeves, *m*, attached to the large cylinder, to revolve by means of the spur-wheel, *Z*. Then the plate which closes

the mouth of the cylinder at the end, *i*, is opened and the surface of the hardened superphosphate is gradually pressed against the wheel, *B*, which carries metallic blades which rapidly revolve over its surface; it is thus cut away and falls into a channel below, the plates which close the horizontal bottom of the cylinder being gradually removed. When the cylinder has been completely removed from the chamber and emptied in the manner described all the movements are arrested automatically.

The gases from the maturing pits must be washed before they are allowed to escape into the atmosphere, as otherwise they would injure vegetation. For this purpose towers 8 to 10 metres high are used, down which a spray of water passes which runs in a thin layer over cement plates and inclined planes arranged in such a manner that the gas pursues a zig-zag path in an opposite direction to the water. The gases may also be washed with an atomised water-spray obtained with a Körting apparatus in a series of special chambers which force the gases to pursue a lengthened path, and finally to escape free from harmful substances. All this plant, consisting of towers or chambers, is constructed in pitch pine, which is the most resistant wood, and the joints of the planks are made good with molten sulphur, pitch or bitumen, otherwise openings would easily form because fluosilicate solutions contract wood instead of causing it to swell.

The water in which the gas has been washed mainly contains fluosilicic acid, H_2SiF_6 (up to 12° Bé.). It is either mixed with lime and discharged into watercourses, or it is mixed with a 10 per cent. solution of sodium chloride, and the sodium fluosilicate, Na_2SiF_6, allowed to deposit, separated in a filter press and then dried, when it contains up to 98 per cent. of fluosilicate. This may be utilised in enamel factories, for the manufacture of opaque glass, or of certain special tiles, and is sold at as much as £16 per ton. The superphosphate is hot when removed from the chamber and contains from 15 to 20 per cent. of moisture. It is in the form of lumps, and is powdered in a crusher formed of parallel vertical revolving discs carrying numerous pins arranged in concentric circles (Fig. 220, Th. Carr's disintegrator). These discs revolve in opposite directions.

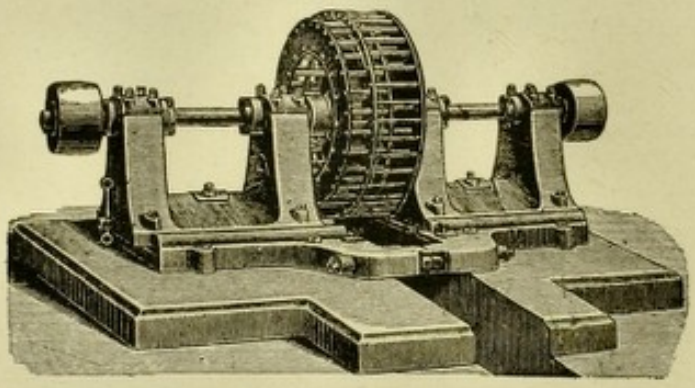


Fig. 220.

Drying by heat, which is carried out in case the product is too damp through an error in manufacture, is a delicate operation, because when the hydroscopic water is evaporated the gypsum loses part of its water of crystallisation at 120° and may then cause reversion. The transformation of monocalcium phosphate into acid calcium pyrophosphate and then into calcium metaphosphate at 200° is most serious, without considering other causes of reversion: $4CaH_4(PO_4)_2 = 3CaH_2P_2O_7 + Ca(PO_3)_2 + 5H_2O$.

Whilst superphosphates containing meta- and pyrophosphates show a smaller proportion of soluble phosphoric anhydride on analysis, these substances are slowly decomposed in the soil by the action of water and CO_2, and transformed into orthophosphates which are assimilable by the plants (Maercker). Therefore the firm of Emilio Giana of Vercelli has expressly manufactured calcium pyrophosphate on an industrial scale since 1908 by direct treatment of phosphorite with sulphur dioxide in presence of air:

$$Ca_3(PO_4)_2 + SO_2 + O = CaSO_4 + Ca_2P_2O_7.$$

This product is a white powder of 96 per cent. fineness with Kahl's sieve, which does not corrode the sacks and is very suitable for acid, humous, or siliceous soils. It contains 26·5 per cent. of total P_2O_5 and only 3 per cent. soluble in dilute citric acid, whilst 12 per cent. dissolves on prolonged contact with water and CO_2 (as in the soil). It becomes almost entirely soluble with one-third its weight of sulphuric acid, which is the amount necessary to convert it into superphosphate.

Of the various types of drying plants the best results are obtained with a long brickwork

chamber (Fig. 221), in which Körting conveniently regulates the distribution of heat by flanged pipes. Small trucks are introduced into the chamber, which are provided with finely perforated iron sheeting on which the superphosphate is distributed in thin layers. The trucks nearest to the source of heat are the first to dry, and whilst the trucks issue on one side with the dry product others with the moister product enter at the other, in such a manner that work is continuous and there is a rational utilisation of heat. The gases which escape during drying should be led to the absorption towers.

Superphosphate ready for sale is kept in storehouses protected from the rain, and is only placed in sacks at the moment of despatch, because these sacks are attacked in time by the acid in the superphosphate.

Various mixtures of superphosphate with other fertilising salts are also prepared and also *double superphosphates* (of almost double the concentration of the ordinary product).

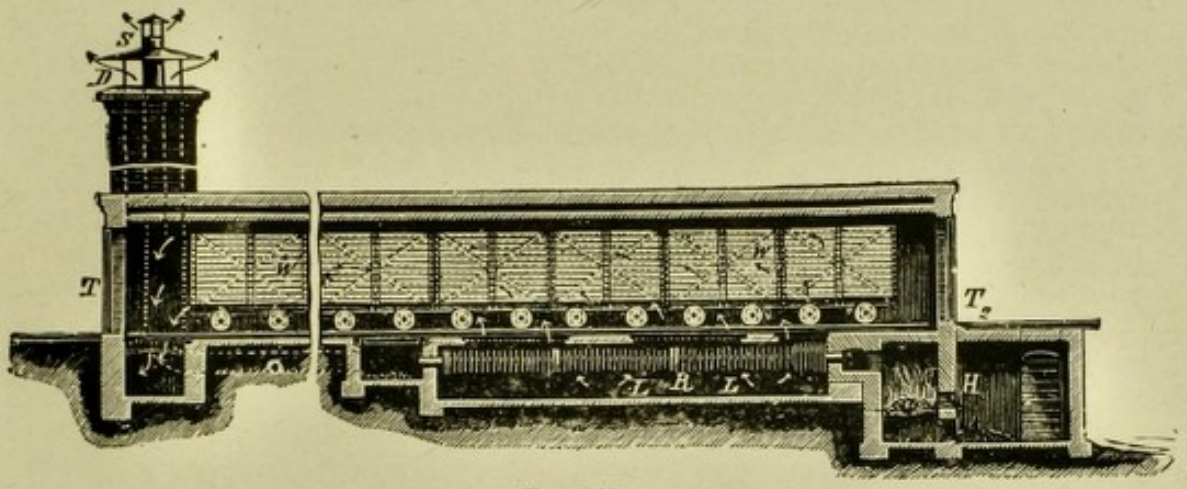


FIG. 221.

STATISTICS AND PRICES. Production of *crude phosphate* (*phosphorite*). In 1906 the American product cost from 4*s*. 10*d*. to 7*s*. 2½*d*. per ton, according to strength, at Hamburg ; the African product cost from 4*s*. to 6*s*. 3½*d*. per ton.

	1893	1898	1906	1908
	Tons	Tons	Tons	Tons
Florida . . .	400,000	650,000	1,250,000	1,692,100
Tennessee . .	40,000 (1896)	500,000	550,000	455,500
South Carolina .	500,000	400,000	300,000	225,500
Algeria and Tunisia	6,000	400,000	1,050,000	1,265,200 (1908) 1,580,000 (1909)
France (Somme) .	400,000	350,000	400,000	200,000 (1909)
Belgium . .	400,000	200,000	155,000	200,000

In 1886 the *world's production of phosphorite* was 200,000 tons, 2,000,000 tons in 1898, 3,000,000 tons in 1904, 4,000,000 tons in 1906, and 5,220,000 tons in 1908.

Of the phosphorite imported into Italy, two-thirds originally came from Africa and one-third from America, but to-day three-fourths comes from Africa (Gafsa, Kalae Djerda, and Constantine), containing 57 to 70 per cent. of tricalcium phosphate, and one-fourth from America. The African phosphorite contains more calcium carbonate and less fluoride than the American.

The Gafsa company for the production of African phosphorite has a capital of £720,000, and is located at Tunis. It commenced by producing 65,000 tons in 1899 ; in 1901 it produced 178,000 tons, in 1905 524,000 tons, in 1907 746,000 tons, and in 1909 908,000

tons. The railway which leads to the coast at Susa is now finished, and when the further railway between Tunis and Kalae Djerda is completed, this source of phosphates will acquire even greater importance. Tunisia will be able to supply an abundance of phosphates for a further century.

In 1908, *France* imported 767,630 tons of phosphorite, and in 1909 645,192 tons, apart from the 200,000 tons produced in the country. The phosphates from the Somme valley contain 70 to 75 per cent. of tricalcium phosphate, 3 per cent. of iron and alumina, and cost 6·4*d*. per unit of phosphate per ton in the ground condition, and loaded into trucks, early in 1910. American phosphate containing less than 5 per cent. of moisture costs £1 4*s*. to £1 8*s*. per ton of 70 to 80 per cent. strength f.o.b. at the port of departure. In France three-fourths of the production of superphosphate is provided by the numerous works of the "Société de produits chimiques de St. Gobain."

In the *United States of America* in 1900 there were 422 chemical manure works with a capital of £12,000,000. In 1905 there were only 400 such works, but their total capital was £13,800,000, and they employed 14,200 workpeople and 1618 other employees. Apart from the manures containing potassium, sodium, &c., they treated 1,300,000 tons of phosphorite. The production of phosphorite is very large as it is largely exported. In 1905 Florida produced 1,200,000 tons, of which 580,000 tons were of *hard rock* quality, containing 76 to 80 per cent. of calcium phosphate, and 530,000 tons of *land pebble* quality, containing 68 to 73 per cent.; South Carolina produced 235,000 tons of *land rock*, and Tennessee produced 440,000 tons of *brown rock* of 78 to 80 per cent. strength, and 45,000 tons of *blue rock*. In 1909 a Franco-American society in Tennessee commenced to exploit a deposit containing 25,000,000 tons. The phosphorite of Florida is always very rich in fluorides.

The amount of phosphorite utilisable in the future in the United States has been estimated as follows: 3,000,000 tons in South Carolina, 15,000,000 tons in Florida, 43,000,000 tons in Tennessee, and 100,000,000 tons in Idaho, Utah, and Wyoming.

The production of superphosphate in the various countries was as follows:

	1900	1904	1908	Imports	Exports	Imports of phosphorite
	Tons	Tons	Tons	Tons	Tons	Tons
United States of America	1,600,000	3,800,000	—	—	—	—
France	1,150,000	1,250,000	1,608,000	—	—	720,000 (1908) 645,000 (1909)
England	750,000	800,000	1,200,000	—	—	530,200 (1908) 451,800 (1909)
Germany	650,000	1,000,000	1,500,000	80,500 (1909)	169,000	—
Italy	350,000	450,000	800,000	—	2,832	567,400 (1908) 509,400 (1909)
Belgium	330,000	400,000	—	—	—	—
Austria-Hungary	300,000	400,000	1,100,000	—	—	—
Russia	—	—	800,000	800,000	—	—
Japan	120,000	—	—	25,000 (1905)	—	100,000 (1905)
Spain	—	—	150,000	120,000 (1907)	—	75,000 (1907)

The world's production of superphosphate in 1904 exceeded 6,000,000 tons, and was 7,500,000 tons in 1906 and about 9,500,000 tons in 1908.

An idea of the rapid development of the superphosphate industry may be gathered from the following Table which refers to the superphosphate production of Italy and Germany:

Germany		Italy	
In 1867	1,000 tons	In 1893	72,000 tons
1872	7,600 ,,	1895	145,686 ,,
1883	400,000 ,,	1899	277,315 ,,
1900	650,000 ,,	1903	400,000 ,,
For 1904 to 1909 *see* last page		For 1904 to 1909 *see* last page	

In 1907 Italy produced 50,000 tons of bone superphosphate.

The price of mineral superphosphate in Italy was about 3·84*d.* per kilo of phosphoric anhydride soluble in water and in ammonium citrate per 100 kilos of superphosphate. In 1904 the syndicate of producers was dissolved and the price fell to 2·88*d.* In 1906 the price rose again to 3·84*d.* through increased cost of raw materials. In 1907 it rose to 4·224*d.*–4·32*d.* and in May and June 1908 reached 4·32*d.*–4·512*d.* per unit for bone superphosphate and 4·224*d.* for basic slag. Then a drop in prices occurred, caused by the world's financial crisis, a considerable drop in the price of raw materials and over-production. In 1909 it was even sold at 2·88*d.*–3·072*d.*, and it was only in May and June 1910 after the syndicate of producers had been reconstituted that a minimal price of 3·264*d.* was fixed. In the Table below the oscillations of prices, production, and imports in Italy during the last few years are shown.[1]

There are to-day about 95 important superphosphate works in *Italy* which consume about 4000 h.p. and employ 4500 workpeople. 75 of these works also manufacture sulphuric acid, and in Sicily a works has been erected for the production of 30,000 tons per annum. 65 of these works are in the North of Italy, 25 in Central Italy, and the remainder in the South.

The Consumption of Basic Slag in Europe was in 1885, 5000 tons, almost entirely in Germany, of the value of £1600; in 1891, 400,000 tons; in 1899, 1,655,000 tons (of which 895,000 in Germany of the value of £2,120,000); in 1907, 2,600,000 tons, of which 1,500,000 tons in Germany.

Italy imported 70,000 tons in 1902, 67,460 tons in 1905, 81,840 tons in 1906, more than 129,000 tons in 1907, and about 93,000 tons in 1909, of which two-fifths came from Belgium, one-tenth from Germany, and one-fifth from England.

In 1908 Russia imported 1,000,000 tons of basic slag. Germany imported 197,000 tons in 1907, more than 279,000 tons in 1909 and exported 361,000 tons. Spain imported 30,000 tons.

1

Year	Price per unit of P_2O	Production in tons	Imports			Exports
			Super-phosphate (?)	Various unnamed fertilisers	Basic slag	
1903	L. 0·40	400,000	—	—	75,000	—
1904	L. 0·30 (after the dissolution of the syndicate) . . .	459,000	30,000	17,500	60,000	—
1906	L. 0·40 (through increased price for phosphorite) . . .	560,000	23,790	20,800	81,840	—
1907	L. 0·44 to 0·45	651,000	46,835	30,049	129,000	2300
1908	L. 0·45 to 0·47	800,000	46,880	23,640	120,000	2800
1909	L. 0·30 to 0·32	700,000 ?	38,300	24,000	93,000	4250
1910	L. 0·32 to 0·34 (reconstitution of the manufacturing syndicate)	—	—	—	—	—

The first syndicate was dissolved mainly on account of disloyal infringement of the mutual compact on the part of many producers. The excessive rise in price caused by the first syndicate and by various powerful industrial groups rendered it possible for many co-operative works to be started by agriculturists, especially by the Federation of Agriculturists of Piacenza, and thus the crisis was still further aggravated.

STRONTIUM : Sr, 87.6

This element is not very abundant in nature and is found in combination as carbonate in *Strontianite*, $SrCO_3$, and as sulphate in *Celestine*, $SrSO_4$. It was already studied as an element by Hope in 1792. He obtained it free by electrolysing molten strontium chloride in presence of ammonium chloride. It is also obtained by heating a saturated solution of $SrCl_2$ with sodium amalgam and then distilling the mercury from the strontium amalgam which is so formed.

It is a shining yellowish metal of sp. gr. 2·5. It decomposes water at the ordinary temperature ; it oxidises in the air and burns with a reddish flame. The heat of formation of the divalent $Sr^{\cdot\cdot}$ ion is 501 Kj.

STRONTIUM OXIDE : SrO. This compound is formed by heating the nitrate to redness or the carbonate to a white heat, or perhaps preferably, by heating a mixture of strontium carbonate and carbide : $3SrCO_3 + SrC_2 = 4SrO + 5CO$.

Strontium oxide dissolves in water with evolution of heat and formation of the hydroxide.

STRONTIUM HYDROXIDE : $Sr(OH)_2$. This is obtained directly by heating the carbonate with carbon in presence of steam which diminishes the partial pressure due to the CO_2 by carrying it away, and thus causes the carbonate to dissociate more easily : $SrCO_3 + C + H_2O = 2CO + Sr(OH)_2$. Industrially almost all strontium compounds are prepared by reducing strontium sulphate to the sulphide by heating with carbon and then transforming this sulphide into other compounds by suitable reagents. The oxide, for example, is obtained by heating the sulphide in steam or preferably by heating the sulphide solution with copper oxide : $SrS + CuO = SrO + CuS$. The aqueous solution of the hydroxide is strongly basic and crystallises with $8H_2O$ from the saturated solution. It has an important application in the extraction of the sugar of beetroot molasses, which contain 45 to 50 per cent. of sugar. This sugar cannot be recovered by crystallisation on account of the numerous impurities in the molasses. Strontium salts, however, form insoluble saccharates which separate and are then decomposed by carbon dioxide with formation of sugar and strontium carbonate, which latter can be used for the production of fresh hydroxide. This process is used in Germany, whilst the Italian sugar works used baryta before the fiscal legislation of 1903 (*see* Sugar, vol. ii, " Organic Chemistry ").

Strontium hydroxide for industrial use costs £14 per ton ; when free from iron £18 per ton, and chemically pure for the laboratory 2*s.* 5*d.* per kilo.

STRONTIUM PEROXIDE : SrO_2. The corresponding hydrate is first prepared by the action of hydrogen peroxide on a solution of $Sr(OH)_2$; at 100° this hydrate forms H_2O and SrO_2, which separates as a white powder.

STRONTIUM CHLORIDE : $SrCl_2$. This is obtained by treating the carbonate or sulphide with HCl ; it crystallises with $6H_2O$ and the white crystals are hygroscopic, readily soluble in water and also in alcohol, by which means it can be separated when present together with barium chloride. It is used for fireworks, and costs £30 per ton.

STRONTIUM NITRATE : $Sr(NO_3)_2$. This compound is obtained by treating the carbonate or sulphide with nitric acid. It forms colourless crystals, soluble in water and almost insoluble in alcohol, by which means it can be separated from calcium nitrate which is soluble. It may also crystallise with $4H_2O$. It is used for fireworks for obtaining a red light and costs £26 per ton.

STRONTIUM SULPHATE : $SrSO_4$, is found naturally as *celestine* in rhombic crystals, isomorphous with anhydrite, $CaSO_4$. It is only slightly soluble in water (1 : 7000), and the solubility is diminished by the addition of alcohol. Celestine containing 95 per cent. of sulphate costs about £3 per ton, whilst pure strontium sulphate obtained by precipitation costs ten times as much.

STRONTIUM CARBONATE : $SrCO_3$. As the mineral *strontianite* this is found crystallised in the regular system, and is isomorphous with *arragonite*, $CaCO_3$. It may be prepared from the sulphide with CO_2, or by precipitating soluble strontium salts with sodium carbonate, also by melting strontium sulphate with Na_2CO_3. At 1100° the carbonate dissociates into $SrO + CO_2$; it is almost insoluble in water.

BARIUM : Ba, 137·37

This element is fairly abundant in nature in the form of *Heavy Spar*, $BaSO_4$, and as *Witherite*, $BaCO_3$, which yields the various salts of barium with the corresponding acids, whilst heavy spar must be reduced to the sulphide by heating it with carbon before other barium salts can be obtained from it. Barium is obtained in the metallic state by the electrolysis of molten $BaCl_2$ in presence of NH_4Cl, or in the same manner as strontium from barium amalgam, but the new electrolytic process of preparation from $BaCl_2$ solution, in which mercury is used as a cathode and forms an amalgam, appears to be better. The amalgam is then distilled in a current of hydrogen, and barium hydride is thus formed which loses H when heated *in vacuo*, so that pure barium remains (Guntz, 1907). It is also obtained on heating barium oxide with magnesium :

$$BaO + Mg = MgO + Ba.$$

Barium when thus obtained is pure ; it has a metallic appearance with a yellowish reflex, a specific gravity of 3·75, melts at 850°, and decomposes water more energetically than calcium and strontium.

Soluble barium salts are poisonous. Metallic barium has no practical application and the impure product obtained from sodium amalgam costs 6*s*. per gramme, whilst the pure, electrolytic product costs 28*s*.

BARIUM OXIDE : BaO. This was once obtained by heating barium nitrate or hydroxide to redness. Frank prepared it by mixing a barium salt, $BaCO_3$, with barium carbide and heating the mixture out of contact with the air. The porous oxide which is used for the preparation of the peroxide is now obtained by melting the hydroxide together with the carbide and a hydrocarbon, for example, heavy petroleum, and then heating until all the hydrocarbon is eliminated. Egly (1905) obtains the porous oxide by heating a mixture of barium carbonate and nitrate mixed with a little hydrocarbon to redness. At Niagara Falls the oxide is industrially obtained in the electric furnace from a mixture of 4 molecules of $BaSO_4$ with 5 atoms of carbon in the form of coke ; SO_2 is evolved, and the oxide is then transformed into barium hydroxide, which is largely used.

W. Feld heats barium carbonate with carbon free from hydrogen to a high temperature. Neither free nor combined hydrogen being present, H_2O cannot be formed, therefore no $Ba(OH)_2$ is formed and the reaction is facilitated.

It forms a white amorphous mass which actively absorbs water. The crude product costs £48 per ton, when purified £96, and the chemically pure product £3 per kilo.

BARIUM HYDROXIDE : $Ba(OH)_2$. This compound is formed with evolution of heat on dissolving the oxide in water. It is also obtained from the carbonate and from the sulphide in the same manner as has been described for strontium hydroxide, or by reducing the sulphate with carbon and treating the barium sulphide so formed with CuO : copper sulphide and barium oxide are thus produced. On lixiviating, the oxide dissolves to form barium hydroxide, and the copper sulphide is then reconverted into copper oxide. It has been observed that the copper sulphide easily retains much barium hydroxide which is then transformed into carbonate or sulphate and renders the regeneration of the copper oxide difficult, so that it is necessary to decompose the copper sulphide by wet methods. The copper oxide may also be replaced by zinc oxide.

Barium hydroxide is also prepared by transforming the sulphide into carbonate by means of CO_2 and H_2O and then preparing the carbide from it by heating with carbon in the electric furnace. With water the carbide forms barium hydroxide and acetylene, which may also be utilised :

$$BaC_2 + 2H_2O = Ba(OH)_2 + C_2H_2.$$

Attempts have also been made to electrolyse a solution of barium sulphide directly.

The hydroxide is soluble in water, forming a strongly alkaline liquid, and crystallises with $8H_2O$. Barium hydroxide is used in large quantity for the extraction of sugar from molasses, as has been explained in the case of strontium hydroxide. The crude commercial crystalline product costs £15 4*s*. per ton, the anhydrous product £46 8*s*., and the chemically pure anhydrous product costs 2*s*. 5*d*. per kilo.

Since 1903 barium hydroxide has not been used in Italy for the extraction of sugar from molasses because this sugar extracted from molasses is no longer exempt from taxation as was formerly the case (*see* vol. ii, "Organic Chemistry," Sugar). In 1902 Italy produced about 3615 tons, in 1903 only 412 tons of the value of £3920, in 1904 about 70 tons of the value of £504, in 1907 about 613 tons, and in 1908 about 45 tons of the value of £4000. In 1909 it imported 530 tons of the value of £4240.

In the United States 50,500 tons of barium hydroxide were produced in 1903 and only 22,500 tons of the value of £15,000 in 1904.

BARIUM PEROXIDE : BaO_2. This is obtained from the oxide by heating to about 500° in presence of air. At higher temperatures the peroxide loses oxygen (*see* p. 180). The crude product forms a greenish mass, but when pure it is a colourless powder insoluble in water and forms hydrogen peroxide with dilute acids. On heating, it evolves oxygen, and is also used as a bleaching agent.

Barium peroxide, like other peroxides, such as hydrogen peroxide, Na_2O_2, &c., contains the group —O—O—, which is relatively unstable, and this explains the oxidising and reducing power of peroxides in general.

The anhydrous commercial peroxide of 85 to 89 per cent. costs £40 per ton, and the pure product £72. In 1905 Italy produced 60 tons, which enjoyed a protective tariff of £4 per ton, equal to that on the oxide.

Germany exported 567·6 tons in 1908 and about 780 tons in 1909, and imported 170 tons.

BARIUM CHLORIDE : $BaCl_2$. This compound crystallises with $2H_2O$, and is not hygroscopic as are $CaCl_2$ and $SrCl_2$. It loses water at 60°, and then melts at about 800°. It is prepared from the carbonate with HCl, or preferably from the sulphide, BaS, by heating it with a metallic chloride, such as $CaCl_2$ or $FeCl_3$: $BaS + CaCl_2 = CaS + BaCl_2$; thus by Kolb's method a mixture of 100 parts of barium sulphate, 36 parts of lean coal, and 68 parts of calcium chloride in very concentrated solution is heated in a furnace to 900° ; the chloride is then dissolved with hot water.

It is used for the prevention of boiler scale, for the preparation of precipitated barium sulphate and as an addition to ceramic materials in order to prevent the efflorescence of soluble sulphates contained in the prime materials. The commercial crystallised chloride costs £6 to £7 4*s*. per ton, and when purified £12 16*s*. Italy produced 490 tons in 1905, 600 tons in 1906, 800 tons in 1907, and 950 tons in 1908 of the value of £7600 ; Germany exported 5340 tons in 1909 and imported 1910 tons.

BARIUM NITRATE : $Ba(NO_3)_2$. This is obtained by dissolving witherite in nitric acid or by treating a solution of $BaCl_2$ in the heat with sodium nitrate, as the barium nitrate, which is comparatively insoluble, then separates. According to Ger. Pat. 198,861 the pure nitrate is obtained in solution by heating a mixture of finely powdered barium carbonate with a solution of calcium nitrate in an autoclave. Undissolved $CaCO_3$ finally remains. Barium nitrate forms shining octahedral crystals which are only slightly soluble in water (7 parts in 100). At a red heat it decomposes, forming BaO.

It is still much used for the manufacture of the peroxide, and is also used for fireworks in order to obtain a green flame. It costs about £20 per ton. Italy produced 90 tons in 1907 of the value of £2160, and Germany exported 613·2 tons in 1909.

BARIUM SULPHATE : $BaSO_4$. This compound is found in nature as *barytes* or *heavy spar* in rhombic prisms, isomorphous with celestine and of sp. gr. 4·6 ; when produced artificially it is employed as a pigment under the name of *permanent white*, and has to some extent replaced white lead (lead carbonate) because it is less poisonous and does not blacken with hydrogen sulphide or metallic sulphides. Natural barium sulphate is also used as a pigment after grinding it very finely, but it is not so valuable as that obtained by

precipitation. The well-powdered natural sulphate is mixed with charcoal and heated to bright redness. The mixture of barium sulphide and oxide thus formed is dissolved in water, filtered and treated with sodium sulphate. Barium sulphate is precipitated and sodium hydroxide remains in solution. The sulphur dioxide which is formed in the furnace in which the sulphate is heated with charcoal is utilised for the preparation of Na_2SO_4 by Hargreaves' process.

If barium carbonate (witherite) is used as a raw material, it suffices to dissolve it in hydrochloric acid and precipitate with sodium sulphate or dilute sulphuric acid in the cold. When mixed with zinc sulphide it forms lithopone (*see* Zinc Sulphide).

It is insoluble in water (1 part to 430,000), and also in acids, and for this reason it is used in analytical chemistry for the separation of barium from soluble salts by precipitating it in the form of sulphate.

The dry, commercial, precipitated sulphate (fixed white) costs £9 12*s*. per ton and in paste form of first quality £12. The second quality costs £6 and finely powdered natural barytes costs £4.

In 1902 Italy produced 220 tons of precipitated barium sulphate and imported 1170 tons; in 1908 the production fell to 56 tons of the value of £380 16*s*.; in 1904 the imports rose to 1875 tons of the value of £9000, in 1907 to 1540 tons, and in 1909 to 2095 tons of the value of £7400. The production of natural barytes in 1904 was 12,300 tons of the value of £10,940, and in 1908 it was 15,730 tons of the value of £13,120.

Barium Persulphate: $BaS_2O_8 + 4H_2O$, is obtained by electrolysing barium sulphate mixed with sulphuric acid.

BARIUM SULPHIDE: BaS, is obtained by heating barium sulphate mixed with coal, tar, or oil in a furnace. It is soluble in water and crystallises with $6H_2O$; it is phosphorescent in the dark. It is used for the preparation of various other barium salts (*see above*), and also replaces barium hydroxide in the treatment of beet-sugar molasses, because on treating it with 7 parts of hot water it is largely transformed into barium hydroxide which partially separates in crystals on cooling. It is also used for the precipitation of arsenic from sulphuric acid to be used in electric accumulators, and is sometimes employed for vulcanising and weighting gutta-percha. Commercial barium sulphide varies greatly in strength and should always be analytically tested. The crude sulphide costs £4 to £4 16*s*. per ton, and when purified £40.

Italy produced 14 tons in 1906, 1960 tons in 1907, and 2260 tons in 1908 of the value of £7240.

BARIUM CARBONATE: $BaCO_3$. This compound exists as *witherite* in rhombic crystals, isomorphous with arragonite and strontianite, and has a specific gravity of 4·3. The temperature of dissociation of barium carbonate in an atmosphere free from CO_2 is very high (1350°), and it is, therefore, not easy to obtain the oxide from the carbonate by heating it. In an atmosphere of CO_2 it half melts at 1350°, perhaps because a basic carbonate, $BaO.BaCO_3$, the melting-point of which would be 1454°, is formed. The thermal equation for the formation of barium carbonate is $BaO + CO_2 = BaCO_3 + 62{,}200$ cals. It may be obtained from the sulphide with CO_2 or from soluble barium salts with sodium carbonate.

According to Fr. Pat. 408,357 of 1909 and the supplementary patent of 1910, barium carbonate may be prepared by heating 100 parts of powdered sodium sulphate with 250 parts of sodium carbonate and 200 parts of water in autoclaves at 5 atmospheres pressure. It is then filtered and decanted and yields of as much as 97 per cent. are finally obtained.

It forms a white substance insoluble in water and in alcohol and soluble in HCl, with which it forms $BaCl_2$. It is used in the manufacture of terra-cotta, glass, and enamels. Powdered witherite costs about £7 4*s*. per ton and the

precipitated carbonate from £8 to £12. In 1902 Italy produced 300 tons of barium carbonate and only imported three tons. In 1908 it imported 13·7 tons and produced 650 tons of the value of £3380.

HYDRAZINE

Just as ammonia has a certain similarity to the alkali metals, so the divalent radical, N_2H_4 (Hydrazine, p. 327), has a certain similarity to the divalent alkaline earth metals, and yields a series of derivatives analogous in constitution and properties.

Thus **Hydrazine Sulphate**, $N_2H_4.H_2SO_4$, which is only slightly soluble in water, is known, and so is a chloride, $ClNH_3.NH_3Cl$, &c. Certain properties of these compounds are similar to those of the alkali metals. Hydrazine also forms compounds with hydrazoic acid, &c.

MAGNESIUM SUBGROUP

This comprises glucinum, Gl = 9·1; magnesium, Mg = 24·32; zinc, Zn = 65·37; cadmium, Cd = 112·4, and to a certain extent mercury, Hg = 200. The basicity of magnesium oxide constitutes a link with the alkaline earth metals which have just been described. The metals of this group, however, do not decompose water even on heating, and their oxides are only very slightly soluble or insoluble in water. The hydroxides and carbonates are less stable and the chlorides are partially decomposed in presence of water into oxides and HCl. [*Translator's note.*—The statement that these metals do not decompose water is only true to a certain extent.] Another important difference between this group and that of the alkaline earth metals consists in the solubility of the sulphates. Zinc and magnesium sulphate crystallise with $7H_2O$ and form mixed isomorphous crystals with other sulphates.

Glucinum and magnesium are light metals (Gl, sp. gr. 1·8, Mg 1·74), whilst zinc, cadmium, and mercury are heavy metals (Zn = 7·1, Cd = 8·6).

The sulphides of the alkali and alkaline earth metals are soluble in water, whilst those of the heavy metals are insoluble in water and in dilute acids. The sulphides of magnesium and glucinum are not precipitated from solutions of their soluble salts by H_2S.

The closest similarity in this group exists between glucinum and magnesium, and the next closest between zinc and cadmium. Mercury is in many ways allied to zinc and cadmium in mercuric compounds, where it behaves as a divalent element, whilst mercurous compounds show a behaviour approaching that of certain derivatives of copper and silver.

MAGNESIUM: Mg, 24.32

This element is not found free in nature, but abounds in various minerals, especially as carbonate in *Magnesite*, $MgCO_3$, and in the double carbonate of calcium and magnesium, *Dolomite*, $MgCa(CO_3)_2$; it is also fairly widely diffused as a silicate, *Asbestos*,[1] as *Talc*, $Mg_3Si_4O_{12}$, *Serpentine*,

[1] **Asbestos** was already known to the ancients who used it in the form of fabrics as winding sheets for corpses which were to be cremated, on account of its resistance to fire, by which means they were able to recover the pure ashes. In its chemical composition it is a magnesium silicate in which varying quantities of magnesia are replaced by lime, together with ferrous oxide and alumina as impurities. It belongs to the group of the *amphibolites*. Its composition varies with the source from which it is obtained; thus, for example, the Canadian asbestos (*chrysotile*) consists of hydrated magnesium silicate mixed with 2 to 6 per cent. of ferrous oxide, whilst that from the Cape contains less magnesia and more iron oxide. It has a more or less pronouncedly fibrous structure.

The most important deposits are found in Canada .then in Russia, the Cape of Good Hope, and a little in the United States and Italy. It is dislodged from the rock and fibrous blocks are liberated which are crushed with suitable machinery in order to separate them from dust and also to separate the long from the short fibres. Asbestos is found in Italy in the Val Malenco and Piedmont (Val d'Ossola and Val di Lanzo) and the deposits are exploited by an English firm. Italian asbestos is inferior to the Canadian product as its fibres are shorter. Italy produced 360 tons in 1908 of the value of £4000 and imported 2550 tons; in 1909 it imported 2285 tons of the value of

$Mg_3Si_2O_8H_2.xH_2O$, as *Meerschaum*, $Mg_2Si_3O_8.2H_2O$, but most abundantly in the form of magnesium salts in the Stassfurt deposits (*see* p. 424), as *Carnallite*, *Kieserite*, ($MgSO_4.H_2O$), *Kainite*, *Schönite* ($K_2SO_4.MgSO_4.6H_2O$), &c. It also abounds in sea water in the form of chloride and sulphate. The Dead Sea contains about 10 per cent. of $MgCl_2$.

Metallic magnesium was once prepared by reducing the chloride, $MgCl_2$, with metallic sodium (Davy's process, modified by Bussy in 1830); to-day, however, it is all prepared electrolytically in the Hemelingen works at Bremen and a small amount in the Elektron works at Griesheim, by the electrolysis of molten magnesium chloride as was proposed by Bunsen in 1852, or preferably from molten carnallite ($MgCl_2.KCl$) which is more easily obtained free from water.

The operation is conducted in a steel crucible which acts as a cathode, the anode being formed of carbon. During the fusion and electrolysis of the carnallite, potassium and sodium chlorides are added in such proportions that the molten mass always contains 41·6 per cent. of $MgCl_2$, 32·6 per cent. of KCl, and 25·66 per cent. of NaCl, thus forming a kind of artificial carnallite. A current of 100 amps. per square metre at an E.M.F. of 7 to 8 volts is used. The magnesium collects in numerous small spheres, which are separated by crushing the mass after cooling. These magnesium spheres are melted together in a crucible with or without the addition of fluxes (CaF_2), and are then cast into bars. According to U.S. Pat. 935,796 of 1909, magnesium is prepared electrolytically by first forming an alloy of aluminium and magnesium.

Magnesium is a metal of silvery appearance which does not alter in dry air. Its specific gravity is 1·7; it is ductile and malleable and on heating may be drawn into wires and thin ribbons. It melts between 700° and 800° and distils at a white heat. It is resistant to the action of alkalis and is easily dissolved by dilute acids with evolution of hydrogen. When heated in a gas flame it catches fire and burns with a very bright light, producing powdery, white magnesium oxide. The magnesium light is very rich in chemically active rays and is, therefore, used for photographic purposes. Fine magnesium powder when projected into a gas flame gives an extremely luminous light, and in photography magnesium flash-lights are used which consist of 1 part of potassium chlorate and 2 parts of magnesium powder, or better still of equal parts of magnesium powder and barium nitrate. It does not decompose water in the cold, but evolves hydrogen abundantly at 100°.

Magnesium reduces many oxides, liberating the corresponding metals or non-metals, such as boron, carbon, silicon, &c. The demand for magnesium is relatively small as it is only used for photographic illumination, for lanterns, and for fireworks. Some magnesium is now used for the preparation of a very interesting alloy, containing 10 to 20 per cent. of Mg with 80 to 90 per cent. aluminium, called **Magnalium** (*see* Aluminium). The world's consumption of magnesium in 1899 appears not to have exceeded 12 tons, but it is now increasing. The price in 1870 was £20 per kilo, but in 1902 it had fallen to 16*s*. per kilo in bars and 32*s*. in wire or ribbon.

The electrolytic process was started in 1884 and from that date the price fell rapidly.

MAGNESIUM OXIDE: MgO (BURNT MAGNESIA)

This compound is obtained on heating the carbonate, $MgCO_3$, to redness, and according to the temperature to which it was heated the product is more or less light. It is ordinarily

£59,400. The exports were 193 tons in 1908 and 527 tons in 1909 of the value of £8440. Canada supplies 80 per cent. of the world's production and exports about 40,000 tons per annum. The following varieties are distinguished commercially according to the varying length of the fibres: Crude, first quality; crude, second quality; fibre; paper stock, and asbestine. It has a specific gravity of 2·5 to 2·9, is resistant to the action of acids and fairly resistant to that of dilute alkalis.

It is used for insulating covers for boilers, for hangings and curtains, as cardboard for lining boiler tubes, joints, &c., by mixing to a paste with sodium silicate, and so on. Incombustible cardboard and paper are also prepared from it. When mixed with cement to a paste it forms *eternite*, which is used in large sheets for covering roofs, &c. (6 parts of cement to 1 part of asbestos).

The price varies with the length of the fibre from £2 (asbestos powder) to £280 per ton when the fibre is long,

obtained as a soft and very white powder by heating basic magnesium carbonate (magnesia alba, *see below*) in stoneware crucibles to a not very high temperature (dark red) until it no longer effervesces with HCl. In order to obtain heavy burnt magnesia, the magnesia alba is well compressed in crucibles and heated to a white heat. The highest degree of compactness is obtained by heating to redness the magnesium carbonate which is obtained by precipitating a boiling solution of magnesium sulphate with sodium carbonate, boiling for some time, washing the precipitate, and drying it. This magnesia is also very pure.

It is obtained at Neustassfurt from $MgCl_2$ as a secondary product in the preparation of chlorine (p. 146). Its heat of formation is 143,900 cals. It is almost completely insoluble in water, and melts at the temperature of the electric furnace with partial evaporation.

Magnesia is used in medicine and also as a refractory and infusible material for furnaces which are required to withstand the highest temperatures, because it is not reduced by carbon even at the highest temperatures which are known.[1] Bricks of molten magnesium oxide are to-day prepared for lining electric furnaces. They are produced in electrical furnaces and are then poured into moulds to cool.

Nernst constructed his incandescent electric lamp by utilising the property of magnesium oxide and other oxides of the rare earths (zirconia, yttria, &c., p. 404) of becoming conductors of electricity when heated. The filament or small cylinder of metallic oxide which is present in the lamp is first heated by means of an electrical resistance and allows the current to pass when it has acquired a certain temperature, so that the oxide then becomes incandescent, emitting a very intense light. The use of this Nernst lamp has gradually established itself, and a powerful company has recently been formed in America for preparing it on a very large scale. In Europe these lamps are already widely used and consume 1·2 watts per candle-power, but after 500 hours their luminosity diminishes by 20 per cent., whilst the consumption of energy rises to 1·7 watts.

Heavy calcined magnesia costs £48 per ton, whilst the light product costs about £56. In 1909 Italy imported 9 tons and exported 38·8 tons of the pure product of the value of £2700, and 38 tons of the impure of the value of £880.

MAGNESIUM PEROXIDE : MgO_2. This is obtained in an impure condition from sodium or barium peroxide with magnesium sulphate or chloride in concentrated solution.

It is used to some extent in the bleaching of woollen and silken fabrics, because the bath has a less energetic alkaline reaction, although it costs more (16*s*. per kilo). A product called "novozon," containing magnesium dioxide, has been introduced medicinally as an energetic antiseptic.

MAGNESIUM HYDROXIDE : $Mg(OH)_2$. If sodium hydroxide is added to a solution of a magnesium salt $Mg(OH)_2$ is precipitated, which is only slightly soluble in water and still less (1 : 50,000) if an excess of the precipitating agent NaOH is present. It imparts an alkaline reaction to water and is able to fix CO_2 from the air.

Aqueous solutions of ammonia and of ammonium salts completely dissolve magnesium hydroxide because the $NH_4^{\cdot}$ ions of these salts unite with a few

[1] In Italy, for the basic lining of Siemens-Martin furnaces, calcined natural magnesia specially imported from Styria is used which contains about 85 per cent. of magnesium oxide, 2 per cent. of calcium oxide, 8 per cent. of iron oxide, and 2 per cent. of silica. This product is more suitable than that from Eubœa in Greece, which contains 94 to 96 per cent. of MgO, 1·25 to 2·9 per cent. of CaO, 0·06 to 0·26 per cent. of Fe_2O_3, 0·16 to 0·42 per cent. of Al_2O_3, and 0·50 to 3·15 per cent. of SiO_2. This contains little or no iron and does not, therefore, form magnesium ferrites in the furnace which increases the stability and permanence of the lining. The *giobertite* deposits of Piedmont contain very much silica (25 to 26 per cent. of SiO_2), and give a very fusible lining, but this product is more suitable for the ceramic industry.

In 1908 Italy imported 12,000 tons of semi-fused calcined magnesite for ceramic and metallurgical purposes.

OH′ ions, which the hydroxide $Mg(OH)_2$ liberates in solution, and form soluble ammonia or $NH_3 + H_2O$; as these OH′ ions react, others are detached from the magnesium hydroxide, and thus the reaction continues until the whole of the hydroxide has dissolved (p. 100). Thus magnesium salts in general are not precipitated by the common reagents for the other heavy metals when ammonia and ammonium salts (NH_4Cl) are present. On heating, magnesium hydroxide loses water, forming MgO.

MAGNESIUM CHLORIDE: $MgCl_2$. This compound is obtained in large quantity from the mother liquors of the Stassfurt salts which contain $MgCl_2$, $MgBr_2$, and $MgSO_4$. These are evaporated in open iron pans to 42° Bé. The salts which are first precipitated are separated and the concentrated solution is then allowed to cool, when it sets to a radiating crystalline mass of $MgCl_2.6H_2O$. If the concentration is carried up to 45° Bé. molten $MgCl_2$ is obtained, but in order to obtain 80 per cent. $MgCl_2$ without decomposition and formation of HCl it is necessary to heat in a vacuum up to 175°.

Magnesium chloride volatilises at a red heat and partially decomposes in presence of minimal quantities of water, forming HCl and magnesium oxychloride, MgCl.OH. Even in hot aqueous solution it already forms HCl at 175°, and for this reason water containing much magnesium chloride, and especially sea water, should not be used in steam boilers. Magnesium chloride has a bitter taste and is very hygroscopic.

It is used for the preparation of HCl and as a dressing for cotton and woollen textiles. Much $MgCl_2$ is also used in the preparation of *lignolite*, *xylolite*, or *magnesia cement*, which is a very hard mixture formed of a paste containing sawdust, magnesium chloride, and magnesium oxide in suitable proportions. It is also called *Sorel cement* from the name of its discoverer (1867). Its composition varies between $MgCl_2.5MgO.13H_2O$ at the commencement of the reaction, and $MgCl_2.2MgO.9H_2O$ at the end of the reaction after the paste has been made up for some days. A cement of this character may be produced as follows: 100 parts of magnesia (a very soft oxide freshly heated to redness) + 300 parts or less of infusorial earth or sawdust, both of which are made to a paste with about 713 parts of a concentrated solution (32 per cent.) of magnesium chloride. These ingredients must be mixed continuously for several hours, sometimes even for more than a day, so that the mass sets almost to a jelly without separation of the components. The maximum hardness is only acquired after exposure to the air for two or three weeks. Sbertoli (Ger. Pat. 221,641 of 1906) mixes $MgCl_2$ and MgO in equimolecular proportions, dries this mixture and thus obtains a powder which is placed on the market as such, and is used in a similar manner to Portland cement.

Lignolite is used for flooring, walls, and various decorations. A magnesium chloride ammonia $MgCl_2.NH_3$, which is of great use in soldering metals, is obtained by heating a mixture of 883 grms. of anhydrous magnesium chloride, dissolved in a little water, with 655 c.c. of ammonia of 22° Bé. until the mass becomes clear. After cooling, it becomes solid and is kept in a dry place. In use it is rubbed over the metals at the points to be soldered before they are heated.

The crude fused chloride costs about £4 per ton and the refined anhydrous product £20. In 1904 Italy imported 480 tons of the value of £1540, and in 1909 1452 tons of the value of £5228. Germany exported 21,862 tons in 1905 at about £2 per ton, and in 1908 it produced 30,000 tons of the value of £28,000.

MAGNESIUM SULPHATE: $MgSO_4$. This salt commonly crystallises with $7H_2O$ in colourless rhombic prisms and then forms so-called *Epsom salts*, which lose $6H_2O$ at a temperature of 150° and the remainder at 200°. It is very soluble in water (1 : 2 in the cold and 1 : 1 on heating), and crystallises from concentrated solutions at 30° with $6H_2O$, but in another crystalline form.

It abounds at Stassfurt in the form of schönite, $MgSO_4.K_2SO_4.6H_2O$, and of kieserite, $MgSO_4.H_2O$. On concentrating solutions of these salts,

$MgSO_4.H_2O$ separates because it is less soluble than the chlorides ; it is purified by recrystallisation from water and then forms $MgSO_4.7H_2O$, which is isomorphous with various other sulphates, such as $NiSO_4.7H_2O$ and $ZnSO_4.7H_2O$; it forms mixed crystals with ferrous sulphate, $FeSO_4.7H_2O$, and cobalt sulphate, $CoSO_4.7H_2O$, forming rhombic or monoclinic crystals according to the preponderance of the one or the other (isodimorphism, p. 112). Numerous double salts, isomorphous with one another, are also known, and are obtained from all these sulphates by addition of potassium or ammonium sulphate. They have all the formula, $X_2SO_4.MeSO_4.6H_2O$, where X represents K or NH_4, and Me may be Mg, Fe, Ni, Co, Zn, Cu, &c. ; thus we have $K_2SO_4.MgSO_4.6H_2O$.

Magnesium sulphate also crystallises with quantities of water varying from 1 to 12 mols. It is used in the preparation of K_2SO_4 and $BaSO_4$, for finishing cotton fabrics, and for weighting silk and paper. It is also frequently used in medicine, and has been proposed as a fertiliser in certain cases. The pure crystallised commercial sulphate costs £2 16*s.* to £3 4*s.* per ton, and when anhydrous £10 per ton. In Italy 1100 tons of magnesium sulphate were produced in 1893, more than 1880 tons in 1905, and 2380 tons in 1908 ; the imports were 114 tons in 1905, 82·9 tons in 1906, 304·4 tons in 1908, and 348·8 tons in 1909 of the value of £1186. Germany produced 58,567 tons in 1905.

MAGNESIUM CARBONATE : $MgCO_3$. This compound is found in nature in the form of *Magnesite* or *Giobertite*, $MgCO_3$, which is found, among other places, in Piedmont and in the provinces of Como, Brescia, Bergamo, &c. ; it is widely diffused as *dolomite*, $MgCO_3.CaCO_3$. The lime is separated from the latter in the following manner : The calcined dolomite is suspended in water which is then saturated with CO_2 ; the magnesia dissolves before the lime, forming the bicarbonate, $Mg(HCO_3)_2$, which loses CO_2 and H_2O on heating, forming $MgCO_3$.

Magnesium carbonate is obtained by precipitating a soluble magnesium salt with sodium carbonate or by heating MgO with sodium dicarbonate, although the white mass which is obtained is a basic carbonate, called *magnesia alba*, $Mg(OH)_2.4MgCO_3.5H_2O$, which on heating with water in presence of CO_2 forms $MgCO_3.3H_2O$. Double salts are also known, such as $MgCO_3.K_2CO_3.4H_2O$.

Magnesium carbonate already decomposes at 300°, forming MgO and CO_2. It is, in fact, used for obtaining CO_2 in large quantities. It is used in medicine, and as a tooth-powder, metal polish, &c. It is also embodied with many pigments in paints. It costs about £24 per ton.

In 1905 Italy produced 210 tons and 220 tons in 1908 of the value of £4740 ; it imported 15 tons in 1905 and 56·4 tons in 1909 of the value of £1444 ; the exports were 74·2 tons in 1907, 63 tons in 1908, and 43·6 tons in 1909 of the value of £1012.

MANGESIUM PHOSPHATES. The primary phosphate is not known and the tertiary phosphate, $Mg_3(PO_4)_2$, is of little importance. The secondary phosphate, $MgHPO_4.7H_2O$, is more commonly obtained in a crystalline form by precipitating a soluble magnesium salt with secondary sodium phosphate, Na_2HPO_4, but in presence of ammonia and ammonium salts magnesium ammonium phosphate $Mg.NH_4.PO_4.6H_2O$ is precipitated, which is very insoluble and is therefore used in the quantitative separation of magnesium from solutions of its salts. On heating to redness it forms magnesium pyrophosphate, $Mg_2P_2O_7$. Magnesium ammonium phosphate is present in guano and urine, and often forms bladder-stones.

MAGNESIUM SILICATES. Numerous silicates of magnesium are found as minerals which have already been mentioned, and a gelatinous silicate, $3MgSiO_3.5H_2O$, is produced artificially by precipitating a soluble magnesium salt with sodium silicate, and is serviceable

for decolorising vegetable and mineral oils. The so-called fullers' earth is also imported into Europe for this purpose.

The production of *talc*, $Mg_3H_2Si_4O_{12}$, in the United States was 96,600 tons in 1905 and 107,000 tons in 1908, of the value of £280,000. In Italy the production of ground talc in 1905 was 6490 tons and in 1908 10,930 tons of the value of £13,312. There are various varieties of talc. It is a soft mineral of hardness 1 on the Mohr scale.

MAGNESIUM NITRATE : $Mg(NO_3)_2.6H_2O$. It is obtained by neutralising MgO with HNO_3, and then evaporating until crystallisation occurs. It is a hygroscopic salt, soluble in both water and alcohol, and is used for strengthening incandescent mantles at the point of suspension.

MAGNESIUM NITRIDE : Mg_3N_2. It is obtained as a yellowish porous mass on heating magnesium in an atmosphere of nitrogen or in a current of ammonia :

$$Mg_3 + 2NH_3 = Mg_3N_2 + 3H_2.$$

When poured into water it becomes heated and ammonia is evolved.

GLUCINUM : Gl, 9.1

This element is also known as **Beryllium.** It is called glucinum on account of the sweet taste of its salts. It occupies a position in the group of divalent metals analogous to that of lithium in the alkali metal group. Thus it has the least atomic weight, and like lithium, which tends in its chemical properties to depart from those of its group, approximating to magnesium, glucinum is similar to aluminium in many of its derivatives ; thus it is only slightly attacked by HNO_3 and dissolves in alkali hydroxides with evolution of H.

Glucinum is very rare and is found in *emerald* and in *beryl*, which is a double silicate, $Al_3Gl_3(SiO_3)_6$, and also in *chrysoberyl*, which is a glucinum aluminate, $GlAl_2O_4$. On decomposing glucinum with K_2CO_3 and then separating the silica with H_2SO_4, a solution of alum and of glucinum sulphate remains, from which alum first crystallises and the iron and aluminium which are present as impurities are separated with ammonium carbonate. The mother liquors which contain the glucinum salt are acidified with HCl, and glucinum hydroxide then precipitated with NH_3. The hydroxide may then be used for the preparation of all the other salts.

Metallic glucinum is obtained by melting the double fluoride, $GlF_2.2KF$, with metallic sodium. It is a white, ductile metal of sp. gr. 1·64, soluble in acids and in dilute alkalis but not in dilute HNO_3. It does not alter in the air and does not decompose water even at 1000°.

Crystallised glucinum is one of the most expensive rare metals and costs £2 per gramme.

GLUCINUM OXIDE : GlO, is obtained by heating the hydroxide. When the oxide has been strongly heated to redness it dissolves in acids with difficulty (similarly to Al_2O_3).

GLUCINUM HYDROXIDE : $Gl(OH)_2$. This compound is obtained in a gelatinous form by precipitating a soluble glucinum salt with NH_3, in a similar manner to Al, and dissolves in ammonium carbonate or in sodium hydroxide solution. It separates from these solutions on prolonged boiling.

GLUCINUM CHLORIDE : $GlCl_2.4H_2O$. This compound is obtained on heating GlO with carbon in a current of chlorine, similarly to $AlCl_3$. It sublimes easily, and the atomic weight of glucinum may be deduced from its vapour density.

GLUCINUM CARBONATE : $GlCO_3$. This is soluble in H_2O and readily evolves carbon dioxide.

GLUCINUM SULPHATE : $GlSO_4$. This compound crystallises from water with 4 or $7H_2O$, according to the temperature. It still retains $2H_2O$ at 105° and becomes anhydrous at 260°.

Glucinum salts cost £4 to £6 per kilo.

ZINC : Zn, 65.37

Zinc is found abundantly in nature as *Blende*, ZnS, and as *Calamine*[1] or *Smithsonite*, $ZnCO_3$, minerals which are often found together with lead ores, and are smelted in Belgium, Silesia, England, Poland, North America, and Sardinia. The deposits of Lombardy, Piedmont, and Belluno are less important.

The manufacture of zinc was started at Bristol in 1743, and then extended in the year 1807 to Liége, and later acquired great importance in Silesia.

The object of the primary treatment of the ores is to obtain zinc oxide, because metallic zinc is then easily obtained from the latter. The operation is simple in cases when zinc carbonate is being treated because it is then sufficient to simply heat in reverberatory furnaces in order to separate the CO_2. The treatment of blende, on the other hand, presents many difficulties, so that it was only about thirty years ago, after repeated attempts, that a profitable smelting process was successfully carried out by employing suitable furnaces which allow of the utilisation of all the sulphur dioxide which is evolved and its conversion into sulphuric acid.

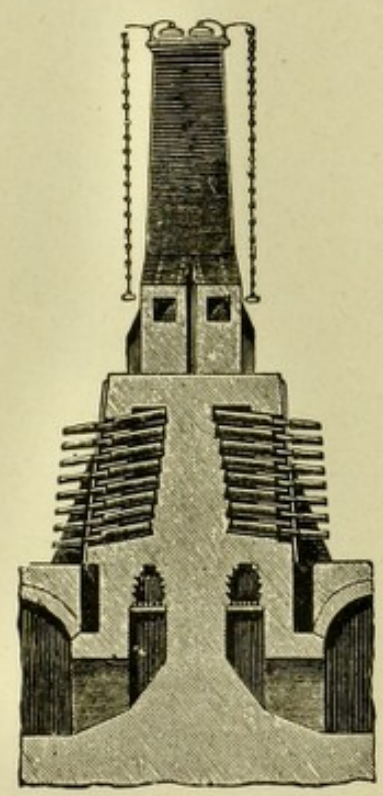


Fig. 222.

In order to obtain zinc from the residues, which contain oxide mixed with other impurities, there are two separate processes, the Belgian and Silesian processes. In the former the powdered mass is mixed with coal (2 : 1), and distilled in numerous retorts of cylindrical form, 1 metre long and of 24 cm. diameter, arranged in double series (up to 150 retorts) in a furnace heated by producer gas (Fig. 222). CO is first evolved, and when zinc vapours commence to be formed the CO flame becomes luminous and the zinc then condenses in several long conical receivers (alembics) which are connected with all the retorts. Zinc dust mixed with oxide (5 per cent.) is first deposited, and is redistilled during later operations or used as such in certain industries as a strong reducing agent. The molten metal which collects in the lower part of the receivers is withdrawn every two hours into large iron ladles, and is then poured into suitable moulds. Hegeler has recently improved the Siemens furnaces used in Belgium very considerably, thus producing more regular and homogeneous heating of all the retorts.

By the Silesian system poor ores can also be treated. A mixture of powdered ore and coal is placed in a large number of muffles arranged in a double row in a furnace (Fig. 223). The muffles have an elbow-shaped delivery tube at the upper part of the outer end, which passes into a common chamber where all the molten zinc and zinc dust is collected.

The crude zinc thus obtained contains various impurities, especially Pb, Fe, Cd, Sb, As, Ag, Cu, and also sulphur derived from the blende. The metal is refined by melting it in iron pans, and allowing it to slowly cool in such a manner that almost all the impurities collect at the bottom and at the surface, and may then be easily separated. To-day, however, refining is more often conducted by melting in a reverberatory furnace with an inclined hearth at a moderate temperature for several days. Zinc oxide and other impurities separate at the surface, whilst Pb and Fe collect below.

The pure molten zinc is poured into moulds in order to be worked later. If an exceptionally pure product is desired, the zinc is dissolved in sulphuric acid, and the solution of the sulphate decomposed electrolytically. The zinc which separates is then distilled *in vacuo*.

[1] *Translator's note.*—There is an obvious error here in the original text.

PROPERTIES. Metallic zinc has a greyish-white appearance, and when pure and fused has a specific gravity of 6·91. At ordinary temperatures it is somewhat brittle, but becomes ductile at 100° to 150°, and can be rolled into sheets at that temperature. At 200° it again becomes brittle, and can then be powdered. It melts at 417·6° and boils at 730°. At higher temperatures it catches fire with a greenish-yellow flame and produces a light white powder of zinc oxide (philosopher's wool); it does not alter in hot air and in non-aerated water. In moist air it becomes covered with a thin layer of oxide and carbonate, which preserves it from further alteration, but when present on galvanised (zinc-coated) iron or zinc-coated wires no oxidation of the iron takes place because the zinc has a higher electric potential and prevents rusting of a metal of lower potential (pp. 419–420).

Zinc dissolves easily in dilute H_2SO_4 and in HCl with evolution of hydrogen, but when very pure it is not attacked by these acids because its surface becomes covered with a very thin layer of hydrogen which protects it. It only decomposes water at a red heat, but when in the form of an extremely fine powder this decomposition of water already occurs in the cold. With hot alkaline solutions it evolves hydrogen:

$$Zn + 2NaOH = Zn(ONa)_2 + H_2.$$

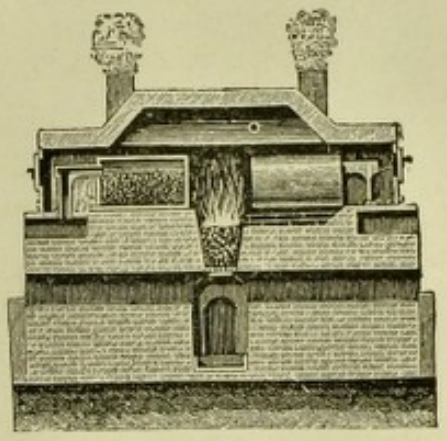


Fig. 223.

Much zinc is used for zinc-coated wires for telegraphy, for roofing, and for the manufacture of zinc-coated ("galvanised") iron. It is also used for gutters, conduits, baths, &c., because it withstands the action of water very well. It is used in the preparation of various alloys, such as brass, German silver, &c. Finely powdered zinc is also used for coating iron and steel with zinc in the preparation of lithographic plates, in which case it is spread in a thin layer over the surface mixed with reducing agents, and then heated in suitable furnaces.

The world's production of zinc in 1880 was 250,000 tons; in 1903 it was 571,000 tons and in 1909 772,000 tons. In 1909 the production in the various countries was 216,000 tons in Germany, 164,500 tons in Belgium, 236,600 tons in the United States (127,000 tons in 1901), 45,000 tons in France, 58,400 tons in England, 9000 tons in Russia, 12,000 tons in Austria, and 1070 tons in Australia; in Italy it was only about 300 tons. In the Iglesias district of Sardinia alone 150,000 tons of zinc ores are produced annually of the value of about £600,000 (in 1908) and the mining of the ore occupies 8000 to 9000 workmen, but it is almost entirely smelted in other countries. In 1905 Italy imported 6000 tons of zinc in bars (9222 tons in 1909 of the value of £192,000), and 4450 tons of zinc in sheets and foil (in 1909 4566 tons of the value of £105,800).

Germany produced 731,200 tons of zinc ore in 1905 and about 70,600 tons in 1907 of the value of £1,760,000.

The price in 1860 was £20 per ton, and in 1902 £18 8*s.* per ton. Zinc dust costs £20 per ton. The price of zinc is now regulated by an international syndicate.

ZINC OXIDE: ZnO. This is obtained by roasting the various zinc ores, or by burning zinc in the air (philosopher's wool), or also by transforming blende into $ZnSO_4$, and then precipitating with NH_3. It may also be obtained by calcining basic zinc carbonate, which forms a white powder which is erroneously called zinc white and is employed in varnishes because it has good covering power and is not blackened by H_2S in the same manner as white lead (basic lead carbonate), but three coatings of white lead on wood produce the same effect as four coatings of zinc oxide, because this latter has less covering power.

On heating, it acquires a yellowish colour, which it loses on cooling.

It costs £20 to £28 per ton (in 1895 it cost £14 16*s.*), and Italy produced 375 tons in 1893, about 1200 tons in 1905, and 860 tons in 1908 of the value of £20,640 ; it imported 1246 tons in 1905, 2025 tons in 1908, and 1570 tons in 1909 of the value of £42,800. The exports were 173 tons in 1905, 727 tons in 1907, 395 tons in 1908, and 282 tons in 1909 of the value of £7680.

In 1900 Germany exported 14,900 tons and imported 4520 tons.

ZINC PEROXIDE : ZnO_2. This compound is obtained from $BaO_2 + ZnSO_4$, and is used medicinally for curing wounds.

ZINC HYDROXIDE : $Zn(OH)_2$. This compound is separated from soluble zinc salts by sodium hydroxide or ammonia, but dissolves in an excess of the precipitating agent, because it forms $Zn(ONa)_2$, which is not stable, and dissolves in ammonium hydroxide for the same reasons as were explained in dealing with $Mg(OH)_2$ (pp. 526–527).

ZINC CHLORIDE : $ZnCl_2$. This compound is formed on dissolving zinc in HCl and evaporating the solution, or by heating zinc in a current of chlorine.

It is obtained on a large scale in concentrated solution by treating a solution of a zinc salt with ferrous chloride and passing a current of air through the liquid ; all the iron is precipitated and pure $ZnCl_2$ remains. The anhydrous compound (butter of zinc) is obtained by heating $ZnSO_4$ with NaCl or $CaCl_2$, when pure $ZnCl_2$ distils. G. Carrara (Eng. Pat. 10,522 of 1908) obtains zinc chloride by treating a mixture of zinc ore, sawdust or peat and other porous substances, such as pumice, with chlorine in a retort at a temperature of 250° to 300°. Zinc chloride is extracted from the residue with water and then freed from iron and manganese. This process was tried on a small industrial scale in a zinc mine in the Bergamasco valley, but was discontinued. This compound is very hydroscopic and very soluble in water. Hot solutions form a little HCl in the same way as those of $MgCl_2$. It is poisonous and abstracts water from organic substances to such an extent that they are carbonised. With ZnO the concentrated solution forms a mass which hardens rapidly, and this is **Zinc Oxychloride, ZnOH.Cl.**

It is employed for impregnating woodwork which is then more resistant against natural decay. It is also used as a disinfectant for preserving certain animal preparations and for preparing parchment paper, &c. Solutions of 50° Bé. cost from £6 to £10 per ton, whilst the pure, white, fused product costs double that amount. Italy produced 150 tons in 1905, 400 tons in 1906, and 500 tons in 1908 of the value of £6000.

ZINC SULPHATE : $ZnSO_4$. This is obtained on dissolving zinc in sulphuric acid, or by roasting the sulphide and then treating it with hot dilute H_2SO_4 ; any copper which may be present as an impurity is removed from this solution by the introduction of a sheet of zinc, and any iron by boiling it for a long time. It forms crystals of $ZnSO_4.7H_2O$, very soluble in water (1 : 1·38 at 10° or 1 : 1·65 at 100°), and is isomorphous with various other sulphates (*see above*). It loses $6H_2O$ at 100°, and the seventh molecule of water on heating to redness.

It is used for the preservation of wood and hides, and for rendering fabrics fireproof. It is also used as a disinfectant, as a mordant in textile printing, and in medicine.

The crude crystalline salt costs £2 8*s.* to £3 4*s.* per ton, and when refined £8 per ton.

In 1905 Germany produced 5896 tons and Italy 5 tons, apart from that which was imported.

ZINC HYDROSULPHITE. This is used in indigo dyeing and is obtained by the action of zinc dust on a sulphite.

ZINC CARBONATE : $ZnCO_3$. This is found as *spathic zinc ore*, *calamine* or *smithsonite* in rhombohedric crystals isomorphous with calcite. It is also formed, mixed with the hydroxide, by precipitating a soluble zinc salt with CO_3Na_2, or with $KHCO_3$, in order to obtain it pure, and is sometimes used instead of zinc white.

ZINC SULPHIDE : ZnS. This compound is found in nature as zinc blende, coloured brown by iron oxide and other impurities, whilst when it is obtained by precipitation of a zinc salt with ammonium sulphide, it forms a white mass, being the only metallic sulphide of this colour.[1] Zinc blende is fluorescent after having been submitted to the action of sunlight and even at the temperature of liquid air if it has been exposed to the action of radio-active emanations (Occhialini and Chella, 1907).

Various patents have been taken out of recent years for the industrial preparation of this sulphide (Ger. Pats. 149,557 and 167,498, &c.).

Molten sulphur reacts with difficulty with zinc, whilst a mixture of zinc dust and powdered sulphur reacts violently on heating.

It is insoluble in water but soluble in dilute acids, excepting acetic acid, and therefore when it is to be precipitated from its salts with H_2S, sodium acetate must be added which saturates the acid which is liberated from the zinc salt. It is phosphorescent, as are the alkaline earth sulphides. When white it costs £48 per ton.

By precipitating a hot solution of zinc sulphate with a hot solution of barium sulphide, a white precipitate is produced which is filtered, 1 per cent. of freshly precipitated magnesium hydroxide added, then dried, pulverised, mixed with 3 per cent. of ammonium chloride, heated to redness, and poured into water whilst still hot. It is then again dried and finely ground ; *lithopone* is thus obtained, which is a mixture of zinc sulphide and barium sulphate, containing 11 to 42 per cent. of ZnS ; the so-called yellow quality contains 11 to 18 per cent. of ZnS, and costs about £14 8*s*. per ton, whilst the blue quality, containing 22 to 30 per cent., costs £18 8*s*., and the green quality, containing 32 to 42 per cent., costs up to £21 12*s*. per ton. It can advantageously be used instead of white lead because it has somewhat better covering power, and is not poisonous (*see* the various patents, Ger. Pats. 166,772, 163,435, 170,478, and 166,717). In analysing lithopone it is desirable not only to determine the zinc, but also the sulphur.

Germany exported 5820 tons of lithopone in 1890, 8623 tons in 1900 and 9500 tons in 1907 of the value of £136,000, and imported 2200 tons.

CADMIUM : Cd, 112.4

This element often accompanies zinc in its ores (about 0·4 per cent., though calamine, for example, sometimes contains up to 5 per cent. in Silesia and Missouri). It is easily separated because it distils before the zinc, or by means of its sulphide which is insoluble in dilute mineral acids, whilst zinc sulphide is soluble. On roasting zinc blende a considerable portion of the cadmium remains in the residue in the form of sulphate and may be extracted with water (U.S. Pat. 799,743). Pure cadmium is obtained by treating a mixture of Zn and Cd with dilute H_2SO_4, as by this treatment all the zinc is first dissolved. Cadmium is a somewhat soft metal, white, of sp. gr. 8·6, which melts at 320° and boils at 770°. It does not alter in the air, but becomes covered with brown oxide on heating. It dissolves more easily in dilute HNO_3 than in dilute HCl or dilute H_2SO_4. It has been found that cadmium vapours at 1700° consist of monatomic molecules. It is used as an addition to various metallic alloys in order to considerably reduce their melting-points. It forms a soft amalgam with mercury which then hardens very easily, and for this reason it is used as a cement for stopping decayed teeth. The world's production of cadmium in 1880 was 3 tons, 13 tons in 1902, whilst in 1905 Germany alone produced 24·5 tons. The price to-day oscillates round 8*s*. per kilo.

CADMIUM OXIDE : CdO. This compound is formed on burning cadmium in the air or on heating the sulphate, carbonate, or nitrate. It is obtained as a brown powder of sp. gr. 6·95, or in bluish-black microscopic crystals of sp. gr. 8·1.

[1] *Translator's note.*—This remark refers to those metallic sulphides only which are encountered in the ordinary course of analysis.

CADMIUM HYDROXIDE, $Cd(OH)_2$, is obtained from cadmium salts with sodium hydroxide and dissolves in ammonia.

CADMIUM CHLORIDE: $CdCl_2 + 2H_2O$, is more stable than $ZnCl_2$ and does not, therefore, yield HCl on heating with water. It melts at 540° and sublimes.

CADMIUM BROMIDE and IODIDE are used in photography.

CADMIUM SULPHATE: $CdSO_4$. This compound is obtained from Cd and H_2SO_4 and crystallises with $7H_2O$ in a form isomorphous with the sulphates of Zn, Mg, &c. A hydrated sulphate, $5CdSO_4.8H_2O$, is also known.

CADMIUM SULPHIDE: CdS. This is obtained from soluble cadmium salts by precipitating them with H_2S or sodium sulphide, and forms a mass of bright orange-yellow colour, which is used in painting, as it is resistant to the action of light and also has very good covering power. It costs from 8*s*. to 12*s*. per kilo.

MERCURY: Hg, 200

In those compounds in which mercury behaves as a divalent element of the type HgX_2, the resemblance with zinc and cadmium derivatives is very marked, so much so that the various double salts are sometimes isomorphous, for example, $HgSO_4.K_2SO_4 + 6H_2O$. But mercury is distinguished from these metals by forming a series of compounds HgX, where the mercury acts as a monovalent element. We shall see below that various other elements exercise variable valency, as was already noted in dealing with the non-metals. When a metal forms two or more series of combinations, the chemical and physical differences

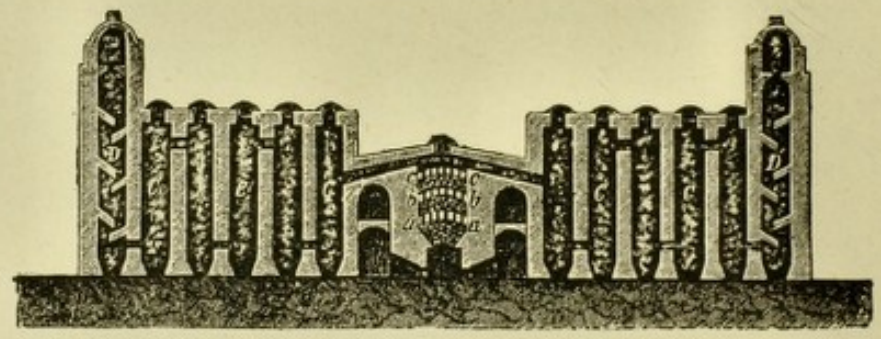


FIG. 224.

between the compounds of such classes are greater than those between two metals of the same group.

Mercury is the only metal which is liquid at the ordinary temperature, and is only rarely found free or as silver amalgam in nature. It is found, on the other hand, almost exclusively as cinnabar, HgS in Spain (at Almaden), Mexico, Austria (Idria), Peru, China, Japan, California, Russia, and Tuscany (at Monte Amiata).

Almost the whole of the mercury is obtained on distilling cinnabar in suitable furnaces in presence of an abundant supply of air. The mercury thus distils together with sulphur dioxide, and on cooling the receivers it condenses, whilst the SO_2 is then dissolved in water. The mercury is obtained practically pure by redistilling it from iron vessels.

The type of furnace which was used some years ago at Idria for the treatment of cinnabar is illustrated in Fig. 224. In the central portion there is a furnace with three perforated hearths, *a*, *b*, and *c*, on to which the ore is charged according to its size, and it is then roasted by the hot gases which are formed in the hearth below. The mercury vapours, mixed with SO_2, condense in a series of lateral chambers, *C*, and the liquid mercury runs on to an inclined floor and collects in a single channel outside.

The uncondensed gases (SO_2) are absorbed in the last chamber, *D*, down which a current of water passes along inclined planes, and the aqueous solution of SO_2 which is so obtained is utilised. This process is, however, not continuous and does not give a good yield. In 1890,

therefore, the above furnaces were replaced by reverberatory and cupola furnaces, which permit of continuous working with yields of more than 90 per cent.

Since 1890 Cermak-Spirek furnaces have been largely used in all localities where mercury is smelted. The engineer Spirek gave an interesting account of these furnaces at the International Chemical Congress at Rome in 1906. The ore falls automatically from above down channels formed of inclined planes down which the ore passes, being thus stirred up, and then along other inclined planes below, which become hotter towards the bottom. The gases rise in a direction contrary to the descending stream of ore and carry off the mercury vapours together with the other gases (H_2O, CO, CO_2, air, H_2SO_4, SO_2, &c.).

The whole of the hot gases pass to the condensers where the vapours of H_2O, SO_2, and NH_4Cl are first cooled in inverted stoneware U-tubes down the outside of which water passes, each of which dips into a wooden vat. The mercury is here separated, together with solid impurities, and collects partly in the vats and partly on the walls of the tubes, forming "soots" which contain some mercury, and are treated separately. The remaining gases,

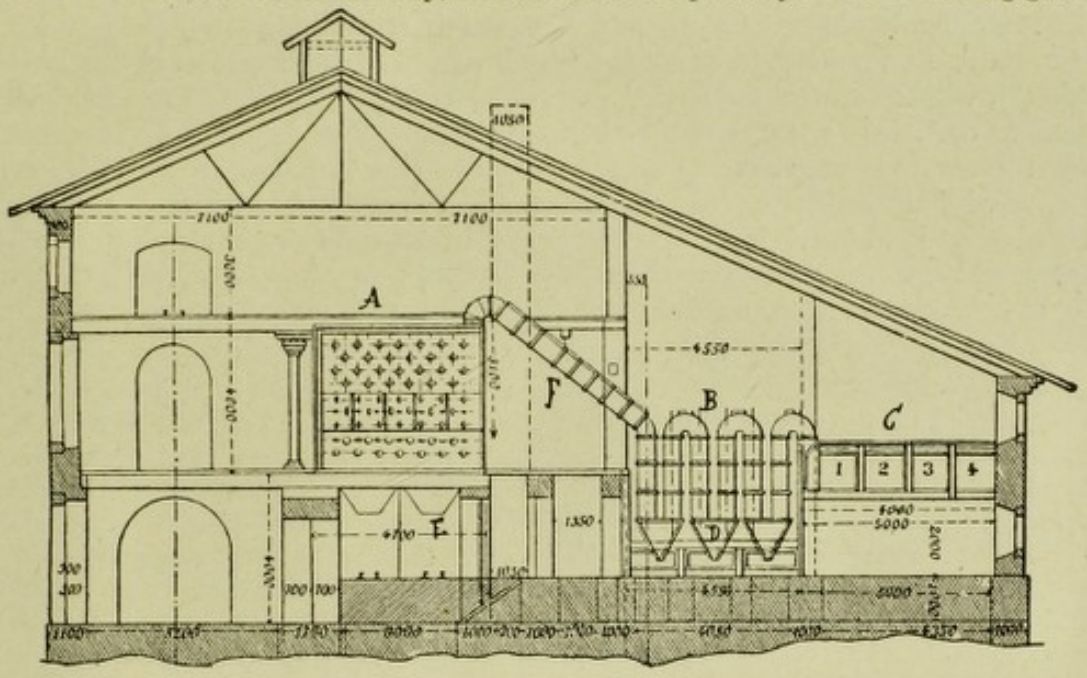


Fig. 225.

which still contain mercury, pass through conduits where they are filtered by traversing a long path through wooden lathes arranged like Venetian blinds. In this way further "soots" are formed and all the mercury is deposited. The whole apparatus is maintained at a slightly diminished pressure by means of a fan in order to avoid leakage towards the outside. With the Cermak-Spirek plant poor ores containing less than 0·1 per cent. of Hg may be treated, and the mean loss does not exceed 5 per cent. of the mercury.[1]

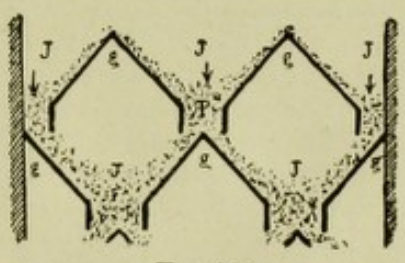


Fig. 226.

In Fig. 225 the complete plant used at Monte Amiata is shown including the furnace, *A*, condensers, *B*, and the filters, *C*. Fig. 226 is a transverse section of the furnace with inclined walls, forming channels down which the ore moves, thus descending from the top to the bottom.

Since a couple of years ago a new furnace has been introduced in some districts called the Dennis furnace, which appears to present certain advantages over the one just described, but it has been working for too short a time to enable any certain judgment to be formed as to its merits.

In some places mercury is obtained by heating a mixture of cinnabar and iron or lime, which retain the sulphur, whilst the mercury distils:

$$4HgS + 4CaO = 4Hg + 3CaS + CaSO_4.$$

Attempts have lately been made to extract the mercury from cinnabar by an electrolytic

[1] This plant was tried in 1907 in a works at Rescaldino, for desulphurising and oxidising cupriferous burnt pyrites which was to undergo electrolytic extraction of the copper, but apparently without practical success.

process by suspending it in a solution of NaCl or KCl. An E.M.F. of 1 volt suffices to cause a separation of mercury at the cathode. This method presents the great advantage of eliminating all danger of poisoning by mercury vapours which is such a cause of anxiety when working by dry methods.

Mercury is purified by redistilling it and then squeezing it through sacks or closely woven cotton fabrics. In order to separate dissolved traces of other metals, the mercury is then poured in a thin stream down tall cylinders containing cold, dilute nitric acid of sp. gr. 1·1, which dissolves the other metals more easily than the mercury ; it is then washed with water and dried.

PROPERTIES. Mercury is a liquid of silvery appearance. It does not alter in the air, has a specific gravity of 13·596 at 0°, solidifies in octahedra at 34·5 and boils at 357·5°. When near its boiling-point it becomes covered with a red layer of HgO, which decomposes at 500° into Hg + O.

Mercury vapours were the first in which monatomic molecules were discovered. In the cold it is only slightly attacked, or not at all, by HCl and H_2SO_4, whilst on heating with H_2SO_4, SO_2 + $HgSO_4$ and H_2O are formed. It readily combines with the halogens and with sulphur. It dissolves almost all the metals excepting iron, forming amalgams. Tin amalgam is used for mirrors. On studying amalgams by means of their freezing-points and also microscopically, it is found that chemical combinations between the components of the amalgams are often formed, such as $HgNa_2$; on the other hand, they often form true solutions or mixtures, and in certain cases mixed crystals are formed.

A new mercury electric lamp (Bastian) has recently found application, and gives an intense and economical but greenish light. It consists of a glass tube, 50 to 60 cm. long, containing a little mercury and two electrodes at its ends. A very high vacuum is then produced in the tube, which is placed horizontally, and an electric current is passed along a thread of mercury uniting the two poles. The mercury is thus rapidly heated and when mercury vapours have been formed these conduct the current, which no longer requires the liquid mercury in order to pass. The vapour then becomes incandescent, emitting a very intense light, and the tube should then be inclined in order to collect all the mercury at one end. The disadvantage of these lamps, which act with an E.M.F. of 50 to 60 volts or even of 100 volts, consists in the fact that the glass tubes sometimes break through the powerful heat, liberating all the mercury vapour, which is poisonous. A further disadvantage for domestic purposes consists in the fact that it has been observed that the light emitted from the most luminous portions exercises a harmful physiological action. They are, therefore, more suitable for lighting public places, as the consumption of electric current is very small. In order to avoid fracture of the tubes through temperature rises, Heraeus constructs these lamps with a quartz tube, but they are then very dear, and Schott prepares a special tube of sufficiently resistant glass, which also corrects the light, which is almost deprived of red and very green rays by the colour of the glass itself. The light of these lamps is rich in ultra-violet rays, and in order to utilise these, for example, for the sterilisation of water, quartz tubes are required which do not absorb these rays. A light which is richer in red rays can be obtained from these lamps by the addition of cadmium or bismuth to the mercury.

The largest quantities of mercury are used for the extraction of gold and silver (*see below*), but it is also used in the construction of numerous physical instruments, thermometers, barometers, pumps, &c. It is used in the preparation of mercury fulminate, corrosive sublimate, &c.

Mercury forms two series of compounds : *mercurous* compounds in which one atom of mercury is saturated by one monovalent atom and which are obtained by various reactions in presence of excess of mercury, and *mercuric* compounds in which the mercury is divalent, which are more stable.

Mercury is placed on the market in iron bottles which contain a definite weight. Spanish, American, and Italian mercury is sold in bottles containing 34·5 kilos of Hg, whilst those from Russia contain 34·7 kilos, and those from Idria 34·05 kilos. The world's production of mercury in 1904 was 4011 tons, distributed as follows : Almaden (Spain), 1020 tons ;

Idria (Austria), 536 tons ; Russia, 393 tons ; United States, 1517 tons ; Mexico, 190 tons ; Italy (at Monte Amiata), 370 tons in 1905, 434 tons in 1907, and 684 tons in 1908. In 1884 mercury cost 3*s*. 2½*d*. per kilo and 5*s*. 2½*d*. in 1902. In 1905 the imports into Italy were 57 tons and the exports 243 tons, whilst in 1907 they were 350 tons, and in 1909 714 tons of the value of £154,280. The imports into Italy have now been reduced to 10 tons. The production of mercury in Russia and America tends to diminish. Germany imported 723 tons of mercury in 1909.

MERCUROUS COMPOUNDS

MERCUROUS OXIDE : Hg_2O. This is obtained by precipitating a mercurous salt with a solution of sodium hydroxide. It has a dark brown colour and is decomposed into HgO + Hg by light and by carbon.

MERCUROUS CHLORIDE : HgCl (Calomel). This compound is prepared by heating an intimate mixture of 4 parts of powdered mercuric chloride, $HgCl_2$, with 3 parts of mercury in a covered iron pan ; the grey mass is heated until it becomes white and on then raising the temperature all the calomel sublimes on to the top of a plate which projects inside the pan. It is then poured into a vat of water and purified by washing it repeatedly with dilute nitric acid to remove remaining traces of unaltered mercury, and finally thoroughly washed several times with distilled water to eliminate the last traces of corrosive sublimate, which would be poisonous, as calomel is administered medicinally through the mouth. Calomel is also obtained by precipitating a solution of mercurous nitrate with NaCl or by passing SO_2 into a solution of corrosive sublimate, or according to the equation :

$$HgSO_4 + 2NaCl + Hg = NaSO_4 + 2HgCl.$$

It forms a white mass, insoluble in water, alcohol, and dilute acids. It slightly decomposes in the light forming Hg + $HgCl_2$, and is also decomposed by boiling water. HgCl is blackened by ammonia because **Dimercuro-ammonium Chloride, NH_2Hg_2Cl**, is formed, mixed with Hg.

At 448° it is converted into vapour, the density of which corresponds to the formula HgCl, but at this temperature it is decomposed into $HgCl_2$ + Hg which recombine in the cold, and it is therefore probable that the constitutional formula of calomel is Hg_2Cl_2.

It is used in medicine when absolutely free from $HgCl_2$, and for colouring porcelain together with gold. It costs from 5*s*. 7*d*. to 6*s*. 5*d*. per kilo.

Mercurous Bromide and **Iodide** are less stable and more soluble than the chloride and separate mercury in the light. **Mercurous Azide, HgN_3**, is also known.

MERCUROUS NITRATE : $HgNO_3$. This is prepared by the action of one part of mercury on one part of not too concentrated nitric acid in the cold. It crystallises with $2H_2O$. It dissolves unaltered in a little water to form a yellowish basic nitrate, $HgNO_3 . HgO$ with much water. It oxidises in the air, forming mercuric nitrate, but it is reduced to mercurous nitrate by excess of Hg. It is a powerful poison.

MERCUROUS SULPHATE : Hg_2SO_4. This compound is formed by the action of concentrated sulphuric acid on an excess of mercury. It is crystalline, only slightly soluble in water, and forms Hg + O_2 + SO_2 on heating.

MERCURIC COMPOUNDS

MERCURIC OXIDE : HgO (Red Precipitate). On gradually heating an equimolecular mixture of mercuric nitrate, $Hg(NO_3)_2$, and Hg in a metallic capsule or in a small muffle furnace, an oxide of a more or less bright brick-red colour is obtained in crystalline scales of sp. gr. 11·2, only slightly soluble in water and very poisonous. The red oxide is also formed on heating mercury for a long time in the air. If, on the other hand, this oxide is prepared by wet

methods, for instance, by pouring a solution of mercuric chloride into a boiling solution of sodium hydroxide, mercuric oxide of an intense yellow colour is obtained which blackens in the light through separation of mercury. The difference between the red and the yellow oxides consists only in the colour due to the different degrees of fineness of the particles.

Mercuric oxide decomposes alkali chlorides, bromides, and iodides :

$$HgO + 2NaCl + H_2O = HgCl_2 + 2NaOH.$$

Mercuric oxide when boiled with aqueous NH_3 forms a yellow solution of **Hydroxydimercuro-ammonium Hydroxide, $OH.Hg_2NH_2O$** (*Millon's base*).

It is used medicinally, for colouring porcelain, and for coating or varnishing keels of vessels in order to prevent shell-fish and marine plants from adhering to them. In this way less friction is caused during navigation and considerable quantities of fuel are economised. In contact with the sodium chloride of the sea water, mercuric oxide perhaps forms a little corrosive sublimate which is poisonous to plants and animals. It costs 4*s*. 9½*d*. to 6*s*. per kilo. Italy produced 25 tons in 1907 of the value of £6000.

MERCURIC CHLORIDE : $HgCl_2$ (Corrosive Sublimate). This compound is obtained by subliming a mixture of mercuric sulphate and NaCl in a clay vessel on a sand bath with the addition of a small quantity of MnO_2 ; the sublimate collects in white crystals forming rhombic prisms of sp. gr. 5·4, which melt at 265° : $HgSO_4 + 2NaCl = Na_2SO_4 + HgCl_2$. It is also obtained by the wet method by dissolving HgO in HCl and then evaporating the solution. It is now industrially prepared by passing gaseous chlorine, produced from liquid chlorine, over mercury heated almost to its point of evaporation, and condensing the sublimate which is so formed in the crystalline condition in the enlarged, cold portion of the glass retort in which the reaction is carried out. 20 to 25 kilos of mercury are treated in each retort in 8 to 10 hours, and the sublimate is removed by breaking the retort after each operation. It is a very powerful poison.

A solution of corrosive sublimate is easily reduced by SO_2 or by stannous chloride with separation of white, insoluble mercurous chloride which becomes grey with an excess of the reagent through the separation of Hg, thus :

$$2HgCl_2 + SnCl_2 = SnCl_4 + 2HgCl,$$

and then $2HgCl + SnCl_2 = SnCl_4 + 2Hg$.

With ammonia it forms a white precipitate of **Mercury Ammonium Chloride, $HgClNH_2$ (White Precipitate).** One part of corrosive sublimate dissolves in 15 parts of cold water or 2 parts of boiling water. It is more soluble in alcohol. The aqueous solution shows an acid reaction because it undergoes slight hydrolytic dissociation, and on adding NaCl the reaction becomes neutral because the double salt $HgCl_2.NaCl.H_2O$ is formed, which has a less energetic antiseptic action than $HgCl_2$. The action of the other halogen salts is also less energetic because they are less highly ionised.

It is used medicinally, as an antiseptic, and also for impregnating the wooden sleepers of railways. It is also used in the manufacture of aniline dyestuffs and in calico printing. It costs 5*s*. 2½*d*. per kilo. Italy exported 22·8 tons in 1904 of the value of £5472 ; 39·5 tons in 1905, 30·2 tons in 1907, 9·8 tons in 1909, and 21·7 tons in 1909 of the value of £4340. The production of sublimate and calomel in Italy was 30 tons in 1905 and 75 tons in 1908 of the value of £15,000. In 1907 Italy produced 100 tons of mercury salts altogether and exported 11·5 tons, exclusive of sublimate. It exported 20 tons in 1908 and 14·8 tons in 1909 of the value of £4120.

Mercuric Bromide, $HgBr_2$, is similar to the chloride.

MERCURIC IODIDE : HgI_2. This compound is obtained by precipitating a soluble mercuric salt with a solution of potassium iodide. A yellow crystalline substance is first

formed which suddenly becomes red and is very insoluble in water. This iodide suddenly acquires a yellow colour at 130° and melts at 223° to form a red liquid, which on cooling first becomes yellow and then red again. These changes are due to isomeric forms of the same substance. HgI_2 is soluble in a solution of KI, and on adding potassium hydroxide to this solution *Nessler's reagent* is obtained, which is used for the detection of minimal traces of ammonia, for instance, in water (p. 214), with which it forms a brown precipitate. Nessler's reagent is prepared by boiling a mixture of 35 grms. of KI with 13 grms. of $HgCl_2$ in 800 grms. of water and then adding a cold saturated solution of $HgCl_2$, drop by drop, until a permanent precipitate is just obtained. 160 grms. of solid KOH are then added and the whole is diluted with water to 1000 c.c., after which a further few drops of mercuric chloride solution are added, the whole is allowed to stand and the clear liquid decanted and kept in well-closed bottles. The **Double Iodide of Mercury and Copper, $HgI_2.CuI$,** behaves in a similar way on heating, but the colour-changes already occur at temperatures below 100°, and it has therefore been suggested as a material for colouring the extremities of the axles of railway waggons so that any overheating through excessive friction may easily be noticed.

The mercuric halogen compounds are very resistant to the action of concentrated H_2SO_4 and also to alkalis.

MERCURIC CYANIDE: $Hg(CN)_2$. This compound is formed on heating mercuric oxide with Prussian blue (*see* Iron) suspended in water. It then separates on cooling in large colourless prisms. It is more soluble in alcohol and in ether than in water. It resists the action of acids and its aqueous solutions are not precipitated either by $AgNO_3$ or by KOH, perhaps because they are only dissociated into ions to a minimal amount, and a precipitate of HgS is only obtained with H_2S or with alkali sulphides, because it is very insoluble, and a small number of dissociated ions of the cyanide separate completely with HgS until all the mercuric cyanide has been decomposed.

MERCURIC NITRATE: $Hg(NO_3)_2$. This compound is not easily prepared in a pure state because a little basic nitrate is always obtained with mercury in excess of hot nitric acid. It is very poisonous. On diluting its aqueous solution the insoluble basic nitrate, $Hg(NO_3)_2.2HgO.H_2O$, separates and produces pure HgO on boiling.

MERCURIC SULPHATE: $HgSO_4$. On heating Hg or HgO with an excess of concentrated H_2SO_4 the sulphate separates as a colourless crystalline mass which becomes yellow on heating. It is insoluble in water, in contact with which it forms a yellow basic salt $HgSO_4.2HgO$, which is insoluble. It forms double salts with the alkali sulphates, for example, $HgSO_4.K_2SO_4.6H_2O$, which are isomorphous with the corresponding double salts of magnesium, zinc, &c.

MERCURIC SULPHIDE: HgS. This is found in nature as *cinnabar*, a bright red mass of radiating crystals. It is almost always obtained artificially by the dry method by heating the crude black sulphide obtained by mixing and stirring a mixture of 54 parts of Hg and 7·5 parts of sulphur in a covered cast-iron pot. The cinnabar which sublimes forms a bright red crystalline mass which is then ground under water to avoid the production of dust, and is purified by heating it with a solution of potassium carbonate, after which it is further washed with water, dried on tiles, and finally ground with special precautions. The brightness of its red colour depends on the fineness of its particles.

It is prepared by the wet method by thoroughly mixing 5 parts of Hg and 1 part of sulphur and then heating the mixture to 45° with a concentrated solution of KOH of 45° Bé. until the black powder becomes bright red. It is then poured into water, washed, and dried.

It is obtained in the laboratory by the action of H_2S on a solution of a mercuric salt. It then forms a black mass which becomes red on sublimation. It is used in painting, but the colour degenerates in time. It is often adulterated with iron oxide, minim, gypsum, &c. It costs 6*s.* to 6*s.* 10*d.* per kilo. Germany exported 199·4 tons in 1905 at £240 per ton. Italy imported 14·7 tons of cinnabar (or vermilion) in 1907, 7·9 tons in 1908, and 7·6 tons in 1909 of the value of £2120.

COPPER, SILVER, AND GOLD

These three elements form a rather heterogeneous group, which is derived from Mendelejew's periodic system of the elements (*see* the end of this work), but forms a weak point in the brilliant conception of the Russian chemist. It is only by forced conceptions that any close analogy can be found between these elements.

Already when we consider their valencies we find that copper is usually divalent in its compounds, whilst silver is exclusively monovalent and gold is sometimes monovalent, but generally trivalent.

Their oxides and sulphides are all insoluble, as are those of the heavy metals, and it is only in some reactions that a certain analogy can be traced between the compounds of this group and those of the group of the alkali metals. The heat of formation of the derivatives of these metals, in which they show minimal valency, decreases with increase of the atomic weight.

COPPER: Cu, 63.57

This element is sometimes found in the native state crystallised in octahedra or cubes, but is usually found in combination in various minerals, coloured black, blue, or red in America, Sweden, the Ural Mountains, Japan, and China. It is found as *Chalcopyrite*, CuS.FeS, as basic carbonate in *Malachite*, $CuCO_3 + 3Cu(OH)_2$, and *Azurite*, $CuCO_3 + Cu(OH)_2$, in *Cuprite*, Cu_2O, and in *Chalcosine*, Cu_2S.[1] It is one of the metals which have been used by man since remote antiquity, but its consumption has increased extraordinarily of late years.

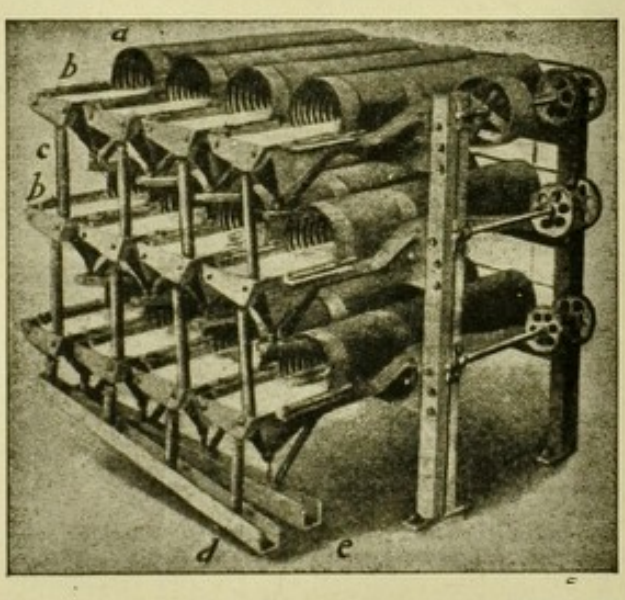


FIG. 227.

The metal may be extracted from poor copper ores by the wet process, whilst in the case of rich ores the dry process is usually applied.

The dry treatment of oxidised ores and of native copper is very simple as it is merely necessary to heat them with carbon and a siliceous flux in a reverberatory furnace. A very impure copper is, however, thus obtained. The treatment of sulphurised ores is considerably more complicated, but produces a much purer metal.

In order to concentrate poor ores these are pulverised and then introduced into horizontal revolving cylinders with an internal spiral channel (Fig. 227) (English Macquisten process) through which a strong current of water passes which does not moisten the particles of mineral sulphide so that these float and are continually discharged along the wide horizontal channels, *b*, which enter the cylinders, and through the tubes, *c*. The ore, which contains ten times as much copper as before, finally passes into the common channel, *d*. The particles of siliceous gangue, which contain no metal, are completely moistened by the current of water, collect at the bases of the cylinders on account of their weight and are carried by the spiral channels into other collecting tubes which lead to the single discharging

[1] In Italy copper ores are worked at Agordo (Belluno) (pyrites with about 1·5 per cent. of copper); in Liguria (at Rovegno, Gallinaria, and especially at Libiola), chalcopyrite is worked containing 5 to 13 per cent. of Cu and up to 49 per cent. of sulphur. In the Val d'Aosta (at San Marcello and at Ollomont) chalcopyrite is also worked. There are various mines in Tuscany, and the ore is more especially treated at Livorno, but if very rich it is sent to England. The mineral which is worked at Massa Marittima also contains tin.

channel, *e*. The cylinders make 30 revolutions per minute and may also be arranged in series so that the ore passes from one to the other and there is no danger of loss. Each tube treats from 5 to 6 tons of ore per day. The concentrated ore cannot be introduced directly into the furnace as a powder, because it would cause obstruction, and is therefore moistened, converted into compressed briquettes, and dried, or is slightly melted so that a species of agglomerate is formed in Danks' furnaces (*see* Iron).

(1) TREATMENT OF SULPHURISED ORES BY THE DRY METHOD. A considerable portion of the sulphur in these ores is utilised by roasting them in suitable furnaces such as are used for the pyrites utilised in the manufacture of sulphuric acid (p. 256).

Where the sulphur is not utilised the roasting is simply conducted in large heaps containing hundreds of tons of ore in the open air on a layer of wood which is then lighted. The roasting lasts from four to five weeks. In this way a portion of the sulphur and certain volatile products such as antimony and arsenic are eliminated. A more or less finely

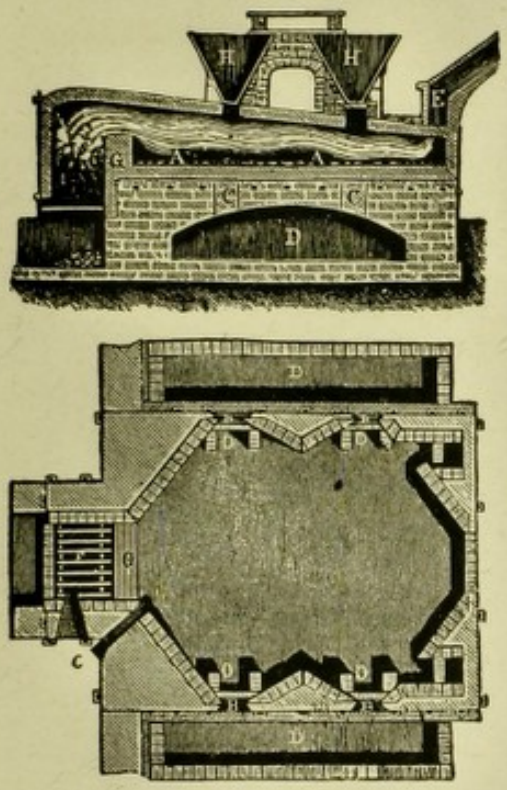


FIG. 228.

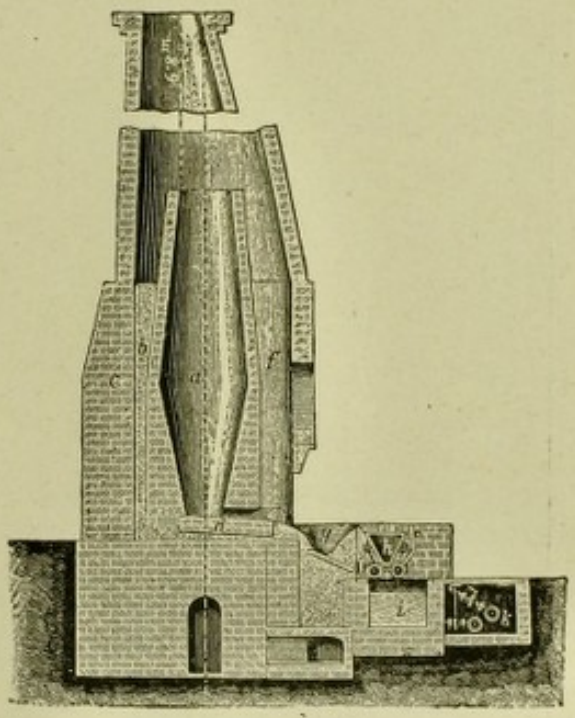


FIG. 229.

divided mass of black colour thus remains, the colour being due to the oxides of copper and iron which are formed. The roasted ore is then treated in some countries in cupola furnaces, whilst in others reverberatory furnaces are used (*see* Fig. 228, section and plan), in which it is mixed with coal (where coal is cheap as in England, or where the ores contain much antimony and arsenic). Since much time and fuel, and also a portion of the sulphur, are lost during roasting, the crude material is often treated directly in a cupola or reverberatory furnace, the SO_2 being then utilised. This utilisation is, however, not easy on account of the large quantities of other gases with which the SO_2 is diluted, and it cannot be used for the manufacture of contact sulphuric acid, because the catalyst (Fe_2O_3, p. 281) becomes covered with a quantity of dust and zinc oxide; moreover, as the gases are moist, dilute sulphuric acid is obtained. The gases are often, therefore, by preference dispersed by means of very high chimneys (there is one at Boston 154 metres high) in order not to injure the surrounding vegetation.

A type of cupola furnace as used at Mansfield is illustrated in section in Fig. 229. The roasted ore, which contains iron oxide and sulphides, and sulphates of copper and iron obtained by oxidation of the sulphides, is mixed with fluxes (silicates, quartz, or slag from preceding operations) and charged into the cupola, *a*. As the temperature gradually rises inside and outside (hot gases circulate in *f*) through the action of the air which passes into

the cupola, a portion of the sulphur is eliminated and also any residual As and Sb. Simultaneously sulphates and oxides of copper, iron, zinc, lead, &c., are formed, and a portion of the copper sulphide remains unaltered because it is less oxidisable than the sulphides of the other metals. When the temperature is sufficiently high a reducing action commences which is more energetic if coal has been added to the ore or if it contains bituminous matter. The sulphates are thus converted into sulphides and the ferric oxide into ferrous oxide which separates as a slag through the action of the molten fluxes, which also dissolve many other impurities, consisting of various metals and their oxides. On the other hand, almost all the copper which was present in the state of oxide is partially reduced to metallic copper and partially to sulphide by reacting with the iron sulphide which is present: $6CuO + 4FeS = 3Cu_2S + 4FeO + SO_2$. The molten mass containing metallic copper, copper sulphide, and copper oxide mixed with other oxides and with sulphides of iron, &c., forms the so-called *coarse metal* (matte) which contains about 35 per cent. of copper. If attempts were made to produce a purer "matte" there would be a risk of copper passing into the slag. The molten mass, mixed with lighter molten slag, runs on to an inclined hearth at the base, *d*, and is discharged by two apertures, *e*, into two crucibles, *g*; the slag, which separates at the surface, overflows into the lateral receivers, *h*. The molten matte is solidified and granulated by pouring it into the vessel, *i*, in which water continually circulates through the tubes, *k*.

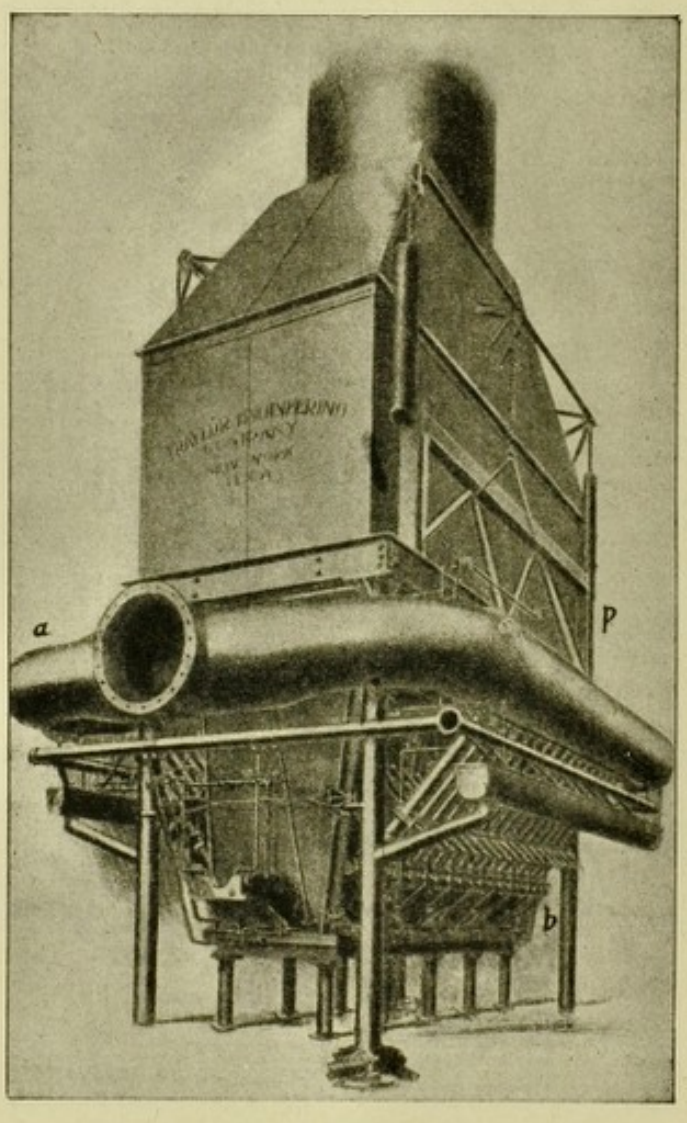


FIG. 230.

The crude matte is then concentrated and purified by submitting it once or twice to the process of roasting and melting as was done before, thus gradually eliminating the impurities by means of the slag in such a way that the greater part of the copper and the iron remains as sulphides. A concentrated matte is thus obtained which contains much Cu_2S and FeS, together with copper oxide, its total contents of copper being 60 to 70 per cent. This regulus is finally treated in reverberatory furnaces where, by the direct action of the flame and of much air, the sulphides are transformed into oxides, the mass being continually stirred with iron tools by hand or suitable mechanical devices: $Cu_2S + 3O = Cu_2O + SO_2$. Furthermore a portion of the cuprous oxide is reduced to metallic copper through the action of the iron sulphide: $3Cu_2O + FeS = 6Cu + FeO + SO_2$. The iron oxide separates in the slag together with the silica remaining in the regulus and partly with silica derived from the furnace hearth. When it is certain that oxidation is complete, powdered coal is introduced into the furnace in order to reduce the metallic oxides energetically. In this manner impure *blister copper*, containing 90 to 95 per cent. of Cu, 1 to 2·5 per cent. of Fe, and 0·5 to 2·5 per cent. of sulphur, is obtained, together with a very little regulus. The slag which separates in these furnaces contains up to 1 per cent. of copper and is used as a flux in the concentration of the grey metal.

Of late years, after the work of Holloway (1879) and of Manhés (1882–1895), the treatment of grey metal is carried out directly in Bessemer converters (*see* Iron), which contain 2 to 3 tons of the regulus. In this case, contrary to the practice in the case of iron, air is merely blown over the surface of the molten mass and rapidly transforms the copper and iron sulphides into cuprous and ferrous oxides with evolution of SO_2. Cuprous oxide forms metallic copper with a portion of the Cu_2S (*see above*), whilst ferrous oxide is transformed into slag by the silica which lines the converter. 50 tons of regulus are treated in twenty-four hours and a *black copper* is obtained containing 95 to 99 per cent. of Cu, a little sulphur, and minimal quantities of other metals. The slag is reutilised.

AMERICAN PROCESS. In cupola furnaces there are notable heat losses, large consumption of refractory materials and fuel, and not more than 20 tons of ore can be treated per twenty-four hours. By the new process of direct smelting of sulphurised or pyritic ore proposed by Holloway, the heat of combustion of the sulphur contained in the ore is partly utilised, and the process is also well adapted for poor ores. In the new type of furnace (Fig. 230) the walls of refractory material are replaced by double walls of steel, which are kept cool by a current of water, whilst the upper part of the furnace, which is of rectangular section, is built of brickwork. A large pipe, *a*, carries in the compressed air from a Root's blower at a pressure of 60 cm. of water. This is injected into the lower part of the furnace through tuyères, *b*, which may amount to 150 in number. The portion enclosed by the steel plates from *a* to *b* has a width of 0·90 metre below and 2·60 metres above and a depth of 4·30 metres. The brickwork portion below the level, *p*, up to which it is charged, has a section of 2·20 by 3 metres and is 3·30 metres high. The water which circulates between the double steel walls escapes at a temperature of 70° to 80°, and 600 to 700 cu. metres of water are used per twenty-four hours. The furnace bottom is formed of a large steel plate which can be raised in one piece for the purpose of discharging the contents. The fused regulus is discharged into suitable crucibles mounted on pivots so that they are reversible, and these are then carried on cars directly to the Holloway-Manhés converters (Fig. 231), which differ somewhat from ordinary Bessemer converters. The furnace is charged through *p* with the ore, mixed with coke and with limestone as a flux. A portion of the fuel is sometimes replaced by pyrites or copper and sulphur, and the consumption of fuel is thus only 3 to 5 per cent. of the ore, whilst in cupola furnaces it may be as much as 20 to 25 per cent. In the converter the fused matte is transformed by a single operation, and without consumption of fuel, into crude copper by means of powerful jets of slightly compressed air which pass over the surface of the fused regulus below the molten slag and carry off the sulphur dioxide, whilst the impurities, consisting of iron, &c., which sometimes form as much as 40 per cent. of the regulus, are combined and absorbed by the quartz lining of the converter, being transformed into a fused vitreous silicate which floats on the copper and may be decanted. The quartz lining is renewed after 7 or 8 operations, and 5 to 6 converters are used for each furnace, so that time is allowed for relining, cooling, &c. Fairly pure copper (up to 98 per cent.) is obtained in the converters, but it may be refined in reverberatory furnaces as described below.

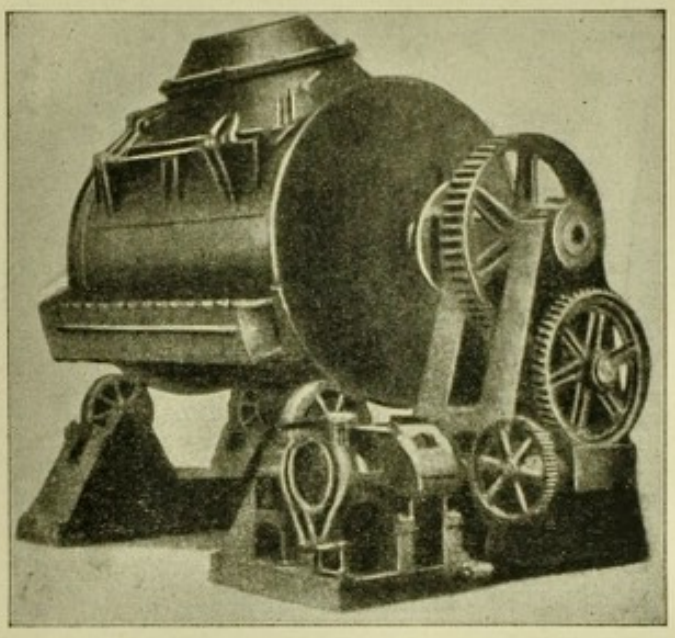


Fig. 231.

COPPER REFINING. The black copper may be refined in reverberatory furnaces or electrolytically. The reverberatory furnaces which are used have a small siliceous hearth, on to which the black copper is introduced and raised to a high temperature for 6 or 7

hours, all the apertures of the furnace being closed (*B*, Fig. 230). High temperatures are more easily reached in small than in large furnaces. When the mass has been thoroughly heated and melted large quantities of air are injected and a portion of the impurities, consisting of Zn, Pb, As, Sb, and S, is thus volatilised, another portion, consisting of Fe, Ni, and part of the Zn and Pb, being converted into slag by the silica of the furnace hearth. This slag floats on the melted copper and can easily be separated. Cuprous oxide, Cu_2O, is formed on the surface and penetrates into the molten metal, giving off oxygen to the copper sulphide which is still present, with evolution of SO_2.

Copper remains, which contains a little cuprous oxide, Cu_2O, and a little SO_2. In order to reduce and eliminate these products, large poles of green wood are introduced into the copper and evolve H_2O, H, CO, and hydrocarbons which stir up the mass. All the SO_2 is thus eliminated and a large portion of the Cu_2O is reduced to metallic copper. The last traces of Cu_2O are reduced by throwing powdered wood charcoal into the furnace ; pure malleable and ductile copper finally remains. The reduction is more effective if a highly reducing substance is added to the fused mass, instead of green wood ; such substances are copper phosphide, containing 9 per cent. of P, or manganous copper, containing 30 per cent. of Mn. Compact copper without blowholes is thus produced. Special Bessemer converters similar to those used for steel are now sometimes used.

The electrolytic refining of copper gives a very pure product. The black copper is cast in moulds 1 metre long, 0·50 metre broad, and about 2 cm. deep, and the slabs thus obtained are subjected to electrolysis, as explained below, by using them as anodes in an electrolytic bath and depositing electrolytic copper on plates of pure copper which form the cathodes.

(2) **WET TREATMENT AND UTILISATION OF CUPRIFEROUS BURNT PYRITES.** This treatment is suitable for relatively poor copper ores. Burnt pyrites containing 4 to 7 per cent. of copper is treated by the wet chlorination process, whilst if it contains more than 7 per cent of copper, dry chlorination is used, but the consumption of NaCl is then more excessive than when the wet method is employed. In this case the ordinary process of oxidation which was first described is preferred.

The cupriferous pyrites which are used for the production of SO_2 in sulphuric acid manufacture are burnt in such a manner that the copper in the ash finally remains partly as cuprous oxide and partly as cuprous sulphide, Cu_2S, whilst the iron is also present as oxide and to a small extent as FeS. The product obtained under these conditions is the most suitable for dry extraction.[1]

Burnt pyrites which only contains 1 per cent. of copper is treated by the wet method. The burnt pyrites is exposed to the air and rain in heaps for some weeks and then treated in vats with dilute (Glover) sulphuric acid with stirring. The resulting liquid is discharged into other vats into which a sufficient quantity of iron turnings, or preferably of sheet iron, is placed. On stirring, a powdery reddish paste is deposited on the bottom which contains all the metallic copper and forms the so-called *cementation copper*, which contains 60 to 70 per cent. of copper when moist, and 75 to 80 per cent. when dry.

This cementation copper is ordinarily used for the preparation of crystallised copper sulphate (*which see*) or is treated as a rich ore for the extraction of copper by the usual processes. 400,000 tons of cupriferous pyrites are annually used in England.

(*a*) **DRY CHLORINATION PROCESS.** The sulphur contained in the burnt pyrites should if possible be present in smaller quantity than the copper and not in larger quantity, because in that case more salt is required and the roasting takes more time. The powdered cupriferous residues are mixed with 10 to 15 per cent. of sodium chloride and heated for 10 to 15 hours in reverberatory or preferably in muffle furnaces, as the temperature is more easily regulated in the latter. This should not exceed 500° (less than a red heat), as otherwise the copper chloride forms volatile cuprous chloride which is lost. In certain cases it is advisable to add 6 to 7 per cent. of ferrous sulphate (for each 4 to 5 per cent. of copper), as time is thus gained in roasting and copper sulphate is more easily formed which is then transformed on heating into chloride by the action of the sodium chloride.

[1] Both Cu_2O and Cu_2S melt comparatively easily and then impede the successful combustion of the pyrites. In pyrites furnaces it is therefore inadvisable to exceed a temperature of 550° to 600° (cherry-red heat). This temperature is more easily maintained in mechanical furnaces ; thus whilst in the Maletra burners (p. 256) only about 80 per cent. of the copper remains soluble in acids, in the mechanical furnaces (p. 257), as much as 95 per cent. remains soluble. This result is obtained with more certainty if the pyrites is previously mixed with a very little sulphuric acid.

In order to determine whether the roasting is completed, a portion of the mixture is removed from the furnace with a ladle, washed with water and then with dilute hydrochloric acid, and copper is tested for in the residue by boiling it with aqua regia, and then dissolving in ammonia. According to the more or less intense blue colour of the solution, the larger or smaller quantity of copper which has not been attacked by the sodium chloride through insufficient roasting is estimated. The roasted product is systematically lixiviated with water in vats similar to those used for soda (p. 470), utilising the mother liquors from a previous treatment. The solution of copper salts, after filtration or decantation, is exposed to so-called *cementation* in wooden or cemented vats, the copper being precipitated by iron filings or preferably by iron turnings, sheet iron, or, better still, spongy iron, with continual stirring and heating to 50° to 60° with a jet of steam. Theoretically 88 parts of iron precipitate 100 parts of copper, but in practice it is necessary to employ at least 200 parts of iron. Sometimes treatment with SO_2 is resorted to in order to obtain a purer cementation copper; as thus obtained it contains from 60 to 85 per cent. of copper, the rest consisting of iron salts and other impurities.

(*b*) **WET CHLORINATION.** Burnt pyrites is treated with a solution containing 1000 parts of water, 280 parts of ferrous sulphate, and 120 parts of sodium chloride, at 80°, the whole being then stirred for three or four days. Ferrous chloride is thus formed, and this transforms the copper oxide into a mixture of soluble copper chloride and insoluble cuprous chloride:

$$3CuO + 2FeCl_2 = Fe_2O_3 + CuCl_2 + Cu_2Cl_2.$$

On adding iron filings, or preferably iron turnings or spongy iron, to this mixture, free copper (cementation copper) is precipitated and ferric chloride is formed which is converted into ferrous chloride by excess of iron:

$$2CuCl_2 + Cu_2Cl_2 + 2Fe = Fe_2Cl_6 + 4Cu.$$

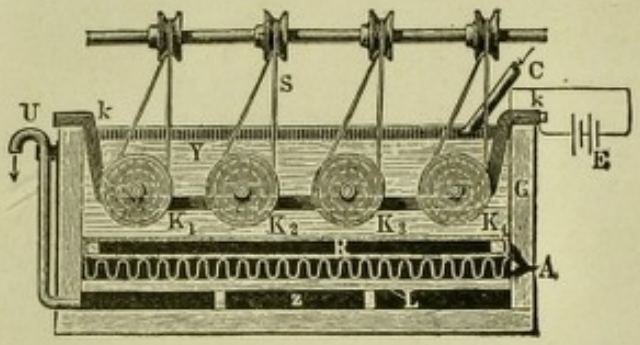


FIG. 232.

The solution of ferrous chloride is used for the treatment of fresh burnt pyrites instead of sodium chloride. The cementation copper is used for the preparation of refined copper or copper sulphate.

(3) **ELECTROLYTIC PROCESS.** At one time only rich ores or the black copper obtained on treatment of the ore (*see above*) were treated by this process. To-day, however, poor ores, especially when they contain sulphur, are also treated by the Siemens-Halske process, which uses a solution of ferric sulphate, or by the Höpfner process in which a solution of cuprous chloride is used. Siemens and Halske treat the powdered ore or cupriferous iron pyrites which has been slightly roasted, with a solution of ferric sulphate containing a little H_2SO_4, in order to increase its conductivity. The copper of the ore passes into solution forming copper sulphate and reducing the ferric sulphate to ferrous sulphate: $Cu_2S + 2Fe_2(SO_4)_3 = 2CuSO_4 + 4FeSO_4 + S$. This solution is electrolysed in a continuous apparatus, which is shown diagrammatically in Fig. 232. There is a wooden vat, *G*, containing a perforated false bottom, *L*, on which a series of carbon anodes, *A*, rest. These are covered by a layer of filtering material, *R* (felt or other material), which separates the anode compartment from the upper cathode compartment. In this latter, which is filled with the solution, a series of cylinders, K_1 to K_4, clad with sheet copper are immersed. These are united with one another and connected to the negative pole, *K*, and are rotated by the belts, *S*, in such a manner that the bath is continuously stirred. When a current is passed copper is deposited on the cathodes, *K*, whilst SO_4 ions are formed at the anodes which oxidise the ferrous sulphate formed in the cathodic compartments; this then passes to the anode through the filter, *R*: $CuSO_4 + 2FeSO_4 = Cu + Fe_2(SO_4)_2$. The solution, almost free from copper and containing regenerated ferric sulphate, escapes through the syphon tube, *U*, and is used to dissolve fresh copper in the vat in which the ore is treated; it is then again passed through the electrolytic apparatus, the process being continuous. After various modifications the Siemens-Halske process is now arranged as indicated schematically in Fig. 233. *A* is a vat containing a solution of copper sulphate and ferrous sulphate. This solution passes through the tube, *B*, into the cathodic compartment, *C* and *K*, and after

having deposited the greater portion of the copper, passes into the anodic compartment, *a*, where it is oxidised, forming ferric sulphate. The ore is crushed in *E*, and the powdered ore passes along the channel, *F*, into the vat, *H*, which is provided with a stirrer. The oxidised solution, containing little $CuSO_4$ and much $Fe_2(SO_4)_3$, also passes into this vat through the tubes, *D* and *G*. In contact with the powdered ore, a solution of $CuSO_4$ and $FeSO_4$ is formed, and the extracted ore is then deposited in *K*, whilst the liquid passes into the vat, *A*, through the tube, *M*. A current density of 16 amps. per square metre is employed at an E.M.F. of 0·7 volt. Ores containing up to 0·1 per cent. of copper can be extracted in 10 hours.

By the Höpfner process the copper is dissolved in a solution of copper chloride instead of one of ferric sulphate.

Another electrolytic process which has yielded good practical results after many improvements is that of Marchese, who uses the matte $Cu_2S + Fe_3S$ as anodes. This regulus is obtained in the initial treatment of the ore (*see above*). The bath consists of a solution of the ore in H_2SO_4 and the cathode of plates of pure copper on which the new copper, which is very pure (99·8 per cent.), is deposited, whilst sulphur is deposited at the anode.

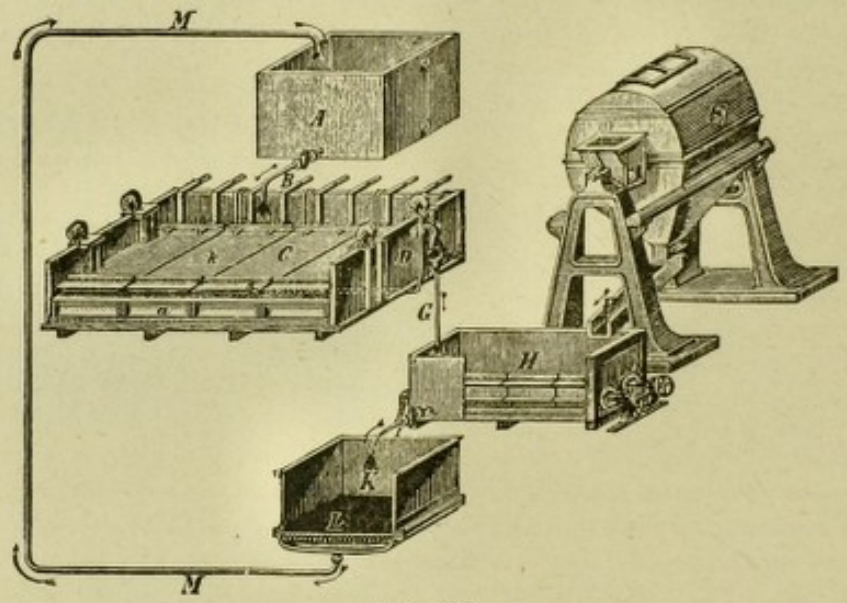


Fig. 233.

PROPERTIES. Pure metallic copper has a beautiful bright red and specially lustrous colour. It is fairly hard (*see* Table, p. 411), but also fairly ductile and flexible, and may be obtained in wires and in very thin foil, which has a green appearance by transmitted light. Its specific gravity is 8·94 ; it melts at 1080° and solidifies to an irregular mass, so that it is difficult to cast. At temperatures near its melting-point it is brittle and can be powdered. It keeps well in dry air, but in presence of moisture becomes covered with a green layer of the basic carbonate, **Verdigris**. When heated in the air it is readily transformed into the black oxide, CuO. It is not appreciably dissolved by HCl or H_2SO_4, although in presence of air, or in the form of oxide, copper is attacked more easily by these two acids. On heating with strong H_2SO_4, SO_2 is evolved and $CuSO_4$ is formed. Dilute nitric acid dissolves it even in the cold with evolution of NO. Zinc, iron, magnesium, &c., separate it from solutions of its salts in the metallic state. When heated with SO_2 under pressure solutions of $CuSO_4$ form a precipitate of pure copper. Ammonia dissolves copper in presence of air, forming an intensely blue solution of **Hydroxyammoniate of Copper**. Certain vegetable organisms are extremely sensitive to the poisonous action of copper and its salts.

APPLICATIONS. Much copper, in the very pure form in which it is obtained to-day by electrolytic processes, is used in electric installations as a good conductor of the current. It is also used in the construction of much industrial machinery, for cooking utensils, for

engraving, &c., but the greater portion of the copper which is used goes to form alloys with other metals.

ALLOYS OF COPPER. We will enumerate the principal alloys of this metal. *Brass* contains 3 parts of Cu and 1 part of Zn, and has a yellow colour. The proportion of zinc may vary somewhat, but never descends below 18 per cent. It is used for many mechanical purposes because it is harder than copper. It sometimes contains 1 to 2 per cent. of lead. *Bronze* is an alloy of copper and tin, and sometimes contains a little zinc and lead. *Bell metal* contains 75 to 80 per cent. of copper and 20 to 25 per cent. of tin ; it also sometimes contains traces of Zn and Pb. It has a greyish-yellow colour, is easily melted, has a fine granular structure, is hard, brittle, and very sonorous. It costs £100 to £112 per ton. *Gun metal* contains 89 to 91 per cent. of Cu, 9 to 11 per cent. of Sn, and sometimes 1 to 1·5 per cent. of Zn. *Phosphor-bronze* is obtained from ordinary bronze by the addition of 0·5 to 0·8 per cent. of phosphorus (in rare instances and for special purposes up to 3 per cent. of phosphorus, which is added in the form of an alloy of phosphorus and copper or phosphorus and zinc) ; phosphor-bronze is harder than ordinary bronze and is suitable for objects which are exposed to tension, for example, the wires in electric conduits, &c. The phosphorus combines with the oxygen contained in the metal. When it contains less than 0·5 per cent. of P it costs £96 to £110 per ton, but when it contains 3 per cent. it may even cost £140. *Statuary bronze* contains up to 5 per cent. of zinc and 2 per cent. of lead. It can be worked with the chisel, and is suitable for artistic objects, because when cast it readily reproduces every detail and has the property of readily becoming covered with a greenish layer which renders it similar to antique bronze. *German silver*, *pakfong*, or *pinchbeck* is an alloy of Cu, Zn, and Ni in varying proportions (for example, 60 per cent. of Cu + 24 per cent. of Zn + 16 per cent. of Ni), and according to the varieties manufactured by the firm of Krupp it is considered to be of first quality when it contains about 17 per cent. of Ni, of second quality with 12 per cent., of third quality with 8 per cent., and of fourth quality with less than 5 per cent. It has an almost silvery-white colour, and is harder and more resistant to chemical reagents than bronze. Objects made of this alloy and coated with silver are called *silver plate*. *Silico-bronze* contains small and varying quantities of silicon, which acts in a similar manner to phosphorus and renders the coefficient of expansion of the metal smaller, although it still remains a good conductor of electricity, so that it is very suitable for the production of telegraph and telephone wires. *Manganese bronze* contains up to 30 per cent. of Mn, which combines with oxygen in a similar manner to phosphorus and may replace a considerable portion of the tin. It is very hard and tenacious and is well suited for the construction of the screws of vessels. There are also bronzes containing aluminium, tungsten, &c.

STATISTICS AND PRICES. The production of copper and its price at various periods and in various countries are shown in the Table on the next page.

In 1905 Peru, Cape Colony, Norway, Bolivia, Austria, &c., also contributed to the total production. 200,000 tons are refined electrolytically in the United States.

The consumption of copper in the United States in 1903 was 190,000 tons and in Germany in 1908 188,000 tons. In 1903 it was 108,000 tons in England, 50,000 tons in France, 19,000 tons in Austria-Hungary, and 18,000 tons in Russia. Germany imported 154,700 tons of copper in 1909.

Prices are referred to the "Lake" brand of copper valued at New York, which is higher than that of Mansfeld, but the variations are all almost always due to financial speculation. In 1906–1907 the price rose to £108 per ton, but during the American crisis in 1907 it fell in a few months to £66. Of the 11,900 tons of copper and its alloys produced in Italy the objects produced with materials imported from abroad are included, whilst the copper actually produced in Italian mines was 3250 tons in 1905. Of copper and alloys of copper Italy produced 15,450 tons in 1906, 17,490 tons in 1907, and 18,280 tons in 1908 of the value of £1,520,000. In 1904 Italy imported about 11,500 tons of crude copper, brass, and bronze, without including 2350 tons of sheets, bars, tubes, and wire. In 1905 Italy imported 15,914 tons, in 1907 22,071 tons, and in 1908 19,622 tons of the value of £1,690,000, and in 1909 about 22,000 tons.

PRODUCTION OF COPPER IN TONS

	1850	1880	1890	1900	1905	1908
Germany . .	1,950	14,250	24,427	30,930	31,700	30,000
France . .	1,925	3,360	2,300	6,450	?	—
England . .	15,420	3,720	940	770	500	—
Russia . .	—	3,200	5,720	8,130	10,000	—
Spain and Portugal	—	23,670	64,370	53,720	49,000	—
United States of America .	914	27,430	117,820	272,500	421,000	440,000
Chili . .	6,000	32,540	24,290	20,340	32,500	—
Australia . .	2,580	8,650	6,225	10,500	30,000	—
Japan . .	—	4,500	18,260	25,700	37,500	—
Italy (copper and alloys) . .	—	300 ?	6,400	9,600	11,900	18,280
Canada . .	—	—	2,730	9,000	21,000	—
Mexico . .	—	—	5,000 ?	33,000	65,000	—
Total world's production . .	57,000	155,000	280,000	490,000	721,550	734,545
Price per ton in pounds sterling	£96	£88	£69·6	£73·6	Variable	£66

CUPROUS COMPOUNDS

CUPROUS OXIDE : Cu_2O. This is found in nature as *cuprite* in red regular octahedra, and is obtained by reducing copper salts in the heat, whilst in the cold yellow cuprous hydroxide, $Cu_2(OH)_2$, is formed. Thus cuprous oxide may be produced with an alkaline solution of grape sugar, which contains an aldehydic reducing group, or with arsenious acid. It is a red substance of sp. gr. 5·35, which is not attacked by the air in the cold. It dissolves in ammonia and then acquires a blue colour in contact with the air. In presence of sulphuric acid it forms copper and copper sulphate,

$$Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O.$$

CUPROUS CHLORIDE : CuCl or Cu_2Cl_2. This compound is formed on burning copper in an atmosphere of chlorine or on boiling a cupric chloride solution with copper and HCl, or also by reducing a solution of copper sulphate in a current of SO_2 in presence of sodium chloride. It then separates as a white powder on pouring the solution into water, but in contact with air it acquires a green colour through the formation of copper oxychloride : $Cu{<}^{OH}_{Cl}$.

It melts at 430°, distils unaltered at 1000°, and has a vapour density corresponding to the formula, Cu_2Cl_2. With HCl or NH_3 solutions a colourless solution is first obtained which rapidly becomes blue in the air with formation of cupric compounds and rapidly absorbs carbon monoxide with formation of $2CuCl.CO.2H_2O$, which separates in colourless crystals.

Cuprous Bromide and **Iodide** are more insoluble in water than the chloride. On adding KI to a solution of copper sulphate, cuprous iodide is formed, and half the iodine is iberated, $2CuSO_4 + 4KI = 2SO_4K_2 + 2CuI + I_2$.

CUPROUS CYANIDE : Cu.CN. On adding potassium cyanide to a solution of copper sulphate, cuprous cyanide is first separated, but this immediately dissolves in an excess of KCN, as it is completely transformed into a double salt, $Cu_2Cy_2.2KCy$ (the symbol Cy

represents the monovalent cyanogen group, CN). This salt no longer shows any reaction for copper as it is dissociated in solution into the anion $(Cu_2Cy_4)''$, and the cations, $2K^{\cdot}$.

A **Cuprous Hydride, Cu_2H_2**, is also known, and is formed as a yellow powder which then turns brown on heating copper sulphate solution with a solution of hypophosphorous acid. It reacts with HCl according to the following equation :

$$Cu_2H_2 + 2HCl = Cu_2Cl_2 + 2H_2.$$

CUPROUS SULPHIDE : Cu_2S. This compound is found in nature as *chalcosine* in trimetric crystals, and is formed on burning copper in sulphur vapour or on heating cupric sulphide in a current of hydrogen.

CUPRIC COMPOUNDS

COPPER OXIDE, CUPRIC OXIDE : CuO. This oxide is a black powder which is obtained by heating copper strongly in the air, or by heating the hydroxide, carbonate, or preferably the nitrate of copper, to redness. When heated it readily gives off oxygen to organic matter when in contact with it, burning it completely and being reduced to metallic copper, the carbon of the organic matter being converted into CO_2 and its hydrogen into H_2O. For this reason it is used in the analysis of almost all organic substances. The crude product costs £90 per ton, when pure £150, and when pure for analysis 5*s*. 7*d*. per kilo. Italy produced 10·5 tons in 1908 of the value of £336.

COPPER HYDROXIDE : $Cu(OH)_2$. On treating the solution of a copper salt with NaOH, a voluminous bluish-green precipitate of $Cu(OH)_2$ is formed which becomes brown and finally black on heating, as it is transformed into CuO. Its solution in NH_3 is intensely blue and has the property of dissolving cellulose. It is called *Schweitzer's reagent*. $Cu(OH)_2$ only dissolves in NaOH in presence of certain organic substances, such as tartaric acid, sugar, &c. It costs a little more than the oxide.

CUPRIC CHLORIDE : $CuCl_2$. This compound is formed on dissolving copper carbonate or oxide in HCl. It crystallises from water in greenish needles with $2H_2O$, whilst when anhydrous it has a yellowish-brown colour and melts at 60°, being then transformed into $Cu_2Cl_2 + Cl_2$. It is also soluble in alcohol. The concentrated aqueous solution is green because it is only slightly dissociated, whilst on diluting with much water it becomes blue because of the presence of blue $Cu^{\cdot\cdot}$ ions, whilst the undissociated $CuCl_2$ molecules are yellowish-brown, which explains the green colour of the concentrated solution, which consists of a mixture of non-dissociated $CuCl_2$ and $Cu^{\cdot\cdot}$. This latter ion is always blue in all cupric compounds.

It forms well-crystallised double salts with HCl and NH_4Cl.

Cupric Bromide is similar to the chloride. **Cupric iodide** is not known because it dissociates into $I_2 + Cu_2I_2$ as soon as it is formed.

COPPER NITRATE : $Cu(NO_3)_2$. It is prepared by dissolving Cu or CuO in nitric acid. It is very soluble in water and forms bright blue crystals with 4 or $6H_2O$. It is also soluble in alcohol and forms CuO on heating to redness.

BASIC COPPER CARBONATE. The neutral carbonate is not known, but th basic carbonate exists in two forms as minerals, *Malachite*, $CuCO_3.Cu(OH)_2.\frac{1}{2}H_2O$, and *Azurite*, $2CuCO_3.Cu(OH)_2$.

COPPER SULPHATE, BLUE VITRIOL : $CuSO_4$. This is the most widely used copper salt. It is very stable and is obtained by dissolving copper and many copper minerals in hot, dilute sulphuric acid in contact with the air. It is necessary, however, to remember that except in the presence of much air copper reacts scarcely or not at all with sulphuric acid (*see* p. 419), and it is therefore preferable in such cases to start from copper oxide. For preparing the sulphate industrially a lead tower is sometimes used, filled with copper turnings down which a spray of dilute sulphuric acid descends which is discharged at the base and repeatedly pumped to the top of the tower. When the reaction between the acid and the copper first starts, heat is produced which causes a strong current of air to be drawn in through an aperture at the base of the tower.

This becomes heated and escapes at the top after having oxidised the copper and thus facilitated its transformation into sulphate. The sulphate is also prepared by lightly roasting copper sulphide in the air and then extracting the resulting copper sulphate with water from which it crystallises in blue triclinic crystals containing $5H_2O$. This is the ordinary *blue vitriol*, which effloresces superficially in the air because it loses a little water. At 100° it loses $4H_2O$, but only loses the final molecule of water at 200°, leaving a white powder of anhydrous copper sulphate which is somewhat hygroscopic, and is used for dehydrating various substances, when it regains its blue colour. 100 parts of water at 20° dissolve 42·3 parts of $CuSO_4.5H_2O$, and the solution has an acid reaction in common with those of many salts of heavy metals because they are hydrolytically dissociated by water. Copper sulphate has various practical applications and is therefore manufactured on a large scale by one of the following industrial processes.

Cupriferous pyrites is now often used after it has been employed for the preparation of SO_2 in sulphuric acid manufacture, and is treated in the manner already described for the preparation of copper, that is, cementation copper is prepared from it which is then used for the manufacture of the sulphate. It is found in practice that much burnt cupriferous pyrites cannot be extracted very easily with water and H_2SO_4, because at the temperature of the pyrites burners (up to 750°) the sulphate and sulphide of copper which are first formed give rise to the oxide and to a regulus which renders it difficult to recover the copper except by the process of chlorination.

In order to prevent a considerable portion of the copper sulphate formed in the pyrites burners from decomposing through the employment of too high a temperature, it has been proposed (Gianoli, *Industria*, 1903, p. 731) to mix the pyrites before roasting with about 10 per cent. of sodium disulphate or sulphate. The lixiviation of the burnt pyrites is then conducted in the usual manner with water and sulphuric acid, and the copper is then much more completely extracted. Copper is separated from the solution by cementation with iron (*see above*).

Cementation or granulated copper obtained by any method is placed in lead-lined wooden vats. Crude sulphuric acid is added and the whole is diluted with mother liquors from a previous crystallisation of copper sulphate until a density of about 29° Bé. is acquired, after which the whole is heated to 85° to 90°. It is necessary to aerate the liquid well as otherwise the copper sulphate which is formed is partially transformed into cuprous sulphate in presence of free copper, and it is necessary to oxidise this with air in order to again transform it into cupric sulphate. The injection of air and the necessary heating can be simultaneously obtained by employing a steam injector. In certain cases it is convenient to heat and oxidise the cementation copper by spreading it out in a reverberatory furnace, carefully regulating the temperature and the current of air and stirring the material so that the copper is almost entirely converted into the black oxide. This then forms copper sulphate on simple solution in sulphuric acid. The aqueous solution of the sulphate is concentrated in large shallow leaden pans (3 × 3 × 0·55 metres), which rest on iron plates under which the hot gases from a furnace circulate in flues. After a certain concentration has been acquired, crude copper sulphate separates abundantly on cooling. This is then redissolved in mother liquors obtained from pure copper sulphate and previously diluted with water to 14° to 15° Bé. ; a solution of crude copper sulphate of a concentration of 26° Bé. when hot is thus obtained. If a more concentrated or saturated solution were employed very small and impure crystals would be obtained. The liquid is then heated until it is completely clarified and the solution is thus slightly concentrated. It is then poured into the crystallising boxes which are lined with lead (3 metres × 1·5 metres × 1 metre deep). According to an American process which has also been applied in certain Italian works (Rifredi) the copper is heated to its melting-point and then poured in a thin stream into water in order to enable it to be easily oxidised and attacked by the sulphuric acid. Small, thin, hollow spheres are thus obtained (although it is necessary to employ very pure copper in order that this should occur) which are placed in a cylinder some metres high, down which a spray of sulphuric acid of 28° Bé. is then poured from above, whilst a current of air ascends from below. When the liquid reaches the base it consists of a hot saturated solution of copper sulphate,

ready for crystallisation. The mother liquors from this crystallisation are again pumped to the top of the cylinder which is always kept filled with new copper spheres, and is always fed with sulphuric acid in such a manner as to obtain a solution of copper sulphate of constant concentration. When pure copper is being treated, the mother liquors may be continuously reutilised. The crystallisation lasts from 8 to 12 days, and occurs on the walls and floor or on leaden strips which are introduced into the solution. The crystals form best if the liquid contains a little free sulphuric acid, and this amount is regulated by the workmen themselves, who mix a given volume in a test-tube with a very dilute solution of alkali of fixed strength until neutralisation occurs, when a precipitate of copper hydroxide just commences to be formed. By making two tests with varying quantities of alkali, the workmen easily control the limit of acidity. In some places the crystals are separated from the mother liquor in a hydro-extractor, but many of the crystals are thus broken and lose their commercial value. They are therefore usually spread on trays with raised rims and allowed to dry in the air in large chambers which are well ventilated in summer or gently heated in winter (to 25° to 30°). Into these drying chambers much light should not be admitted and care must be taken that the crystals are not dried too much or they lose their clearness. One kilo of copper theoretically produces 3·934 kilos of $CuSO_4.5H_2O$. The mother liquors are used in the treatment of the raw material as was explained above.

According to Gin's process (International Congress of Applied Chemistry at Berlin, 1903) copper sulphate can be profitably prepared by lightly roasting ores containing copper and iron in such a way that a large portion of these metals is obtained in the form of sulphates. These are then extracted with water and a current of SO_2 passed into the solution to reduce the ferric sulphate to ferrous sulphate. The whole is then heated in autoclaves to 180°. At this temperature the ferrous sulphate separates from solution, whilst copper sulphate remains dissolved and is easily separated from the iron by straining or centrifugating. According to U.S. Pat. 875,012 of 1907 burnt pyrites is treated with dilute sulphuric acid and 2 to 5 per cent. of calcium hypochlorite ; the whole is then heated to 70° to 80° for 12 to 24 hours, in which manner the copper only is dissolved and not the iron.

APPLICATIONS AND STATISTICS. Copper sulphate is used for copper-plating, in dyeing and printing, in the manufacture of pigments containing copper powder, for preserving wood and hides, and in considerable quantities in wine culture as a remedy for peronospora. The price varies with the price of copper and was about £20 per ton in 1904, then rose to £26 in 1906–1907, and dropped after 1907 to below £18 per ton, rising again to £20 per ton in 1910.

The production and imports of copper sulphate for Italy are given in the following Table :

	Production in tons	£	Imports in tons
1893	900	—	—
1896	4,756	86,934	—
1900	13,191·4	346,960	31,000
1905	26,212	553,560	30,684
1906	34,270	926,840	25,030
1907	45,263·5	1,174,680	15,974
1908	42,600	935,120	25,031·5
1909	—	—	9,040

In 1906 Italy exported 102·1 tons and in 1908 612·9 tons of copper sulphate.

In 1904 the production of copper sulphate in the United States was 30,000 tons and it is estimated that in 1900 the world's production was a little more than 100,000 tons. Germany produced 6984·4 tons of copper sulphate in 1905 and imported 2200 tons in the same year, whilst in 1908 it imported 5080 tons and in 1909 6550 tons. In 1909 England exported 45,000 tons.

COPPER SULPHIDE: CuS. This compound is obtained as a black precipitate on passing a current of H_2S into a solution of a copper salt, even in presence of acid. It is insoluble in water and in dilute acids. When exposed to moist air it is slowly converted into sulphate; when heated, on the other hand, in a current of hydrogen it is transformed into cuprous sulphide. A theoretical explanation of the fact that certain oxides are completely precipitated by H_2S from acid solution, whilst under the same conditions others are not precipitated, may be deduced from the study of electrolytic dissociation. In the case of copper sulphide the reaction only occurs between the ions of copper sulphate, which is almost completely dissociated into $Cu^{\cdot\cdot}$ and SO_4'', and the few free $H^{\cdot}$ and S'' ions. The copper sulphide, CuS, which results, is very insoluble and is deposited, but as fast as the $Cu^{\cdot\cdot}$ and S'' ions are eliminated, the equilibrium which first existed between the H_2S ions and its undissociated molecules is disturbed. A further portion of the H_2S molecules then dissociates into the corresponding ions and these unite with further $Cu^{\cdot\cdot}$ ions, forming fresh copper sulphide which separates, and the reaction thus continues until the copper is completely precipitated in the form of CuS, so long as the solution of copper sulphate is sufficiently dilute to permit of its complete dissociation: $CuSO_4 + H_2S = CuS + H_2SO_4$. If, however, a strong, free, dissociated acid is present, the new $H^{\cdot}$ ions will hinder the ionisation of the H_2S and then no precipitate of copper sulphide will be formed.

We may also explain the laws which regulate the equilibrium of any given reaction and the conditions under which a precipitate in general can be formed by certain general considerations. This copper sulphide, CuS, which is separated from solutions of $CuSO_4$ by H_2S, is very slightly soluble in water, and its complete separation depends on the following circumstances: The minimal quantities of CuS which dissolve and are dissociated into $Cu^{\cdot\cdot}$ and S'' are in a certain equilibrium with the precipitated and non-dissociated CuS: $Cu^{\cdot\cdot} + S'' \rightleftharpoons CuS$; and according to the mass law (p. 66) we may always represent this equilibrium by a mathematical expression, taking the concentration of the ions (a for $Cu^{\cdot\cdot}$ and b for S'') and the concentration of the undissociated substance ($CuS = c$) into account; at a given temperature the general formula will be $a.b = k.c$, where k is the equilibrium constant (p. 66) which depends on the temperature only (the concentration of the saturated solution is different at different temperatures).

The product, $a.b$, which has a definite value for each saturated solution, is called the *solubility product* and indicates for any given temperature the concentration limit which must be exceeded in order that a precipitate may commence to be formed. $a.b$ is also the *concentration product*, that is, it represents the concentration of the ions at a definite temperature. The two products coincide in the case of saturated solutions, but sometimes the concentration product exceeds the solubility product. This is the case for supersaturated solutions in which, as soon as the labile equilibrium ceases, so much salt separates that the concentration product becomes equal to the solubility product. If in the case of a given salt the concentration product is inferior to the solubility product, we have an unsaturated solution. In the case of slightly soluble salts the solubility product is very small, whilst in the case of very soluble salts it is comparatively large. In the case of precipitates, these are not able to form and separate until the product of concentration of their ions has reached the value of the solubility product. When we increase the number of $H^{\cdot}$ ions in a solution of copper sulphate through which H_2S is passing, by the addition of a strong mineral acid, the ionisation of the H_2S is lessened, and the concentration product of the S'' and $Cu^{\cdot\cdot}$ ions becomes less than the solubility product, that is to say, it does not reach the saturation limit and consequently no CuS precipitate is formed. If we now alter the concentration of the $H^{\cdot}$ ions by considerably diluting the solution with water, then as further H_2S passes in, its ionisation and the concentration of the S'' ions may reach and exceed the value of the solubility product and the CuS will be precipitated.

This precipitate is very insoluble, that is, its solubility product is very small, and if, therefore, CuS is suspended in water acidified with a strong mineral acid, very little CuS will pass into solution because very few $Cu^{\cdot\cdot}$ and S'' ions suffice to attain the value of their solubility product which is minimal, and then no further traces of CuS will pass into solution. If, on the other hand, we are dealing with a metallic sulphide which is more soluble than that of copper, such, for instance, as ferrous sulphide, or to a still greater extent zinc sulphide, the solubility product will always be higher than the concentration product because H_2S is always only slightly dissociated, and thus these sulphides dissolve in mineral acids and are not precipitated in presence of sulphuric acid. These sulphides however can be

precipitated by employing precipitating agents which do not contain $H^{\cdot}$ ions, which would cause the solution of the sulphide, and of these ammonium sulphide is very suitable:

$$ZnSO_4 + (NH_4)_2S = SO_4(NH_4)_2 + ZnS.$$

In the case of metals which give sulphides which are still more soluble than zinc sulphide, it is not possible to precipitate them with H_2S or even with $(NH_4)_2S$. The sulphides of the alkali and alkaline earth metals come under this category.

GENERAL REACTIONS OF COPPER COMPOUNDS

Copper salts, excepting the sulphides, when treated with ammonia first form a hydroxide which then immediately dissolves in excess of ammonia, producing an intensely blue solution which on evaporation separates crystals which have a constitution similar to double or basic salts such as $CuSO_4.4NH_3.H_2O$, which forms $CuSO_4.2NH_3$ at 150°. These salts contain complex ions and therefore only show a few of the general reactions for copper. Thus they are precipitated by H_2S but not by KOH. Volatile copper compounds colour the flame blue or green. The blue ammoniacal solutions are decolorised by addition of potassium cyanide, as compounds are obtained which no longer contain the $Cu^{\cdot\cdot}$ ion. With potassium ferrocyanide (*see* Iron), cupric salts give a reddish-brown coloration or precipitate of copper ferrocyanide.

On immersing a bright strip of iron in a solution of a copper salt it immediately becomes covered by a layer of metallic copper.

SILVER: Ag, 107.88

Silver is a metal which has been known since remote antiquity, as it is often found free in nature.

The principal minerals from which it is extracted are *Argentite*, Ag_2S, *Pyrargyrite*, $3Ag_2S.Sb_2S_3$, *Strohmeyerite*, $Cu_2S.Ag_2S$, and *Horn Silver*, AgCl.

It often accompanies lead in galena in quantities sufficiently large to enable it to be profitably extracted. Argentiferous galena ordinarily contains 0·01 to 0·05 per cent., and occasionally 1 per cent. of Ag, and constitutes the most important ore from which silver is extracted.

Silver ores abound in California, Mexico, Chili, Saxony, Hungary, the Altai Mountains, and a little in Sardinia

The metallurgy of silver is fairly varied, and according to the local circumstances silver is sometimes extracted by one method and sometimes by another. In the past amalgamation processes were used, but solution processes are now gaining ground. We will concisely describe the more important processes.

(1) **Extraction by Lead.** This is based on the property of lead and lead oxide of moving silver from its combinations on heating. Whilst the other metals separate in the form of oxides, silver is not oxidised and remains dissolved in the molten lead. The argentiferous ore is mixed with lead (galena containing at least 0·15 per cent. of Ag is treated as such), and is melted in a cupel furnace (Fig. 234), which is a reverberatory furnace with a circular brickwork hearth lined with stamped calcareous marl and containing a depression in the centre in which the molten silver collects. The cupel, which may contain as much as 40 tons of lead, is closed by a sheet-iron cover which may be raised and removed and is lined internally with clay. During smelting a current of air is injected by a mechanical blower and two tuyères which pass into the cupel; oxidation is continued until all the lead is transformed into the molten oxide (litharge). The cupel is heated by a furnace at the side, separate from the cupel itself, and in order to discharge the molten litharge which floats on the surface, there are two lateral openings, the sills of which can be lowered so that all the PbO can be removed continuously whatever may be the level of the molten mass.

Finally molten silver alone remains, covered by a thin layer of PbO which bursts

every now and again and allows the shining surface of the molten silver to be seen, this phenomenon being accompanied by iridescent light.

A portion of the lead oxide, together with other impurities, is absorbed by the porous floor of the cupel. When the shining silver surface appears the cupellation is finished and the cooling of the silver is accelerated by water. This final product is still impure, containing 95 to 98 per cent. of silver, together with other metals, which are then separated by refining in another much smaller reverberatory furnace with a porous floor, by the help of a strong air-blast, which oxidises and separates all the other oxidisable metals in the form of slag, with the addition if necessary of a little marl or bone ash. When the metal is pure it is removed from the furnace and may be granulated by pouring it into water, or it is poured into moulds in order to be cast into bars.

(2) Another dry process is that proposed by **Pattinson** in 1833, which is well adapted for the treatment of lead containing less than 0·01 per cent. of Ag. In the same way as on freezing the aqueous solution of a substance the solid solvent is almost exclusively separated in the form of ice, so on slowly cooling a large mass, even 10 tons or more, of molten argentiferous lead in a cast-iron pan, octahedral crystals of lead separate which are much less argentiferous (liquation). The solid portions are removed with perforated ladles, and the remaining liquid lead containing more silver is continuously allowed to cool, the solid lead being removed as fast as it forms. An argentiferous lead containing 1 to 2·5 per cent. of Ag finally remains, whilst the separated portion does not contain more than 0·001 to 0·003 per cent. The argentiferous lead which has thus been enriched is then subjected to cupellation as described above.

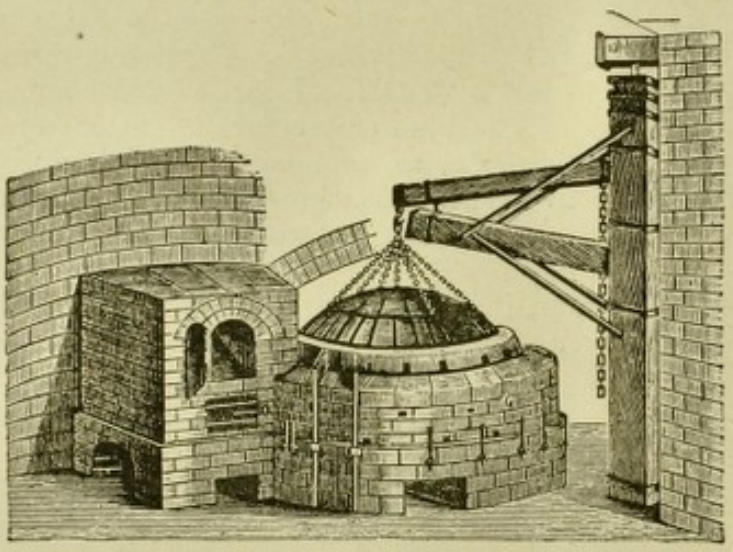


Fig. 234.

When argentiferous ores are treated by Pattinson's process it is necessary to mix them with much pure lead.

(3) A third dry process for which pure lead is not required, as in Pattinson's process, is that proposed by Karsten in 1841 and applied unsuccessfully by Parkers in 1850. After various improvements by Roswag, Cordurié, and others, the process was successfully introduced industrially. It is based on the fact that zinc has a greater affinity for silver than lead.

The argentiferous lead under treatment is melted in large cast-iron pans of a capacity of 2 tons or more and heated to a temperature of above 450°, that is, a little higher than the melting-point of zinc. About one-fifth of a ton of zinc is then added in several portions and the mass is kept mixed for a long time, the impurities which collect at the surface being separated.

The zinc combines with all the silver, a little lead, and any impurities such as copper and gold. A dense scum then collects at the surface and solidifies on slowly cooling, floating on the molten lead so that it is easy to separate it a little at a time. The remaining lead should not contain more than 0·001 per cent. of silver. The argentiferous zinc is then treated in one of two ways. It may be cupelled in the same way as argentiferous lead, or preferably it is distilled in a graphite crucible mixed with a little carbon (1 per cent.). The zinc which distils is condensed and reutilised.

Schnabel, on the other hand, melts the zinc scum in a closed iron pan provided with a delivery tube for the gases, H, air, &c., and passes in a jet of steam at a pressure of 2 atmospheres. In this way zinc oxide and lead oxide are formed and separate. The hydrogen which is evolved mixes with air and produces slight explosions now and again.

All the silver remains mixed with the lead, which is finally treated in the cupellation furnace.

WET PROCESSES. These comprise the European and American amalgamation processes and the solution process.

(1) **European Amalgamation Process.** This is based on the fact that mercury easily alloys with and dissolves silver, and reacts with certain silver compounds, such as AgS_2 and AgCl, forming amalgams. The powdered ore is mixed with sodium chloride and gently roasted in a reverberatory furnace, in cupola furnaces or in a Brückner rotary furnace. Sulphates and oxides are formed and the silver is converted into chloride. After cooling, the powdered mass is placed in a revolving barrel with a little water and lumps of iron, and is kept in motion for some hours.

The silver chloride which was dissolved in the sodium chloride is decomposed by the iron: $2AgCl + Fe = FeCl_2 + 2Ag$.

The free silver is amalgamated by adding an excess of mercury in the same barrel and rotating it for 18 to 20 hours. The amalgam, containing all the silver, is filtered through sacks in order to separate the excess of mercury and the aqueous solution, which pass through the cloths. By applying a little pressure to the cloths, a little further mercury is pressed out, and the remaining amalgam is distilled in various ways in order to separate the mercury, which is easily volatile, from the less volatile silver.

The distillation is conducted in either cylindrical or horizontal iron retorts with a delivery tube which dips into a vessel of water where the mercury vapours are condensed. The remaining silver is then refined in any suitable manner.

(2) **American Amalgamation Process (Patio Process).** This process is especially used in Mexico. The ore is finely powdered and is then placed in large flat heaps in yards with an inclined pavement, and is sprinkled with water and salt (2 to 5 per cent.). An intimate mixture is obtained by causing men and mules to trample on the heaps for some days and 2 to 3 per cent. of cupriferous chlorinated burnt pyrites or roasted chalcopyrite is then added. The mixing is continued and finally the necessary quantity of mercury is added to each heap, namely, 6 to 8 kilos for each kilo of silver contained in the ore.

The whole is incessantly mixed for 40 to 50 days by making horses trample over it in such a way that complete amalgamation is secured. The chalcopyrite forms ferrous chloride with the sodium chloride and copper, and also sodium sulphate.

The silver chloride forms silver subchloride which remains dissolved in the excess of sodium chloride and forms calomel (HgCl) and free silver by interaction with the mercury. This silver then dissolves in the mercury forming an amalgam. The amalgam is separated from many impurities with water in revolving barrels, and is then filtered through sacks, after which it is distilled as described above. This process is very lengthy and causes considerable loss of mercury, as HgCl, and of silver, but it has the advantage of not requiring fuel until the amalgam is formed, and it is possible to treat ores which cannot be utilised by other methods.

(3) **Kröhncke's Process.** This treatment takes place in revolving barrels with a hot solution of cuprous chloride and sodium chloride. Silver and AgCl are so obtained, even in presence of arsenic and antimony sulphides. Mercury is then added, together with zinc or lead, so that amalgamation may take place without loss of mercury in the form of HgCl. The process is rapid and rational and is accompanied by a minimum of losses.

The amalgam which is finally distilled ordinarily contains about 10 per cent. of silver.

(4) **Various Processes.** Francke's process is an improvement of the American process. The ore is partially roasted with NaCl, and the silver is thus obtained partly as chloride and partly as sulphate. The silver is then separated from solution by copper plates and is finally amalgamated. Another process consists in treating minerals containing native silver or much silver chloride or sulphides with a hot solution of NaCl in copper vats furnished with copper stirrers, and heated over direct fire. Cuprous chloride is formed and decomposes the silver sulphide. The silver is then amalgamated with mercury.

(5) **Solution and Precipitation Processes.** (*a*) Augustin's process. This process is useful for pure sulphides or argentiferous copper matte, as far as possible free from Pb, Zn, Sb, and As.

The powdered ore is mixed with sodium chloride and roasted, and is then extracted with a solution of sodium chloride in revolving barrels ; this dissolves the silver chloride forming a double salt. The silver is first precipitated from the solution by copper plates and the copper is then recovered by dissolving it and precipitating it with iron.

Gibbs modified this process by precipitating the last portions of silver mixed with cuprous chloride fractionally with sulphuric acid ; all the silver is found in the portions which separate first.

An advantageous simplification of Augustin's process, especially for the treatment of argentiferous alloys and rich ores, is that introduced by Ziervogel, who roasts in the absence of sodium chloride in such a manner that silver sulphate is obtained mixed with copper sulphate and basic ferric sulphate. This process is not suitable when the mineral contains Sb or As, because silver arsenate and antimonate are then formed during roasting and are insoluble in water, being thus lost. Recently C. Goldschmidt has advantageously replaced the copper or iron plates used to separate the silver from the sulphate by cobalt plates ; the silver is at once deposited partly in an amorphous and partly in a crystalline condition.

There are other wet processes which use **Sodium Thiosulphate** (Patera) or **Calcium Thiosulphate** (Kin), which very easily dissolve the silver chloride contained in ores which have been roasted with NaCl. A portion of the heterogeneous chlorides is, however, first removed by lixiviation with water. The solution of silver thiosulphate is precipitated with sodium or calcium sulphide and thus Na or Ca thiosulphate is regenerated, the silver being separated as sulphide. By this method, which has been improved by Russel, any gold which may be present in the ore is also separated. The silver sulphide is then treated in the usual way by the processes already described.

Crude copper matte or black argentiferous copper may also be lixiviated with dilute sulphuric acid ; this dissolves all the copper, and the argentiferous residue is then treated with lead by the dry process.

Pure silver is obtained in the laboratory by dissolving commercial silver which always contains a little copper, lead, &c., in nitric acid. Silver chloride is then precipitated with HCl. The chloride may be fused with soda, when silver remains : $2AgCl + Na_2CO_3 = 2NaCl + CO_2 + O + 2Ag$. Or it may be boiled with dilute potassium hydroxide and glucose. The silver which is thus separated is distilled in a crucible of quicklime by means of the oxy-hydrogen flame.

PROPERTIES. Silver conducts heat and electricity better than any other metal (Table, p. 411). It has a white lustrous colour and a specific gravity of 10·4 to 10·6 ; it melts at 962° and boils at 2070°. When evaporated in the oxy-hydrogen flame, it forms bluish vapours. It does not oxidise in the air, either when hot or cold, and is therefore classed amongst the noble metals (Pt, Au, Ag). When molten it is able to absorb 20 times its volume of oxygen which it suddenly loses on cooling (spitting). It crystallises in octahedra, and melts to a compact mass if it contains traces of Pb and Cu. It is not attacked by weak acids in the cold, with the exception of nitric acid which dissolves it easily. Hydrochloric acid does not attack it appreciably, but H_2SO_4 dissolves it on heating. Silver soluble in water has been obtained in the form of a colloidal solution of the metal only (p. 105), or more easily by adding a solution of $AgNO_3$ to a concentrated solution of sodium silicate containing formaldehyde. It forms a reddish-brown solution, though other colorations are obtained by other methods (*see* Gold). It is oxidised by ozone in the cold and is blackened by H_2S. Silver is a relatively soft metal, and for practical purposes it is, therefore, alloyed with other metals, especially with copper, which renders it harder. The fineness of silver alloys is given in thousandths, and that of coinage is $\frac{900}{1000}$ (in Italy), that is, it contains 900 grms. of silver and 100 of copper for coinage of above the value of two lire. For coinage of lower value, the fineness is $\frac{835}{1000}$ (in Italy). Silver articles ordinarily have a fineness of 750. The addition of very

small quantities of zinc or cadmium tends to the production of alloys free from blow-holes and irregularities. Alloys containing much copper—50 per cent.—can be rendered white by the addition of Al or Ni.

Much silver is used for silver-plating other metals or alloys, by using the object to be plated as a cathode and a silver plate as anode, the bath being formed of a solution of silver cyanide in an excess of potassium cyanide. The dissolved double salt, AgCN.CNK, is dissociated, forming $Ag(CN)_2'$ and $K^{\cdot}$. The $K^{\cdot}$ acts on the double cyanide and separates Ag ; thus

$$Ag(CN)_2K + K = 2KCN + Ag.$$

STATISTICS AND PRICES. In 1880 the world's production of silver was 2482 tons, in 1890 4180 tons, and in 1900 5600 tons, of which last quantity 1855 tons were produced in the United States (1650 tons in 1908), 1175 tons in Mexico, 400 tons in Germany (the same quantity as in 1905), 290 tons in Bolivia, and 337 tons in Australia. The price is steadily falling ; in 1870 silver cost £9 per kilo, in 1890 £6 13*s.*, and in 1903 £3 5*s.* 6*d.* In Italy 33·6 tons of silver were extracted in 1899 from the argentiferous galena of Sardinia, which is treated in the works of Pertusola and Monteponi. In 1905 the Italian production was 20·215 tons ; 20·7 tons were imported and 25·95 tons were exported ; in 1907 the production was 20·5 tons of the value of £90,600, and the imports were 22·45 tons (36·0 tons in 1908 and 43·0 tons in 1909 of the value of about £160,000, whilst the exports in 1909 were 34·6 tons, valued at £138,800).

SILVER OXIDE : Ag_2O. This compound is obtained as a brownish-green precipitate from a solution of silver nitrate when treated with sodium or potassium hydroxide. It is slightly soluble in water to which it imparts an alkaline reaction, which leads one to suppose that the hydroxide Ag.OH may be formed in the solution, and acts as a strong base. This hydroxide has, however, not yet been isolated.

At 250° the oxide dissociates into $Ag_2 + O$, and is reduced to metallic silver by hydrogen at 100°. The freshly precipitated oxide dissolves in ammonia, and its solution on evaporation leaves black crystals of $Ag_2O.2NH_3$, which when dry explode with a minimum amount of friction.

SILVER SUBOXIDE : Ag_4O, and **SILVER PEROXIDE : Ag_2O_2.** The first compound is very unstable and the second is obtained from silver or silver oxide in contact with ozone. It forms black crystals which yield oxygen and silver oxide at 100°.

SILVER CHLORIDE : AgCl. This compound is found ready formed in nature as *horn silver* and may be obtained as a white curdy mass by precipitating a soluble silver salt with HCl or with a soluble chloride such as NaCl. It blackens in the light. It is very insoluble in water (1 : 716,000 at 14°), but is easily soluble in ammonia, potassium cyanide and sodium thiosulphate solutions, forming various complex ions. It is insoluble in dilute acids, but dissolves in fuming HCl and in a concentrated solution of NaCl (*see* Processes of Silver Extraction).

It melts easily, forming horny masses on solidification. It is transformed by HI into AgI.

SILVER BROMIDE : AgBr. It is formed in an analogous manner to the chloride, and has a pale yellow colour. It is soluble in sodium thiosulphate and slightly soluble in ammonia. It forms AgI with HI. It blackens in the light more rapidly than the chloride.

SILVER IODIDE : AgI. This has a more marked yellow colour than the bromide, and is obtained under the same condition as the chloride and bromide, but blackens more easily in the light when it contains traces of impurities, such as silver nitrate, tannin, &c. It is insoluble in ammonia and dissolves in HI forming crystalline AgI.HI.

It is transformed by bromine or chlorine into AgBr or AgCl as might be foreseen from its heat of formation.

SILVER FLUORIDE : AgF. This compound is readily soluble in water and has been proposed as an energetic antiseptic by Paterno and Cingolani, who placed it on the market under the name of *tachiolo*. They proposed it for the sterilisation of water, but the favourable results obtained by them were contested by others (*see* Water, p. 216). Lo Monaco recommended its use for disinfecting the mulberry leaves in order to prevent certain diseases

of the silkworm. The results obtained were, however, not decisive. According to observations made by G. de Rossi, silver nitrate is as sufficient an antiseptic as the fluoride. Paterno and Cingolani stated (1907) that whilst the nitrate sterilises water at a dilution of 1 : 200,000, the fluoride sterilises it more persistently even at a dilution of 1 : 400,000.

SILVER NITRATE : $AgNO_3$ (Lunar Caustic). This substance is easily obtained by dissolving commercial silver in dilute nitric acid and then evaporating. In order to eliminate the copper nitrate present as an impurity, the mass is melted and heated to a dull red heat in order to separate the copper in the form of oxide insoluble in water. It is obtained crystallised from an aqueous solution in rhombic tablets, isomorphous with KNO_3; it melts at 118°, and when solidified in the form of sticks forms *lunar caustic*, which is used in medicine as an energetic caustic for wounds and sores. It is very soluble in water and shows neutral reaction. It also dissolves in alcohol, and is poisonous. When pure it is not discoloured by light.

It is used in photography, in medicine, for silvering mirrors, &c. The price varies somewhat. The crystalline product costs £2 12*s*. to £2 16*s*. per kilo, and when fused in sticks £3 per kilo. Italy imported 6325 kilos in 1906, 3358 kilos in 1907, 2216 kilos in 1908, and 2990 kilos in 1909 of the value of £7200. A considerable portion of the imports came from Germany.

SILVER NITRITE : $AgNO_2$. This compound is formed by precipitating a concentrated solution of $AgNO_3$ with KNO_2. It crystallises from hot water in yellow needles.

SILVER SULPHITE : Ag_2SO_3. This is prepared as a gelatinous white precipitate by adding sulphurous acid to a solution of silver nitrate. It blackens in the air and decomposes at 100° with formation of silver.

SILVER SULPHATE : Ag_2SO_4, is obtained by dissolving spongy silver in hot H_2SO_4, and evaporating until crystallisation commences.

The colourless crystals dissolve in 200 parts of water and more easily in water acidified with HNO_3 or H_2SO_4.

SILVER AZIDE : AgN_3. Angeli prepared this substance from an aqueous solution of silver nitrate by the addition of an aqueous solution of hydrazine sulphate. It is not affected by light and is explosive.

THE PHOTOGRAPHIC PROCESS

It is generally known that the photographic process is based on the alteration of certain silver salts under the action of luminous rays, especially of the violet and ultra-violet rays. The first photographic processes were the *daguerreotype* process and the wet-plate collodion process, but these are now of historic interest only.[1] To-day dry-plates sensitised

[1] **History of Photography.** The true photographic process commenced to acquire practical importance only after the beautiful experiments made by Daguerre in 1838, following which he succeeded in fixing the images of objects and persons in an easy, rapid, and permanent manner by the action of light. His success and the general admiration were so great that the French Government, on the advice of the celebrated Arago, offered Daguerre an annual pension of 6000 francs on condition that he made his discovery public. On August 19, 1839, at a memorable meeting of the Académie des Sciences, Arago communicated in detail the photographic process of Daguerre, and the daguerreotype process dates from that time. The substance sensitive to the action of light was silver iodide, which Daguerre produced on a silver plate by exposing it in the dark to the action of iodine vapour. In the camera this plate was rapidly affected by luminous rays emitted by the object to be photographed, although the image was not at once visible on the exposed plate. On exposing this plate to the action of mercury vapour, the mercury was deposited in extremely fine drops only on those parts which had been influenced by the light, and the image then appeared in full detail. All that was required in order to fix the image and render it stable in the light was to dissolve the unaltered silver iodide with a solution of sodium thiosulphate.

The essential difference between the daguerreotype process and those which had preceded it consisted in the fact that it was not necessary to expose the sensitive surface for a long time in order to produce the image, but by utilising the extraordinary sensitiveness of silver iodide it was produced in an extremely short time, so that it became possible for the first time to obtain a latent, invisible image even from moving objects, which could then be fully developed in all details by the above-mentioned indirect process.

By the daguerreotype process reproductions of the original photograph could not be obtained, but in the same year (1839) Talbot communicated to the Royal Society of London a method of obtaining several copies from one transparent original. He superposed the negative plate on paper sensitised with chloride and silver nitrate, and then on exposure to the sun he obtained the positive. In this manner he succeeded in obtaining any number of copies by repeating the same operation. On this principle, Talbot also obtained impressions directly in the camera on sheets of transparent paper coated with silver iodide, then developing the latent image with gallic acid which precipitated black silver at the points influenced by the light. With this negative Talbot obtained the positive by

with gelatine containing silver bromide are exclusively used. They are prepared as follows in a dark chamber: A mixture of gelatine and silver nitrate is admixed with another mixture of gelatine and ammonium bromide at such concentrations that the gelatine sets on cooling.

The silver bromide so produced is so finely divided that the solution only becomes opalescent and is not very sensitive to light, because it is still too transparent. In order to render it more sensitive, this solution is heated for a long time so that the silver bromide aggregates into larger particles (Colloidal Solutions, p. 102), thus rendering the mass opaque (mature). This gelatine is then spread in thin layers on glass plates which are dried in the dark.

These are the ordinary photographic plates which are exposed in the photographic camera and receive light impressions from the illuminated object, the image of which is to be produced. Their sensitiveness is twenty times greater than that of the collodion plate, and Rayleigh has succeeded in producing a photographic impression on such plates with an exposure of a twenty-five-millionth of a second.

At the points which are exposed to the light, the silver bromide appears to be instantaneously transformed into silver subbromide, Ag_2Br, which is not visible, but forms a latent image which may then be rendered visible by treating it in a developing bath containing a reducing solution of ferrous potassium oxalate, ikonogen, hydroquinone, &c., in a chamber illuminated by red light which has no action on the sensitised gelatine.[1]

In this way the Ag_2Br is reduced to black, finely divided, metallic silver which is deposited more or less abundantly on the plate, according to the intensity of the luminous impression. It is maintained by some that the latent image is not due to chemical reactions but only to physical modifications, because the latent image is obtained even at temperatures of $-252°$, at which it is difficult to imagine any such chemical action.

When the image is well developed the plate is immersed in a bath of sodium thiosulphate

superposing it on a sheet of sensitised paper and exposing to the sun. After developing the new exposed sheet with gallic acid a positive was obtained in the same manner as before, and any number could be obtained at pleasure.

A further important step in the development of photography occurred in 1847 when Niepce, a nephew of Daguerre's first assistant, obtained the first sensitive glass plate by fixing silver iodide on it with a layer of albumen which, however, very easily altered. Fry and Archer obtained much better results in 1851 by coating the glass plate with a thin layer of collodion in which they had previously dissolved a bromide or an iodide. On immersing these plates in a bath of silver nitrate they obtained plates covered with an extremely sensitive film containing silver bromide or iodide, which after being exposed in the camera and developed with pyrogallic acid allowed extremely fine positives to be obtained which were faithful images of the object which had been photographed.

This convenient process with the collodion plate rapidly and completely replaced the daguerreotypes.

The collodion plate was supplanted in turn by a still more perfect process by which it was not necessary to prepare the plates a few minutes before use. In place of the wet collodion plate, Bennet succeeded in preparing sensitive dry-plates coated with silver-bromide-gelatine, which could be kept for years, after the fruitless attempts of Maddox and Wortley.

[1] Ferrous oxalate dissolved in excess of potassium oxalate or a mixture of ferrous sulphate and potassium oxalate was first used as a developer, the bath being acidified slightly by preference. A more energetic alkaline developer, which had already been used for wet-plates, was very soon used for dry-plates, namely, an alkaline solution of pyrogallic acid treated with sodium sulphite. Later a slower developer was advantageously used for over-exposed plates, namely, hydroquinone and also its isomer, pyrocatechin. For instantaneous negatives the best results are obtained with ikonogen, which is a very energetic developer consisting of the sodium salt of α-amino-β-naphtholsulphonic acid. It would be impossible to enumerate all the various developers which have been placed on the market during the last few years, such as metol, rhodinal, &c., which are suitable for even the finest work, but are only used, like those just mentioned, in a weakly alkaline bath.

Amidol, on the other hand, which is a sulphate of diaminophenol, develops the plate in a weakly acid bath in the same way as ferrous oxalate, and has less action on the gelatine film of the plate.

Only a few years ago photographic plates still had a great disadvantage, namely, that they were not uniformly influenced by the various colours of the objects which were photographed. The silver halides which are contained in the gelatine are very sensitive to blue and violet light, that is, to the more refractive rays of the spectrum, but are almost unaffected by green, yellow, or red light. It thus happens that a green or red flower or ribbon remains darker in the photograph than one of blue or violet colour. The credit for having indicated a way of obviating this difficulty as long ago as 1873 belongs to H. W. Vogel, who suggested the addition of substances capable of absorbing red, yellow, and green rays (*optical sensitisers*) to the silver-bromide-gelatine emulsion. At first mixtures of silver bromide with green or red aniline dyestuffs were made, but to-day silver salts are directly prepared from such colours, especially from eosin, &c. *Orthochromatic plates* are thus obtained which enable landscapes to be more faithfully depicted, and to-day still more perfect plates are produced by Miethe called *perchromatic* or *panchromatic* plates with ethyl red (iodoethylquinaldine-quinoline) which are not only sensitive to the green and yellow rays, but also to an equal extent to all the rays of the spectrum including red. It has thus become possible to reproduce any painting with a sufficient truthfulness of shade, which was not possible in the past.

Among the improvements introduced into photography we will also mention the preparation of *films*, which are celluloid sheets covered with gelatine-silver-bromide emulsions like the glass plates. The films have the advantage that they can be produced in the form of rolls which take up little space and are also very much lighter than the glass plates.

(*fixing bath*) which only dissolves the unaltered silver bromide, which has not been acted upon by the light, and the image thus remains fixed on a plate of transparent glass, but with shading opposite to that of the actual object, that is, the luminous portions of the object appear the darkest as they have influenced the plate to the greatest extent. In this way the so-called *negative* is obtained. Fixation is carried out in a place illuminated by a yellow light.

In order to obtain *positive* copies from the negative, that is, copies which reproduce the object in its true relations of light and shade, the negative plate is placed over a sheet of sensitised paper prepared by an analogous method to the plate, but with a gelatine which is less sensitive to light. On exposing the plate to the light this allows more or less light to pass through its more or less darkened parts and thus produces the complete positive on the paper in a few minutes with shading corresponding to that of the photographed object. This printed paper is then treated in a dilute bath of gold chloride in order to obtain more intense and pleasing tints. This operation is called *toning* of the positive, and is due to very fine blackish particles of gold which are deposited at those parts of the paper more or less influenced by the light, because the partially reduced silver salt acts in turn as a reducing agent on the gold salt. After toning, the positive is treated in a bath of sodium thiosulphate in order to dissolve the silver salt which has not been influenced by the light, and the positive is then said to be *fixed*. In order that the prints may remain stable and unaltered in the air, it is necessary to complete the operation by abundant and prolonged washing with water, as otherwise traces of thiosulphate remain and these slowly decompose, separating sulphur and forming silver sulphide which has a yellow and unsatisfactory appearance even in thin layers. This disadvantage is sometimes also caused by the decomposition of the albumen of the paper, which also contains sulphur.

The **Platinotype Process** is free from similar disadvantages and forms prints of black shade, harmonious and similar to wood-cuts, and is greatly valued. Platinotype paper is prepared with ferric oxalate and potassium chloroplatinate. The ferric oxalate is reduced to insoluble ferrous oxalate by the action of light, and this is then able to reduce the platinum salt on simply immersing in water or in a solution of potassium oxalate, thus separating very fine black particles of platinum which form and intensify the shades of the printed copy. Simple washing in water acidified with hydrochloric acid then suffices in order to obtain a suitable print without any further fixing, which is almost completely resistant to the action of chlorine.

It is thus clear in what manner as many copies as are desired may to-day be printed from a single negative.

The **Catatype Process.** Before closing this very short chemical account of the origin and development of photography, we must record an interesting discovery due to Ostwald and Gros jointly in 1903, based on purely theoretical considerations on *catalysts*, which has met with practical success. In chemistry various reactions are known which occur more or less slowly, for instance, the action between pure zinc and pure sulphuric acid which produces a minimal or almost zero quantity of hydrogen. If, however, a drop of platinum chloride is added, the development of hydrogen becomes abundant and tumultuous. Again, hydrogen peroxide slowly decomposes, forming oxygen and water, but if a trace of manganese dioxide is added, oxygen is evolved very abundantly. These substances, such as platinum chloride, finely divided platinum, manganese dioxide, &c., which take no part in the reaction, but notably accelerate it by their presence, are called *catalysts* (*see* p. 68).

Ostwald and Gros applied a very simple catalytic process to the copying or printing of photographs on paper without the action of light, starting from another photograph. It is known that a solution of pyrogallic acid oxidises slowly in presence of potassium bromate, forming reddish-brown colorations. If, however, a trace of powdered platinum or silver is added, the coloration is rapidly produced. In the ordinary photographic positive the image is formed by a deposit of finely divided silver or platinum. If a sheet of paper prepared with pyrogallic acid and potassium bromate is brought into contact with this positive in the dark, then after some time a positive copy with reddish-brown tones will be obtained. It is clear that the original positive used in this way will rapidly lose its colour and become quite useless. This objection can, however, be avoided by modifying the process in the following manner, which also permits a positive to be obtained from a negative.

If the negative plate is placed in an ethereal solution of hydrogen peroxide this is decomposed at the points of contact with the silver deposited on the plate and water alone remains, whilst at the more or less dark portions of the negative the hydrogen peroxide still remains unaltered. If after evaporation of the ether this negative is then applied with slight pressure to a dry gelatinised paper, the hydrogen peroxide brought on to this sheet remains unaltered, thus forming an invisible positive. If this sheet is then immersed in a solution of manganese chloride or sulphate, a brown deposit of manganese dioxide is formed at those points where the hydrogen peroxide is present, so that all the shades of the photograph are faithfully reproduced. If, on the other hand, it is placed in an alkaline solution of a silver salt a black deposit of silver will be formed and other similar tints may thus be produced with other solutions.

This process of copying or photographic printing is known by the name of *catatypy*, and it is believed that it will soon acquire practical importance, especially for platinum negatives or positives which have a more marked catalytic power than those of silver.

During the last few years, after fruitless or almost fruitless attempts by Ritter, Wollaston, Davy, Becquerel, Ducos, Cros, and many others, a practical method of *colour photography* has acquired certain importance, and has approached a practical solution. At first the most varied chemical processes were tried without much practical success, and it was only in 1891, when G. Lippmann, by making use of an interference process, succeeded in faithfully reproducing all the colours of the solar spectrum in a permanent manner, that this branch of photography disclosed new and enormous horizons. Lippmann solved the problem in a very simple manner by placing the film of silver bromide, finely subdivided in gelatine, in contact with a mercury surface in the dark chamber of a photographic camera, and then allowing the coloured object to act on the plate. The plate is developed in the usual manner, but the photograph shows by reflection all the colours of the depicted object.[1] In 1908 the firm of Lumière, of Lyons, simplified and improved colour photography with their *autochromatic plates*, which are coated with starch grains coloured red, green, and blue, so that the plate is only influenced by colours corresponding to those of the starch grains. The red grains only allow red light rays to pass and retain all the others ; the same applies to the green grains and the green rays. Contrary to what might be supposed, even the most delicate intermediate shades are faithfully reproduced. The Lippmann process required a long exposure, whilst with the autochromatic plate even instantaneous photographs may be taken, but they cannot be reproduced. They are very suitable for projecting coloured pictures (in a lantern).

Since 1906 *catachromic* experiments have been proposed and made by K. Schinzel in which the exposed plate takes an inverse picture, and on printing thus reproduces the original colours of the object which is photographed.

[1] F. Grassi summarises this interesting process of *colour photography* in his " History of Physics in the Nineteenth Century," as follows : " Lippmann uses a small vessel filled with mercury of which one wall is formed by the sensitised plate which is placed with the gelatine film inwards. The vessel is then placed in an ordinary dark slide in such a manner that the film is in the normal position. The rays proceeding from the object, which we will suppose, in order to simplify the reasoning, to consist entirely of the red rays of the solar spectrum, pass through the film and encounter the surface of the mercury which reflects them in the same direction as the incident light. Stationary waves are thus formed and the film may be imagined as divided into many layers parallel to the surface of the glass, bounded by the planes in which the action of the light is at a maximum, and where, consequently, the sensitive substance of the plate will be most largely changed. Between the one plane and the other there will be half-way a plane in which the reflected light destroys the incident light and in which the sensitive matter will not have been in the least changed, because it has not actually been exposed to light. On developing the plate in the ordinary manner and fixing it, the film is now formed of many very thin layers each of which will have precisely that thickness which, as in certain portions of a soap bubble, appears red.

" When a multi-coloured object is photographed each of these colours will appear at the corresponding point in the image when it is looked at by reflected light, as each colour is determined by the thickness of the thin layers which have been developed on the gelatine according to the characteristic wave lengths of that particular colour. The method requires special precautions on account of the varying velocities characteristic for the different colours.

" We may finally note that these colour photographs are permanent because the coloration does not depend on chemical substances, which may become modified by light, but on the properties of thin plates, which properties are permanent because they depend on the thickness alone. It is thus evident that Lippmann photographs cannot undergo alteration."

Photography has given rise to numerous new and flourishing industries which have acquired enormous importance in certain countries. It will suffice to note that already in 1885 the United States consumed 40 tons of silver and 3 tons of gold for photographic preparations alone. In 1901 Germany exported for photographic purposes silver salts to the value of more than £48,000, and gold preparations to the value of more than £120,000. If we include in the photographic industries optical apparatus as well as chemicals then it is estimated that in 1904 the world's production exceeded £20,000,000 and that this industry occupied tens of thousands of workpeople.

GOLD : Au, 197.2

Gold is often accompanied in nature by silver (from 1 to 40 per cent.) and occasionally by mercury. It is generally found in the free state in quartzose or alluvial rocks and in the sand carried down by certain rivers. Thus we have the gold-bearing sands of Tessin and of the Adda. Gold is widely diffused throughout the earth's crust, but in such small quantities that it only pays to extract it in regions where it is relatively abundant, such as the United States, California, Alaska, Hungary, Transylvania, Russia (Ural), and the Transvaal. In Italy the production is minimal and the gold is found in grains imperceptible to the naked eye contained as small veins in quartz and in auriferous pyrites in Monte Rosa, in the province of Novara, and is extracted by an English company in the Val Sesia, Val Ansaca, and Val Toppa. A little gold is also found in the Val d'Aosta ; at Bovisa, near Milan, the firm of Vogel extracts gold from roasted auriferous pyrites. Gold is rarely found in compact masses—nuggets—although in Australia a nugget weighing 87 kilos has been found. The ore which is treated in the Transvaal contains 20 grms. of gold per ton, and is considered to be a rich ore.

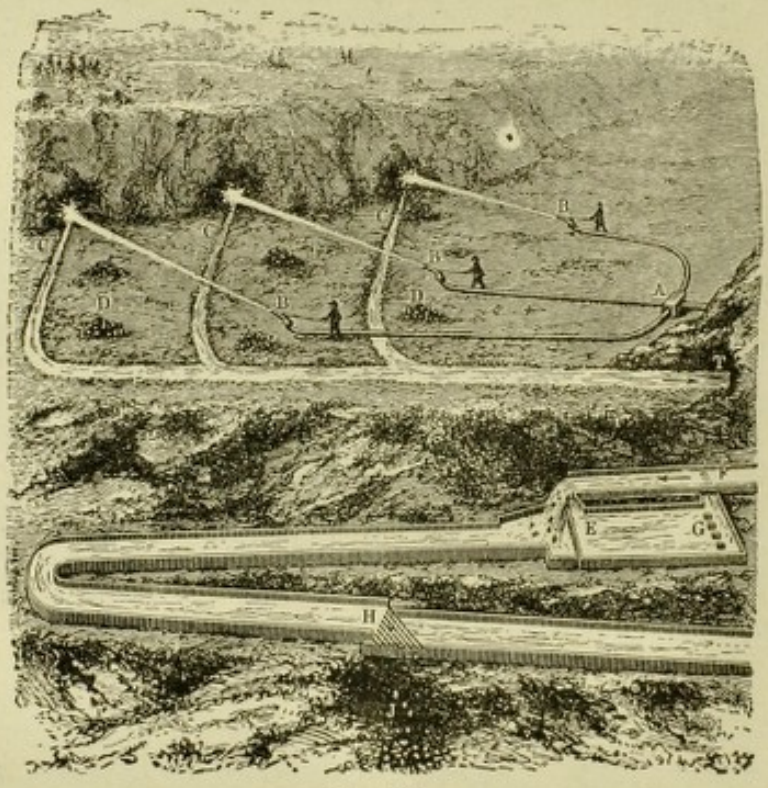


FIG. 235.

Gold was once entirely extracted by levigation of sand and disintegrated auriferous rocks ; the water carries away the sand, which is lighter, leaving the heavier grains of gold behind, but in this way much gold was lost, much labour was required, and the resulting product was impure. A great advantage was gained when the disintegration of auriferous quartz rock by means of powerful jets of water at a pressure of 4 to 5 atmospheres was thought of (Fig. 235) ; the rivulet thus formed is subjected to levigation by passing it along inclined channels in which the heavier particles of gold are deposited, whilst those of the gangue are carried away by the water. In order to avoid losses, a little mercury is placed in these inclined channels in order to dissolve and retain the gold. The amalgam is then treated in the manner described below. When mercury is not used, the impure gold residues are passed over a magnet in order to remove any iron and are then fused with borax, soda, and nitre in order to separate impurities in the form of slag.

When gold-bearing deposits do not contain sulphides (pyrites, &c.), or after these have been decomposed by roasting, good results are obtained by extracting the gold by amalgamation. In this case the ore is very completely crushed and is carried by a stream of water into a rotating vat in continuous contact with mercury which dissolves a large portion of the gold. In order to recover the small quantities of gold which are carried away with the mineral pulp together with the water, it is passed over amalgamated or silvered copper plates, to which an oscillatory movement is imparted. Now and again these plates are removed and the amalgam is distilled in the usual manner in iron retorts in suitable furnaces, when the mercury evaporates and the gold remains. In order to avoid minimal losses, the almost exhausted pulp is afterwards treated by the cyanide process described below.

In order to amalgamate the gold in ores containing pyrites and arsenic, Rae has introduced with advantage electric amalgamation (Fig. 236), which is carried out in a wooden vat into which the auriferous pulp is passed with a current of water. An internal stirrer provided with perforated discs, *b*, forms an anode and is connected to the dynamo, *A*, by the leads, *a* ; the cathode is formed of mercury on the floor of the bath, and is connected with the dynamo through the leads, *c*. By this process much labour and mercury are saved.

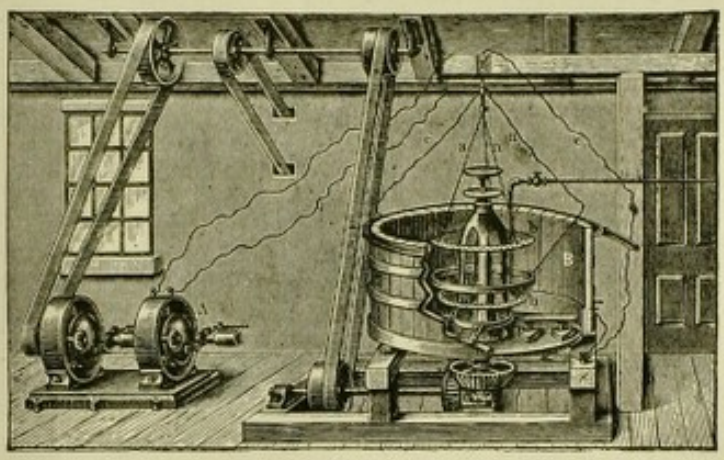


Fig. 236.

Amalgamation is not suitable for ores of complex composition, and these are treated by fusion with lead which dissolves the gold, and the impurities are then eliminated by fluxes in the form of slag. The auriferous lead is then treated by cupellation (*see above*, under Silver).

A very advantageous process by means of which up to 90 per cent. of the gold contained in ores is extracted, is that of Plattner, which consists in the chlorination of the ore. It is first roasted in order to eliminate the sulphur and arsenic, and is then moistened with water in a wooden vessel with a double bottom lined with paraffin or tar, in which it is then exposed to the action of chlorine. All the gold is transformed into gold chloride which is soluble in water, and the solution is treated with ferrous sulphate in order to separate the gold in the form of a brown powder which is then washed, dried, and fused with borax in order to obtain pure gold.

During recent years the process of A. Forrest, modified by Siemens, has come into general use. It is the most efficient of all processes and enables gold to be extracted even from very poor ores, and in general it can be employed without previous roasting. This process is based on the solubility of gold and of gold sulphide in sodium or potassium cyanide. The finely divided ore is generally first passed over oscillating amalgamated plates, and the pulp carried away by the washing water is then collected in large tanks of wood or masonry with a double bottom, which hold the product of the whole day's working—sometimes holding 800 cu. metres. To every ton of ore, half a ton of an aqueous solution of potassium cyanide of 0·6 to 0·8 per cent. is added. The solution is changed every 24 to 48 hours, being replaced by a weaker solution, and the complete extraction lasts from 4 to 6 days, so that four to six vats are employed in order to permit of continuous working.

The reaction is given by the following equation, the oxygen being furnished by the air which is present in the ore and in the water :

$$Au_2 + 4KCN + H_2O + O = 2KOH + 2KAu(CN)_2.$$

In order to separate the gold from the solution of gold potassium cyanide Forrest precipitates it by introducing zinc or aluminium shavings. W. Siemens, on the other hand, devised a considerable improvement by submitting the cyanide solution to electrolysis

in vessels divided into several chambers in which anodes formed of iron plates or of lead peroxide are placed ; the cathodes consist of thin sheets of lead on which the gold is deposited. At the anode Prussian blue is formed from which KCN is again obtained. Every month the leaden sheets, which now contain 1 to 10 per cent. of gold, are removed, and the gold obtained by cupellation, whilst the lead oxide which is formed is again reduced to lead. The residues from the electrolytic baths still contain 1 to 1·5 grms. of gold per 1000 litres, whilst in the zinc precipitation baths only 0·2 grm. remains. By means of the cyanide process, even 98 per cent. of the gold contained in the tailings and residues from the amalgamation process are to-day recovered, though they sometimes only contain 0·0002 per cent. of gold. These residues are separated by a process of decantation or are extracted two or three times in a filter press with cyanide containing 0·02 per cent. of KCN.

The treatment of gold ores is now facilitated by powdering them more finely than was previously the case, and then using a filter press and cyanide baths which circulate continuously ; in this way the treatment costs less than £1 4*s*. per ton of ore.

One of these electrolytic plants, 7 metres long, 1½ metres wide, and 1 metre high, consumes about 100 amps. at 2 volts and treats 50 cu. metres of solution per twenty-four hours. Since 1900 great economies have been effected in the cost of cyanide by employing the crude cyanide prepared by the Cyanid-Gesellschaft of Berlin from calcium carbide, atmospheric nitrogen, and potash (*see* p. 309).

GOLD REFINING. When gold is admixed with silver and a little copper it is refined by heating it with nitric acid which dissolves all the copper and silver if the silver is present in amount more than double that of the gold, otherwise it is necessary to add some silver.

A better method of refining, accompanied by less loss of silver, is carried out by heating with strong sulphuric acid in which the gold only is insoluble. To-day the electrolytic process of refining by Möbius' process has become common, because it is very economical and yields very pure gold without noticeable losses of silver. The electrolytic bath consists of nitric acid or preferably of a weakly acid solution of silver nitrate. The mass of gold and silver under treatment is used as anode and is surrounded by cotton sacks ; the cathode is formed of silver plates. All the metals of the anode, excepting the gold, which collects in the sacks, pass into solution, and at the cathode all the silver is recovered in a crystalline form.

If an electric current of 350 amps. per square metre at 1 volt is used, the silver has a purity of $\frac{999\cdot5}{1000}$, and the gold after fusion contains $\frac{999}{1000}$.

PROPERTIES. Pure gold is a metal of a lustrous yellow colour, somewhat soft and extraordinarily ductile and malleable (p. 408) ; when in very thin sheets it shows a bluish or greenish colour by transmitted light. Its specific gravity at 17·5° is 19·33 ; it is an excellent conductor of electricity and heat and melts at 1064° forming a green liquid. It is the most resistant of the noble metals because it is only attacked and dissolved by aqua regia (also a little by boiling nitric acid of sp. gr. 1·42), by chlorine and by potassium cyanide in presence of oxygen (*see above*). Mercury dissolves it without alteration, whilst it does not dissolve platinum, so that it is easily separated by this means. It is not oxidised in the air and always preserves its lustre. The compounds of gold are rather unstable, and are decomposed by heat with formation of metallic gold.

Gold has recently been produced in colloidal aqueous solution (p. 105) of red colour, by reducing a dilute solution of a gold salt with formaldehyde, preferably in the presence of sodium silicate. Blue colloidal gold solution is obtained by reducing a dilute and perfectly neutral solution (1 : 10,000) of $AuCl_3$ with a dilute solution (1 : 2000) of hydrazine hydrate.

In dilute solutions of gold salts, carbon monoxide produces a purple coloration due to colloidal gold, and this solution is very sensitive towards electrolytes. Alcoholic solutions of gold chloride, when poured into water, form hydrosols of various colours.

APPLICATIONS. As gold is very malleable, it is employed in the form of leaf for gilding works of art, fabrics, &c. For use in jewellery and coinage gold is always alloyed with copper, and then acquires a redder colour, or if it

is alloyed with silver it acquires a lighter yellow colour. The fineness of gold in jewellery is expressed in carats. The pure metal is called 24-carat gold, and thus 18-carat gold contains 18 parts of gold in 24 (= 75 per cent.).

Gold coinage has a fineness of $\frac{900}{1000}$ (English, Russian, and Turkish coins contain $\frac{916{\cdot}5}{1000}$ of gold). Jewellers produce a pure gold colour on the surface of 18-carat gold by dissolving a large part of the copper from the surface by immersion in a bath of ammonium nitrate, alum, and salt, or in HNO_3 or H_2SO_4. Gold is soldered with an alloy of silver, gold, and copper. In order to recognise gold objects and determine their quality approximately, the object under examination is rubbed on a *touchstone* and compared with another streak made with gold of known strength, by moistening both streaks with HNO_3; the effects obtained are then compared and according as the streak of the object under examination disappears to a greater or less extent the purity of the gold is estimated. Objects are gilded by means of gold amalgam or gold leaf, or electrolytically in the same way as silver.

The world's production of gold in 1895 was 155,160 kilos; in 1904 it was 510,000 kilos of the value of £70,160,000, which was supplied by the principal centres of production (in 1901) as follows: the United States 120,700 kilos, Australia 124,950 kilos, Russia 35,990 kilos, the Transvaal 7433 kilos (in 1898, before the war, the production had reached 117,470 kilos, and to-day it tends to regain its former importance; thus in 1909 21,000,000 tons of ore were treated and gold to the value of £30,920,000 was obtained), Canada 36,807 kilos. The world's production of gold in 1909 represented a value of £91,520,000, of which about one-third was produced in Africa, one-sixth in Australia, and about one-fifth in the United States. The production of gold in Italy was 206 kilos in 1890, 349 kilos in 1894, 15 kilos in 1905, and 72 kilos in 1908. The imports were 5758 kilos in 1905, 4860 kilos in 1907, 5400 kilos in 1908, and 4575 kilos in 1909, and the exports were 1731 kilos in 1905, 298 kilos in 1907, 0027 (?) kilos in 1908, and 828 kilos in 1909. In Italy only two mines are now working, those of Creas and Feuillaz in the province of Novara. They treated 6543 tons of ore containing 10·8 grms. of gold per ton in 1906, and 13,475 tons of ore containing 6·12 grms. per ton in 1907 of the value of £8200. In 1905, Germany produced 3933 kilos of pure gold. The *price* of gold is £137 10*s.* per kilo, and has undergone only very slight variations during the last hundred years, the maximum variation being 8*s.* per kilo, because it serves to establish the value of all other goods and of coinage.

COMPOUNDS OF GOLD

As has already been stated, gold forms two sorts of compounds: *aurous* compounds in which gold behaves as a monovalent element, which are less stable, and *auric* compounds in which it is trivalent.

AUROUS COMPOUNDS

AUROUS OXIDE: Au_2O. This is formed as a dark violet powder when potassium hydroxide is added to aurous chloride, AuCl. It decomposes at 250° into $Au_2 + O$.

AUROUS CHLORIDE: AuCl. This compound is formed by heating auric chloride, $AuCl_3$, to 180°. It forms a white powder insoluble in water, by which it is decomposed on heating.

AUROUS IODIDE: AuI. This separates as a yellow powder on treating a solution of auric chloride with potassium iodide, in an analogous manner to cuprous iodide: $AuCl_3 + 3KI = 3KCl + AuI + I_2$. On heating, AuI decomposes into its components.

POTASSIUM AUROCYANIDE: KCy.AuCy. This compound is formed on dissolving gold in excess of KCN in presence of oxygen, and is thus formed in the industrial extraction of gold. It is readily soluble in water, and is used for electro-gilding.

AUROUS SULPHIDE: Au_2S. This is separated as a grey powder, soluble in pure water, by passing H_2S into a hot solution of gold trichloride. It is reprecipitated from aqueous solution by HCl. It is used in gilding.

AURIC COMPOUNDS

AURIC OXIDE: Au_2O_3. This is obtained on heating a solution of auric chloride with magnesium oxide; the precipitate contains magnesium because it consists of magnesium aurate, $Mg(AuO_2)_2$, and is treated with strong HNO_3; a brown powder of Au_2O_3 then remains, which, after drying, is decomposed at 250° into 2Au + 3O. It is insoluble in water and acids, but is dissolved by alkalis because it has an acid character.

AURIC ACID: $Au(OH)_3$. If the precipitate obtained as above with magnesia is purified with *dilute* nitric acid, a reddish-yellow powder of $Au(OH)_3$ remains. This product does not show any basic reactions, but behaves as an acid and not as a hydroxide. It is insoluble in water and in acids and dissolves in alkalis on account of its acid character, forming salts of a hypothetical **Meta-Auric Acid, AuO.OH**, which may be considered to be derived from auric acid by the separation of one molecule of water. **Potassium Aurate** forms yellow needle-shaped crystals, $AuO.OK + 3H_2O$. It is soluble in water, and has an alkaline reaction. It is formed from the oxide and KOH; on treating it with other soluble salts it forms other aurates. Thus with silver nitrate it forms silver aurate:

$$AuO.OK + NO_3Ag = NO_3K + AuO.OAg.$$

Salts of normal auric acid are not known.

AURIC CHLORIDE: $AuCl_3$ (Gold trichloride). When chlorine or aqua regia act on metallic gold a brown-red deliquescent mass is formed which is soluble in water, alkalis, and ether, and consists of $AuCl_3$. On evaporating the aqueous solution it is partially decomposed into Cl_2 and AuCl. It is soluble in HCl, and on concentrating this solution by heating, long yellow needles separate, which consist of chlorauric acid: $HAuCl_4 + 4H_2O$, of which various well-crystallised salts are known, such as potassium chloraurate, $KAuCl_4 + 2H_2O$, and the ammonium salt, $NH_4AuCl_4 + H_2O$, which may also be considered as double salts, $AuCl_3.NH_4Cl.H_2O$ and $AuCl_3.KCl + 2H_2O$. Sometimes in solution these salts do not form an anion $AuCl_4'$, but behave like gold chloride.

GOLD SULPHIDES: Au_2S_3 and Au_2S_2. On passing a current of H_2S into a *cold* solution of auric chloride, a blackish-brown mass separates which is formed of a mixture of these two sulphides, together with a little sulphur. It is soluble in alkali sulphides, and then forms sulpho-salts (K_3AuS_2, &c.).

Solutions of *gold salts* in general are easily reduced to finely divided metallic gold by ferrous sulphate, oxalic acid, stannous chloride, &c. With this latter reagent, a precipitate of purple-violet colour is obtained which is known as *Purple of Cassius*, and is probably nothing else than a colloidal complex of finely divided gold and stannic acid, and is used for colouring glass and porcelain. This characteristic reaction of gold salts is not always easily produced, and it is necessary to add the stannous chloride slowly drop by drop to an excess of the gold solution.

THIRD GROUP. TRIVALENT METALS

These form the group of the so-called earths or earth metals, a name derived from the properties and appearance of the corresponding oxides, of which aluminium oxide (alumina) is the type. This group is formed of elements with a trivalent cation and includes **Aluminium** (Al = 27·1), and a special group of very rare elements: **Scandium**, Sc = 44·1; **Yttrium**, Y = 89; **Lanthanum**, La = 139; **Ytterbium**, Yb = 172; **Gallium**, Ga = 69·9; **Indium**, In = 114·8; **Thallium**, Tl = 204.

Aluminium has certain resemblances to boron in its valency and in the constitution of many of its derivatives. Thus both the elements are insoluble

in nitric acid and soluble in boiling solutions of alkali hydroxides. Thus, also, boron hydroxide has decidedly acid characteristics and aluminium hydroxide is also acid with respect to strong bases, with which both form salts of the same constitution : $B(ONa)_3$; $Al(ONa)_3$; still, aluminium, on account of its higher atomic weight, also possesses basic and metallic characteristics much more pronounced than those of boron. In general the elements of the sub-group have less basic characters in spite of their high atomic weights.

ALUMINIUM : Al, 27.1

This is an important element, not only on account of the applications which it has found as metal during recent years, but also because it is abundantly and widely present in nature in a state of combination and its derivatives form products of great practical importance. It is not found free in nature, but is abundant in the form of oxide, Al_2O_3, which when pure and crystalline forms *corundum*. When coloured red or blue by small quantities of metallic oxides, it forms *ruby* or *sapphire*. When subdivided into very small rather hard crystals it forms *emery*. It also abounds in the form of hydrates of varied composition and then forms *Diaspore*, $Al_2O_3.H_2O$, in rhombic crystals; *Bauxite*, $Al_2O_3.2H_2O$, and *Hydrargillite*, $Al_2O_3.3H_2O$. In the form of silicate it enters as a most important element into the composition of many rocks and then, when it forms pure white deposits, takes the name of *kaolin*, which forms the prime material for the manufacture of porcelain. In large impure deposits it forms *common clay*, and when combined with various other silicates forms *Felspar*, $(SiO_3)_2Al.KSiO_3$, &c. Aluminium is also abundant in the form of *Cryolite*, which is a double fluoride of sodium and aluminium, $3NaF.AlF_3$ (*see* Soda, p. 476), and is supplied by Greenland to the whole world, more especially for the manufacture of enamels (*see below*), and partly for the manufacture of aluminium and of opaque white glass.

It was first prepared by Wöhler in 1827 in the free state as a grey powder by heating a mixture of aluminium chloride and metallic potassium to redness, and is more easily obtained in small spheres by passing the vapours of aluminium chloride over red-hot potassium.

Aluminium was first prepared electrolytically by Bunsen in 1854 by decomposing a double salt, the double chloride of aluminium and sodium, after others had attempted to decompose aluminium chloride alone without success. The difficulty was caused by the high melting-point of the chloride, and Bunsen lowered this considerably by mixing it with NaCl as Dumas had already done in 1832 in the preparation of potassium, and Wöhler in the preparation of magnesium. In 1854 St. Claire Deville made various attempts to prepare aluminium industrially by employing sodium instead of potassium, together with the vapours of aluminium chloride. He also improved the process of preparing sodium, and thus lowered its price, and consequently the price of aluminium dropped from £48 per kilo in 1855 to £15 in 1856, and in that year Deville succeeded in preparing 30 kilos.

The attempts made by various chemists to obtain aluminium electrolytically, especially from cryolite, $3NaF.AlF_3$, remained without practical results until 1886 when Deville prepared aluminium by a more or less improved process.

In 1883 the first patents of Grätzels on the electrolysis of cryolite were taken out, and in 1884 the brothers Cowles attempted to prepare aluminium from alumina with carbon by heating the mixture with an electric current, but obtained a product of small value. In 1887 the important French patent of P. Héroult appeared, by which it was possible to obtain aluminium at a very low price by the direct electrolysis of fused alumina. The enormous aluminium works at Neuhausen on the Falls of the Rhine were then erected in 1888 and this company immediately united with the Allgemeine Elektricitätsgesellschaft of Berlin, which obtained aluminium by the same method at a low price, according to a patent by Kiliani. In America the manufacture of aluminium in large quantities was started in

1890 by the process of Hall, who electrolysed fused alumina dissolved in fluoride. When these patents were first applied grave difficulties were encountered in the preparation of pure aluminium, and various alloys of aluminium with copper were alone prepared. Pure aluminium was only produced after 1890. To-day aluminium is produced entirely by these two processes, which are constantly being improved.

The technical details of these processes are jealously kept secret by the manufacturers. The great difficulties consisted in finding vessels which would resist external heating to the extremely high temperature of molten aluminium, and were overcome by melting the alumina by means of an electric arc by immersing the electrodes directly into the mass. The electric furnace for the manufacture of aluminium is illustrated diagrammatically in elevation and plan in Fig. 237. The hearth, *K*, of the furnace is formed of suitably arranged compact graphite bricks, *A*, and is held firmly together by an iron box, *a*, through which the copper terminals, *a'*, which are united to the negative pole of the source of current are passed. The anode, *B*, consists of a bundle of carbon plates, *B'*, held together by an armature *g* and *h*, the interspace between these plates being filled with a well-conducting material, such as copper or green wood. This anode is connected with the positive pole through the ring, *h*. The anode is suspended at *e* by a chain in order to be able to immerse it more or less deeply in the molten electrolytic bath. The furnace is covered by a graphite plate, *k*, which allows the anode to move in a vertical direction only in the opening. The furnace is charged and the gases (CO) escape through the openings, *m* and *n*.

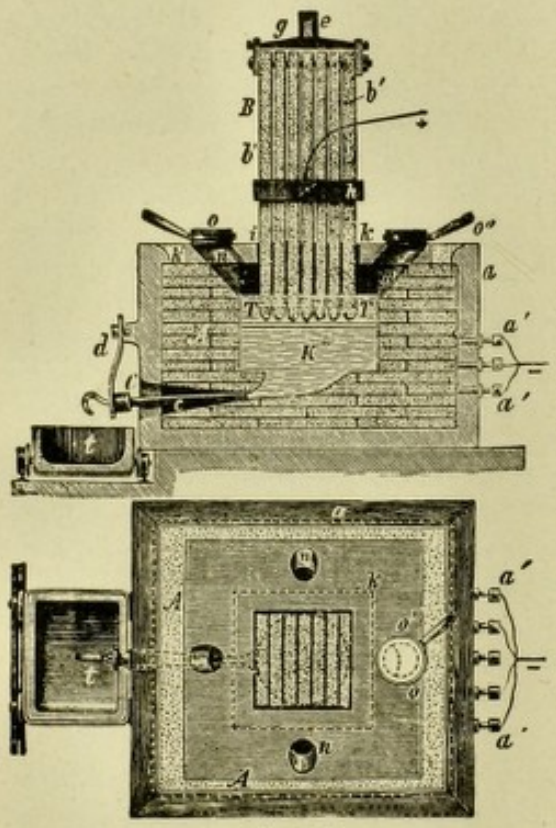


Fig. 237.

In the preparation of aluminium bronze the operation is started by introducing a certain quantity of copper through *k*, and the anode is then lowered until it touches the copper, when this is melted by the passage of the current. Alumina (Al_2O_3) obtained from bauxite (*see below*, Oxide and Hydroxide of Aluminium) is then charged into the furnace, and the anode is raised slowly so that the electric arc between the copper and the carbon passes through the alumina. This melts and gives up oxygen to the carbon of the anode, which is oxidised with formation of CO, and the aluminium which is formed alloys with the copper. The fused alloy is discharged into the carbon vessel, *t*, where it solidifies in blocks.

When metallic aluminium is to be produced, cryolite is added as a flux in a furnace lined with alumina, in the absence of copper, and alumina is then gradually added and rapidly forms molten aluminium. The anode always consists of carbon and the cathode is of iron, but as soon as molten aluminium is formed this acts as a cathode. The molten aluminium, which is formed under a layer of molten material, is extracted by immersing tubes into the melted mass which syphon off the aluminium from below.

The process encountered another difficulty in the impurity of natural alumina, which yielded aluminium containing 2 to 3 per cent. of silicon, which was therefore useless. To-day pure aluminium oxide is artificially prepared from bauxite (*see below*) and thus pure aluminium is obtained which only contains 0·15 per cent. of SiO_2.

According to a recent patent it appears that aluminium can more easily be obtained by the electrolysis of aluminium sulphide, but nothing is yet known as to the practical results.

PROPERTIES. Aluminium is a metal of silvery appearance with a specific gravity of 2·64 to 2·70, which melts at 700°. It is ductile and malleable, but more so at about 100°. It is not altered in the air, because it immediately becomes covered with a very thin layer of air and of adherent oxide which

preserves it from atmospheric corrosion. Hydrochloric acid dissolves it easily and therefore also acetic acid mixed with NaCl, whilst, on the other hand, it is very resistant to the action of cold dilute nitric acid and of sulphuric acid. On account of these properties it is used for the manufacture of tanks and other objects for many industries (cheese factories, fats, eatables, &c.). It also dissolves in alkali hydroxides, especially on heating, with evolution of hydrogen : $Al + 3KOH = Al(OK)_3 + 3H$. Compact blocks of aluminium are oxidised with difficulty on heating, whilst when in the form of very thin foil or as fine powder, it is easily set on fire by a gas flame, emitting a very bright light (*aluminium lamp*). If aluminium filings are brought into contact with a solution of mercuric chloride, *aluminium amalgam* is formed, which is a very active reducing agent, and thus immediately evolves hydrogen in contact with water, forming aluminium hydroxide.

If aluminium is employed as an electrode in a voltameter, it only allows an alternating current to pass when it is connected with the negative pole—cathode—whilst if an aluminium plate is allowed to act as cathode, it does not let the current pass within certain limits, and on account of this property it is utilised as a "rectifier" for alternate currents.

APPLICATIONS. On account of its physical and chemical properties aluminium gave rise to great hopes that it would be employed on an enormous scale, and it was even supposed that it would replace iron and other metals in common use. But its exceptional lightness, its appearance, and its resistance to atmospheric influences did not suffice to establish its general use as had been hoped, and this is more especially due to its lack of hardness. It also easily alters its properties when it contains minimal traces of impurities, such as a trace of sodium, which causes it to be attacked by water. Moreover, it cannot be worked with a file, because it "smears," that is, fills the interstices of the file. Some of these disadvantages can be overcome by suitable additions, such as 2 to 15 per cent. of phosphorus. An important application of aluminium has now been found in *thermite* (*see below*), and it is also used in the form of very fine foil for packages to replace tin foil. In France it is now used for coinage. The automobile factory of Rochet and Scheider at Lyons alone used 28 tons of aluminium in 1904 in the manufacture of 280 motors, in the form of various alloys.

A very important application of metallic aluminium is in the manufacture of its alloys, which are largely used. We will mention the most important of these. *Aluminium bronze* is an alloy of copper containing 3 to 10 per cent. of Al. It has a specific gravity of 8·37 to 7·65, and a golden colour which varies from reddish to bright yellow. When it contains 10 per cent. of Al it melts at 1100°, and is obtained directly in the electric furnace (*see above*), or by pouring Al into molten copper. Its electric conductivity is 13·6 per cent. of that of copper. It is very resistant to the action of acids NaCl, NH_3, S, alkalis, alum, Cl, sulphite, &c.

Aluminium Brass is ordinary brass containing 33 per cent. of zinc, to which 0·5 to 4 per cent. of Al is added. It is easily malleable at a dark red heat, and is sometimes used instead of aluminium bronze, but is less resistant to various reagents. *Magnalium* is an alloy of aluminium with less than 2 per cent. of magnesium (often 1 per cent.), and is obtained by adding Al to an electrolytic bath of molten carnallite. Whilst the two metallic components of this alloy have many disadvantages for practical purposes, magnalium enjoys many advantages, and its properties are so useful that they guarantee it a prosperous future. It has a specific gravity of 2·4 to 2·5, is easily melted and cast ; it does not smear under the file, has a very fine grain, may be turned in the lathe even at high speed, and may be polished like a mirror. It is used for many parts of machinery, for cooking utensils and scientific apparatus, and as it retains its silvery lustre very well, it is suitable for optical mirrors, &c. It costs about £200 per ton. *Zimalium*, a cheaper alloy of aluminium with a little manganese and zinc, has also been recently prepared.

For many years, and to a certain extent to-day, serious difficulties have been encountered

in soldering aluminium. Of the various alloys which are to-day used for soldering, we will only mention one, patented in 1905, formed of 64 parts of tin, 30 parts of zinc, 1 of lead, and 1 of aluminium. To-day, however, aluminium can be perfectly welded autogenously by the oxy-acetylene blow-pipe (p. 176) by coating the point to be welded if necessary with a thick aqueous solution of potassium chloride, sodium chloride, lithium chloride, and potassium disulphate mixed in various proportions in order to prevent oxidation during heating. In order to determine whether other foreign metals are present in a soldered part, M. Schoop in 1907 immersed the soldered portion in water feebly acidified with HCl ; hydrogen is only evolved at the soldered point when foreign metals are present.

We have mentioned above that finely divided aluminium easily burns in a flame forming Al_2O_3. This property was ingeniously applied in 1898 by Hans Goldschmidt of the firm of Krupp in order to obtain very high temperatures (over 2000°), at which even the more resistant oxides, excepting MgO, are reduced to the free metals :

$$Cr_2O_3 + 2Al = Al_2O_3 + Cr_2.$$

It is possible in this way to obtain extremely pure metals by the reduction of their oxides, whilst they were formerly obtained by reduction with carbon and the resulting metals were impure. The heat of formation of aluminium oxide is 1255 Kj. (300,000 cals.), and this explains the great stability of this oxide even at the highest temperatures, and the enormous quantity of heat which is evolved in its formation.

H. Goldschmidt prepared **thermite**, which is a mixture of equal parts of iron oxide and finely divided aluminium. If the temperature at one point of this mass is raised by heating it with a match formed of a magnesium wire, which ends in a small sphere of aluminium powder and barium peroxide, then the mass becomes heated at that point and the ignition gradually extends throughout the whole of the mixture, reducing the iron oxide to metallic iron with formation of aluminium oxide and evolution of an extraordinary quantity of heat, which melts the iron which is formed. Thermite thus renders it possible to weld wrought and cast iron objects and broken parts of machinery by surrounding the point to be welded with a metallic box filled with thermite. On starting the ignition, the molten iron accumulates at the point to be soldered and the repairs are so reliable that there is no further danger of breaking at that point. Repairs to ships and very heavy machinery are thus carried out at a minimal expense, whilst at one time it was necessary to dismount the large pieces in order to transport them to workshops at an expense of hundreds of pounds. The rails of tramways and railways are to-day welded in this manner, so that they form single pieces a mile or more in length, in which form they last much longer ; it has now been found that it is not necessary to leave a small space between one length of rail and another as was formerly believed. Of recent years better results have been obtained with a mixture of powdered aluminium and calcium or with a powdered alloy of these two metals instead of aluminium alone. Pure powdered silicon is also used, mixed with calcium, instead of aluminium.

PRICES AND STATISTICS. Whilst there were only 2 or 3 aluminium works a few years ago, there are more than 10 in full activity to-day, which together employ about 60,000 hydraulic horse-power, of which 10,000 are utilised at Niagara Falls, 4500 at Neuhausen on the Rhine, 5000 at Rheinfelden, &c. In 1908 a new English company was formed for the production of aluminium in Switzerland, with a capital of £1,200,000. The world's production in 1883 was 2 tons, in 1888 71 tons, in 1893 716 tons, in 1896 1790 tons, in 1898 4024 tons, in 1900 7743 tons, in 1905 10,000 tons, in 1906 14,500 tons, and in 1907 19,800 tons, of which 8000 were produced in the United States, 6000 in France, 4500 in Germany, Austria, and Switzerland, and about 1000 tons in England. In 1904 France produced 1500 tons and in 1903 exported 662 tons; in 1906 about 1470 tons and in 1909 more than 4400 tons. In Italy the manufacture of aluminium was only started in 1906 at Bussi in the Valle di Pescara by treating bauxite of Lecce nei Marzi by the "Società italiana per la fabbricazione di alluminio," which has a capital of £120,000 and is affiliated to the "Società elettrochimica" of Rome ; in 1908 3 series of small furnaces were working, comprising 50 furnaces in all, and produced 600 tons of aluminium ; in 1910 a fourth series of furnaces was at work. Bauxite deposits have recently been discovered on the left bank of the Liri. In 1907 Italy imported 538·3 tons of aluminium and its alloys, in 1908 442·1 tons and in 1909 490 tons.

The movements of the price of aluminium illustrate the development of this interesting

industry very effectively. In 1855 1 kilo of aluminium cost £50, in 1857 £12 (*see above*), in 1874 £8, in 1886 £3 8*s*., in 1890 12*s*., in 1895 3*s*. 2½*d*., in 1902 2*s*.; in 1906 it rose to 3*s*. 7*d*. per kilo on account of the large demand, and in 1909 it fell again to 1*s*. 2½*d*. and to 1*s*. 5*d*. in 1910 on account of the large production by the older and newer works, which attempted to form an international trust in 1909 in order to raise the price, but did not succeed in coming to an agreement. In spite of the present low price, the Aluminium Gesellschaft of Neuhausen in Switzerland has paid the following dividends to shareholders: 16 per cent. in 1904, 18 per cent. in 1905, 22 per cent. in 1906, and 26 per cent. in 1907.

ALUMINIUM COMPOUNDS

ALUMINIUM OXIDE: Al_2O_3 (Alumina). In nature this occurs as *ruby*, *sapphire*, *corundum*, and *emery*, which are very hard and have a specific gravity of about 3·9. Rubies and sapphires may be prepared artificially by melting alumina with lead oxide at a red heat in a porcelain capsule. The lead aluminate which is first formed decomposes by acting on the silica of the capsule and deposits crystals equal to those found in nature, which are coloured ruby red if a little potassium dichromate is added to the fused mass, or blue if a little cobalt oxide is introduced.[1]

Amorphous Al_2O_3 is obtained by heating aluminium hydroxide or other compounds. It is soluble in acids, but if it has been previously heated to redness for some time it becomes insoluble, and the only way of then obtaining it in solution is to fuse it with potassium carbonate or potassium disulphate.

The industrial preparation of pure aluminium oxide has to-day acquired great importance because it forms the prime material for the manufacture of aluminium (*see above*). It is obtained from cryolite and to a larger extent from *bauxite*, in various ways. According to Bayer's process, the bauxite, $Al_2O(OH)_4$,[2] is calcined and pulverised, mixed with a little lime and then treated with a sodium hydroxide solution of 45° Bé. at a pressure of 3 to 4 atmospheres. (Bauxite for the manufacture of aluminium should not contain more than 0·2 per cent. of silica.) Sodium aluminate soluble in water is thus obtained. It is filtered hot, washed, and to the clear solution after suitable dilution about two-thirds of pure gelatinous aluminium hydroxide is added. The whole is then stirred continuously in large vats for 5 or 6 days, after which time all the sodium aluminate is dissociated and all the alumina is precipitated in the pure state, together with that originally added. It is separated in a filter press and all the sodium hydroxide then remains in solution and is reutilised (*see also* Fr. Pat. 373,070 of 1906). Formerly a current of CO_2 was passed into the sodium aluminate solution and this first precipitated pure aluminium hydroxide and afterwards the silicates, whilst a solution of sodium carbonate remained which was reutilised in the process. An excess of sodium hydroxide is more effective in preventing the precipitation of silica. The hydroxide obtained by the Bayer process is free from iron and silica, contains 40 per cent. of water, and after drying forms a white powder consisting of the oxide, Al_2O_3.

Pure alumina is also prepared in the electric furnace by mixing powdered bauxite with coal, and with a flux, such as Na_2CO_3, cryolite, or calcium fluoride, and also sometimes Al and Fe_2O_3 (a borate is still more effective; Ger. Pat. 205,790 of 1908). All the impurities collect as a slag in the very fusible alloy of aluminium and iron or iron silicide which is easily separable.

[1] **Artificial Rubies.** Of the various methods of manufacture, the most recent, Verneuil's process, deserves mention. A solution of aluminium sulphate containing iron as an impurity is mixed with one of chrome-alum and precipitated with ammonia; the precipitate is first dried in the air, then raised to a cherry-red heat and finally melted in the oxy-hydrogen flame. Drops weighing about 20 grms. and 1·5 cm. in diameter are removed from the molten mass and allowed to solidify; all gradations of colour are so obtained varying with the quantity of chrome-alum which was added. About one ton of artificial rubies is manufactured yearly.

[2] The question whether there are important deposits of bauxite in Italy has been discussed for some time, but until a short time ago it was almost unknown. Recent researches of Mattirolo and analyses by Formenti have however proved the presence of notable surface deposits (1,000,000 sq. metres of a thickness of 3 metres) at Lecce nei Marzi on the slope of Monte Turchio. This bauxite contains 50 to 55 per cent. of aluminium and 3 to 4 per cent. of silica (SiO_2), but the contents of iron sometimes exceed 25 per cent. of Fe_2O_3, and this explains how the engineers of the Bureau of Mines erroneously classified these minerals as iron ores. They are now the property of the "Società italiana per la fabbricazione di alluminio," who treat and purify these ores in their works at Bussi.

When aluminium oxide is heated in a current of chlorine in presence of carbon, it forms aluminium chloride, $AlCl_3$. Refined anhydrous alumina of 98 to 99 per cent. in the form of a heavy powder costs £40 per ton, whilst in the form of a light powder it costs £84.

ALUMINIUM HYDROXIDE: $Al(OH)_3$. As already noted above, this compound occurs in nature as *diaspore*, *bauxite*, and *hydrargillite*. It is obtained as a gelatinous mass by treating a soluble aluminium salt with NH_3, alkali hydroxide, or alkali carbonate: $2AlCl_3 + 3CO_3Na_2 + 3H_2O = 2Al(OH)_3 + 3CO_2 + 6NaCl$. The hydroxide is soluble in NaOH, but not in NH_3 (*see below*). The hydroxide is prepared industrially by Löwig's process, by treating a solution of sodium aluminate with milk of lime:

$$2AlO_2Na + Ca(OH)_2 = 2NaOH + (AlO_2)_2Ca.$$

The dissolved sodium hydroxide is reutilised for the preparation of sodium aluminate, whilst the precipitated calcium aluminate is dissolved in HCl:

$$(AlO_2)_2Ca + 8HCl = CaCl_2 + 2AlCl_3 + 4H_2O.$$

On then mixing the solution of $AlCl_3$ with calcium aluminate in the exact proportions indicated by the following equation, pure aluminium hydroxide is precipitated:

$$2AlCl_3 + 3(AlO_2)_2Ca + 12H_2O = 8Al(OH)_3 + 3CaCl_2.$$

The purification of bauxite has also been described in the preceding pages.

The freshly precipitated hydroxide can be dissolved in a solution of aluminium chloride or acetate, and on then subjecting this solution to dialysis (p. 102) the chloride or acetate diffuses through the membrane, whilst a colloidal aqueous solution of the hydroxide remains. This has a weakly alkaline reaction and is coagulated by traces of acids, alkalis or salts.

Freshly precipitated aluminium hydroxide dissolves in acids and in alkali hydroxides, forming *aluminates* AlO.ONa; when the hydroxide is dried it no longer dissolves in acids.

The aluminates may be considered as derivatives of **Aluminium Meta-hydroxide**, AlO.OH, which is formed by cautiously heating the ordinary hydroxide until one molecule of water is eliminated. If a soluble salt of the alkali earth metals, magnesium, &c., is added to the aqueous solution of an alkali aluminate, a precipitate of the aluminate of calcium, magnesium, &c., is formed:

$$2AlO.ONa + CaCl_2 = 2NaCl + (AlO.O)_2Ca.$$

Various crystalline minerals, known as *spinelles*, are found in nature, which correspond in constitution to these aluminates, for example:

$$\begin{matrix} AlO.O \\ AlO.O \end{matrix}\!\!>\!Mg, \quad \begin{matrix} AlO.O \\ AlO.O \end{matrix}\!\!>\!Be, \quad \begin{matrix} AlO.O \\ AlO.O \end{matrix}\!\!>\!Zn, \text{ &c.}$$

Aluminium hydroxide behaves both as a weak base and as a weak acid, so that it is able to form salts both with strong acids and with strong bases.

Thus freshly precipitated $Al(OH)_3$ dissolves in NaOH or in HCl, but these salts are not very stable and are already decomposed by carbon dioxide or ammonium chloride with precipitation of the hydroxide. Salts which are formed with strong acids have an acid reaction in aqueous solution and those formed with strong bases have an alkaline reaction because they are in part *hydrolytically dissociated* by water in a similar manner to any other salts of strong acids with weak bases or weak acids with strong bases. Their general behaviour is explained by hydrolytic dissociation due to the ionisation of minimal traces of water into $H^{\cdot}$ and OH'.

In the salts formed from weak bases and strong acids in aqueous solution one part of the cation unites with a few OH' anions of ionised water forming neutral molecules, and free $H^{\cdot}$ cations of the water thus remain and produce an acid reaction. The OH' anions having disappeared, other molecules of water are ionised and a further portion of the cations of the salt is hydrolysed, thus increasing the acid reaction until a certain equilibrium is reached. In the case of salts formed of strong bases with weak acids, their aqueous

solution has an alkaline reaction because a portion of their anions are hydrolysed with the $H^{\cdot}$ cations of the ionised water molecules, and OH' anions of the water are liberated, which impart the alkaline reaction to the solution. The strong alkaline reaction of sodium and potassium carbonate (p. 436) is thus explained, as their aqueous solutions are strongly hydrolysed.

When sodium carbonate or ammonium sulphide is added to a solution of an aluminium salt aluminium hydroxide is precipitated instead of the carbonate or sulphide as occurs in the case of various other salts; chromium salts behave similarly. This apparent abnormality is logically explained by the instantaneous hydrolysis of the carbonate or sulphide of aluminium (or of chromium) which occurs at the instant of their formation in presence of much water, because, being formed of a very weak base and very weak acids (H_2CO_3 and H_2S), they are completely hydrolysed by excess of water with evolution of CO_2 or H_2S and separation of gelatinous aluminium hydroxide.

Freshly prepared aluminium hydroxide precipitates many dyestuffs (alizarine and anthracene dyestuffs) from their solutions, forming insoluble combinations of various colours which are called *lakes*. This reaction is utilised with the help of solutions of aluminium acetate or also of sodium aluminate, for mordanting fabrics by impregnating them with these solutions. On heating, the acetate is then decomposed with formation of acetic acid, and aluminium hydroxide remains in the fibre. On then immersing the fabric in a bath containing the dyestuff, the colour is fixed in the tissues through the formation of these lakes.

Waterproof fabrics are obtained by impregnating the materials with aluminium acetate and then heating them. All the pores of the fibres are thus filled with the gelatinous hydroxide which is then transformed into insoluble aluminium oxide. The fabrics lose all their capillarity and are no longer wetted by water.

STATISTICS AND PRICES. Commercial aluminium hydroxide in paste form costs £20 per ton; the dry substance in powder costs £52 per ton; sodium aluminate in solution (25° Bé.) costs £18, and the solid with 40 per cent. of Al_2O_3 £28 per ton; commercial aluminium acetate in solution (10° to 12°) costs £9 4*s.* per ton, and of 14° to 15° Bé. £14. Bauxite of good quality costs £2 to £2 8*s.* per ton, and Germany imported 39,325 tons in 1905. The purest product is used for the manufacture of aluminium and the least pure for the production of refractory materials. In 1908 Italy produced 7000 tons of bauxite of the value of £2520, and in 1902 imported 420·4 tons of aluminium hydroxide of the value of £4010; in 1907 390 tons, in 1908 360 tons, and in 1909 455 tons of the value of £4360. France possesses the largest bauxite deposits in the world, especially in the Department of Var; in 1907 it produced 430,000 tons of bauxite and in 1908 191,000 tons, and in 1907 it exported 110,000 tons of the value of £88,000. Austria imported (from Germany) 2657 tons in 1905, 3160 tons in 1906, 4840 in 1907, and 3670 tons in 1908 of the value of £40,000. The United States of America produced 48,130 tons of bauxite in 1906 of the value of £48,000.

ALUMINIUM CHLORIDE: $AlCl_3$. This substance is prepared by passing a current of dry gaseous HCl over fragments of aluminium heated in a porcelain tube or also from Al_2O_3 and carbon when heated in presence of chlorine. The chloride which distils condenses as a white crystalline mass of hexagonal scales which are deliquescent and very hygroscopic. It is easily hydrolysed by water, and in order to maintain it in solution without separation of $Al(OH)_3$ it is therefore necessary that a little HCl should be present. On concentrating the aqueous solution by heating it is easily hydrolysed with evolution of HCl and separation of the hydroxide. One method of carbonising wool is based on this reaction. Wool is carbonised in order to destroy the vegetable residues which are found mixed with it, and this is affected by aluminium chloride because whilst wool itself resists the moist HCl vapours at 120° quite well, the straw and cotton are attacked and carbonised or incinerated. Ordinarily, however, dilute sulphuric acid is used for carbonisation. When aluminium chloride is pure it fumes in the air and boils at 183°. At 440° its vapour density corresponds to the formula Al_2Cl_6, whilst at 760° it corresponds to $AlCl_3$.

It is soluble in water, alcohol, and ether. A solution of $Al(OH)_3$ in HCl is used as a disinfectant. Certain double salts of little importance are also known :

$$AlCl_3.NaCl\ ;\ AlCl_3.PCl_5,\ \&c.$$

A commercial solution of $AlCl_3$ of 30° Bé. costs £10 per ton. The anhydrous solid costs £58 per ton.

ALUMINIUM SULPHATE : $Al_2(SO_4)_3 + 18H_2O$

This compound is formed on dissolving clay (aluminium silicate) or preferably bauxite or aluminium hydroxide, free from iron, in sulphuric acid of 66° Bé., heated to 100° in a copper vessel. When the solution is saturated, that is, when on adding further aluminium hydroxide no more frothing occurs, the solution is poured whilst still hot into large leaden pans $2\frac{1}{2}$ to 3 metres long, 2 metres wide, and 15 to 20 cm. deep. The mass is then stirred continuously with wooden spades to avoid the formation of lumps during solidification. The blocks which are formed are then broken and enclosed in barrels.

In order to obtain the purest product, free from acid, it is redissolved in hot water and the aluminium sulphate is allowed to crystallise in scales of sp. gr. of 2·71. The aqueous solution, when treated with an insufficient quantity of NH_3, separates a basic sulphate, $Al_2\begin{cases}(OH)_4\\SO_4\end{cases} + 7H_2O$ (*aluminite*). Lately the price of aluminium sulphate has fallen somewhat—to £4 16*s* to £6 per ton—and it may therefore be employed in place of alum as a mordant in the dyeing of alizarine and anthracene colours, but it must be free from iron as otherwise this forms dark violet lakes which deaden the other shades ; it may also be used for tanning hides, for hardening cardboard, purification of water, &c.

Aluminium sulphate unites with the alkali sulphates to form double salts which crystallise in large octahedra or cubes and are called *alums*, such as potash alum, $Al_2(SO_4)_3.K_2SO_4 + 24H_2O$, and there are many such alums, because the potassium sulphate may be replaced by the sulphates of other monovalent metals, Na, Rb, Cs, Tl, and NH_4 ; and, on the other hand, Al may be replaced by other trivalent metals, such as Fe, Cr, V, Mn, Co, Ti, &c. Thus, for instance, there is an iron potash alum, $Fe_2(SO_4)_3.K_2SO_4 + 24H_2O$; a chrome sodium alum, $Cr_2(SO_4)_3,\ Na_2SO_4 + 24H_2O$, &c. All these alums are isomorphous (p. 111) and form mixed crystals in any proportions (p. 112), and since they are differently coloured (chrome potash alum has a violet-red colour and iron alum a deep violet colour) they may be superposed in the same crystal, forming variously coloured layers. The constitution of alum may be more simply represented by the following formula :

$$\begin{matrix}SO_4 \equiv Al\\SO_4 < K\end{matrix} + 12H_2O,$$

but in aqueous solution the alums have no characteristic ions of their own, but show the reactions of the component salts (aluminium sulphate and potassium sulphate), so that they must be considered as true double salts (p. 414), and not as complex salts, like the ferrocyanides, potassium ferricyanide, &c. (*see* Iron).

Potassium Alum, $Al_2(SO_4)_3.K_2SO_4 + 24H_2O$, is called *common alum*, and is prepared at Tolfa, near Rome, from an abundant mineral, *alumite*, which is a basic alum, $(SO_4)_2AlK.Al(OH)_3$. This is first roasted at 500° and then extracted with hot water, when the hydroxide remains undissolved. On concentrating and cooling the solution, pure *Roman alum* crystallises in cubes. Alum is also prepared from cryolite and from bauxite or from aluminium

silicate with H_2SO_4, by adding a solution of potassium sulphate to the aluminium sulphate solution which is so obtained, and then allowing the alum to crystallise.

Potash alum dissolves in 10 parts of cold water or in 0·75 part of boiling water, and shows an acid reaction because it is hydrolysed (p. 239). Alum heated to 120° loses water and forms *burnt alum* as a white voluminous mass.

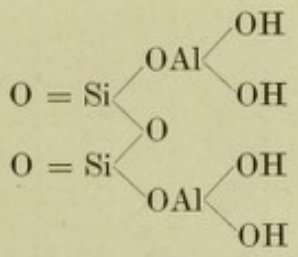
Alum is used for the same purposes as were mentioned for aluminium sulphate ; it is also employed in medicine and for hardening plaster of Paris.

STATISTICS. Commercial crystallised alum costs £8 per ton ; the refined product, free from iron, costs £14, burnt alum £24, and Roman alum £30. Chrome alum and commercial iron alum cost about £16 per ton.

In 1893 Italy produced 2000 tons of aluminium sulphate, 2200 tons in 1904, and about 3000 tons in 1907 of the value of £10,760 ; in 1909 Italy imported 1650 tons of aluminium sulphate and alums, and exported 580 tons ; 3170 tons of alum were produced in Italy in 1907, and 2900 tons in 1908 of the value of £13,320. Germany produced 2500 tons of alum and 500 tons of aluminium sulphate in 1874, and 4460 tons of alum and 3100 tons of sulphate in 1890 ; in 1902 it produced 50,000 tons of aluminium sulphate (4270 tons of alum and 5580 tons of aluminium sulphate in 1905) and in 1909 it exported 28,600 tons. Austria consumed 12,000 tons of aluminium sulphate in 1909.

ALUMINIUM SILICATE (KAOLIN, CLAY)

CERAMIC INDUSTRY. Various double silicates of aluminium and the alkali metals occur abundantly in nature in the various rocks, *leucite* $(SiO_3)_2AlK$, *albite* $(SiO_3)_2AlNa.SiO_2$, and *orthoclase* or *felspar* $(SiO_3)_2AlK.SiO_2$. On exposure of these rocks rain water removes alkali silicates, and large deposits of aluminium silicate are formed which, when pure and white, is known as *kaolin,* which is a pure aluminium silicate, $Al_2O_3.2SiO_2 + 2H_2O$, or :



When impure and transported to some distance from the original rock it is coloured brown by various iron oxides and forms *common clay,* which is one of the principal constituents of the soil. Pure, finely divided clay possesses marked plasticity, that is, it has the property of taking up much water to form a paste capable of being moulded, which becomes very hard and contracts to the extent of 20 to 40 per cent. on baking in suitable furnaces and melts if the temperature is sufficiently high. After baking, it has lost all plasticity, even when powderd very finely. Clay and kaolin constitute the prime materials of the ceramic industry for the manufacture of bricks, earthenware, and porcelain. However, apart from plasticity, it should be refractory to a high degree, that is, it should resist the action of heat without melting, because in order to render the porcelain hard and compact, it must be heated to very high temperatures.[1] Kaolin for porcelain manufacture should not become

[1] *High temperatures are measured* with electric pyrometers (*see* Rhodium) or more commonly by means of the so-called Seger cones, which are small lengthened triangular pyramids, 6 cms. high and with a base of 2 cm., formed of aluminium silicate and more or less alkali and lime. They are stamped with conventional numbers to which definite temperatures correspond (*see* Table on next page). If they are introduced into a furnace of which the temperature is to be measured, then by observing which cone commences to be vitrified and then softened;

coloured on fusion and should not effervesce with acids (absence of carbonates). Clay for castings, fireclay, pumice stone, &c., have all a basis of aluminium silicate, but also contain free siliceous quartz and other impurities.[1]

Sand as an impurity influences the plasticity unfavourably, whilst iron and lime alter it very little. Magnesia, and also lime to a less extent, diminish the refractory properties. Good commercial kaolin contains 43·5 to 46 per cent. of SiO_2, 39 to 39·8 per cent.

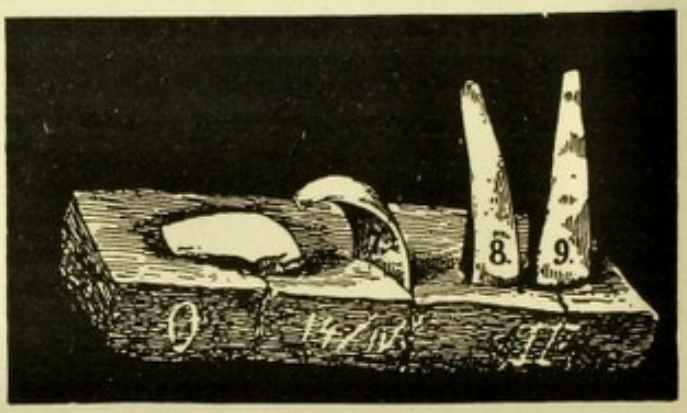


FIG. 238.

of Al_2O_3, and 13 to 13·9 per cent. of water. Ceramic materials may be divided into two groups: **Compact** materials which are semi-vitrified and semi-fused, translucent, very hard,

and bends until its point touches the floor or the tile on which it is placed, the temperature is determined (*see* Fig. 238).

Number of cone	Melts at about	Number of cone	Melts at about	Number of cone	Melts at about	Number of cone	Melts at about
022	590°	08	990°	7	1270°	26	1650°
021	620°	07	1010°	8	1290°	27	1670°
020	650°	06	1030°	9	1310°	28	1690°
019	680°	05	1050°	10	1330°	29	1710°
018	710°	04	1070°	11	1350°	30	1730°
017	740°	03	1090°	12	1370°	31	1750°
016	770°	02	1110°	13	1390°	32	1770°
015	800°	01	1130°	14	1410°	33	1790°
014	830°	1	1150°	15	1430°	34	1810°
013	860°	2	1170°	16	1450°	35	1830°
012	890°	3	1190°	17	1470°	36	1850°
011	920°	4	1210°	18	1490°	37	1870°
010	950°	5	1230°	19	1510°	38	1890°
009	970°	6	1250°	20	1530°	39	1910°

[1] **Fireclay** for the preparation of firebricks should not only have a definite chemical composition and a high melting-point, but also a dense and compact physical constitution. The composition of fireclay should be about 43 to 47 per cent. of SiO_2, 37 to 39 per cent. of Al_2O_3, 1 to 1·5 per cent. of Fe_2O_3, 0·2 to 0·8 per cent. of CaO, 0 to 0·4 per cent. of MgO, 0·4 to 0·7 per cent. of alkali, and 12 to 15 per cent. of loss in weight on ignition; but in order to render it more infusible this clay is mixed with other clay previously baked several times, for instance, with fireclay bricks which have been previously used and are then called *chamotte*. It is then coarsely ground and is used to thin down other fatter clays which have, however, the density and compactness of fireclay and renders it less easily attacked by basic ashes in the furnace in which it is employed. Clay and chamotte are mixed by millstones or vertical stones; after the mass has been slightly moistened, it is then compressed into bricks in suitable moulds. The bricks are baked in furnaces at a temperature between Seger cones 10 and 20 (*see* preceding Note).

Still more infusible materials (for example, *Dinas bricks*) are obtained by adding quartz or by starting from quartz sand which is mixed with 2 per cent. of gypsum and 1 per cent. of aluminium sulphate, as the particles of quartz then become cemented at the plastic point during baking.

A mass containing 92 to 94 per cent. of SiO_2 and 4·5 to 5·5 per cent. of Al_2O_3 is thus obtained; these bricks are used for building the arches of glass kilns, but are sensitive to temperature fluctuations and slightly increase in volume on baking.

The infusibility increases with *Bischoff's coefficient*: $\frac{Al_2O_3 + SiO_2}{\text{bases}}$; by the term "bases" the sum of the oxides of Fe, Ca, Mg, K, and Na is here understood and should not exceed 3 per cent. of the total altogether, but for inferior materials is sometimes as much as 7 per cent. Increase of Al_2O_3 increases the refractory properties of the brick and its resistance to chemical agents. The melting-point is lowered to the same degree whatever

impermeable to water and do not adhere to the tongue, and comprise true *glazed porcelain* (soft and hard), *statuary porcelain* or unglazed biscuit-ware, and *stoneware*, glazed or unglazed, semi-vitrified, but not semi-fused, and non-adherent to the tongue.[1]

Porous Ceramic Materials which are not vitrified, have an earthy fracture, absorb water, adhere to the tongue, and include (1) *majolica*, with an opaque superficial glaze and dark internal body; (2) *terraglia* (*fine faience*) with a white, porous internal body and transparent glaze; (3) *coarse earthenware*, more or less coloured with an opaque glaze of various colours; (4) *bricks* or constructive materials of baked clay, unglazed and refractory; (5) *plaques, tiles, and terra-cotta*, ordinarily coloured red.

PORCELAIN is manufactured by working up kaolin to a paste with felspar and well-powdered quartz in definite proportions, so that the porcelain may become less porous, contract less and take a better glaze. At high temperatures in suitable furnaces the felspar and quartz melt, and are incorporated by the kaolin, forming a very hard compact mass. The kaolin is obtained in a very fine powder by means of systematic levigation; the felspar and the quartz are rendered more friable by first heating them in a furnace and then powdering them in ball mills (p. 512), or by submitting the powder to regular levigation with water. The pulverised material is freed from iron particles from the machinery by passing it over magnets during levigation. The paste is prepared in various proportions in different works, for example, 45 to 65 parts of kaolin, 10 to 30 parts of quartz, and 5 to 20 parts of felspar, and these ingredients are intimately mixed in large vats by stirring with water; the homogeneous paste is collected in filter presses in a compact form, and is then allowed to stand for some time in a moist spot where it undergoes a kind of putrefaction (maturing) which somewhat increases its plasticity by the formation of colloidal substances (*see* p. 102); during this maturing process there is a slow evolution of CO_2, NH_3, and H_2S. After this it is repeatedly kneaded and rekneaded until it is ready

may be the base which is introduced if equimolecular proportions are taken, so that 1 mol. of MgO produces the same depression as 1 mol. of CaO, and thus for equal weights of MgO and CaO it is lowered more by the MgO because this has a lower molecular weight. In very basic minerals, such as *talc* ($3MgO.4SiO_2$), the alumina, Al_2O_3, lowers the melting-point. Thus, on mixing talco, which melts with Seger cone 31, and kaolin ($Al_2O_3 + 2SiO_2$), which melts with cone 36, a product is obtained which melts with cone 11. The addition of silica to clay lowers the melting-point (acid silicates) and the maximum depression is obtained with a proportion of 1 mol. of clay and 17 mols. of SiO_2, and for equal contents of SiO_2 that mixture melts at a lower temperature which contains the SiO_2 in a more finely divided state. Materials of coarse grain resist temperature fluctuations better than those of fine grain.

In 1907 Italy imported 8450 tons of fireclay bricks and in 1908 5500 tons of the value of £112,000.

In 1909 Germany exported 170,000 tons of refractory materials and imported 35,000 tons.

Foundry clay. The best qualities contain 80 to 90 per cent. of SiO_2, almost entirely in the form of siliceous quartz, and 15 to 18 per cent. of alumina with traces only of lime and magnesia. This product comes from France (Boulogne) and costs 2*s.* 5*d.* to 3*s.* 2*d.* per ton on the spot; at Milan it costs £1 to £1 4*s.* per ton, including freight.

The clays which are found in Italy are of poor quality and cost 4*s.* 10*d.* to 9*s.* 8*d.* at Milan. Near Pavia and Cavamanara there are poor qualities of foundry clays which cost 4*s.* 10*d.* per ton at Milan.

Pumice stone is a volcanic mineral forming a more or less spongy mass, often of fibrous structure and of grey colour, of sp. gr. 2·2; it is used for polishing stones and metals. When powdered it is agglutinated with sodium silicate and then forms bricks and artificial pumice. In powder form it costs £6 to £10 per ton; in large pieces it is much lighter and costs up to £20. Italy produced 15,000 tons in 1908, valued at £24,000.

[1] Stoneware has acquired great importance to-day for the manufacture of drain-pipes and conduits for impure liquids of acid or weakly alkaline reaction. It is also very largely used for the most varied chemical plant (receivers, rings for towers, cocks, heating stoves, serpentine coils, various condensing and distilling plant, &c.), and generally has a semi-vitrified surface and brownish-grey or yellow-brown colour, which varies according to the quantity of iron silicate contained in the clay from which it is formed. This should contain little or no calcium carbonate, but sufficient quantities of fluxes (alkali silicates, felspar, and quartz) to allow the paste to be directly exposed to baking, because the higher the fusion point of these fluxes, the higher will be the softening point of the clay, up to Seger cone 26, and if they are present it may fall to a much lower temperature (cone 4).

The colour varies also with the reducing or oxidising character of the flame in the kiln, being grey when this has a reducing action and yellow when it has an oxidising action, and the colour is more intense with rise of temperature. The best qualities of clay for stoneware are found in Germany along the Rhine and the Elbe and in Nassau; much is also found in Bohemia, and it is not lacking in various parts of Italy, but is of inferior quality. The composition varies considerably, but may be corrected by levigation or by addition of fatter or leaner clay and also by addition of chamotte powder (*see* preceding Note); the chemical composition generally varies between the following limits: SiO_2 60 to 70 per cent., Al_2O_3 20 to 25 per cent., Fe_2O_3 0·8 to 1·8 per cent., CaO + Mgo 0·5 to 1·2 per cent., $K_2O + Na_2O$ 1·5 to 3·5 per cent., H_2O 4 to 9 per cent. (together with organic matter). The best clays approximate to 70 per cent. of SiO_2 and 22 to 23 per cent. of Al_2O_3. The ware is baked in the same manner as porcelain, and in order to obtain the surface glaze sodium chloride is thrown into the furnace or into the gases during burning towards the end of the baking when the furnace has a temperature of 7–8 Seger cone. The sodium chloride is decomposed by the steam in the gases into HCl and NaOH. This latter forms a mist which covers the surface of the stoneware objects and vitrifies it, forming an alkali aluminium silicate. The vitrification may also be obtained by dipping the unbaked ware into a glaze consisting of a suspension of brick clay and a little limestone, or of a pulverised mixture consisting of 17 parts of felspar, 7 parts of marble, 5 parts of kaolin, and 11 parts of quartz. On baking at 1300° to 1400° the articles should undergo practically no alteration of shape if the raw materials are homogeneous and of good quality. The finished and baked ware should show no efflorescence on the surface when filled with water, even after 20 or 30 days.

for modelling, which is carried out with various instruments and perfected machinery which allow the work to be performed rapidly and exactly—wheels, moulds, &c. The modelled objects are allowed to dry slowly in the air, and then undergo a first baking in suitable furnaces so that they may acquire a certain degree of hardness, after which they are more readily handled and glazed. A type of furnace commonly used is that illustrated in section in Fig. 239, and contains three floors communicating with one another by flues left open in the vaults. In the upper floor, *A*, the first baking of the porcelain is carried out by setting it down cautiously in boxes of refractory clay covered and placed on one another in stacks in such a way that the gases from the hearth, *e*, do not stain the articles. In this chamber the temperature reaches 900°, and this suffices to remove all the chemically combined water from the porcelain. When the objects have cooled they are removed from the chamber and are glazed in a bath containing an aqueous suspension of a powdered mixture, the glaze or enamel, composed of kaolin or felspar, sand, and marble.

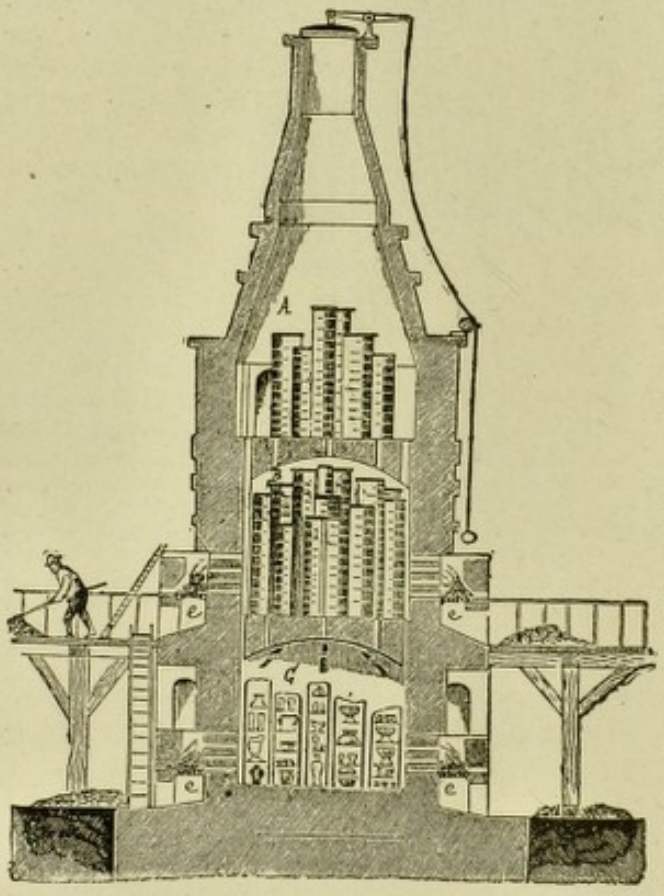


Fig. 239.

The components of the glaze melt at the temperature at which the porcelain is baked, forming an enamel which becomes transparent and hard in the cold.[1]

The objects are then placed in their respective clay boxes and arranged in stacks in the two other chambers of the furnace, *B* and *C*. It is necessary to carefully regulate the temperature, and also still more the nature of the gas which is used for heating the porcelain. The furnaces are heated with wood or coal by means of five hearths (*e*) on each floor. To-day Siemens' regenerative furnaces are often used (p. 500) and allow an almost white heat to be attained. Before reaching this temperature, however, the gases should be of a reducing character in order to destroy the yellowish colour of the porcelain due to iron oxide, Fe_2O_3, but at certain periods the gas should be slightly oxidising in character in order to burn the carbon which is enclosed in the material. The temperatures are nowadays exactly determined by means of electric pyrometers which read the temperature of the kiln at any moment, even at a distance. The kilns are to-day constructed of refractory material and work continuously, and when one chamber is heating the other is cooling, whilst the third is discharged and recharged. The cooled material is removed and is checked in order to remove defective pieces from those which are satisfactory.

Egg-shell porcelain is much used in France and in England. It does not contain kaolin, but is formed of a vitreous mass consisting of an alkali earth silicate which is covered with a lead glaze of the same composition as flint glass. It melts easily and has

[1] Enamels for metallic objects (for cooking and for chemical purposes) are to-day prepared from mixtures free from lead and containing a little tin oxide. On the tile or iron object heated in a muffle a fusible enamel is first placed, for example, 17 parts of quartz, 30 of felspar, 46 of borax, 2 of soda, 3 of sodium fluosilicate 2 of saltpetre, 0·18 of cobalt oxide, 0·42 of nickel oxide, and 0·03 of copper oxide; the whole is melted and, after cooling, is ground with the addition of 7 per cent. of clay or kaolin. On to this fusible enamel an opaque, white shining enamel is then superposed, consisting of the following mixture: quartz 10·5, felspar 37·5, borax 18, cryolite 12, and nitre 0·7 parts. This mixture is melted and after cooling is ground with the addition of 7 per cent. of kaolin and 8 per cent. of tin oxide. At one time tin oxide was used in order to obtain white, opaque enamels to the extent of 40 per cent., but it is now partially replaced by cryolite, and this has recently been replaced by sodium fluosilicate which is still cheaper.

the appearance of a milky glass, translucent and devitrified. It is obtained by mixing 60 parts of sand, 23 of potassium nitrate, 7 of sodium chloride, 3·5 of soda, 3·5 of gypsum, and 3·5 of burnt alum. This mixture is heated (*fritted*), and the product is pulverised and mixed with 17 per cent. of chalk and 8 per cent. of *marl* (aluminium silicate mixed with calcium carbonate). Egg-shell porcelain, glazed or unglazed, is used for many ornamental objects and is better suited than hard porcelain for coloration in very varied tints.

Bricks and Tiles are to-day manufactured with the help of highly perfected machinery. Comparatively impure and coloured clay is more or less suitable for the manufacture of bricks. Chalky clay, which contains much calcium carbonate and gypsum, forms bricks which change their volume greatly in the kiln, as they lose CO_2 and H_2O, but then swell up and crumble on exposure to the air. The composition of clay for bricks should be within the following limits: SiO_2, 43 to 61 per cent.; Al_2O_3, 26 to 39 per cent.; MgO, 0 to 1·5 per cent.; CaO, 0 to 1 per cent.; Fe_2O_3, 0 to 2·5 per cent.; $Na_2O + K_2O$, 0 to 5 per cent.; SO_3 (as sulphates), 0 to 2 per cent.; loss on ignition (CO_2, &c.), 7·35 to 18 per cent. Fragments of small siliceous pebbles are harmful as they swell during baking and then burst the bricks. Pyrites is also harmful because the iron sulphide which

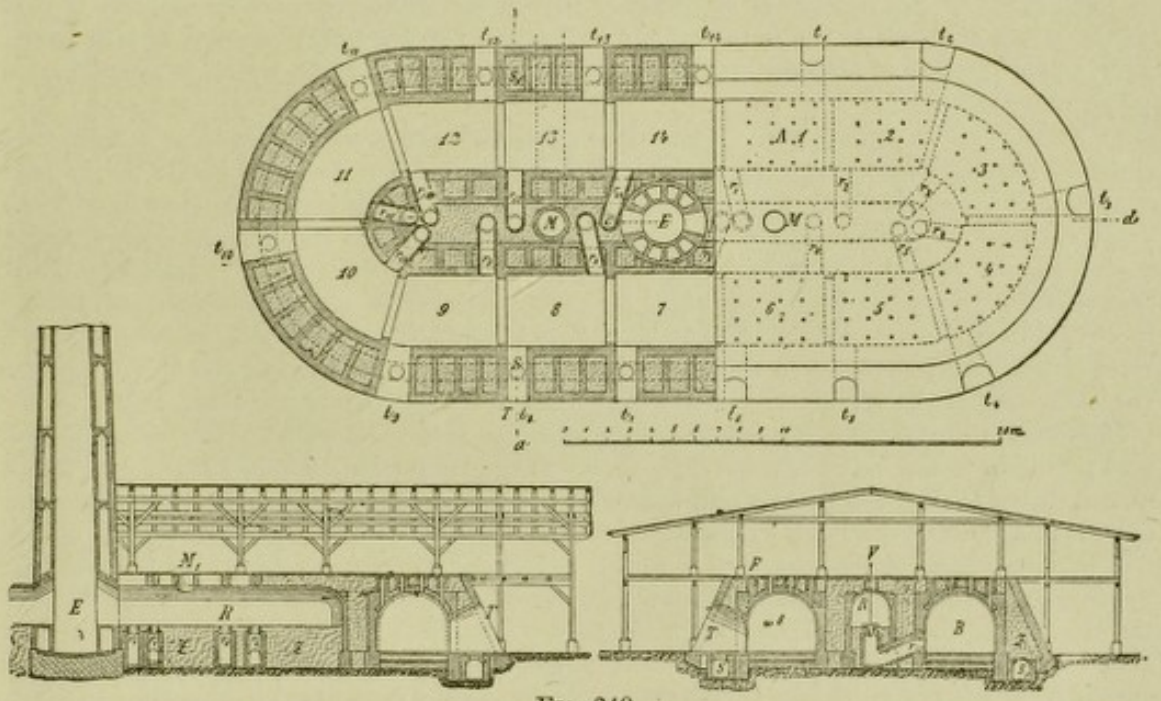


Fig. 240.

is formed in the kiln becomes oxidised to the soluble sulphate in the air, and the bricks become friable. One cubic metre of clay weighs 1·5 tons. After the preparation and maturing of the clay it is worked to a paste and the mixture is shaped into bricks, which operation is now carried out by highly perfected machinery which we cannot describe here. The crude bricks, after drying in the air or in hot gases, are baked in suitable kilns, either open or closed, which at one time worked intermittently, but are now generally worked continuously. Of late years the annular kiln of Hoffmann (1860) has been much used and has undergone many improvements. In Fig. 240 we see it in section, and at the bottom to the right is a transverse section of the chambers, 8–13, or *B*, and to the left a longitudinal section of the kiln which has fourteen chambers, 1 to 14, forming a long single passage in which the walls dividing one chamber from the other are removed provisionally when one or the other is to be emptied or filled with the material. Each chamber has a door (t_1 to t_{14}), and at the diagonally opposite corner an outlet flue (r_1 to r_{14}) for the gases, with an opening adjustable by the valve, *V*, leading into a common flue, *R*, which carries the products of combustion to the chimney, *E*. Of the 14 chambers, 12 are charged with bricks (each of them being capable of holding more than 10,000), whilst one chamber, for example, No. 1, stands empty, and the last one, for example, No. 14, is being charged. If an iron dividing wall is introduced between chambers 13 and 14, and all the doors, t_2 to t_{14}, and all the flues, r_{14}, r_1 . . . r_{12}, shut down, the door, t_1, and the flue, r_{13}, being left open, then the chimney, *E*, will draw in a current of gas and air, which, entering through

the door, t_1, will pass into the chamber, A_1, then into A_3 . . . up to chamber 12, and will then escape along the flue, r_{13}, and reach the chimney.

The current of gas cannot travel in the opposite direction, because the wall between 13 and 14 is closed, whilst all the other chambers are without dividing walls.

The heat is produced from wood or coal which is introduced into several vertical channels, F, in the vault of each chamber, and the gas and the air which enters cold at t, cool the already baked material and enter hot into the first chamber, and thus in turn the gases get continually hotter, so that near chamber 8 they acquire a maximum temperature which suffices, together with the fuel, to bake the bricks in the sucessivee furnaces. Work is continuous, because with one movable door one may successively isolate one chamber for discharging and another for charging. The Hoffmann kiln has undergone various small modifications, but the fundamental principle on which it is based is always the same.

For several years this same furnace has also been applied in the hydraulic cement industry, for which very high temperatures are required, higher than those which are necessary for the preparation of bricks (*see below*).

The more or less red colour of bricks is due to the greater or smaller amount of iron oxide in the clay. The tile industry has undergone notable improvements of late years, and Upper Italy has already started an important export trade which is certain of a successful future.

STATISTICS. Considerable quantities of kaolin are also employed as a weighting material in the manufacture of paper. In Italy there are deposits of kaolin in the provinces of Saluzzo, Novara, Vincenza (at Tretto near Schio), Civitavecchia (at Tolfa), Pisa, Bologna, and in Sicily. These kaolins are well adapted for the preparation of white majolica, and 15,500 tons were produced in Italy in 1902, whilst that required for hard porcelain was imported from England. In 1902 about 14,000 tons of the value of £2200, in 1907 16,534 tons, in 1908 22,877 tons, and in 1909 22,900 tons of the value of £38,496 were imported ; four-fifths of this came from England, which supplies the best qualities. Germany imported 248,736 tons of kaolin in 1909 and exported 27,000 tons.

The ceramic industry is continuously progressing in Italy, and whilst in 1885 earthenware and porcelain to the value of more than £120,000 were imported, in 1901 the imports diminished to less than £80,000, over and above an internal production of more than £600,000, of which £320,000 is provided by the works of Richard-Ginori at Florence and Milan alone, which is the most important in the world, especially for artistic ware and for ceramic paintings. In 1903 Italy produced 23,000 tons of refractory materials and stoneware (25,500 tons in 1908 of the value of £68,000), 36,000 tons of majolica and common earthenware (in 1908 more than £540,000, and 2280 tons of majolica and artistic ceramic ware for £67,240), and 4000 tons of porcelain (the exports of porcelain in 1908 were worth £143,520). In 1904 1400 tons were imported at £80 per ton, and 2400 tons were exported of the value of £15,200.

The Italian imports were 10,200 tons of stoneware in 1907, 9500 tons in 1908, and 8500 tons in 1909 of the value of £9600, one-fifth of which was fine stoneware, and the exports were 224 tons in 1909 ; the imports of majolica were 1050 tons in 1907, 1350 tons in 1908, and 850 tons in 1909 of the value of £9440. The exports were 320 tons in 1907, 310 tons in 1908, and 225 tons in 1909 of the value of £3600. The imports of pottery were 820 tons of white and 7414 tons of coloured and ornamental pottery in 1907, 115 tons of white and 804 tons of coloured and ornamental in 1909 of the value of £60,000 ; the exports in the same years were 448, 348, and 538 tons of white, and 1817, 1357, and 446 tons of coloured and decorated respectively of the value of £18,400 altogether in 1909 ; the imports of white *porcelain* were always about 1850 tons of the value of £84,000, and of coloured and decorated porcelain about 1000 tons of the value of £84,000 ; the exports were about 120 tons of white and 90 tons of decorated, of the value of £14,800 altogether.

In 1909 Italy imported only 900 tons of bricks, tiles, &c., and 5000 tons of terra-cotta of the value of £42,000, whilst the exports were 12,500 tons of bricks and common and glazed tiles in 1907 and 8000 tons in 1909 of the value of £34,400.

The Italian production of bricks and tiles in 1908 was 6,087,380 tons of the value of £2,064,680, and that of terra-cotta (stoves, pipes, flower vases, &c.) was 80,100 tons of the value of £281,120 (in 1890 the production of these articles was 3,600,000 tons, and in 1903 4,793,000 tons).

ARTIFICIAL BRICKS AND STONES (Arenolite or siliceous-argillaceous-calcareous stone). This industry has now acquired great importance in various countries after twenty years of experiment and persistent work,[1] and it will certainly not be long before it also develops in Italy where there are already two works. Of the numerous patents which now exist, those based on the Girard-Meurer process possess special industrial importance.

When intimately mixed and compressed, lime and silica combine rapidly under the simple action of high-pressure steam, forming a compact mass of calcium silicate which is more or less hydrated.

Girard improved the materials by adding a very small quantity of raw clay which gives a harder stone in a shorter time. The artificial stones are thus siliceous-argillaceous-calcareous agglomerates, forming a hardened hydraulic cement under the action of high-pressure steam.

Powdered quicklime is used in the proportion of 1 part of lime to about 10 parts of hot, dry, siliceous sand; a little powdered, raw clay (not calcined; to the extent of about 3 per cent. of the lime) is then added, and after moistening with hot water (30 per cent. of the weight of the lime in order to just obtain the hydroxide) the whole is well mixed and a

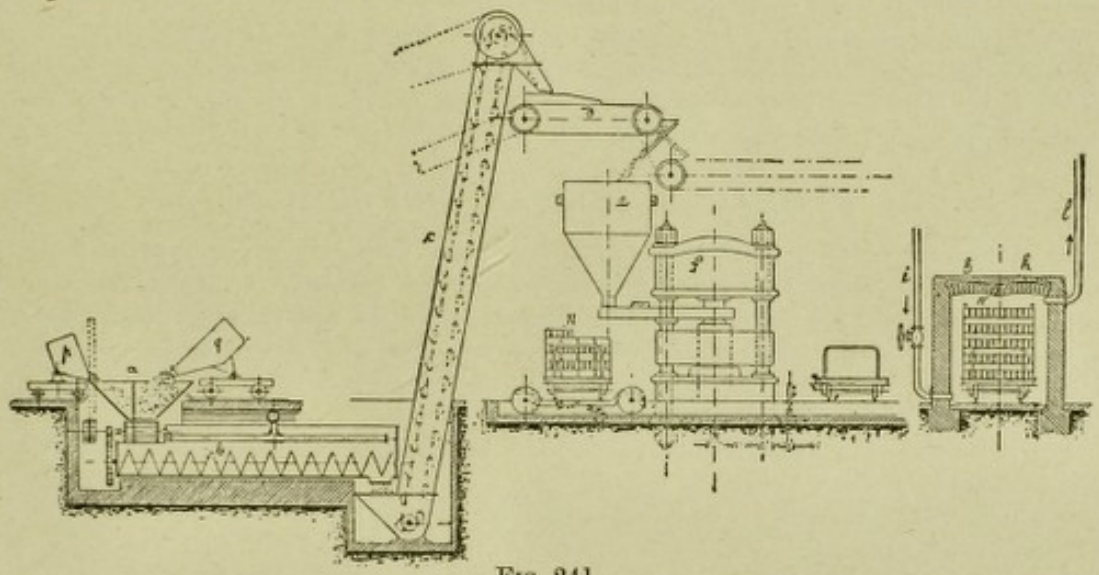


FIG. 241.

further 7 per cent. of the total weight of hot water is added in order to enable bricks of compact form to be more easily obtained in the presses. On removal from the press, the bricks are arranged on cars and introduced into suitable furnaces in which they are exposed to high-pressure steam.

In order that the final result should be good, it is indispensable that the quicklime should be completely slaked and that the physical nature of the sand (fineness and the round or jagged form of its particles, &c.) should be taken into account. In the case of fine quartzose sand, a comparatively small quantity of lime is needed.

An excess of lime must be avoided because if this remains unaltered, it absorbs CO_2 from the air and deteriorates the quality of the bricks. When these have been moulded, they should not remain exposed to the air, but should immediately be treated with steam under pressure.

The necessary arrangements are shown diagrammatically in Fig. 241. The hot material is carried to the hopper, *a*, in cars, *p* and *q*; from these it passes into the mixer, *b*, and thence

[1] Dr. Zernikow in 1877 was the first to mix siliceous sand with freshly slaked lime, and he exposed the mixture to the action of steam under pressure (5 to 8 atmospheres) for 6 to 12 hours. After this the mass was moulded into shapes and compressed. Stone of the highest qualities, which is more fully described above, thus resulted. In 1880 Michaelis showed that this was due to the action of steam at high pressure on silica. Others, on the other hand, first pressed the bricks and then exposed them to the action of high-pressure steam for 3 to 6 days (Gressy, Neffgen, Meurer, Becker and Klee, 1882 to 1898). Pfeiffer in 1894 and then Olschewsky in 1898 endeavoured to produce hardening of the stone by utilising the heat which is evolved in the slaking of the lime, but did not meet with much success. The manufacture of artificial stone only became practical in 1899, when every uncertainty was removed through the improvements of Meurer and the modification then introduced by Girard, that is, by adding clay as a new component. Many works now use the process of Girard-Meurer in almost every country. In Germany there are more than 200 works, and of these the Guttmann works near Berlin alone produce more than 200,000,000 bricks per annum.

along the elevator, *c*, and an endless band, *d*, to the vessel, *e*, from which the homogeneous mixture passes into moulds in order to be strongly compressed in the press, *f*. The bricks which are thus compressed are loaded on to cars, *n*, and passed into the furnaces, *h*, which now consist of horizontal iron autoclaves up to 20 metres in length and 2 metres in diameter, into which compressed steam at a pressure of 8 to 10 atmospheres is introduced through the pipe, *i*. After 8 to 10 hours the reaction is complete and the bricks are immediately ready for use (they are placed in the furnace in the morning, the steam is let off in the evening and they are removed on the following morning). In order to increase the compactness of the surface of these bricks, they are exposed to the action of hydrofluoric acid vapours, or are immersed in a solution of HF, and an extremely hard surface layer of calcium fluoride is thus formed, which resists the action of moisture, carbon dioxide, &c.[1]

The advantages of these artificial stones consist in the great regularity of shape, without deformation, and of resistance to pressures of 400 kilos and more per square centimetre ; they may also be employed for work under water ; they are bad conductors of heat, very resistant to fire, as hard as cement, are able to be painted or varnished directly, and can be used immediately after manufacture ; they absorb less water than ordinary bricks and dry rather more rapidly. Light artificial bricks, either compact or perforated, are now produced with infusorial earth (kieselguhr).

The installation of a works for manufacturing such stone costs less than that of a brick-kiln and requires less space and less manual labour. The price of 100 bricks of the ordinary size (6 × 13 × 26 cm.) varies from 9*s*. 7*d*. to 12*s*. 10*d*.[2] The works in Berlin and neighbourhood annually produce 400,000,000 arenolite bricks.

HYDRAULIC MORTAR AND CEMENT

In almost all modern brickwork construction the employment of hydraulic mortar and cement is continually acquiring greater importance, not only for special work under water, but partially for replacing ordinary mortar. In the hardening of mortar (p. 490) we have seen that the silica of the sand does not take part except to an insignificant extent, and that the hardening depends almost exclusively on the action of CO_2 on lime with formation of hard calcium carbonate.

But if, on the other hand, ordinary limestone containing a little clay and sand is heated to a temperature much below its melting-point, and the resulting lime then quenched with a little water, reducing it to powder, then on heating gently it hardens very quickly without any considerable increase in volume and forms *hydraulic cement*. The proportion between the clay (aluminium silicate) and the lime is called the *hydraulic index* (*see below*), and this in the case of *weakly hydraulic cements* (which give a residue of 10 to 15 per cent. with acids) formed from limestone with 5 to 8 per cent. of clay oscillates between 0·10 and 0·15 ; for *medium hydraulic cements* yielding 15 to 20 per cent. of residue with acids and produced from limestone containing 8 to 15 per cent. of clay, it varies from 0·15 to 0·30 ; for *common hydraulic cements* yielding a residue of 20 to 25 per cent. with acids and formed from limestone containing 15 to 19 per cent. of clay, the hydraulic index varies

[1] In the preparation of bricks by Michaelis' process, that is, by treatment with compressed steam, it has been observed that the amount of silica which combines with the lime to form calcium hydrosilicate increases with the pressure, and that at 10 atmospheres twice as much is combined as at 5 atmospheres. When fine sand is used, twice the amount of combined silica (7 to 8 per cent.) is obtained as when coarse sand is used (3 to 4 per cent.). In any case, however, only half the sand which is employed takes part in the reaction, but the amount which reacts may be increased slightly by compressing the bricks very strongly and employing fine sand. The hardness of the bricks is proportiona' to the quantities of combined silica and of uncombined lime, which in the course of time is transformed into carbonate. The use of superheated steam (200°) is not found to offer any advantage.

In the manufacture of artificial stone by Neffgen's process (the action of steam for 3 to 6 days without pressure at 99 to 99·5°) it has been observed that only 0·5 to 1 per cent. of the silica combines, whether little or much lime is used, or whether the sand is fine or coarse, or whether the steam acts for a longer or shorter time. The hardening these afterwards acquire is due to the formation of carbonate.

In either case the addition of clay does not appear to be of any advantage; in fact the addition of any other ingredient to the mixture of lime and silica is generally harmful or superfluous. The employment of lime produced from dolomitic materials, that is, materials rich in magnesia, does not matter, and only causes the cooling to be a little slower. Apart from pure fat limes, excellent results have also been obtained with medium hydraulic limes, for example, with one containing 12 per cent. of SiO_2, 1·85 per cent. of Fe_2O_3, 3·10 per cent. of Al_2O_3, 79·6 per cent. of CaO, 0·61 per cent. of MgO, and 3 per cent. of CO_2, water, &c.

[2] A works for the production of 50,000 artificial bricks daily would cost about £12,000 in all, and the daily expenditure would be as follows : 150 cu. metres of sand, 12*s*. ; 12 cu. metres of lime, £5 12*s*. ; 2·8 tons of coal, £3 12*s*. ; lubricants, repairs, and various expenditure, £1 12*s*. ; 40 workmen, £4 16*s*. ; supervision, administration, general expenditure, &c., £2 ; amortisation and interest, £4 12*s*. ; daily total £29, so that each 1000 bricks will cost about 11*s*. 7*d*. (These figures add up incorrectly.—*Translator*.)

between 0·30 and 0·42, whilst for *strongly hydraulic cements*, yielding up to 30 per cent. of residue with acids, the index varies from 0·40 to 0·45, and they are obtained from limestone containing 19 to 21 per cent. of clay.

Above these limits we enter the category of true cements which harden more rapidly and strongly and are produced by heating argillaceous limestone, marls, &c., or from artificially prepared but chemically similar mixtures.

The **Hydraulic Cement of Palazzolo on the Oglio** is obtained from a deposit in a hill on the lake of Iseo. It is placed in kilns similar to lime-kilns and mixed with 12 to 14 per cent. of coal. Burnt lime more or less rich in free calcium oxide is formed at the bottom, mixed to form a conglomerate, that is, partially semi-molten into lumps. It is placed in heaps and then moistened after one or two days with a little water in order to slake the quicklime, remixed, then heated till it swells and falls to powder, and then after 7 to 10 days it is passed into a stamp and then to mills (tube mills, *see below*, Cement). This hydraulic lime is sold at 12*s.* per ton.

In 1906 Italy produced 466,000 tons of hydraulic cement of the value of £289,600, and in 1908 481,000 tons ; the exports were 1230 tons.

We have already seen in connection with the production of arenolite that lime combines with silica with formation of calcium hydrosilicate if the mixture is heated in presence of steam under pressure, but if heated until they commence to fuse, certain rocks formed of aluminium silicate and calcium carbonate (calcareous marls) liberate CO_2 from the limestone, and a mixture (cement) of calcium silicate and aluminate remains, which is more or less basic and capable of being rapidly decomposed by water, forming a very hard mass :

$$6CaO + Al_2Si_2O_7 = 2Ca_2SiO_4 + Ca_2Al_2O_5.$$

With water this mixture reacts as follows :

$$(a) \quad Ca_2Al_2O_5 + 5H_2O = 2Ca(OH)_2 + Al_2(OH)_6$$

$$(b) \quad Ca_2SiO_4 + 2H_2O = CaH_2SiO_4 + Ca(OH)_2.$$

If the hardening of cement takes place in the air, the calcium hydroxide which is formed combines with the CO_2 of the air and forms calcium carbonate. Cements are partially attacked by mineral acids, but less by sulphuric acid (*see below*, Theory of the Setting of Cement).

NATURAL CEMENTS. In ancient times mortars for use under water were already known, and the Romans used the volcanic material of Pozzuoli and other places (from the neighbourhood of Viterbo, &c), the *terra di Santorino* (a Greek island), and the *trass* which abounds in the Rhine Provinces.[1] After the time of the Romans these natural hydraulic cements were no longer used for many centuries, and it was only in 1841 that Weiler showed the importance of the earth of Santorino for the preparation of modern cements. These products, which are generally known as hydraulic cements, do not harden under water, even if finely powdered, but acquire this property on mixing them with fat limestone, without the necessity for previous baking. For instance, 1 part of the natural cement may be mixed with 1 to 2 parts of lime and 1 part of sand.

ROMAN CEMENT. This product is obtained by calcining argillaceous limestone containing much silica in continuous furnaces mixed with coke, but maintained at a temperature lower than that of a lime-kiln and always below the melting-point of the mixture. In this way all the CO_2 is driven off, but the whole of the lime should not combine with the silica and alumina. Since the ground and finished product contains uncombined calcium oxide, it becomes slightly heated on mixing it with water but hardens rapidly, even in fifteen minutes. though it gives a product which is less resistant than Portland cement. For masonry which is to be constantly covered by water it is used in the pure state, but for

[1] The compositions of these three products which form natural cements are as follows :

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	$Na_2O + K_2O$	H_2O
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Pozzuolana . . .	45–60	15–20	12–20	6–9	4–6	4–6	8–10
Terra di Santorino . .	68·5	13·3	5·5	2·4	0·7	7·7	1
Trass	55–58	22–24	0·7–1·6	2·5–3·9	1·3–1·8	4·5–9·6	3–7·5

other work it is mixed with from 1 to 6 parts of sand. The composition of Roman cement ordinarily varies within the following limits: SiO_2, 13 to 29 per cent.; $Al_2O_3 + Fe_2O_3$, 10 to 20 per cent.; CaO, 40 to 58 per cent.; MgO, 2 to 5 per cent.

NATURAL AND ARTIFICIAL PORTLAND CEMENT

In 1756 J. Smeaton perceived that all burnt cements which contained alumina and silica, which were thus, therefore, only partly soluble in nitric acid, differed from ordinary limestones and mortars through the property of hardening even under water; this important observation was confirmed and applied practically by J. Parker in 1796. From that time attempts were made in many countries to discover natural cements, and very important deposits were actually found, especially in France, England, and Belgium. In the Grenoble mountain a seam 4½ metres thick was discovered, which from 1842 until to-day has furnished the famous cement of the Porte de France.[1]

So far only natural cements obtained by burning argillaceous limestone had been used,[2] but Vicat in France showed by a series of experiments, started in 1812 and continued for many years, that still better cements, which set more rapidly, could be prepared artificially from mixtures of suitable chemical composition. Important practical applications of

[1] In Italy the first and most important region where cement-forming materials were found is that of Casale Monferrato where more or less hydraulic mortar has been prepared from time immemorial. In 1850 there were 10 cement factories in work at Casale, and the production was about 5000 tons per annum, but the first rational cement furnace was constructed in 1859 by Costantino and Ubaldo Cerrano when the railway to Casale was constructed.

The prime material was obtained from the hills of Casale, Pontestura, and especially of Ozzano, where the better limestone was mixed with layers of siliceous limestone (marly limestone), from which it was carefully separated, and the siliceous material was thrown away. It was only later, about the year 1876, that the manufacture of true Portland cement was started by utilising precisely that same siliceous and marly material which had been thrown away for so many years.

It was mainly on the initiative of G. Cerrano and P. Sosso that the "Società anonima, fabbrica calci e cementi," of Casale Monferrato, was founded in 1873, and in time became the most important works in Italy for the production of natural slow-setting Portland cement, producing 50,000 tons in 1907. The share capital of this concern is £200,000. Casale cement has a tendency to set rather too rapidly, and is therefore corrected during manufacture by the addition of 2 to 3 per cent. of gypsum. The importance of the Portland cement industry in Italy to-day is shown by the statistics given later.

The surface of available limestone in Casale has been estimated at about 20 sq. kilometres, but of late years other important deposits have been found below those of Casale, Ozzano, and Pontestura. These various deposits are superposed and were formed at various epochs, separated by centuries, at the bottom of a prehistoric sea, were then dislocated and raised by cataclysms and earth movements, and to-day the stratifications of the Casale hill dip at an angle of 40° to 60° to the horizon. The various banks of argillaceous limestone which form the available seams are 4 to 6 metres thick, and of graduated composition, which ranges from a marl for hydraulic cements with limestone of micro-crystalline structure, to a more siliceous marl for slightly hydraulic cements and a very argillaceous limestone and finally clay of earthy appearance. They do not contain free silica and the combined silica is always present in double the quantity of the alumina and iron. The ratio between the clay and calcium carbonate is very variable and the deposits are richest in clay at the lower part, and thus various qualities of limestone are obtained which are called by various local names: *marmorina* (the richest in limestone), *dura*, *bastardella*, *molle*, *magra* (the richest in clay), &c.

During the first few years the most advantageously placed deposits, that is, those nearest the surface, were exploited or excavated to a depth of a few dozen metres into the same. For some years past, however, the exploitation of the less accessible seams has been started by excavating galleries several hundred metres long and shafts down to a depth of 100 metres. For this reason the prime material costs more than double that which was at first obtained, namely, up to 6*s*. 5*d*. per ton at the works.

It is generally considered that the Casalese deposits belong to the upper layers of the eocene period, and it is probable that they originally had a thickness of 1000 metres or more. It is now maintained by others that these deposits do not belong to the eocene, but to the miocene period, and they deduce this from the fact that imprints of fossil shells, characteristic of the latter period, are sometimes discovered in the seam. These imprints are, however, extremely rare and certainly doubtful. Others also do not admit that the actual position of these seams is due to upward displacement due to earth movements, but to other causes which have not yet been properly determined.

Not long ago a calcareous deposit was discovered in Dalmatia, suitable for slow cements. According to the geologists, this also belongs to the eocene period and differs from the Casale deposits in the fact that these seams are 20 metres thick and are considerably more homogeneous than the Monferrino deposits.

[2] The compositions of certain natural rocks, argillaceous limestones, marls, &c., used for natural cements are:

	SiO_2	Al_2O_3	CaO	CO_2	MgO	Fe_2O_3
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Stone for Portland cement . .	12·05	20·3	34·58	27·17	—	3·0
,, from Porte de France (slow) .	15·8	26·6	28·91	22·72	0·20	—
,, ,, Palazzolo (slow) . .	7·7	12·9	40·72	32·50	1·00	2·0
,, ,, Casale Monferrato . .	11·1	18·7	33·21	26·50	1·20	4·0
,, ,, the shores of the Black Sea	13·5	4·8	44·40	35·00	0·10	1·35

these studies were made in England by J. Aspdin in 1824, who obtained a high-class hydraulic cement which he called *Portland cement* by heating a mixture of slaked lime and clay to a very high temperature. He called it Portland cement because on treatment with water it formed a hard mass of similar colour to the Portland stone which was at that time highly prized for building purposes in England.

From that time the Portland cement industry developed very greatly in England. The first French works was erected in 1850 and the first German works in 1852. In Italy the first attempts were made at Palazzolo in 1858, and these have led to the formation of a great national industry of recent years, the principal centres of which are in Bergamasco,[1] at Ponte Chiasso in Como, in Veneto, and to-day also in various other parts of Italy. In all these places modern plants and perfected machinery are used.

From the first chemical investigations of the cement showed that this was almost entirely formed of calcium silicate and aluminate, together with iron, magnesium, and alkali silicates as impurities. It has also been found that the best qualities of natural cement contain the lime, alumina, and silica in very definite proportions, varying within narrow limits. There is generally limestone (calcium carbonate) and clay (aluminium silicate) mixed very intimately, almost molecule to molecule, without the necessity for any machinery to mix it more completely. On burning at 1300° to 1400° carbon dioxide is evolved and a partial chemical combination occurs between the lime, alumina, and silica, although the mass is simply sintered by the heat, and not fused. The resulting product has very great powers of reaction with water with which it sets and generally forms very stable and compact hydrates, insoluble in water, and almost unattacked by dilute acids.[2]

[1] The first attempts to manufacture artificial Portland cement in Italy were made at Palazzolo on the Oglio in 1858, but were only successful about the year 1864. In 1865 the Ministry of Public Works already prescribed the use of the products of the new "Società Bergamasca per la fabbricazione dei cementi e delle calci idrauliche" for all public works, and this company thus became the powerful "Società Italiana dei cementi e delle calci idrauliche di Bergamo," with various works at Villa di Serio, Pradalunga, Comenduno, and Palazzolo on the Oglio (1872). In these latter works, since 1877, apart from the preparation of hydraulic cements, a great impulse was given to the manufacture of artificial Portland cement by coarsely grinding a mixture of marl and pure limestone obtained from the hill on the Lake of Iseo, and then adding by means of an automatic balance a definite quantity of lime which is produced as a residue in the manufacture of hydraulic cements. It is not necessary to dry this mixture because the quicklime serves as a drying agent, and it is finally ground in a tube mill (*see below*), and is then moistened and transformed into bricks which are dried in the air under a shed for a couple of months. After this it is dried, baked in Dietzsch furnaces, and then ground in the usual manner (*see below*).

The Società di Palazzolo amalgamated in 1906 with the works of Filli Pesenti with a total share capital of £240,000 and a possible output of 300,000 tons per year of hydraulic, natural, and artificial Portland cements.

[2] *Theory of the setting and hardening of cement.* Cut and polished plates of Portland cement were microscopically examined almost simultaneously in 1897 by Törnebohm and by Le Chatelier, and led to the discovery of four fundamental components of cements:

(1) *Alite* is the most abundant. It forms colourless crystals which are very refractive, feebly doubly refract ve, and of rectangular or hexagonal section.

(2) *Belite* has a dirty yellow colour and is slightly opaque; it shows vivid interference colours. It has two optical axes and its refraction is fairly strong. It forms small round grains without recognisable crystalline form. These are sometimes striated, sometimes in two directions which cut one another at variable angles.

(3) *Celite* is of a deep orange-yellow colour. It is strongly doubly refractive. It is sometimes present in the form of small rods, especially in cements which have been only slightly burnt. In well-burnt cements it forms a filling between the other elements of the stone and gives the cement its colour because it contains a maximum quantity of iron.

(4) *Felite* is colourless, has two optical axes and shows very strong double refraction. Its refractive power is about equal to that of belite. This mineral is present in the form of the largest grains which have sometimes a slightly lengthened shape, but do not show crystalline contours.

Apart from these four minerals, Törnebohm recognised the presence of a mass which was probably amorphous and isotropic, colourless, and very strongly refractive, being superior to alite in this respect. It forms a filling between the minerals and is not always easily distinguishable from alite.

From the chemical point of view the most recent and likely hypotheses to explain the setting and hardening of cement are the following:

According to Rohland (1909) the setting and hardening occur because the lime in burnt cement is in a state of solid solution or rather of "absorbent combination." When it is then worked up with water, the cement separates the silica, iron oxide, and alumina in the form of colloidal hydroxides which are coagulated by the calcium hydroxide which is simultaneously separated by hydrolysis. The more colloidal substances are present, the more carbonate can be formed by the lime with CO_2.

According to E. Stern, crystallised calcium hydroxide is present abundantly in hardened cements, together with dry colloidal substances already observed by Bucca and Oddo in 1896, by Törnebohm in 1897, and by Michaelis in 1891. In fact the calcium aluminate of the cement may be decomposed by water forming crystalline calcium hydroxide and gelatinous aluminium hydroxide, and this may be shown by shaking up cements or specially prepared pure calcium aluminate with water and pouring the whole on to a filter. Calcium and aluminium are then present in the filtered liquid, and if this liquid is exposed to dialysis, calcium passes through the dialyser without any trace of alumina, because this latter is present in the colloidal condition.

In the first phase of the phenomenon of setting through the action of water, the colloidal substance which is formed, which is probably aluminium hydroxide, envelops each granule of cement, at the surface of which many hard crystals of calcium hydroxide are gradually formed. The phenomenon of hardening is thus started and is accompanied by the formation of other crystals of calcium aluminate and silicate occluded in the gelatinous mass.

That calcium hydroxide is present in hardened cement is argued from the fact that on dialysing it in the state

Sea water slowly attacks cement structures and solutions of calcium sulphate are still more harmful.

Artificial Portland Cement has acquired extremely great importance in recent years, especially outside Italy, and more particularly in Germany and in the United States. Thus in Germany the Government prescribes the employment of artificial cement for many public works, because by means of the perfected machinery introduced into this industry to-day products are obtained of which the constant composition and properties can more certainly be relied on.

Selections and Proportions of Prime Materials for Cement Manufacture. Theoretically, in the case of pure materials, it would be necessary to mix 19 to 20 per cent. of clay with 80 to 81 per cent. of calcium carbonate in order to obtain a Portland cement on burning. In practice, in order to prevent any excess of lime (0·5 per cent. more than is necessary may already be harmful to the finished cement when used) a little more clay is added so that ordinarily, according to the nature of the prime materials, 20 to 25 per cent. of clay and 75 to 80 per cent. of limestone are used. But an excess of clay may also be prejudicial during burning as dicalcium silicate may be formed instead of tricalcium silicate, and this increases the friability of the cement, even in the furnace itself, so that during cooling it is easily transformed into powder.[1]

Except in those cases in which the marl or stone gives a cement in which the clay and limestone are naturally present in the right proportions, it is necessary to suitably correct the natural marl or to add the prime materials to one another from the first in exactly the right proportions to form artificial cement, bearing in mind the type of cement which is desired, and which corresponds to a definite hydraulic index (*see above*).

In the case of **Slow-setting Cements,**[2] the hydraulic index, x, varies from 0·45 to 0·60, and in **Rapid-setting Cements** from 0·6 to 1·2. The value of x may always be calculated by introducing the percentages of the various compounds as found by an accurate analysis into the following formula :

$$x = \frac{Al_2O_3 + Fe_2O_3 + SiO_2}{CaO + MgO + K_2O + NaO_2},$$

of a suspension of the powder in water, lime only is found in the liquid which passes through the membrane, whilst a flocculent, colloidal residue, richer in silica and alumina, but poorer in lime, than the original cement, is left above the membrane.

Crystals of calcium carbonate are always found together with those of calcium hydroxide, and are formed by the action of the carbon dioxide which is always present in the water which is used. The colloidal matter protects the crystals of calcium hydroxide from the action of the water in structures formed of hydraulic cement ; the lime would otherwise be gradually dissolved by the water.

In any case, the phenomenon of setting and hardening presents problems which are not yet completely solved.

It has been noted that cements which are very rich in alumina set more rapidly, and the manufacturers avoid this disadvantage by adding 1 to 2 per cent. of natural gypsum, or sometimes even calcium chloride, to the cement before grinding.

The action of $CaSO_4$ or of $CaCl_2$ on the setting of cement was explained by Candlot by the formation of a double compound of gypsum and calcium aluminate as soon as these are brought into contact with water (it is the calcium aluminate which causes rapid setting). The compounds which are formed are $(Al_2O_3.3CaO + CaSO_4) + 30H_2O$, or $(Al_2O_3.3CaO + 2CaCl_2).16H_2O$, which are crystalline and insoluble. It may also be that the gypsum retards the setting because it renders the calcium aluminate less soluble and thus less liable to react with water.

[1] This disadvantage may be prevented by keeping the temperature a little lower in the furnace and thus avoiding a softening of the red-hot mass, but then a larger quantity of calcium aluminate remains which causes the cement to set more rapidly, and thus as a mortar it makes less resistant brickwork, but all the same does not undergo any deformation and does not give cracks as is the case with cement containing an excess of lime.

[2] Those cements are called slow-setting cements which set in the form of mortar within 10 hours by the needle test of Vicat (*see below*), and a wall constructed with such a cement is thoroughly resistant after 8 days, although the hardening continues slowly and in a year or a little more the whole mass acquires the same hardness as the most compact stone.

Rapidly setting cements set in from 2 to 30 minutes, although the best qualities set in from 6 to 10 minutes.

It has been noticed in practice that various causes influence the rapidity of setting : the temperature of the water and of the atmosphere (climate), the nature of the water used in making the mixture, the quantity of water used in the paste, &c.

If a cement or a mortar is used after the period of setting has already started or ended, it no longer has the necessary resistance, and it is a mistake to powder and re-employ such dead cement, because when once it has reacted with the water, it no longer has any value. For this reason it is obviously necessary to preserve powdered cements in dry localities.

The hydraulic index for contracts in France may vary between 0·42 and 0·48 (or 0·47 for a cement containing 8 per cent. of alumina), but must be diminished by 0·02 for each 1 per cent. of alumina below this figure. Those cements are considered good of which the hydraulic index is less than 0·60. Of two cements of equal hydraulic index, the one which contains the most silica sets the more slowly, and the one containing most alumina sets the more rapidly. It sometimes occurs that the rapidity of setting of a cement increases simply through the fact that it has become heated in the sun or in the trucks in which it is transported.

but ordinarily the alkali, $K_2O + Na_2O$, is neglected in this calculation. Some use the *hydraulic modulus*, which is the inverse of x, that is:

$$y = \frac{CaO + MgO + K_2O + Na_2O}{Al_2O_3 + Fe_2O_3 + SiO_2}$$

and here also the quantity of alkali is often neglected. y varies within the limits 0·8 to 2·2. Thus, if we indicate the quantity of iron and aluminium silicate in the limestone by S_1, that of the clay by S_2, of the lime and magnesia of the limestone by C_1, and the lime and magnesia of the clay by C_2, then given the modulus, y, which is required, the relation between the limestone and clay is given by the general formula $\frac{yS_2 - C_2}{C_1 - yS_1}$, which is sufficiently close for use in daily practice [1] if care is taken that materials containing much magnesia or calcium sulphate are rejected, because they form a less resistant cement. When there is a deficiency of iron the prime materials are corrected by the addition of burnt pyrites, and if there is an insufficient quantity of alkali, wood ashes are added, because the alkalis both act similarly to lime and magnesia, that is, lower the temperature of fusion and of reaction of the silica, and also form cements which set more rapidly. In clay which is to be used for cements it is only the combined silica and not the free silica which is of value, therefore in some cases it is better to eliminate the latter by suitable levigation. The composition of Portland cement varies within the following limits: [2] SiO_2 = 20 to 26 per cent.; $Al_2O_3 + Fe_2O_3$ = 7 to 14 per cent.; CaO = 57 to 65 per cent.; MgO = 0·3 to 2·5 per cent.; alkali = 0 to 1·2 per cent.; SO_3 (sulphates) = 0 to 3 per cent. Cements containing the most silica set slowly, whilst those containing much alumina set rapidly.

It is clear that in the analyses, both of the prime materials and of the finished cement, the silica contents must be understood to be combined silica and not free or quartzose silica which takes no part in the formation of the cement.[3] In argillaceous limestone

[1] If we have prime materials giving the following figures on analysis,

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Alkali	Co_2
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Clay . .	55·7	17·2	8·3	1·4	2·4	1·6	3·3	10·1
		81·2						
Limestone .	2·5	1·4	1·1	53	0·2	—	—	41·8
		5·0						

we have the following values: $C_1 = 53·2$; $C_2 = 3·8$; $S_1 = 5$; $S_2 = 81·2$; if we now wish to obtain a cement with a hydraulic modulus, $y = 2$, the ratio between the limestone and the clay will be the following:

$$\frac{(2 \times 81·2) - 3·8}{53·2 - (2 \times 5)} = \frac{158·6}{43·2} = 3·7,$$

that is to say, 1 part of clay must be mixed with 3·7 parts of limestone, and this ratio must be altered a little if we take the alkali also into account.

[2] We here give the mean composition of cements produced in various countries:

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Hydraulic index
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
French cement . .	21–26	5–8	2–4	57–68	0·7–2	0·48–0·54
English ,, . .	20–24	6–10	2·4–5	59–63	0·3–1	0·47–0·60
German ,, . .	20–25	5–11	2·5–5	58–68	0·9–2	0·46–0·58
Belgian ,, . .	23–26	5–9	2–4	60–65	0·6–1	0·49–0·59
Russian ,, . .	21–23	6–8	3–4	62–65	1–2	0·47–0·52
Casale Monferrato cement I	22·73	8·64		64·04	1·40	0·47
Casale Monferrato ,, II	23·47	8·59		63·60	1·48	0·49
Palazzolo ,, .	21·45	9·15		63·12	1·48	0·47
Civitavecchia ,, .	24·60	11·35		58·75	1·54	0·59

[3] F. Coppola, of the Torres Works at Vittorio, maintained (1909) that a cement of good quality may also be obtained by starting from an argillaceous limestone rich in active silica (quartzose silica insoluble in acids and in alkalis), if sufficiently finely ground, because the inactive silica then becomes active during burning.

which is to be used in the manufacture of cements, the portion insoluble in acids should be completely soluble in alkali, otherwise it consists of free silica or quartzose sand.

MANUFACTURE OF ARTIFICIAL CEMENT. This industry has to-day acquired so much importance in all civilised countries, and is connected with such important technical problems, chemical, physical, and mechanical, that it deserves to be treated in greater detail than ordinary in order to give our chemical students an idea as to which factors conduce to the perfection of an industrial process, and how apparently secondary or comparatively unimportant factors may in many cases decide the life and future of an industry. Each operation must be conducted with the maximum precision and studied in all its smallest details in order to obtain the best results, and if possible arrive at improvements. We will now treat shortly and clearly of the principal operations connected with the preparation of cements, a portion of which are common to the preparation of both the natural and artificial product.

GRINDING OF THE PRIME MATERIALS. The very finest grinding and intimate mixture of the limestone and clay are of great influence on the good qualities of the final product.

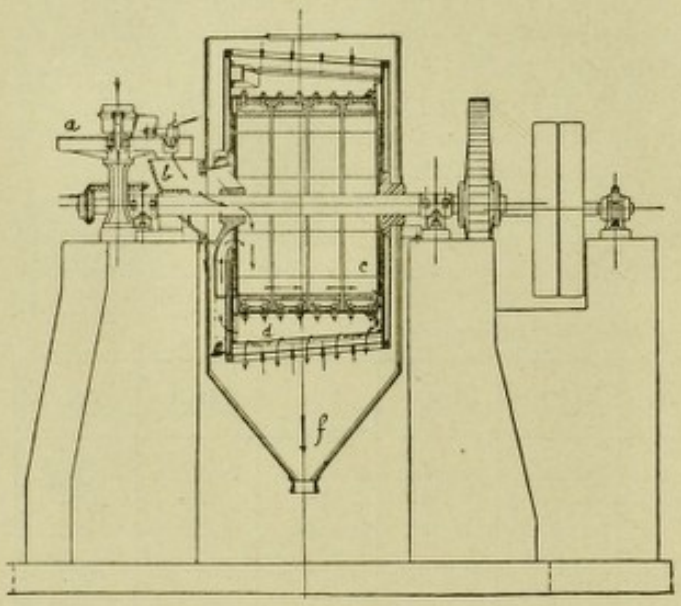


FIG. 242.

In the past the materials were exclusively ground by dry methods, but to-day wet grinding has in many cases been advantageously applied.

(*a*) **Dry Grinding.** In order to pulverise the two prime materials, clay and limestone, finely, it is indispensable that they should be thoroughly dry and contain less than 4 to 5 per cent. of moisture, otherwise in modern ball mills the ground powder will form lumps, which render the work irregular and difficult and lower the yield.

The prime materials are dried in a species of conical brickwork tower, being charged in above and discharged at the base, whilst a current of hot air passes into the lower portion of the tower. Finely divided materials may also be dried in rotary iron cylinders inclined at a very slight angle to the horizontal, into which the material to be dried enters continuously at the top and issues at the base, being met by a current of hot air which passes in from below.

The limestone, before or after drying, is coarsely crushed in a rock-breaker (*see* Fig. 96, p. 256), which crushes up to 15 tons per day with a minimal expenditure of energy. At one time the material was finely crushed by pressing it between two laminated cylinders and then pulverising it in mills with two horizontal stones, such as were used in old-fashioned flour mills. A minimal production is, however, thus obtained (less than one ton per hour) and very much power is required (20 to 30 h.p. per mill), and therefore ball mills were resorted to with advantage about 20 to 25 years ago, and were soon generally used in all works (*see* Figure and description on p. 512). Since 1900 the work in the ball mills has been modified in the direction of first producing a kind of coarse flour, and then completing the fine grinding in other apparatus. Ball mills with sieve plates Nos. 70 to 80 (*see* p. 512) gave 2 tons of finest limestone powder per hour, but required up to 40 h.p.; now, on the other hand, a plate with larger meshes, Nos. 20 to 25, is used, and with an equal consumption of power 6 tons of limestone are treated, the final grinding of which is then completed in tube mills. In 1900 F. L. Smidth, of Copenhagen, constructed a small improved ball mill called a "kominor" (Figs. 242 and 243) in which the plates of the internal drum are not perforated, and thus the meal to be ground, which enters at the one end, *a* and *b*,

is slowly transported by the rotation of the drum to the opposite end before passing into the exit fissure, *c*, and thus remains in contact with the steel balls for a longer time and pursues a longer path, dependent on the size of the kominor which may be up to 2 or 3 metres. The balls are of hard steel weighing 2 to 3 tons, and have a diameter of 5 to 12 cm. A larger production of meal is thus obtained for the same consumption of energy or greater fineness for an equal production. The fineness may be increased at pleasure by diminishing the production. On escaping from the drum the meal falls on to a conical sieve, *d*, which surrounds the drum, and the fine meal is thus collected in *f*, whilst the coarser portion which remains on the sieve is carried to its extremity, *e*, from where the rotary movement of the drum and of the sieve carries it back into the drum again when it again passes through the ball mill. The yield of the kominor is 20 per cent. greater than that of the old ball mills. It requires fewer repairs and may also be constructed in very large sizes, up to 5 tons weight of balls. By diminishing the production one may also dispense with the sieve. With 1·2 tons of balls, 1·8 tons of meal may be obtained per hour, passing through sieves Nos. 20 to 25, and 20 h.p. is then used. A kominor, the weight of the balls of which is 5 tons, requires 85 h.p. Ball mills similar to the kominor have been given various names by the various firms who construct them (Krupp, Löhnert, Pfeiffer, &c.); the firm of Smidth alone constructed 500 kominors up to 1909 for various cement works throughout the world.

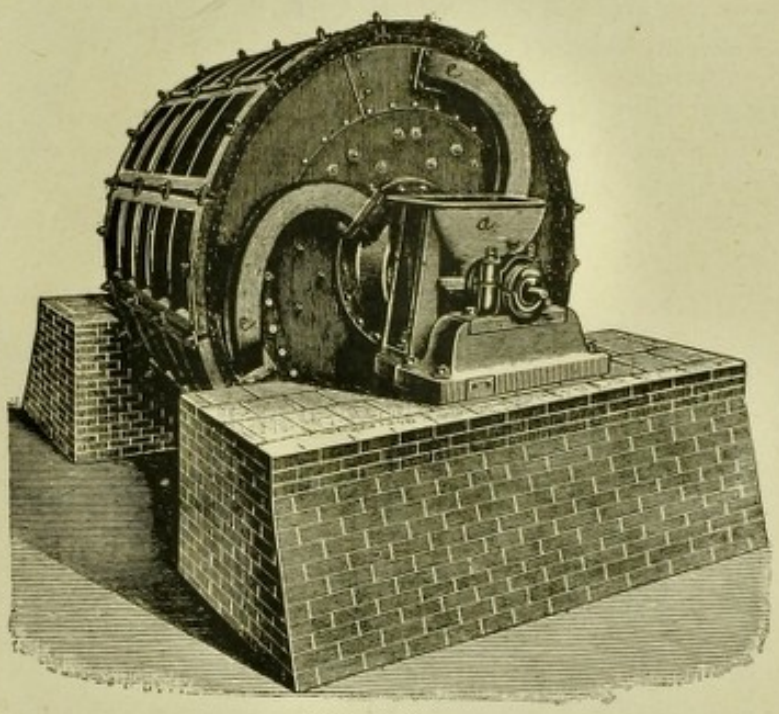


FIG. 243.

The limestone and clay which have been reduced to meal by ball mills or by the kominor then undergo finer grinding in the tube mills or Dana tubes, or by means of pneumatic separators, which separate the finest flour already contained in the meal by means of an air-blast, and regrind the coarser meal. These pneumatic separators are directly connected with the kominor and require very little power—5 to 6 h.p.

The *pneumatic separator* as it is constructed, for instance, by the firm of Pfeiffer, consists essentially of two large concentric cones of sheet iron pointing downwards (Fig. 244). The meal which is discharged by the kominor is carried by bucket elevators into the hopper, *A*, of the separator, from whence it falls regularly over a horizontal plate, *B*, supported by a vertical shaft, *S*, actuated by cog work. On this plate arms, *D*, are fixed, which carry peripheral blades, *C*, which act as a fan when the plate revolves. The meal is thus projected from the plate through the slits, *E* and *F*, and the strong current of air caused by the fan carries the finer powder to the wall of the larger cone, *K*, at the base of which it collects and is discharged through the opening, *H*, whilst the coarser portion of the meal only passes into the smaller cone and is discharged below through the opening, *I*, being then returned to the ball mill (*see* Figs. 245 and 246, view and section of the plant, including a kominor and wind separator with bucket elevator). The fineness of the product collected in *H* is increased on diminishing the velocity of the fan, which thus causes less flour to pass over the regulator, *K*, so that more is returned to the mill.[1]

[1] At first doubts were expressed whether wind separators would not alter the proportions of clay and limestone which were present in the ball mill because they have different specific gravities, and the blast would, therefore, accumulate the denser and the lighter material separately. In reality, however, this does not occur because even if this were the case when working was started, after a very few minutes of continuous feeding in of meal of definite composition from the kominor, the conditions inside the apparatus must soon establish such an equilibrium

Tube mills or *Mill tubes* or *Dana tubes* are still more widely used than pneumatic separators for the production of the finest powder without the need of sieves from the meal of the ball mill or kominor. On crushing a grain of limestone of 10 mm. diameter 1000 grains of 1 mm. diameter may be formed, or 1,000,000 grains of $\frac{1}{10}$ mm. diameter. Although, at first, in order to crush the larger grains mills with few but large and heavy balls are required, for the final pulverisation of the numerous small grains smaller spheres will be required, but in great numbers, that is, one requires a larger grinding surface and a prolongation of the time of contact of the grinding balls with the meal which is to be powdered. The idea of tube mills simply formed of long horizontal iron tubes half-filled with large numbers of small steel balls or hardest flints arose from this consideration (Figs. 247 and 248).

Tube mills are now constructed up to 10 metres in length of a diameter of 1 to 6 metres, which are charged with 15 tons of flint pebbles and make eight to twelve revolutions per

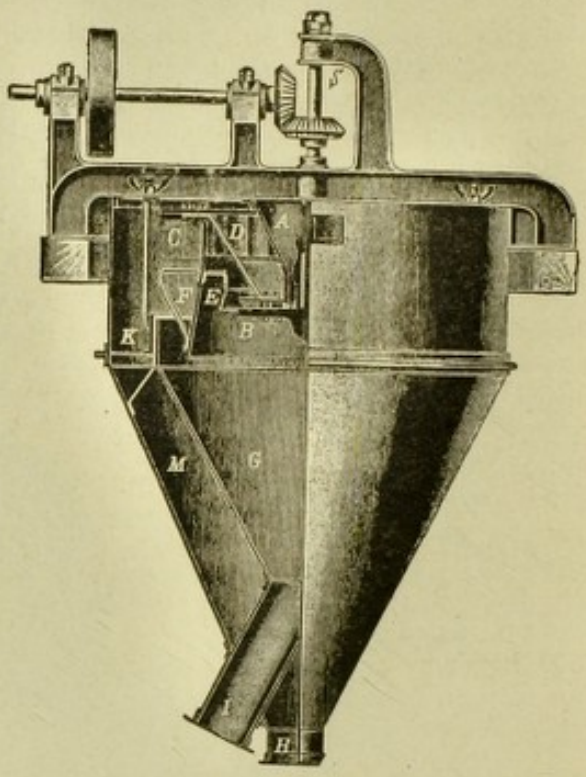


Fig. 244.

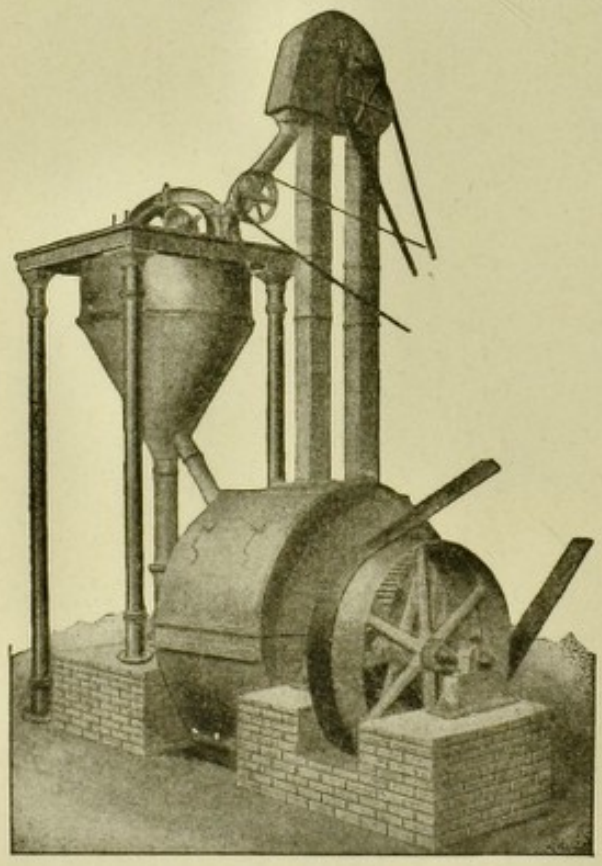


Fig. 245.

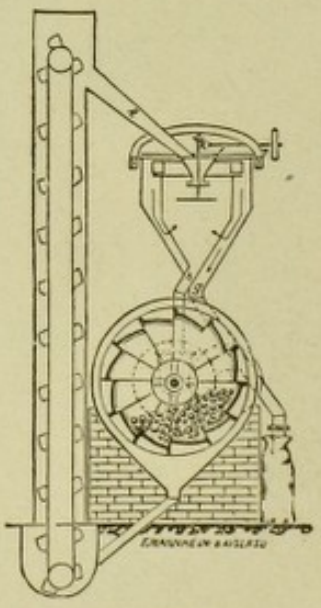


Fig. 246.

minute, absorbing 80 to 100 h.p. The internal surface of the tube is lined with hardened steel or with very hard flint tiles. The meal which is to be ground enters through the tube, *a*, which acts as a hollow pivot for the cylinder and passes out through a peripheral opening provided with a grill at the opposite end of the tube. As is seen in Fig. 247 the quantity of meal indicated by dark shading, *b*, diminishes gradually as it approaches the exit opening, whilst the quantity of steel balls remains the same at all points, so that as the meal is ground the proportion of spheres constantly becomes greater compared with the quantity of meal

or proportion between the two materials of different nature that the fine powder after a time assumes the same composition as the meal.

to be pulverised. The fineness may be increased at pleasure by diminishing the quantity of meal which enters. The product which escapes does not need to pass through a sieve, but is already so fine that sieves with 900 meshes per square centimetre do not retain more than 1 to 2 per cent., and sieves with 4900 meshes per square centimetre retain less than 25 per cent.

(*b*) **Wet Grinding.** This was first applied to friable or powdery limestone and to clay which was mixed with pebbles and coarse sand, introducing it in the necessary pro-

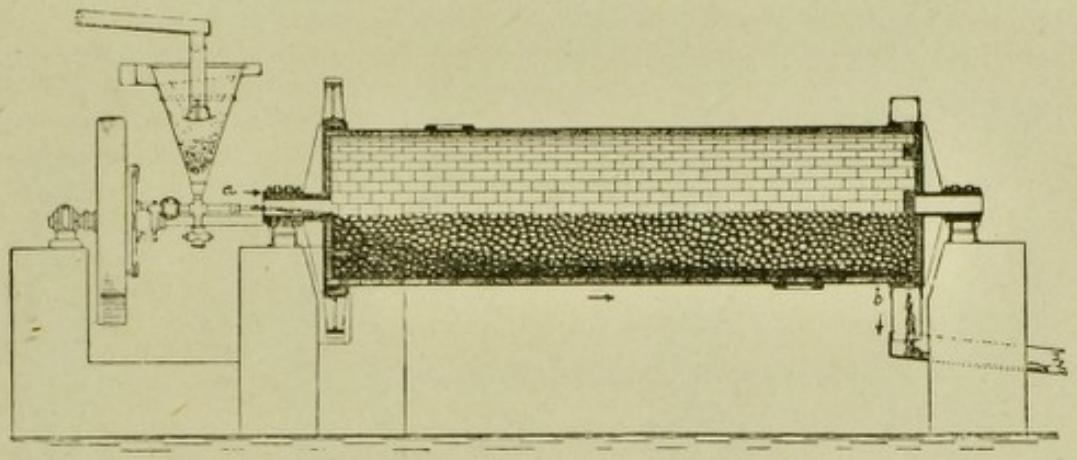


Fig. 247.

portions, together with water, into a large circular brickwork vat, *A* (Fig. 249), in the centre of which a small pillar supported a revolving head carrying horizontal iron arms, from which a sort of very heavy harrow was supported by chains and dragged along the bottom of the vat on turning. After 30 to 50 minutes all the pebbles and heavy sand were deposited at the bottom, whilst the clay was transformed into a liquid paste supported in the agitated water, and was discharged into the vat, *B*, placed below, through a metallic sieve, which retained the stones and coarser sand. In the second vat the paste was remixed

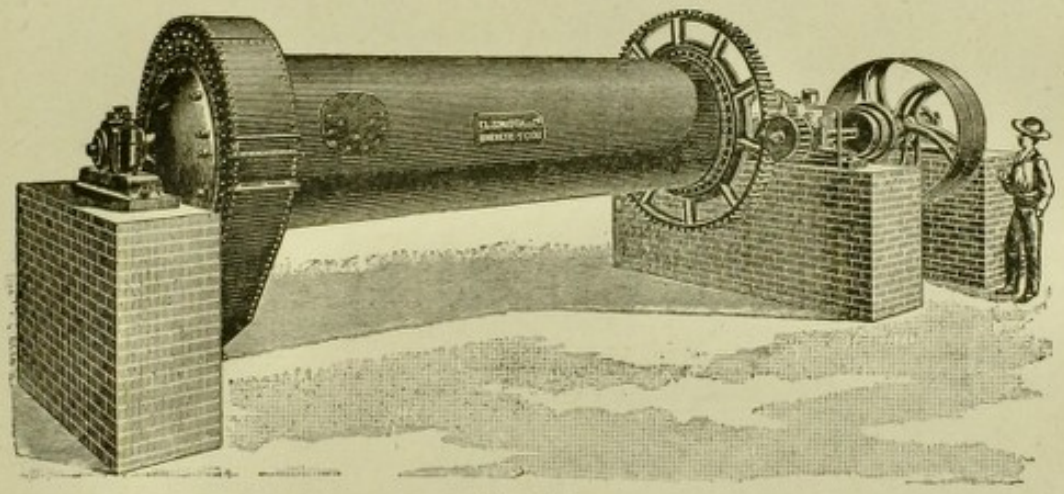


Fig. 248.

by agitation and in the meantime samples were removed for rapid analysis in the laboratory (by determining the carbon dioxide of the carbonate), and if the relation between the clay and the limestone did not correspond to the required values, a definite quantity of another paste, richer in limestone or clay, was added from another vat which was always kept in readiness. This paste was passed by a suitable pump into tube mills which work very well even with a wet mixture, and give a finer product than when a dry mixture is used of which only 15 per cent. remains on a 4900 mesh sieve. If the paste which escapes from the tube mill has been prepared with 35 to 38 per cent. of water only, then it may be directly passed into rotary kilns; if, on the other hand, vertical kilns are used, the paste must be allowed to settle and the water decanted and the mass then dried slowly and converted into bricks as will be described below.

The firm of Smidth of Copenhagen advises the grinding even of hard limestone directly in the wet way in the kominor, and the mixing of the calcareous paste with a clay suspension in the required proportions before being passed through the tube mills. Tube mills are constructed by the same firms which construct ball mills and the kominor (*see above*).

CEMENT-BURNING KILNS. The intimate mixture of limestone and clay having been obtained by the grinding machinery, it is necessary before burning to first shape the powder into bricks by mixing it with 8 to 10 per cent. of water and passing it into ordinary brick-making machines; that used for the preparation of fuel briquettes as already described on p. 370 also serves very well. The bricks are allowed to dry in the air under cover for some weeks, or are preferably placed on cars and then dried by hot air in a long drying chamber.

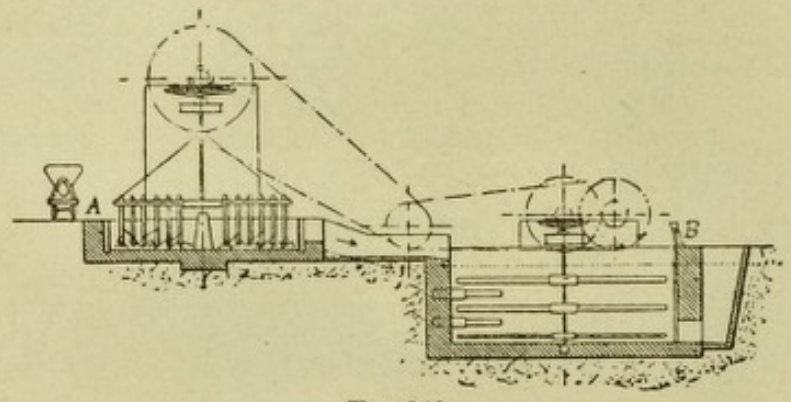


FIG. 249.

After this point the burning and the subsequent operations are the same for either natural or artificial cements. The temperature of burning (incipient fusion) is 1300° to 1400°, although the engineer Bonde, of Copenhagen (1909), has shown that the best results are obtained at 1500°.

The first continuous kilns which were used in large cement works were the *stage kilns of Dietzsch*, more or less modified, which led to considerable economy of fuel compared with the old intermittent kilns (from 25 to 30 kilos of coke per 100 kilos of cement the amount of fuel was reduced to 14–18 kilos). In Fig. 250 we see the original form of Dietzsch kiln. The charge was introduced by means of cars, *C*, and consisted of alternate layers of coal and of dried bricks of cement or of the natural-cement forming rock, and fell into the two or more lateral chambers, *BB*, of the kiln, which terminated below in grates, *a*, *a*, which supported a portion of the weight of the charge. When the combustion was once started through the openings, *E*, in the platform above the two lateral chambers, the regular working of the furnace was soon established and the coal was completely burnt, so that the maximum temperature was produced in the upper part of the chambers, *B*, and drew in a current of air through the grates, *a*, whilst the hot gas escaping through the chimney dried and preheated the materials which were charged into *V* as fast as corresponding quantities of burnt cement were discharged below by removing a few bars of the grate, *a*. The burnt cement which was discharged below was almost cold because the cold air which entered through *a* to sustain the combustion in *B* cooled the burnt cement in *K*; thus also the heat remaining in the burnt cement was utilised and it was possible to attain the necessary temperature of 1400° to 1500° to soften and partially fuse the crude cement in the burning zone. The passage of the material from the chimney, *V*, to the chambers, *B*, was facilitated by long iron shovels worked by operators through the various openings of the furnace, and enabling the combustion to be sustained by the addition of coal through the opening, *E*.

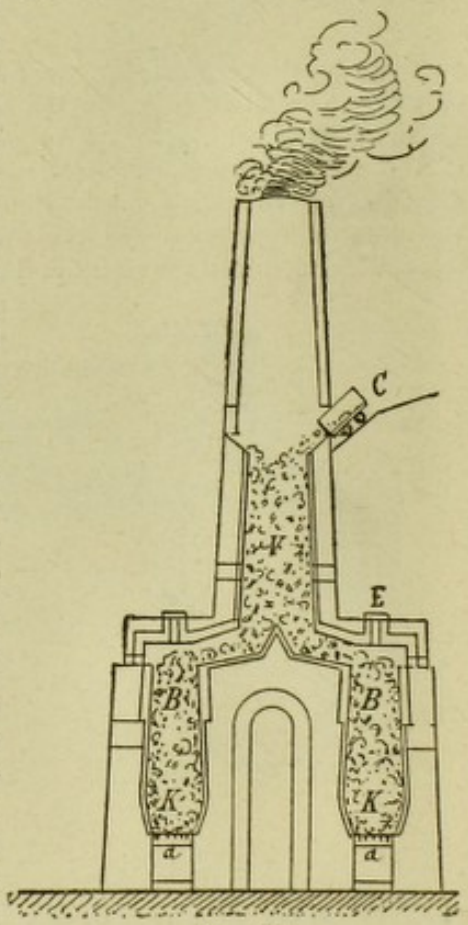


FIG. 250.

The Schöffer or Aalborg kilns were first used in Denmark at Aalborg, and then in other countries and were found to be advantageous (Figs. 251 and 252). The material is charged in at the top at *A*, and the furnace is constricted at *B* to a cone, and is thus better able to support the weight of material which afterwards enters the combustion chamber, *C*. The furnace is again enlarged at the cone, *D*, where there are several inclined flues, *K*, through which the fuel (long-flamed coal) is charged, and the material is removed with long iron tools when it is to be discharged through the lower grate, *R*. The consumption of fuel in these furnaces, which yield 15 tons of burnt cement per twenty-four hours, is 13 to 15 kilos for each 100 kilos of cement. The kiln is lined internally with refractory bricks which sometimes last two years, during which time the furnace is in uninterrupted work without the necessity for any repairs.

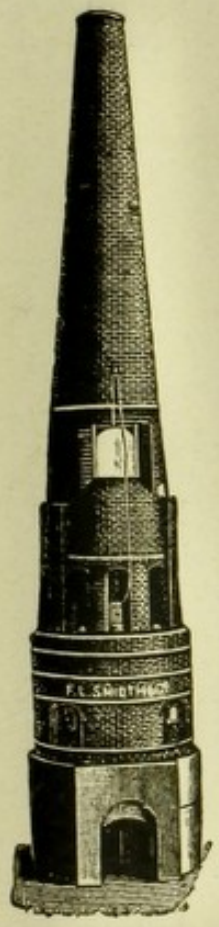


Fig. 251.

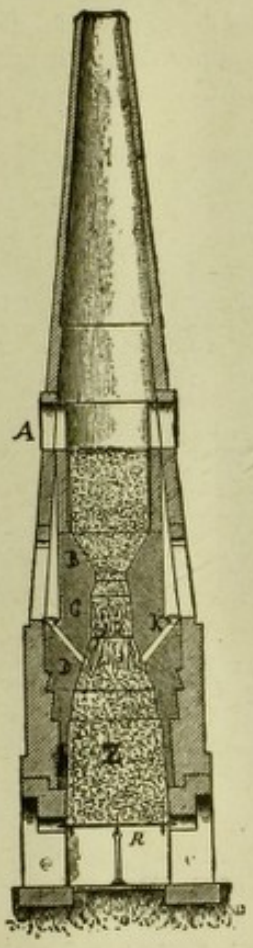


Fig. 252.

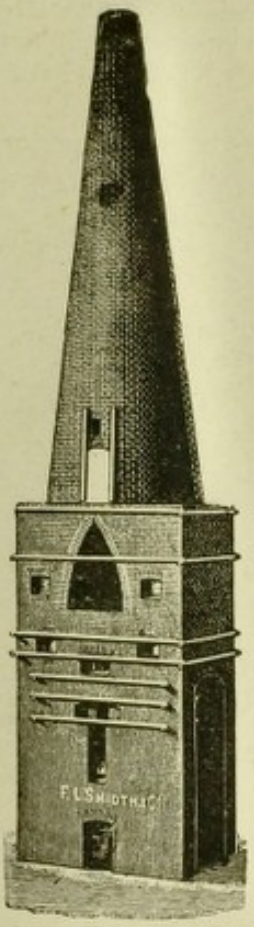


Fig. 253.

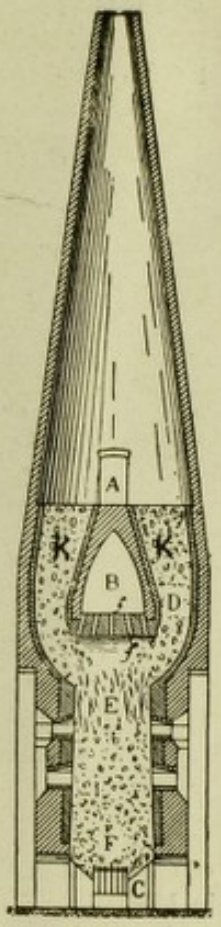


Fig. 254.

Another form of cement kiln which has partially replaced the Aalborg kiln is the Rysager or R-kiln, which was first applied in Denmark by the firm of F. L. Smidth of Copenhagen. It has almost the form of an inverted Dietzsch kiln (Figs. 253 and 254). There are two drying and preheating chambers, *KK*, which lead the material charged in at *A* into the single heating chamber, *E*, into which the coal is charged through various passages, *f*. In this way the maximum temperature is not obtained near the furnace walls and the refractory lining is thus better preserved, avoiding clogging of the cement, which is facilitated by coal ash which acts as a flux. The cold burnt cement is discharged in the usual way by removing several bars of the grate, *C*. With this kiln three workmen are required by day and three by night for all necessary operations, and the consumption of coal is 12 to 14 kilos per 100 kilos of burnt cement.

The burnt cement which is produced in the kiln is called *clinker*.

Fig. 255 shows the exterior of a cement works. *A* is the drying tower for the clay, *B* the two towers for drying the limestone which arrives along an overhead ropeway, *C*, and *D* are the chimneys of the kilns, *R*, for burning the cement which pass through the roof of the works.

ROTARY KILNS. Amongst all the great improvements introduced into the cement industry of late years, the most remarkable is certainly that of the application of rotary kilns.

These kilns allow the cement to be burnt without any necessity for first forming it into bricks or for previously drying the mixture. The mixture is introduced directly into the furnace in the form of a slightly moistened powder containing 8 to 10 per cent. of water, or as a liquid paste containing 30 to 33 per cent. of water.

The first attempts on a small scale to apply these rotary kilns were made by Ransome in England in 1885 without success, whilst a little later, about 1890, they were successfully applied in the United States by using as fuel heavy petroleum oil, atomised in the furnace itself.

In 1895–1897 Hurry and Seamann of the Atlas Cement Company of Northampton, Pennsylvania, replaced the petroleum residues by finely pulverised coal (powdered in tube mills), and it then became possible to also apply rotary kilns in Europe. The first plants, after the attempts of Forell and Lollar in Germany, were constructed by the firm

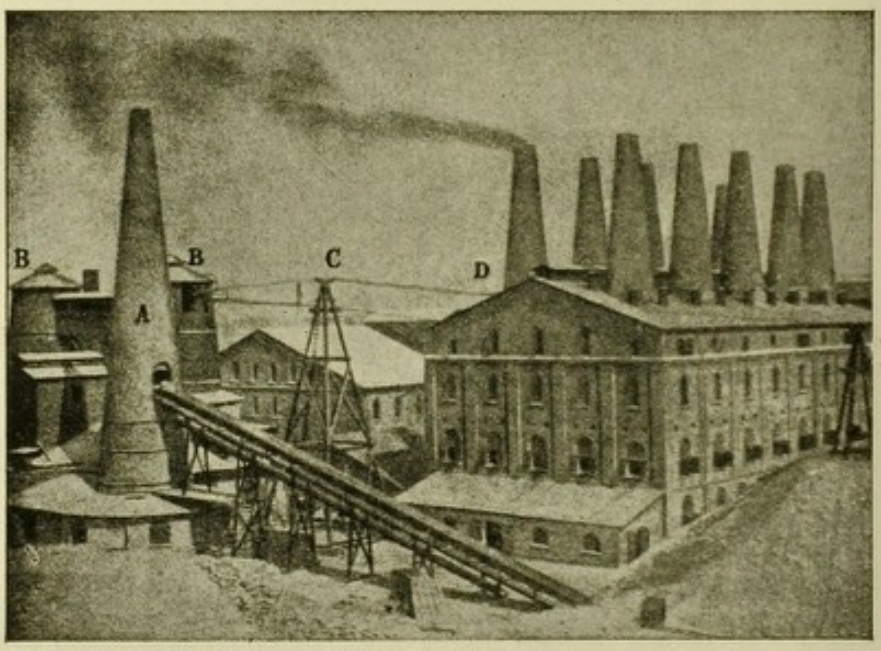


FIG. 255.

of Smidth at Aalborg in 1898 and by Dr. Prüssing of the Brennofen Bauanstalt of Hamburg in 1899.

These first rotary kilns were 10 to 20 metres long, but to-day they are built 45 metres and more in length and 2 to 2½ metres in diameter, especially if the material is charged in as a soft paste containing much water.

The large cylinder of the rotary kilns (Fig. 256) is inclined at an angle of 4° to 6° according to the degree of moisture in the paste. It is mounted on large pillars and revolves on loose rollers. It is constructed of large riveted iron plates which are lined internally, but especially at the burning zone, *B*, with refractory bricks or special bricks made of cement and clinker.

The upper part of the tube, *A*, is connected with the smoke flue which communicates with the chimney through which the steam formed by the drying of the paste continuously passes from the upper part of the tube above *A* and is carried away.

The cylinder is rotated at the rate of one to two turns per minute, and this carries the mass of crude cement slowly downwards. It forms granules of the size of nuts and peas, and is gradually dried and heated by dry, finely powdered coal which is blown in at the lower end of the tube at *B* (Fig. 257). This coal is powdered in a small kominor and a small tube mill or with a pneumatic separator. It burns completely and instantaneously. The hot air by which the coal is blown in and by which it is burnt passes in through the tube, *O*, from the cooling cylinder for the burnt cement, *D*, which consists of a revolving cylinder inclined towards the kiln through which the semi-fused cement

falls in separate granules. A large fan cooled by a current of water is placed at the top of the cooling cylinder, and draws in a current of cold air through the red-hot clinker; the air is thus gradually heated by the agency of the clinker and then blows in the coal at a temperature of 200° to 300°.

The fan is now placed by preference at the lower end of the cooling cylinder so that it blows in cool air at a slight pressure and the complicated and inconvenient cooling of the fan is not necessary. At the top of the cooler the air arrives similarly at a high temperature. The instantaneous combustion of the coal produces a very high temperature of 1500° and more, but the refractory material which lines this part of the tube to a length of 4 to 5 metres (burning zone, *B*) is easily destroyed, and if the foreman does not regulate the heat carefully the cement may melt and agglomerate to a single mass which may finish by obstructing the furnace. These difficulties have recently been overcome by making the part of the kiln corresponding to the burning zone very large and thus increasing the capacity of this zone, and also the output of the kiln itself. The lower mouth of the kiln is closed by a large vertical cast iron plate, *B*, covered internally

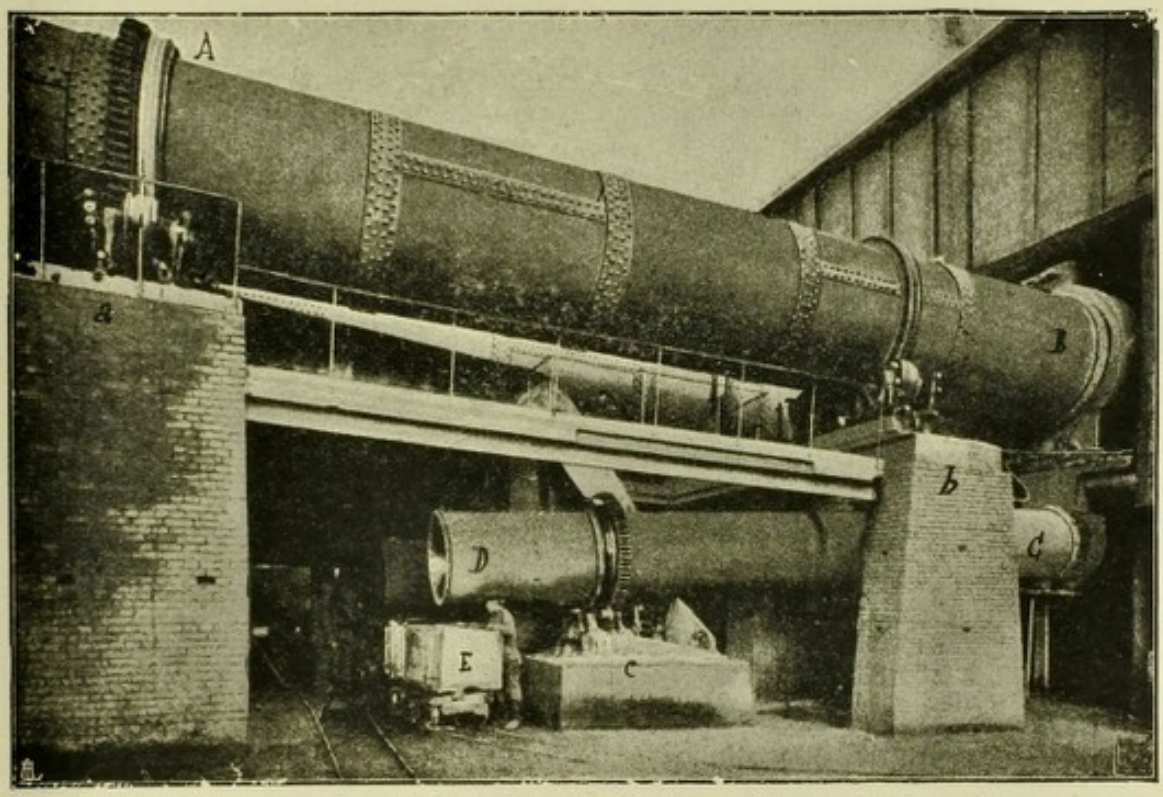


FIG. 256.

by refractory material and carrying the large pipe for the hot air and the smaller pipe for the powdered coal. This plate is mounted on wheels in such a way that it may be approached to within a few millimetres of the furnace mouth, whilst leaving the furnace free to rotate.

The excess of hot air, which is not used for the combustion of the coal, is used for drying it before grinding.

The consumption of fuel in rotary kilns varies according as the material is used in paste form or as a moist powder, and may be from 22 to 30 kilos.[1] Low-grade coal may also

[1] The theoretical consumption of fuel for burning cement in fixed vertical kilns would be 9 kilos of coal per 100 kilos of burnt cement. In practice, the best kilns consume 13 to 14 kilos. In rotary kilns the theoretical consumption of fuel, according to Newberry, on working by the dry method (with a paste containing 8 to 10 per cent. of moisture) would be 17·5 to 20 per cent., according to the lesser or greater excess of air. The practical consumption in the best rotary kilns has to-day been reduced to 22 to 24 per cent., whilst a few years ago 30 to 32 per cent. was still employed. With a paste containing 35 to 40 per cent. of water and assuming an excess of air for the combustion, the theoretical consumption of coal would be 25 to 26 per cent.; in practice in the best furnaces, 28 to 30 per cent. is consumed to-day, whilst formerly more than 40 per cent. was used.

It has been calculated that the motive force required in a cement works corresponds to a daily consumption of coal equal to 3·5 to 4·5 per cent. of the weight of burnt cement, or according to the various types of plant 1 h.p. will be required per 2 to 3 kilos of cement per day.

be employed or even coal waste, because, being finely powdered, it burns even if it contains 10 to 15 per cent. of ash. The consumption of power to drive a large rotary kiln and the corresponding cooler is 20 to 25 h.p.

When the clinker is discharged from the cooler of a rotary kiln, it is gently sprayed with 1 to 2 per cent. of water, and may then be stored for grinding. This water saturates a portion of the calcium oxide and a cement which sets rather more slowly is thus obtained; in any case it acquires greater stability according to the volume test because the calcium oxide is slowly transformed into hydroxide and carbonate and undergoes further alteration.

The cement from rotary kilns differs in general from that obtained in vertical kilns by its greater resistance to compression (*see below*, Cement Testing).

One of the great advantages of rotary kilns consists in the great saving of hand labour. One good foreman can simultaneously supervise two rotary kilns. In a large works visited by the writer at Rudersdorf-Kalkberg, near Berlin, two complete plants of equal output were working side by side. One produced 240 tons of cement daily with 4 small rotary kilns and employed 35 workmen in all by day and 35 by night. The other

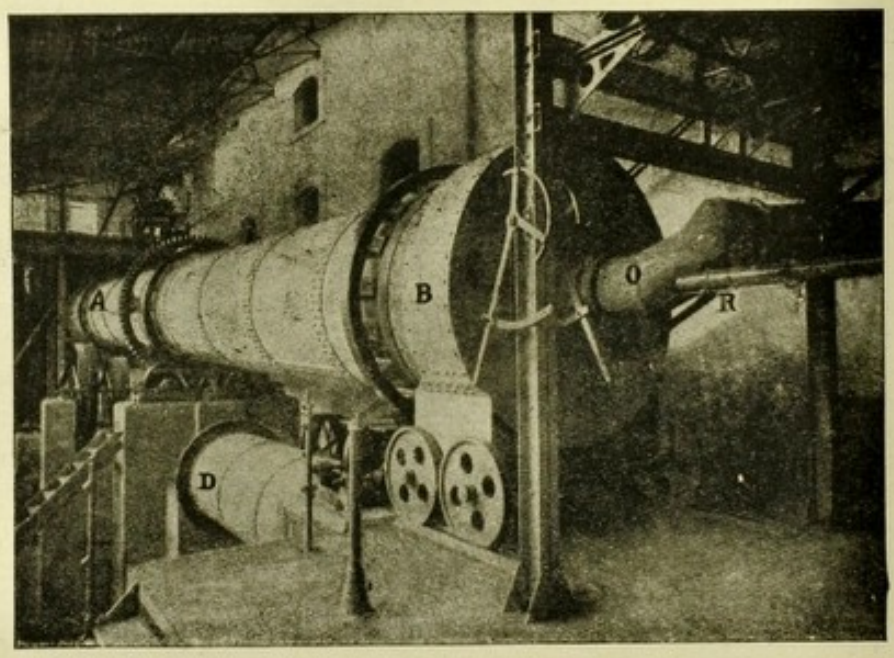


FIG. 257.

produced 240 tons with 12 vertical kilns, and employed 98 workmen by day and 98 by night.

The Atlas Company in America alone possesses more than 140 rotary kilns. In Europe at least 150 such plants have been erected of recent years. In Italy there are now three or four works using rotary kilns.

Rotary kilns are more especially built by the firms of Polysius, Krupp, Smidth, Lönhert, Pfeiffer, &c.

GRINDING OF THE GROUND CEMENT (CLINKER). It is now generally admitted that the good qualities of Portland cement are largely dependent on the degree of fineness of the ground clinker. The best ground cements to-day leave a residue of less than 25 per cent. on a sieve of 4900 meshes per square centimetre, and this result has been obtained by using more perfect machinery, which has already been described in connection with the grinding of the prime materials.

In modern works the clinker is passed through ball mills, or preferably through kominor mills, and the product coarsely ground; the meal is then passed through the tube mills which have already been described. Since the finished clinker is much harder than the limestone and clay or marl, these tube mills are lined with flint, and the crushing material also consists of flint pebbles.

Both in the grinding of the prime materials and in that of the burnt cement, the tube mills may be replaced by pneumatic separators of the Pfeiffer type, which have already been illustrated and lead to an economy of power. In either case sieves are now dispensed with.

In almost all cement works the finished product has of recent years been subjected to a very simple treatment in order to lengthen the time after which it will set when mixed with sand and water, by mixing it, on introduction into the grinding plant, with 1 to 2 per cent. of natural gypsum in lumps.

This gypsum appears to combine in the presence of water with a portion of the calcium aluminate of the cement, thus lengthening the time of setting, which would occasion many difficulties if it were too short. For buildings cements containing more than 3 per cent. of gypsum are not accepted.

The more important works have a very good system of storing the cement after grinding before it is placed on the market, because in this way if a small quantity of free quicklime is present, it is slowly hydrated and carbonated by the moisture and carbon dioxide of the air, and the resulting cement is more stable as judged by the test of deformation or of stability of volume.

For this reason the cement which is discharged from the grinding apparatus is carried by means of elevators or endless rubber bands to the upper portions of large warehouses, which sometimes have a capacity of thousands of tons, and is gradually discharged at the base after some months by means of helical transmitters, which correspond to the various charging doors, and thus it is filled, weighed, and the packages containing 50 kilos each automatically closed.

For foreign or oversea markets the cement is filled into barrels lined with paper.

In America the use of paper sacks has been tried for transport to short distances, and these cost less than 1½*d*.

Other cement-forming substances, analogous to Portland cement, are, for example, the "grappier" cements prepared by the partial utilisation of the argillaceous residues from hydraulic cements which do not crumble with water, and correcting them with clay and lime before burning. It is obvious that these cements are of inferior quality to Portland cement.

Of late years the utilisation of blast-furnace slag has acquired great importance for the preparation of *slag cement*. The annual production of blast-furnace slag is 50,000,000 tons. The composition of this slag varies within the following limits: SiO_2, 27 to 35 per cent.; $Al_2O_3 + Fe_2O_3$, 8 to 20 per cent.; CaO, 44 to 52 per cent.; MgO, 0·6 to 5 per cent.; H_2SO_4 (sulphates), 1·2 to 3 per cent.; those slags in which the ratio of CaO to SiO_2 is greater than 1 are most suitable. Cements of the true Portland characteristics are obtained from slags containing large amounts of silica and alumina by adding lime. In 1861 the firm of Fr. Wilhelm, of Mülheim, attempted to use a cement made of slag only by modifying the fluxes in the blast furnace when necessary, but the results were not of practical value. The molten slag from the blast furnace is to-day obtained in a friable and easily ground condition by pouring the molten slag into water. A powder is thus obtained which is mixed with 30 to 40 per cent. of fat slaked lime or hydraulic lime and then burnt in the usual kiln. Slag cements have a specific gravity of 2·7 to 2·8, and usually contain calcium sulphide (up to 4 per cent.), and they set in more than 10 hours. In the United States these cements are also called *pozzolana*, of which 20,000 tons were manufactured in 1906 and about 600,000 tons in 1909.

A so-called *white Portland cement* has also been placed on the market, which is obtained by heating a mixture of pure calcium carbonate with pure kaolin and about 3 per cent. of gypsum to 1200°, or also from a mixture of 100 parts or less of felspar, 100 parts of kaolin, about 30 parts of magnesite, and about 4 parts of sodium chloride to from 1400°–1500°. This cement is also used for statuary.

CEMENT TESTING. Portland cements form a fine powder of a grey, greenish-yellow or reddish-yellow colour; they require 30 per cent. of water in order to be converted into a paste of normal consistency, whilst cements of other qualities require up to 45 per cent. of water, and hydraulic cements even more. In practice, the cements are used as a paste to which pure, fine sand is added in the proportions of 1 to 3 parts of sand, 1 part of cement, and 0·5 to 0·7 part of water.

The *absolute density* of Portland cement varies from 3·10 to 3·25, whilst that of other cements is lower than 3, and varies from 2·7 to 3, whilst that of hydraulic cements is between 2·50 and 2·85. The specific gravity is determined with a pyknometer or with a graduated cylinder (*see* pp. 72 and 107), turpentine oil or preferably carbon tetrachloride being

employed as the liquid, and the cement is used after passing through a sieve of 900 mesh (per square centimetre).

The *apparent density* is determined by the weight of one litre of powdered cement, collected and weighed with prescribed precautions in suitable vessels.

The *degree of fineness* is also of great practical importance. The best qualities yield a residue of less than 10 per cent. when they are passed through a sieve containing 4900 meshes per square centimetre, and ordinary qualities less than 20 per cent., or less than 3 per cent. with a sieve containing 900 meshes per square centimetre. For this purpose the Tetmajer sieve (Fig. 258) is used, sieving 100 grms. of the cement, until less than 0·1 grm. passes through on giving 25 turns to the handle.

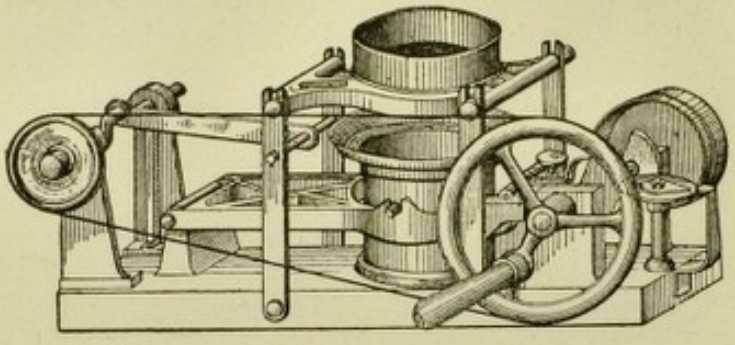


FIG. 258.

In valuing a cement it is necessary to take the *time of setting* into account. This is done by working the cement up to a paste with about 30 per cent. of water (at 15° to 18°, the quantity of water varying with the fineness) added all at one time, and stirring it with an iron spatula for 1 to 5 minutes. The paste is immediately placed in the mould, *a* (Fig. 259), 4 cm. high and 8 cm. in diameter, and setting is said to have commenced when the needle, *c* (Vicat's needle, of a weight of 300 grms. and a point of 1 mm. cross-section), does not succeed in penetrating through the mass contained in the mould; setting is said to be finished when the same needle does not scratch it and does not even penetrate the surface of the block of cement in the mould.

Rapid-setting cements are no longer scratched after 15 to 30 minutes, whilst slow-setting cements require 5 to 10 hours and hydraulic cements exceed 24 hours (excepting those which are strongly hydraulic).

The determination of the *resistance to compression and tension* is also important. The first is determined by submitting a brick of cubical shape and 50 sq. cm. cross-section to pressure in a hydraulic press, furnished with a mercury manometer. The brick is obtained by mixing 1 part of cement with 3 parts of *normal sand* (clean quartzose sand containing at least 90 per cent. of SiO_2, which should pass completely through a sieve with holes of 1·35 mm. diameter, and should all be retained by a sieve with holes of 0·77 mm. diameter) and about 8 per cent. by weight of water, and then compressing the whole with a mechanical hammer (*see below*), and exposing it to the air for one day and in water for 27 days before the test is made.

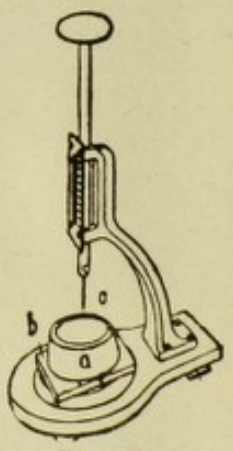


FIG. 259.

It may also be tested after 7 or more days, and the resistance is expressed in kilos of pressure per square centimetre of surface of the face exposed to the pressure until it crumbles or breaks. For good Portland cement, the resistance after 8 days varies between 190 and 180 kilos, and after 28 days between 200 and 220, whilst after 90 days it exceeds 250 kilos.

For these determinations Amsler and Laffon's hydraulic presses are used in many laboratories (Fig. 260), and with these pressures up to 600 kilos per square centimetre can be exerted on the little cube, 5, which is held down by the screw, 6, whilst the piston, 2, is lowered by the handle, 1, and transmits the pressure to the oil which raises the piston of the bell, 10, and the pressure is simultaneously transmitted below to mercury in a vessel which communicates with the manometer, 9.

Resistance to tension is determined on a cement brick which, immediately after being made with water and sand as above, is compressed in a dumb-bell shaped mould (Fig. 261), of exactly prescribed dimensions, and compressed with a mechanical hammer (Fig. 262) which weighs 2 kilos and gives 150 blows. The tension test is made with the Frühling-Michaelis balance (Fig. 263) which has a ratio of 1 : 50 between the

two arms. The cement brick to be tested, *a*, which has first been left in the air for 1 day and then in water for 27 days, is clasped by two pairs of pincers, *A*, and then, when equilibrium has been established, the pan, *B*, is suspended and the mouth of the reservoir, *D*, is opened so that the lead shot contained in it are allowed to fall into the reservoir, *B*, until the test piece, *a*, breaks at the narrowest point, where its cross-section is 5 sq. cm. ; at the moment of fracture the discharging mouth of the vessel *D* automatically closes and all that is now necessary is to weigh the pan, *B*, with the lead shot. From

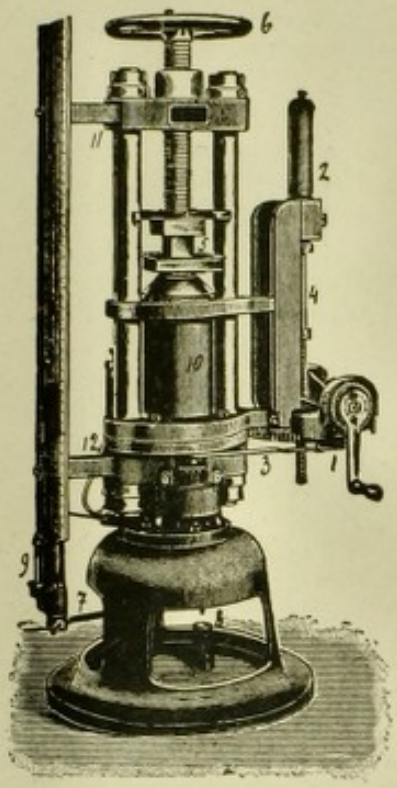


Fig. 260.

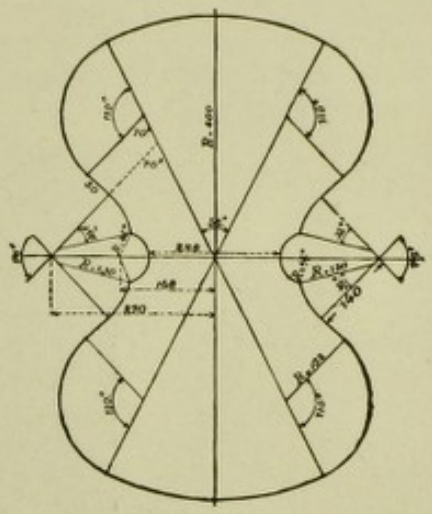


Fig. 261.

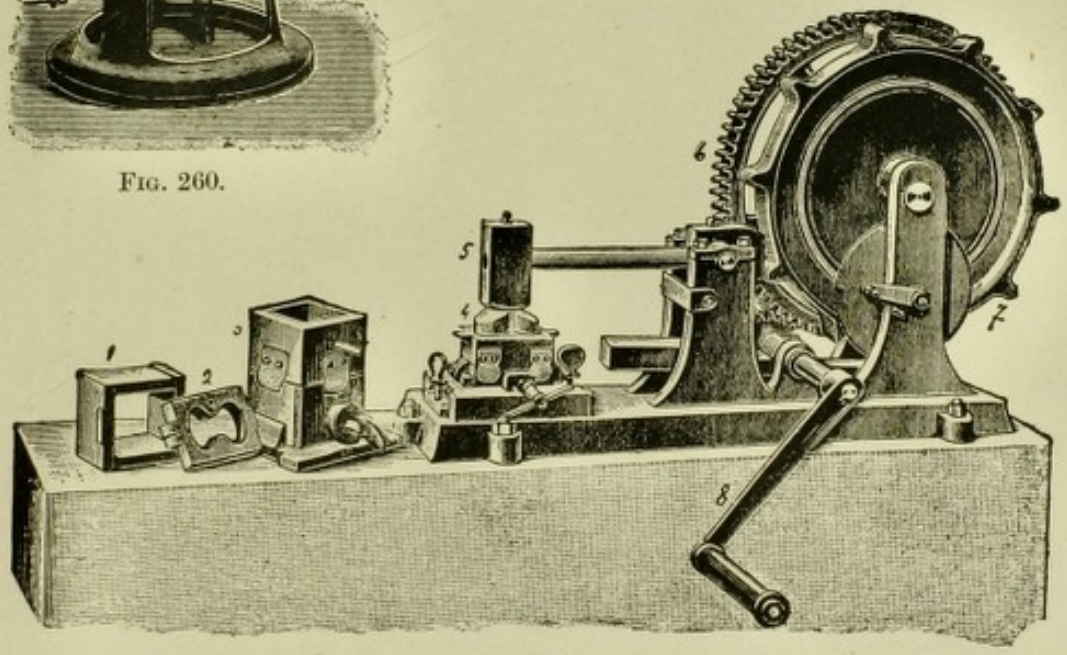


Fig. 262.

this weight multiplied by 50 and divided by 5 (number of square centimetres) or by simply multiplying the number by 10, the resistance to tension is obtained, expressed in kilos per square centimetre. After lying in water for 7 days a normal cement shows a resistance of 16 to 20 kilos, after 28 days of 21 to 25 kilos, after 90 days of 25 to 32 kilos, and after 3 years of 36 to 38 kilos. In general the resistance to pressure is 9 to 10 times greater than the resistance to tension during the first days, but after some time it is 12 to 16 times greater, although in rapidly setting cements after 28 days in water the resistance to pressure is slightly lower than during the first days.

A most important property of cement is that of giving mortars *which do not swell.* This means that in the test in which the bricks are formed these must not show deforma-

tion, cracking, radial cleavage, or enlargement towards the edges after soaking in water for 28 days. Cakes of soft mortar prepared with the cement may be placed on a glass plate ; the cake, 10 cm. in diameter and about 2 cm. thick in the centre, is allowed to stand in the air in a moist spot for 24 hours and then immersed in water at 15° to 20° and observed once a week as described above. This is called the cold test, but a hot test is now generally used because it is more rapid and also enables a clear opinion of the quality of the cement to be obtained ; it is usual to prepare a little cylinder of mortar from the cement which is placed in Le Chatelier's ring (Fig. 264), which has a diameter of 3 cm. and is 3 cm. high, and is formed of a flexible metallic sheet split at one

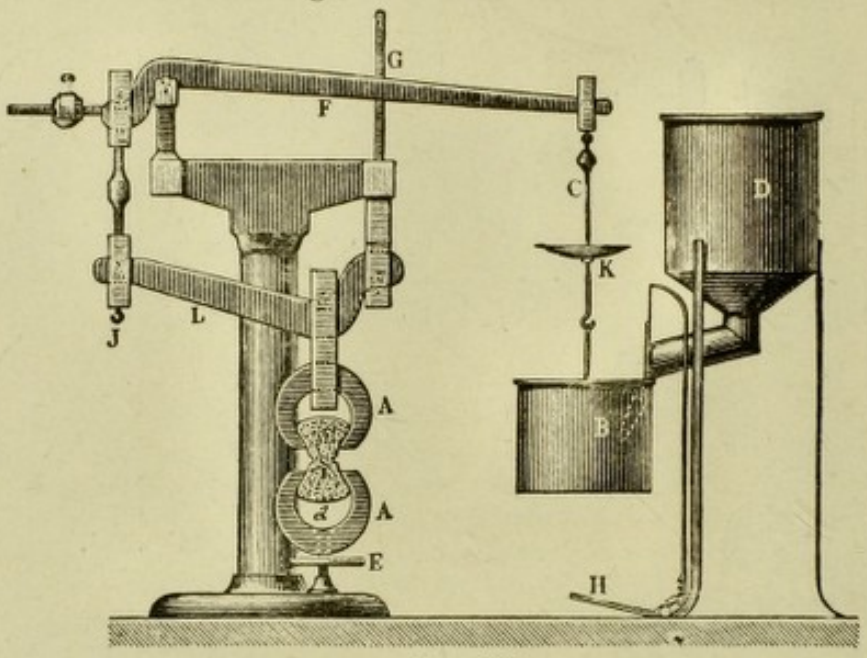


Fig. 263.

point where two long needles are fixed to it at right angles. These indicate the increase of volume of the cement cylinder on a quadrant after the cake has been dried for 24 hours in the air, left in boiling water for six hours, and then cooled in ordinary water for 24 hours. The deformation and expansion are proportional to the distance which separates the two needle points of the apparatus. Defects of swelling or expansion may be caused by bad grinding and mixing, by insufficient burning (in which case much free lime remains), by excess of lime, of gypsum, or of magnesia ; in fact, if during setting there is continuous formation of crystalline calcium hydroxide, due to excess of lime, throughout the mass, it is not sufficiently resistant, and so much pressure is produced that it breaks to pieces. For similar reasons more than 2 per cent. of SO_3 in the form of sulphates or 5 per cent. of magnesia (MgO) cannot be tolerated in cement ; a cement containing 1·5 per cent. of free lime is very expansive and this is corrected during manufacture by the addition of gypsum.[1]

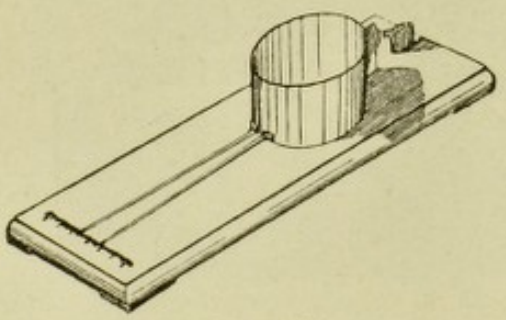


Fig. 264.

An unadulterated cement should lose less than 2·6 per cent. on ignition, and the alkalinity produced in water with which 0·5 grm. of the cement has been mixed should require

[1] The *determination of free lime* in cement is difficult, because neither water nor an aqueous solution can be used. In 1910 A. W. White proposed the following test, which is, however, qualitative only.

A few milligrammes of the powdered cement are placed on a microscope slide and treated with a drop of a reagent consisting of a mixture of 5 grms. of phenol, 5 grms. of nitrobenzene, and two drops of water. The whole is then covered with a cover slip and observed under the microscope by polarised light. If free lime or calcium hydroxide is present small bundles of shining needle-shaped crystals are seen in the dark field in a short time. Dolomite, calcined magnesia and calcium silicate do not give such crystals.

In 1909 R. Brandenburg proposed a quantitative test by distilling a given weight of the cement with a solution of ammonium bromide in absolute alcohol and absorbing the ammonia which distils over in a given volume of normal sulphuric acid.

4 to 6·5 c.c. of $\frac{N}{10}$ hydrochloric acid for saturation. On treating 1 grm. of cement directly with normal hydrochloric acid, 18·8 to 21·7 c.c. are required for saturation; 1 grm. of cement dispersed in water should not reduce more than 2·8 mgrms. of potassium permanganate.

We have already stated that it is only the combined silica and not the free silica which is of value in cements, and therefore in the chemical control of cements the total silica is first determined by the usual methods and that portion which is soluble on boiling in a solution of 5 per cent. sodium carbonate is then also determined; that portion which remains undissolved is free silica (sand) and is dried and weighed.[1]

APPLICATIONS AND STATISTICS. Cement has to-day acquired extraordinary importance because it is used in all works under water or in moist localities, and is also used as *concrete* in prisms or large blocks formed by mixing the cement with sand and water and then allowing it to dry in the air.

Extremely large quantities are used to-day for structures made of *armoured concrete* which has partially replaced iron and wood for the construction of buildings. Armoured concrete is a network of cast-steel bars and wires embedded in and supported by cement. The tensile strength of iron is 10 times greater than that of cement, and the resistance to compression of the latter is 10 times greater than that of iron. On the other hand, the coefficient of linear expansion of iron and of cement are almost equal, being 0·000,013,5 for cement, and 0·000,012,3 for iron, so that by using iron and cement together the advantages of both materials are united, and the disadvantages of either avoided, so that a constructive material is produced which is relatively cheap and of great strength. Steel girders or wires do not rust when they are surrounded by the mortar which consists of 1 part of cement and 3 parts of pure, washed sand, and the adhesion is extremely good. Entire buildings, from basement to roof, are to-day constructed of armoured concrete, including the dividing walls and the flooring.

Cement is transported for long distances in wooden barrels lined with cardboard of 170 kilos net weight, and 180 kilos gross weight. In the United States these weights are 127 and 135 kilos respectively. Half-barrels are also used. In small quantities and for immediate consumption it is despatched in small sacks containing 50 kilos, which must be kept in a dry spot. In America the use of paper sacks which cost 1*d.* to 1·2*d.* each has been recently tried. The best quality of Portland cement was sold in Italy in 1906–1907 at about £2 per ton, and cement of second quality at about £1 12*s.* per ton, but during the crisis of 1907 the price dropped to below £1 4*s.* The various qualities are distinguished by various coloured bands. In Italy there is a protective tariff of 10*s.* per ton and in France of 4*s.*

The production of cement in various countries is shown in the Table on the following page.

In the United States the capital invested in about 100 cement works is approximately £60,000,000. In 1909 attempts were made to form a trust of cement works with a capital of £40,000,000, but were not successful.

ULTRAMARINE

This is a compound which is found in nature in Persia and Turkestan under the name of *lapis lazuli*, and forms a hard mass of sp. gr. 2·75 to 2·95, of beautiful blue colour. It may be polished and is then used as an ornamental stone. Its composition has not been clearly elucidated. It was obtained artificially by Gruelin in 1882 and is prepared to-day in large quantities by heating a mixture of about 100 parts of kaolin, containing less than 1 per cent. of Fe_2O_3, 46 parts of soda, 41 parts of sodium sulphate, 13 parts of sulphur free from arsenic, and 17 parts of coal, resin, or pitch in crucibles to a white heat for 40 hours out of contact with the air. Sodium sulphate may be used instead of soda, and thus there is both *sulphate ultramarine* and *soda ultramarine*. Reactions occur between the kaolin and the sodium sulphide which is produced by the interaction of the sulphate and the coal.

[1] In Italy it has been established by the Ministry by a decree of January 10, 1907, that for public works cement must satisfy the following requirements: Its volume must be constant by the hot and cold test; its absolute density must be not less than 3·05; the maximum residue on a 900-mesh sieve must be 2 per cent., and on a 4900-mesh sieve, 20 per cent.; the setting of the mortar must not commence before 1 hour and must not finish before 5 hours or after 12 hours; the resistance to tension must be at least 16 kilos after standing in water for 7 days, and 20 kilos after 28 days. The resistance to pressure on the seventh day must be 180 kilos and on the twenty-eighth day 220 kilos; the contents of gypsum, expressed as SO_3, must be lower than 1·2 per cent., and the amount of magnesium oxide, MgO, must be less than 3 per cent.

PRODUCTION OF CEMENT IN VARIOUS COUNTRIES

Country	Year	Quantity in Tons	Notes Imports and Exports
Italy . .	1890	104,000	And 368,000 tons of hydraulic cement.
	1905	333,400	at £1 4*s.*, and 435,000 tons of hydraulic cement.
	1906	389,000	at £1 6*s.*, and 466,000 tons of hydraulic cement.
	1907	—	Imports 27,500 tons. Exports 3000 tons.
	1908	514,700	,, 21,000 ,, ,, 4200 ,,
	1909	—	,, 21,500 ,, ,, 6800 ,,
United States.	1882	260,000	Natural (called " Rosendale ") from calcareous clay, rich in magnesia.
	1892	1,000,000	Natural, and a little artificial.
	1905	4,500,000	35,300,000 barrels of 127 kilos net or 135 kilos gross, mainly artificial.
	1906	5,900,000	Mainly artificial.
	1907	6,100,000	at £3 per barrel. Imports 400,000 tons; exports 115,000 tons.
	1908	5,000,000	Imports 168,000 tons. Exports 106,000 tons.
	1909	7,800,000	Artificial at 3*s.* 9*d.* per barrel, more than 250,000 tons natural cement at 2*s.* per barrel. Imports 86,000 tons. Exports 135,000 tons.
Germany .	1882	510,000	Both natural and artificial.
	1899	3,400,000	Exports 693,000 tons in 1907.
	1907	4,700,000	,, 582,000 ,, 1908.
			,, 612,000 ,, 1909.
			Imports 241,400 ,, 1907.
			,, 168,500 ,, 1908.
			,, 224,000 ,, 1909.
France . .	1900	907,000	Both natural and artificial.
England .	1907	1,500,000	From 1885 to 1905 lower and almost constant.
Belgium .	1895	200,000	In 4 works } Exports 588,000 tons in 1904.
	1906	700,000	In 16 ,, }
Russia . .	1905	1,100,000	In 1880 cement was mainly imported, but in 1890 there was already over-production. In 1898 the exports were 2600 tons, in 1900 3800 tons, and in 1903 11,000 tons. The imports were 41,000 tons in 1898; 28,000 tons in 1900; and 14,000 tons in 1903. In 1900 there were 35 works, 3 of which produced more than 200,000 tons in 1904.
Norway. .	1908	46,000	All imported.
Roumania .	1908	60,000	
Japan . .	1905	100,000	
	1907	220,000	1,300,000 barrels.
Australia .	1907	—	40,000 tons imported from Germany and the United States, sold at 16*s.* per ton in Sydney.
Canada . .	1908	550,000	In 1908 4,000,000 barrels were consumed.
Chili . .	1907	—	Imports 98,434 tons.
	1908	—	,, 53,000 ,,
Switzerland .	1892	86,350	
	1896	114,000	

According to Ger. Pat. 206,466 of 1907, the reaction may be completed in 5 hours by regulating the temperature to produce three phases, and by adding nitrate or another oxidiser during the last phase.

The kaolin which is used contains more than 3 per cent. of water of hydration causing a loss of 5 to 10 per cent. of sulphur, which escapes up the chimney as H_2S, to the detriment of the neighbourhood. If green ultramarine is required instead of blue, the mass is heated to redness with 5 per cent. of sulphur in a muffle in a current of air, and the quantity of sodium in the ultramarine is thus diminished. The crude ultramarine so formed is slowly cooled and repeatedly boiled with water in order to remove the excess of Na_2SO_4, Na_2CO_3, Na_2SO_3, &c. ; the ultramarine is then separated in a hydro-extractor or a filter press. It is mixed with 4 times its weight of magnesium carbonate, calcium carbonate, gypsum, or kaolin, and finely ground. The addition of a little glycerine renders the colour more intense. Products containing more SiO_2 may be violet or even red. By the action of HCl or HNO_3 vapours at 130° blue ultramarine becomes red.

Ultramarine contains sulphides and polysulphides, and thus with acids or even with salts of an acid reaction such as alums H_2S is evolved and decolorisation takes place, but the cause of the blue colour is not exactly understood. It is insoluble in ordinary solvents. To the ultramarines containing most sulphur and silica, the formula, $Si_6Al_4Na_6S_4O_{20}$, is assigned, and it may be stated that no good ultramarines contain more than 66 per cent. of silica and alumina ($SiO_2 + Al_2O_3$). The green, blue, violet, and red ultramarines are distinguished by various proportions of sodium and sulphur.

Ultramarine is used in painting (in the Middle Ages natural ultramarine in powder cost up to £120 per kilo), for tinting and printing wallpaper, &c., and it is also much used for correcting the yellowish shade of linen, starch, sugar, paper, &c.

Whilst ultramarine cost 12*s.* 10*d.* per kilo in 1862, the price to-day is less than 9½*d.* The European production was 8500 tons in 1872 of which two-thirds was produced in Germany, but the production is not increasing to-day, because of the many substitutes which have the advantage of being more resistant to the action of acids. All the same, Germany exported 4840 tons of ultramarine in 1905 at a price of £25 12*s.* per ton.

GALLIUM : Ga, 69.9 ; INDIUM : In, 114.8 ; THALLIUM : Tl, 204

These are three rare elements which have much similarity with one another and with aluminium. Their basic character increases with rise of the atomic weight. Thallium also forms a lower oxide in which it behaves as a monovalent element, and yields a strongly basic hydroxide, Tl.OH. The specific gravity and boiling-point rise with increase of the atomic weights.

Before **GALLIUM** was discovered spectroscopically in a blende by Boisbaudran by means of two violet lines, it had been theoretically predicted in 1869 by Mendelejew, by means of his periodic system of the elements, and had already been called *eka-aluminium* by him. It is a white, tough metal which may be cut with a knife ; it melts at 30°, and has a specific gravity of 5·9. It does not react with water and is only slightly attacked by HNO_3, but dissolves in HCl and in alkalis. With aluminium it forms liquid alloys which easily decompose water.

The **Chloride**, Ga_2Cl_3, the **Hydroxide**, $Ga(OH)_3$, and the **Sulphate**, $Ga_2(SO_4)_3$, have similar chemical and physical properties to the corresponding aluminium salts. The sulphide is white and insoluble in acetic acid like that of zinc. An **Oxide**, Ga_2O_3, a **Chloride**, $GaCl_2$, a **Nitrate** and a **Gallium Alum** are also known, among other compounds.

INDIUM. This element was discovered by Reich and Richter in 1863 by means of its spectrum which contains two remarkable blue lines. It is found in certain zinc blendes. It is a softer metal than lead, white, has a sp. gr. 7·4 and melting-point 176° ; it does not alter in the air and burns with a blue flame, forming an **Oxide**, In_2O_3. It dissolves more rapidly in HNO_3 than in HCl or H_2SO_4. The **Chloride**, $InCl_3$, does not form HCl with hot water, thus differing from those of Al, Mg, &c. The **Hydroxide**, $In(OH)_3$, is insoluble in alkalis, and the sulphate forms **Alums**. The **Chlorides**, $InCl_2$ and InCl are also known.

THALLIUM. This is a much less rare metal than the two preceding, and was discovered by means of its spectrum, which shows a fine green line, by Crookes in 1861, and by Lamy in 1862 in the sludge of the lead chambers, being contained in certain pyrites and blendes (and also in the sylvine and carnallite of Stassfurt). It is a metal which is rather less soft than sodium, and is separated from the above products by dissolving in H_2SO_4, and reprecipitating with HI in the form of TlI. The metal is of a leaden colour, of sp. gr. 11·8, and boils at 290°. It is somewhat oxidised in the air, but remains unaltered under water. It is soluble in H_2SO_4 and in HNO_3, but is only slightly soluble in HCl, because it becomes covered by insoluble chloride. It burns with a bright green flame.

Thallium when acting as a monovalent element forms *thallous* compounds, which are similar to those of the alkali metals. Thus the hydroxide and the carbonate show an alkaline reaction and form salts similar to those of potassium with which they are isomorphous; thus also thallous sulphate forms an alum, &c. As a trivalent element, thallium forms thallic compounds which have a certain similarity with those of aluminium, but thallic sulphate forms an alum containing 8 molecules of water instead of 24.

The halogen compounds of thallium are very insoluble, and in this respect it resembles silver. Glass containing thallium is now produced and refracts light very strongly like lead glass.

ELEMENTS OF THE RARE EARTHS

This group comprises numerous more or less rare elements and they have not been all sufficiently studied to make it certain that they are all true elements. The better known are: **Scandium, Sc, 44·1; Yttrium, Y, 89; Lanthanum, La, 139; Cerium, Ce, 140·25; Praseodymium, Pr, 140·6; Neodymium, Nd, 144·3; Samarium, Sa, 150·4; Gadolinium, Gd, 157·3; Terbium, Tb, 159·2; Erbium, Er, 167·4; Thulium, Tm, 168·5; Ytterbium, Yb, 172.**

These elements are often found together with the rare oxides of thorium, &c., which have already been described on p. 403, and are separated from one another by complicated methods which utilise certain special properties of their salts, as in the case of the earths already described on that page.

SCANDIUM. Mendelejew had already predicted the existence of this element before it was discovered, and called it *ekaboron*, on account of its position as a neighbour to boron in the periodic system. The hydroxide, $Sc(OH)_3$, is obtained in a gelatinous form by the action of alkalis, and is insoluble in excess of the latter.

CERIUM is found in *cerite*, $Ce_4Si_3O_{15}H_6$, which contains 60 per cent. of this element. It has an appearance similar to iron, but does not alter in the air, although it burns at high temperatures (*see also* p. 403). It forms an oxide, Ce_2O_3, from which the *cerous* compounds are derived, and another oxide, CeO_3, which forms *ceric* salts.

LANTHANUM (*see* p. 403) is a trivalent element, and forms an oxide, La_2O_3, and various salts.

PRASEODYMIUM and **NEODYMIUM.** These were at one time believed to form a single element, **Didymium**, which was later separated into the two others by Auer. Neodymium salts are red, whilst those of praseodymium are green, and the two elements also show different spectra.

YTTERBIUM. This is obtained from the earth erbia, which mainly consists of the oxide, Yb_2O_3, and is formed from *Gadolinite*, $(Be_2Fe)(YbO)_2(Sio_4)_2$. Its salts give no emission spectrum and are colourless. In 1908–1909 Auer showed that ytterbium is formed of two elements, **Cassiopeium** and **Aldebaranium.**

YTTRIUM is found in *Gadolinite*, *Yttrialite*, &c., and may be separated from the cerite earths by means of the solubility of its double potassium sulphate in concentrated sulphuric acid. The oxide, Y_2O_3, is present in the filament of the Nernst lamp.

SAMARIUM. This element is found in monazite. An oxide, Sa_2O_3, and a well-crystallised chloride, $SaCl_3$, are known.

FOURTH GROUP: TETRAVALENT METALS

GERMANIUM : Ge, 72.5 ; TIN : Sn, 119 ; LEAD : Pb, 207.1

These elements also form oxides of the type MeO in which they are divalent and which have a basic character which increases with rise of the atomic weight. The derivatives of the dioxides, in which the metals are tetravalent, have a weakly acid character which diminishes with rise of the atomic weight. Thus such derivatives of lead are immediately decomposed by water. These elements have a certain similarity with silicon and carbon, although their character is more metallic.

GERMANIUM : Ge, 72.5

Mendelejew had predicted this element in 1871 and called it *ekasilicon*, also predicting its physical and chemical properties. It was discovered in 1886 by Winkler in the mineral, *Argyrodite*, which is a sulphide of silver and germanium, $GeS_2.3Ag_2S$, when all the predictions of Mendelejew were fully and exactly verified. He obtained the free metal by heating this mineral with carbon in a current of hydrogen. It is a very rare element which has a white metallic lustre, gives a characteristic spectrum, crystallises in octahedra, of sp. gr. 5·472, and melts at 900°. It is stable in the air, is insoluble in HCl (like silicon), and forms a hydroxide with nitric acid (like tin) ; it dissolves in molten alkalis. The derivatives of the oxide, GeO, which are called *germanous* compounds, are rather unstable, and those of the oxide, GeO_2, are called *germanic* compounds, and are characterised by their greater stability.

GERMANOUS OXIDE : GeO. This is obtained from the hydroxide which is formed by adding potassium hydroxide to germanous chloride.

GERMANIC OXIDE : GeO_2. This is formed from germanium with HNO_3, or by roasting the sulphide or hydroxide. It separates as a white powder, which is stable on heating. It is insoluble in acids, slightly soluble in water with acid reaction and forms salts with bases.

GERMANIC SULPHIDE : GeS_2. This compound is obtained as a white precipitate from a hydrochloric acid solution of GeO_2 with H_2S ; it evolves H_2S in the air and dissolves in alkali sulphides and in alkalis forming sulpho-salts.

TIN : Sn, 119

Tin is a metal which has been known to man since remote antiquity. It abounds in the form of oxide (*cassiterite*, *tinstone*, SnO_2) in certain deposits in Cornwall, Saxony, Peru, Tuscany, the island of Banka, &c., and the largest tin works existing to-day are in the island of Pulo Brani, near Singapore.

The extraction of tin from cassiterite is relatively simple. The mineral is first crushed, levigated with water in order to separate it from much gangue, and is then roasted in a furnace with a revolving hearth. In this way the sulphur and arsenic are eliminated. After this the residue is again levigated and in certain cases is also treated with crude HCl in order to separate Fe, Cu, and Bi. Finally it is mixed with coal and completely reduced in a cupola or reverberatory furnace.

The tin drops to the bottom into a separate vessel. The slag which remains is again treated in a reverberatory furnace. The refining of the tin is carried out by melting it at a fairly low temperature in such a way that the impurities collect, together with foreign metals, into easily separable lumps. The tin which has thus been purified is again melted and is continuously stirred with rods of fresh wood as in the refining of copper (p. 544), in such a manner that the oxidisable metals separate at the surface and pure tin remains.

The recovery of tin from scrap or turnings of tinplate (tinned sheet-iron containing 3 to 5 per cent. of tin) is an important operation. At one time these turnings were simply

heated and the molten tin collected ; but it is preferable to treat them with hydrochloric acid or a mixture of HCl + HNO_3, slightly dilute and in the cold ; thus 10 parts of crude HCl, 1 part of crude HNO_3, and 10 parts of water may be used per 100 parts of tinplate. From the solution so obtained the tin is precipitated by zinc foil after it has been almost neutralised. Of late years the electrolytic process has acquired importance in various modifications. According to the process of Siemens and Halske, the bundle of tinplate scrap is used as the anode in a bath of hydrochloric acid (1 vol. of 60 per cent. acid + 9 vols. of water), in which 1 per cent. of free acid must always be present during electrolysis ; spongy tin thus collects at the cathode which consists of a tinned copper plate. A current of 100 amps. per square metre is used.

Better results are obtained by electrolysis in a hot bath at 70° to 80°, containing 10 per cent. of sodium hydroxide and 10 per cent. of NaCl as proposed by Keith in 1876 (U.S. Pat. 176,658). In this way any varnish and grease on the scrap are removed. The scrap is compressed into bundles and used as the anode, the cathode being formed of sheet iron on which the tin separates. At the anode electrolytic oxygen is formed which, in presence of NaOH, forms sodium stannate with the tin which dissolves in the hot solution :

$$Sn + O_2 + 2NaOH = SnO_3Na_2 + H_2O.$$

At the cathode electrolytic hydrogen is formed, and reduces the stannate, separating spongy tin and regenerating the sodium hydroxide :

$$SnO_3Na_2 + 4H = H_2O + 2NaOH + Sn.$$

The scrap iron which remains may be used in open-hearth furnaces for the preparation of steel if it contains less than about 0·08 per cent. of tin. It is necessary to work at a low tension with a potential difference between the one bath and the other not greater than 2 to 3 volts, and a current density not greater than 0·75 amp. per square metre of cathode surface. L. Annoni in 1909 increased the surface of the cathode in order to obtain less difference between the extent of the anodic surface, which is formed of bundles of tinplate, and that of the cathodic surface, by forming the latter of iron wire netting. There should not be more than 5 per cent. of sodium stannate nor more than 3 per cent. of sodium carbonate in the bath. The bath should be in continuous circulation from one vessel to the other so that the stannate may not be dissociated and may not be transported to the cathode by the current. It is also necessary to heat the bath in order to maintain it at constant temperature. The tin is removed every 12 hours by carefully removing the cathode with the adherent grey and spongy tin, immediately immersing it in a vessel of water and detaching the tin with a small scraper whilst it is immersed in order to avoid oxidation which easily occurs. It is then rapidly and repeatedly washed and compressed into blocks which still contain 10 to 15 per cent. of water. These are melted in graphite crucibles, sprinkling the surface with a little colophonium in order to avoid oxidation. The slag and the tin residues are resmelted with coal in a reverberatory furnace. Tin from detinning works containing 98 to 99 per cent. of Sn is not suitable for the preparation of fresh tinplate, but is satisfactory for other purposes. In order to maintain the composition of the electrolyte constant it is necessary to continually replace a portion, and the tin is regenerated from the portions which are removed by saturating them with CO_2, and thus precipitating H_2SnO_3 which is sold to enamel works.[1]

Another process which appears to give better results than the electrolytic process is the chlorination process proposed by Higgins in 1854 (Eng. Pat. 767) and perfected by Parmelee in 1870, Lambotte in 1884 (Ger. Pat. 32,517), and still further by Th. Goldschmidt in 1905 (Ger. Pats. 176,457, 181,876 and 188,018), who compresses the scrap into compact bundles, perforates them in all directions, washes them with a solution of hot sodium hydroxide and then with water, dries them, and heats them until the lead solder is melted. He then finally brings them into contact with dry chlorine in cooled vessels under pressure. Pure stannic chloride collects below and pure iron remains, which is not attacked if the scrap and the chlorine were dry.

[1] According to L. Annoni, half a ton of scrap can be detinned in two hours in the detinning establishment of Pont St. Martin in nine vessels arranged in series, each of which has a capacity of 2 cu. metres, and contains 4 bundles of scrap, each weighing 15 kilos and 5 cathodes using a current of 300 amps. at 20 volts. Supposing that the scrap contains 2·5 per cent. of tin on the average, the current efficiency will be 70 per cent. of the theory, as in theory 1 amp.-hour deposits 1·72 grms. of Sn^{iv}, and practically 0·85 grm. is obtained. (*Translator's note.*—There is obviously something wrong with these figures.)

Traces of $FeCl_3$ easily cause the iron to rust, and this is avoided by subjecting it to mild electrolysis.

The Goldschmidt Company in Germany annually treats 50,000 tons of tinplate by this method.

In Germany 75,000 tons of tinplate scrap are treated annually in 8 to 10 works, about 30,000 tons in the rest of Europe, and about 60,000 tons in the United States. In Italy there are four works which are able to treat 10,000 tons of tinplate, as much as is produced in the country, but actually a smaller quantity is treated, and new tinplate costs up to £4 per ton, whilst that from objects which have been used only costs £1 4*s.* to £1 12*s.*, and the detinned iron is sold at £2 8*s.* per ton. Tinplate scrap pays 8*s.* per ton import duty on entering Italy, and there is no export duty. In 1909 the firm of Th. Goldschmidt established a German-American company with a capital of £600,000, for the exploitation of the process of detinning with chlorine throughout the world.

PROPERTIES. Tin is a metal of silvery appearance which melts at 233° and distils at 1500°. It has a specific gravity of 7·29. At the ordinary temperature it is pliable and malleable, and may be converted into extremely thin foil (tin foil), whilst at 200° it is brittle. It has a crystalline structure, and on bending sticks of tin the so-called *cry* of tin is heard, which is due to the friction of the crystalline particles. On pouring HCl on to a surface of tin, radiating crystalline markings remain which give the metal a frosted metallic appearance. At a temperature of −40° it modifies its structure and powdery **Grey Tin** is obtained of sp. gr. 5·8. It is not altered in the air or by water. If kept fused for some time it becomes covered with a grey layer of tin oxide. It is soluble in cold, dilute nitric acid, in HCl, in concentrated H_2SO_4, and in hot NaOH, with evolution of H. With concentrated HNO_3, however, it directly forms metastannic acid without dissolving. It resists alkalis and weak acids, such as acetic acid and the other organic acids, very well in the cold.

Tin forms two series of derivatives, *stannous* compounds, in which it behaves as a divalent element, and *stannic* compounds, in which it is tetravalent.

On account of its resistance to ordinary reagents, tin is much used for objects and vessels in common use, and for tinning copper and iron utensils (kitchen utensils, &c.[1]); tinplate, which consists of tinned iron, is obtained by immersing iron plates previously washed with HCl or H_2SO_4 into baths of molten tin. Tin foil is used for mirrors and for wrapping up foodstuffs. Much tin is used alloyed with other metals. Ordinary *solder* contains tin and lead in almost equal proportions and melts at a lower temperature than either of its components.

Bronzes contain tin and copper (*see* p. 547). *A tin amalgam* is also prepared for silvering mirrors.

The *world's production* of tin was 40,000 tons in 1880, and rose to 91,000 tons in 1903, of which 38,000 tons were used in the United States, 15,000 in Germany, and 11,000 tons in England; in 1907 the world's production was 98,700 tons, of which 56,550 tons were produced in the United States, and 6500 tons in Germany; the consumption in 1907 was 20,500 tons in England and 15,100 tons in Germany. The world's production in 1908 was 105,500 tons. The *price of tin* varies greatly on account of speculative operations. In 1880 it cost £88 5*s.* per ton; in 1895 £66 per ton; in 1902 £120 per ton, and rose in 1906 up to £152 to £160. Italy produced 14 tons of tin from scrap in 1905 and imported 2300 tons, including its alloys with lead and antimony. In 1906 it imported 3361 tons and in 1909 2554 tons of the value of £347,400, apart from 200 tons of worked objects—wire, capsules, &c.—of the value of £26,000.

The production of *tinplate* in the United States of America in 1891 was only

[1] The firm of Postler & Co., of Dresden, placed a paste on the market in 1908 (*Löt-Blitz*), which when stirred up with water is spread on to well-cleaned metallic parts without dismounting them: the object is then heated directly with a benzene lamp and a homogeneous tin surface is thus obtained directly.

999 tons, and rose to 458,000 tons in 1904, without including 65,000 tons imported from England, which produced 600,000 tons in 1908.

Italy produced 28,277 tons of tinplate in 1908 of the value of £517,538, and imported 14,000 tons of tinned, coppered or oxidised iron sheet in 1909 of the value of £320,000.

STANNOUS COMPOUNDS

STANNOUS OXIDE: SnO (Tin Monoxide). This is a black powder which is formed on heating stannous hydroxide in a current of CO_2, and readily oxidises in the air, forming stannic oxide, SnO_2.

STANNOUS HYDROXIDE: $Sn(OH)_2$. This compound is obtained as a white precipitate by the action of sodium carbonate on a solution of stannous chloride,

$$SnCl_2 + Na_2CO_3 + H_2O = Sn(OH)_2 + 2NaCl + CO_2.$$

It is insoluble in NH_3, but dissolves in sodium hydroxide forming **Sodium Stannite**, Na_2SnO_2, which is transformed on heating into soluble **Sodium Stannate**, Na_2SnO_3, with separation of metallic tin.

STANNOUS CHLORIDE: $SnCl_2$. This compound is obtained on treating tin with the calculated quantity of HCl according to the equation, $Sn + 2HCl = SnCl_2 + H_2$, and crystallises with $2H_2O$, forming common *tin salt*, which loses water at 100°, melts at 250°, and distils unaltered at 606° with a vapour density corresponding to the formula, Sn_2Cl_4, whilst at 900° it corresponds to $SnCl_2$. It is soluble in a little water, more especially in presence of HCl, and is a strong reducing agent (p. 538); with much water a white powder of the oxychloride $SnOH.Cl$ is formed and is also formed together with $SnCl_4$ on allowing a slightly acid solution to stand in the air. Stannous chloride is decomposed by strong H_2SO_4 with evolution of HCl. It also forms double salts such as $SnCl_2.2KCl$.

It is used as a mordant. Germany produced 810·5 tons in 1905.

STANNOUS SULPHIDE: SnS. This is precipitated as a brown, amorphous powder on treating a stannous salt with H_2S, or as a blue crystalline powder on melting tin with sulphur. It is insoluble in alkali sulphides, but dissolves in polysulphides on heating to form a sulphostannate: $SnS + Na_2S_2 = Na_2SnS_3$. On treatment with HCl, H_2S is evolved and $SnCl_2$ is formed.

STANNIC COMPOUNDS

STANNIC OXIDE (Tin Dioxide): SnO_2 (Stannic Anhydride). This is found in nature as *cassiterite* of sp. gr. 6·8, and is also formed on heating molten tin in the air. It is a white amorphous substance which only melts at the temperature of the electric furnace. It is insoluble in alkalis and acids. When fused with NaOH it forms soluble stannates.

Italy imported 32·5 tons in 1907 and 53·7 tons in 1909 of the value of £8240.

STANNIC HYDROXIDE. The compound $Sn(OH)_4$ is not known, but the *meta-hydroxide*, H_2SnO_3, has been well studied. It has an acid character and occurs in two modifications:

α-Metastannic Acid forms as a white precipitate on treating a solution of stannic chloride with NH_3 or NaOH, or an alkali stannate with HCl:

$$SnCl_4 + 4NaOH = 4NaCl + H_2O + H_2SnO_3.$$

This compound is soluble in alkalis, in HCl, and in strong HNO_3.

β-Metastannic Acid is formed on treating tin with strong nitric acid. It is insoluble in alkalis and only combines with an excess of these to form sodium metastannate, which is soluble in water, but not in alkali. On heating with HCl it forms **Metastannic Chloride, $SnCl_4$**, which is not identical with the ordinary stannic chloride, and is insoluble in strong HCl, but soluble in water.

The β-acid is transformed into the α-acid on boiling or on fusing it with alkali hydroxides. The β-acid is probably a polymer of the α-acid. According to W. Mecklenburg (1909) the various varieties of stannic acid are best accounted for by supposing them to consist of particles of varying size, which separate from the alkaline, acid, or neutral colloidal solution, and that the α-acid consists of smaller particles than the β-acid.

Amongst the various salts of α-metastannic acid, the sodium salt, $Na_2SnO_3 + 3H_2O$,

which is used in dyeing, deserves mention. It is more soluble in cold than in hot water, and is obtained on fusing the oxide, SnO_2, with NaOH.

STANNIC CHLORIDE : $SnCl_4$. This is a liquid which fumes strongly in the air and is obtained by the action of chlorine on tin or stannous chloride. It has a specific gravity of 2·27 and boils at 114°. In contact with moisture or a little water it is transformed into a crystalline mass, $SnCl_4.5H_2O$, of the consistency of butter (butter of tin). It is prepared industrially by dissolving granulated tin, obtained by pouring molten tin into water, with concentrated hydrochloric acid of 20° Bé. Stannous chloride of 60° Bé. is thus obtained and this is then neutralised and heated with 40 per cent. of concentrated HCl of 20° Bé. in presence of a little sodium chlorate as an oxidising agent :

$$3SnCl_2 + NaClO_3 + 6HCl = 3H_2O + NaCl + 3SnCl_4.$$

The resulting solution is placed on the market under the incorrect name of "Pink Salt."

It is advantageously prepared to-day by the Goldschmidt process (*see above*, Tin) by treating tinplate scrap (tinned iron) directly with dry chlorine gas from liquid chlorine. If the chlorine and the scrap are dry the iron is not attacked (*see also* U.S. Pat. 877,261 of 1908).

According to U.S. Pat. 874,040 of 1907 the tin can be dissolved from the plate with an anhydrous solution of stannous chloride (*see also* Perino, Ger. Pat. 212,757 of 1907 and Fr. Pat. 401,125 of 1909).

On diluting the aqueous solution, HCl and metastannic acid are formed : $SnCl_4 + 3H_2O = SnO_3H_2 + 4HCl$. It is unaltered, on the other hand, by hot sulphuric acid.

Well-crystallised double salts are known, of which *pink salt*, so called on account of its pale pink colour, $SnCl_4.2NH_4Cl$, was at one time much used in dyeing and in weighting silk. It may be considered as the ammonium salt of chlorostannic acid, H_2SnCl_6, and is obtained by saturating an aqueous solution of 2 parts of tin salt, $SnCl_2.2H_2O$, with chlorine, and then pouring the whole into a hot solution of 1 part of NH_4Cl in 2 parts of water. The concentrated aqueous solution does not decompose on heating, but when dilute metastannic acid separates. Solid pink salt costs £80 per ton, and in solutions of 50° Bé. £44 16*s*. Stannic chloride, crystallised or in solution, is usually placed on the market to-day under the denomination of pink salt.[1]

Italy imported 2·9 tons of stannic chloride in 1906, 29·2 tons in 1907, 84·2 tons in 1908, and 172·2 in 1909, of the value of £16,532. In 1905 Italy produced 250 tons of pink salt and 200 tons in 1907 of the value of £8400

[1] Table showing the densities and concentrations of solutions of stannic chloride at 15° :

Degrees Bé.	Specific gravity	$SnCl_4+5H_2O$ Per cent.	Degrees Bé.	Specific gravity	$SnCl_4+5H_2O$ Per cent.	Degrees Bé.	Specific gravity	$SnCl_4+5H_2O$ Per cent.
1·7	1·012	2	26·6	1·2268	34	50·5	1·538	66
3·3	1·024	4	28·1	1·242	36	52	1·563	68
4·8	1·036	6	29·6	1·259	38	53·5	1·587	70
6·2	1·048	8	31·2	1·2755	40	54·9	1·614	72
7·9	1·059	10	32·6	1·293	42	56·4	1·641	74
9·6	1·072	12	34·2	1·310	44	57·8	1·669	76
11·1	1·084	14	35·7	1·329	46	59·4	1·698	78
12·5	1·097	16	37·2	1·347	48	60·8	1·727	80
14·2	1·110	18	38·7	1·366	50	62·2	1·759	82
15·8	1·1236	20	40·2	1·386	52	63·8	1·791	84
17·3	1·137	22	41·7	1·406	54	65·2	1·824	86
18·9	1·151	24	43·2	1·426	56	—	1·859	88
20·3	1·165	26	44·6	1·447	58	—	1·893	90
22	1·180	28	46	1·468	60	—	1·932	92
23·5	1·195	30	47·5	1·491	62	—	1·969	94
25	1·210	32	48·9	1·514	64	—	1·988	96

STANNOUS SULPHIDE: SnS_2 **(Artificial Gold).** This is formed as a yellow amorphous mass by the action of H_2S on solutions of $SnCl_4$, in the form of light scales of a golden colour. It is also obtained on heating 18 parts of tin amalgam (12 parts of molten tin and 6 parts of Hg) with 7 parts of sulphur and 6 parts of NH_4Cl; HgS and NH_4Cl then distil and "artificial gold" remains, which is used for imitation gilding of many objects—cornices, &c.

It is soluble in strong HCl, forming $SnCl_4$. With HNO_3 it forms metastannic acid. It is soluble in alkali sulphides with which it forms sulphostannates (SnS_3Na_2), from which SnS_2 is reprecipitated by acids. When freshly precipitated it dissolves in aqueous ammonia to form a red liquid which is decolorised by the air and separates **Tin Oxysulphide, SnSO,** with acids. This latter is a white powder, soluble in ammonium carbonate.

LEAD: Pb, 207.1

This element is found abundantly in nature in *Galena*, PbS, and in smaller quantities in *Cerussite*, $PbCO_3$, in *Crocoisite*, $PbCrO_4$, *Wulfenite*, $PbMoO_4$, and *Anglesite*, $PbSO_4$. The greater quantity of lead is obtained from galena which abounds in the United States, Spain, Germany and England. Its extraction is not very difficult and is carried out by various methods. The most abundant deposits of lead ores in Italy are in Sardinia (Iglesias), where, after preliminary treatment, the final smelting occurs at Pertusola (Spezia) and at Battino (Serravezza). Much less important galena deposits are found in Veneto, Lombardy, and Tuscany.

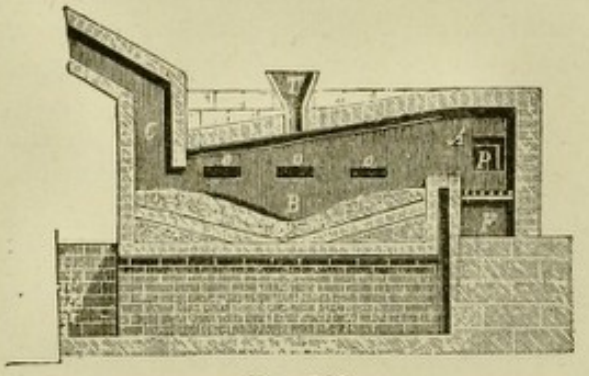


FIG. 265.

(1) EXTRACTION BY ROASTING AND SMELTING. This process is used when the ore is pure and contains no silica, or less than 4 to 5 per cent. The ore is first roasted in a reverberatory furnace and the lead sulphide thus partially transformed into the oxide, PbO, and partially into the sulphate, $PbSO_4$, whilst a portion remains unaltered. On then raising the temperature considerably these three products react with one another yielding molten lead, whilst SO_2 is evolved:

$$PbS + PbSO_4 = 2Pb + 2SO_2, \text{ and also } PbS + 2PbO = 3Pb + SO_2.$$

The unaltered lead sulphide is again roasted and smelted until completely extracted. The smelting furnace (Fig. 265) is that which has for some time been used in England. The hearth is lined with molten slag and inclined towards the middle, *B*, and also towards one side, so that the molten lead may readily be collected. The mass is kept stirred through the openings, *o*, and is heated by the fuel which burns in *F*. The ore is charged in through the funnel, *T*. The operation lasts 6 to 7 hours for each 800 to 1000 kilos. The crude lead which is obtained by these various processes still contains considerable quantities of impurities and is known as "work-lead."

(2) PROCESS OF ROASTING WITH REDUCTION. This is the process commonly used, especially in North America, and is suitable for all grades of ore, even when poor and very impure. The ore is first roasted in the usual reverberatory furnaces with the addition of SiO_2 as a flux, until nothing remains but PbO and lead silicate. The mass is then mixed with half its weight of coke and reduced in special cupola furnaces, constructed of sheet iron with double walls (Fig. 266) between which cold water circulates. During the smelting process, compressed air is injected through tubes which pass in at the bottom of the furnace. In order to be able to obtain the metal from an ore which is difficult to reduce, lime or iron ore is added.

An improvement (Huntington and Heberlein) which facilitates the reduction and roasting without loss of lead vapour and without formation of lead sulphate or compact stony masses, consists in roasting the galens at 700° in a mechanical furnace with 6 to 15 per cent.

of lime, CaO, 6 per cent. of fuel, and an excess of air. 50 to 60 tons of ore are treated in each furnace in 24 hours. $PbSO_4$, $CaSO_4$, a little PbO, but no lead, are formed. The roasting of the product, which contains 1·5 per cent. of sulphur, is completed in a converter (*see* Iron) of 15 tons capacity into which air is blown for 4 to 6 hours, after which PbO and $CaSO_4$ alone remain, SO_2 being evolved. After this treatment the reduction in the cupola furnace takes place much more easily.

CaO acts as a catalytic agent and does not form calcium plumbate as was once believed, as iron oxide produces the same effect. Galena may also be roasted directly in a converter with 10 to 35 per cent. of $CaSO_4$ (Carmichael process) by means of compressed air, and is then reduced in the usual manner, but this method is most suitable for ores containing little sulphur.

(3) **PRECIPITATION PROCESS.** This is now little used, but serves well in the case of ores containing much silica. The galena is melted together with a substance which readily removes the sulphur, such as iron (that is, its oxides), $PbS + Fe = Pb + FeS$. The operation is conducted in a cupola furnace such as is used for copper, but the necessary temperature is so high that appreciable loss of lead occurs.

(4) **ELECTROLYTIC PROCESS.** The powdered galena is placed in capsules of hard lead and dilute sulphuric acid is added. The lead sulphide forms the cathode and the bottom of the capsule the anode. When the current is passed, H and H_2S are evolved and the lead collects as a spongy mass.

REFINING OF WORK-LEAD. The crude lead obtained by various processes contains considerable quantities of impurities, and is purified by liquation (p. 414) if the lead contains copper (*see* Treatment of Water), or by oxidation, the crust or scum which forms on the surface of the molten lead being separated; or the lead may be reduced by means of poles of green wood (*see* Copper, p. 544).

Numerous electrolytic refining processes have also been proposed but have not yet proved to offer any advantages. It appears that lead fluosilicate is very suitable for electrolysis because it yields compact blocks of lead at the cathode. The formation of crystals is avoided by adding a little gelatine to the bath.

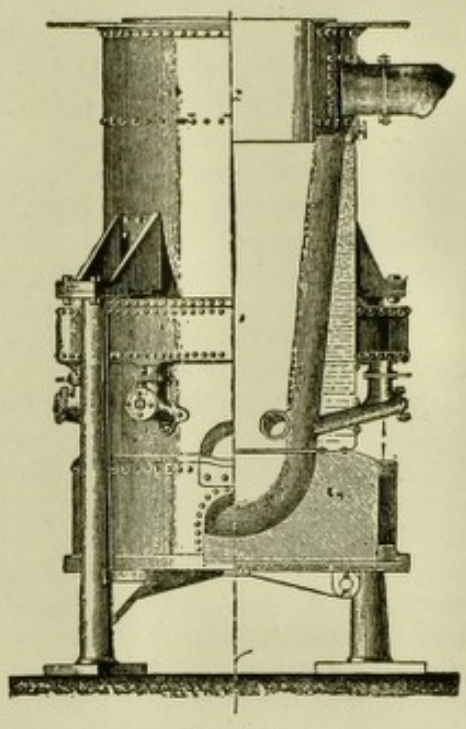


Fig. 266.

PROPERTIES. Pure lead (refined lead of 99·99 per cent. of Pb) has a bluish-grey colour, is very soft and ductile and in the air becomes covered with a thin layer of oxide which destroys this lustre but protects it from atmospheric corrosion. It has a specific gravity of 11·37, melts at 334° and boils at 1600°. When lead is obtained in a state of extremely fine division, for instance, by igniting lead tartrate or citrate in a test-tube out of contact with the air, it catches fire spontaneously and is then known as *pyrophoric lead* (p. 174). It is not attacked by HCl or H_2SO_4 in the cold, because the first layer of insoluble lead chloride or sulphate which is formed at the surface protects the rest of the metal, but if the lead is very finely divided it is completely attacked. Even acetic acid and other organic acids attack lead, and nitric acid dissolves it in the cold forming the nitrate. Zinc and iron separate crystalline lead from solutions of its salts. If a zinc rod is placed in a vessel containing a solution of lead acetate, the zinc quickly becomes covered with many lustrous and branching crystals of lead (lead tree).

Lead salts are poisonous and lead should therefore be absent from all utensils used for the preparation of food, so that solders containing lead and earthenware glazed with lead should be avoided (*see* Lead Poisoning, in the section on White Lead); it should also be avoided for water-pipes (p. 211).

USES AND STATISTICS. Large quantities of lead are used in various chemical industries, but especially for sulphuric acid tanks, lead chambers, the manufacture of hard lead (pp. 249 and 320), pipes, small shot (containing 0·2 to 0·8 per cent. of arsenic), and certain important alloys, such as solder and type metal (p. 320).

The *world's production* of lead in 1880 was 380,000 tons. It was 586,000 tons in 1890, 871,000 tons in 1900, 992,000 tons in 1907, and 1,052,500 tons in 1908. The production in the United States in 1900 was 253,000 tons ; it was 414,000 tons in 1907, and 396,400 tons in 1908. Spain produced 176,000 tons of lead in 1900 and 186,000 tons in 1907. Germany produced 121,000 tons in 1900 and 140,000 tons in 1907. In 1908 84,000 tons came from Mexico, 67,000 tons from Australia, 35,000 tons from England, 26,500 tons from Italy (1902) (and 23,000 tons in 1907 of the value of £440,000), 15,000 tons from France, &c. The price was £16 16*s*. per ton in 1880, and about £12 8*s*. in 1902 ; it then oscillated between a minimum of £12 in 1904 and a maximum of £20 in 1906, finally sinking to £14 8*s*. (?) in 1909 and 1910. Italy imported 6764 tons in 1905, including alloys with antimony. In 1906 the imports were 10,958 tons, in 1908 11,741 tons, and in 1909 10,011 tons of the value of £144,000, to which must be added 250 tons of foil, pipes, type metal, &c., of the value of £11,200.

The lead ores produced in Italy in 1908 amounted to 46,650 tons, of the value of £267,268.

LEAD COMPOUNDS

In its more stable derivatives lead is divalent, but less stable tetravalent compounds exist, and it forms five oxides.

LEAD SUBOXIDE : Pb_2O, is a black powder which is converted on heating into the more stable oxide, PbO.

LEAD MONOXIDE : PbO. On heating lead for a prolonged period in the air (or on heating the hydroxide, nitrate, or carbonate) an amorphous yellow powder of PbO is formed, the common name for which is **Massicot.** On melting massicot and then allowing it to cool more or less rapidly a more or less reddish-yellow scaly mass of PbO results, which is called **Litharge.** This is obtained in large quantity in the extraction of silver (pp. 553, 554). Lead oxide has a markedly basic character and saponifies the fats. It is slightly soluble in water with which it forms the hydroxide. It has a specific gravity of 9·2 to 9·5 and is easily reduced to lead by H, CO, or carbon on heating. PbO is used for the preparation of many other lead compounds, such as the acetate, &c., for glazes, in glass-making, and in the manufacture of earthenware. Crude litharge costs about £16 per ton ; when refined it costs double. Massicot costs £26 to £28. In general the prices vary with those of lead. In 1903 Italy produced 883 tons and about 580 tons in 1905, in addition to which about 600 tons were imported. In 1907 it produced 770 tons and in 1908 780 tons of the value of £14,000. The imports were 883 tons in 1908 and 586 tons in 1909. The exports in 1909 were 106 tons. Germany exported 4450 tons of litharge in 1905 at £15 per ton.

LEAD HYDROXIDE : $Pb(OH)_2$. On adding sodium hydroxide or NH_3 to a solution of a lead salt a voluminous white precipitate of lead hydroxide is produced which is soluble in an excess of sodium hydroxide, but insoluble in excess of ammonia. It is slightly soluble in water, has an alkaline reaction and absorbs CO_2 from the air forming a basic lead carbonate, that is, a mixture of hydroxide and carbonate which is used in painting under the name of *white lead*. At 130° it decomposes into H_2O and PbO.

MINIM : Pb_3O_4 (Red Lead or Red Lead Oxide). This compound is obtained by carefully heating PbO in a reverberatory or muffle furnace at about 450° in such a manner that it does not melt, but the best qualities of minim are obtained on heating the pure oxide with sodium nitrate or potassium chlorate in an oxidising flame to a dark red heat, or by heating lead sulphate mixed with the nitrate and sodium carbonate. It has a bright scarlet colour and may be considered to have the constitution, $2PbO + PbO_2$; in fact on treatment with HNO_3, PbO is dissolved and PbO_2 remains. It has a specific gravity of 8·6 to 9.

On heating strongly it first becomes dark red, then violet, and finally almost black, and on cooling regains its original colour. Powdered minim is used with

oil in painting and for coating machinery. It is also used in glass manufacture, &c. It is now partially replaced by red iron oxide, Fe_2O_3. It costs from £14 to £20 per ton according to its purity and the price of lead.[1]

Italy produced 4175 tons in 1897, only 1340 tons in 1905, and 1580 tons in 1907, and the imports were 725 tons in 1905. Germany exported 8900 tons of red lead in 1905 at £1 16*s*. 10*d*. per ton, and 9114 tons in 1909, whilst it imported 1193 tons.

LEAD DIOXIDE, BROWN LEAD OXIDE: PbO_2. This compound is also inappropriately called *lead peroxide*. It is obtained on treating red lead with dilute HNO_3:

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O,$$

or by passing chlorine into an alkaline solution of a lead salt or by adding calcium hypochlorite to a solution of a lead salt:

$$2PbCl_2 + Ca(OCl)_2 + 2H_2O = CaCl_2 + 2PbO_2 + 4HCl,$$

the hydrochloric acid which is formed combining with the lime. It is now also electrolytically prepared from lead nitrate. PbO_2 is an amorphous powder of dark brown colour.

With cold HCl it forms lead tetrachloride, $PbCl_4$. PbO_2 readily evolves oxygen on heating, being transformed into PbO, and with hot KOH it forms **Potassium Plumbate, K_2PbO_3**, which thus shows an analogy with potassium stannate. Potassium plumbate is decomposed by much water into KOH and PbO_2. A **Calcium Plumbate, $CaPbO_3$** or **Ca_2PbO_4**, is obtained on heating a mixture of PbO and $CaCO_3$ in the air to 700°, CO_2 being evolved. On heating the plumbate to 700° in presence of pure CO_2 oxygen is evolved and calcium carbonate and PbO are formed, which then regenerate the plumbate in contact with air. A continuous process for manufacturing oxygen can be based on this process and was applied industrially by Kassner in 1900 (*see* p. 182).

Lead dioxide is of great importance in connection with the manufacture of electric accumulators (p. 421), as an energetic oxidising agent in various chemical processes, and also in the manufacture of matches. The commercial product of 80 per cent. strength costs £38 per ton, whilst the more concentrated product of 96 to 98 per cent. costs £46, and when purified £128 to £160.

In 1905 Italy produced 1 ton, and in 1908 20 tons of the value of £480.

LEAD CHLORIDE: $PbCl_2$. This is formed as a white precipitate by the addition of dilute HCl or NaCl to a fairly strong solution of a lead salt. It is very insoluble in cold water, but dissolves in 30 parts of water at 100°, and separates in white, shining crystals on cooling this solution. The separation of $PbCl_2$ is facilitated by the addition of dilute HCl, because this increases the concentration of the Cl' ions and the concentration product exceeds the solubility of $PbCl_2$ (pp. 100 and 432).

LEAD TETRACHLORIDE: $PbCl_4$. On dissolving $PbCl_2$ in concentrated HCl and saturating the solution with chlorine, a heavy yellow oil separates of sp. gr. 3·18, which consists of $PbCl_4$. On heating this product $PbCl_2$ and Cl_2 are formed, and with NH_4Cl it forms a yellowish, crystalline double salt, $PbCl_4 . 2NH_4Cl$, which is analogous to pink salt (p. 609).

LEAD IODIDE: PbI_2. This compound is obtained from a solution of a lead salt by the addition of potassium iodide and forms yellow crystals soluble in hot water to a colourless solution.

LEAD NITRATE: $Pb(NO_3)_2$. This compound is obtained in a crystalline condition by concentrating a solution of lead or PbO in dilute nitric acid. It is isomorphous with barium nitrate. 100 parts of water at 10° dissolve 48 parts of the nitrate, and at 100° they

[1] **Analysis of Red Lead.** The amount of impurity is determined by the residue insoluble in dilute nitric acid mixed with an aqueous sugar solution. It is sometimes artificially coloured, and alcohol then dissolves the admixed coal-tar dyestuffs. The percentage of PbO_2 is determined by dissolving 1 grm. of red lead by heating it with 3 c.c. of nitric acid of sp. gr. 1·2 and then treating it with 50 c.c. of $\frac{N}{5}$ oxalic acid. The whole is boiled for some minutes and the excess of oxalic acid titrated back with a $\frac{N}{5}$ solution of potassium permanganate. By deducting from the 50 c.c. of oxalic acid used the amount of permanganate required, the amount of oxalic acid oxidised by the PbO_2 is found, and the percentage present in the red lead is calculated, knowing that 1 c.c. of $\frac{N}{5}$ oxalic acid corresponds to 0·02389 grm. of PbO_2. In another portion of the red lead dissolved in nitric acid, the total lead is determined by precipitating with H_2SO_4 and calculating the amount of lead from the weight of $PbSO_4$. The lead which remains after deducting that corresponding to the peroxide is calculated as PbO, and by adding this to the PbO_2 the total amount of red lead is found.

The best qualities only contain 1 per cent. of impurities, whilst it ordinarily contains 10 per cent., but products are often found in trade which only contain 50 to 70 per cent. of true Pb_3O_4.

dissolve 140 parts. On heating the solid salt it decomposes into $PbO + 2NO_2 + O$. It is used, mixed with PbO_2, for match heads and fireworks, and also to some extent in the printing of textile fabrics, &c. It costs £40 to £48 per ton. 53 tons were produced in Italy in 1905, and 86 tons in 1907 of the value of £2864.

LEAD SULPHATE : $PbSO_4$. This compound is found in rhombic crystals as *anglesite*, and is isomorphous with barium sulphate. It is formed as a white, heavy, insoluble, crystalline mass on adding sulphuric acid or a soluble sulphate to a soluble lead salt. It is slightly soluble in strong H_2SO_4 (p. 249), and in concentrated alkalis, as basic lead sulphate is formed, $2PbSO_4.Pb(OH)_2$ (*see* White Lead). It dissolves in ammonium tartrate and sodium thiosulphate solutions. It is only soluble in water to the extent of 1 part in 12,135 parts both on heating and in the cold. When heated with sodium carbonate it forms $PbCO_3$, and it is reduced by carbon at a red heat to PbS.

LEAD PERSULPHATE : $Pb(SO_4)_2$. This compound is formed in an impure condition, and mixed with $PbSO_4$, by electrolysing strong H_2SO_4 between two lead electrodes in the cold. It is soluble in concentrated H_2SO_4 and precipitates PbO_2 with water ; it is thus an energetic oxidising agent.

LEAD CARBONATE : $PbCO_3$. This is obtained as a white, insoluble, heavy mass on treating lead nitrate with ammonium carbonate or lead acetate with CO_2. It is found naturally as *cerussite*. **Basic Lead Carbonate**, which forms *common white lead*, $Pb\begin{<}{CO_3 - PbOH}{CO_3 - PbOH}$, is much more important, having been used in paint (for artistic and other purposes) since antiquity, as it has very good covering powers, that is, compared with other white mineral pigments it covers a larger surface of wood when suspended in linseed oil, forming a perfectly white surface through which the wood which it covers can no longer be seen. There are various forms of apparatus for comparing the covering power of various pigments. White lead has, however, the disadvantage that it is poisonous and that it is blackened by hydrogen sulphide vapours, as it then forms black PbS. For these reasons it is gradually being replaced by zinc oxide and antimony oxide.[1]

White lead is prepared industrially by various processes which all start from very pure lead and dilute reagents in order to obtain an amorphous (non-crystalline) final product of good covering power. In the *Dutch process*, which is still sometimes used, plates of lead rolled into spirals are placed in receptacles containing a little acetic acid and these vessels are then placed on shelves surrounded by horse-dung. Through the heat and the carbon dioxide formed by the fermentation of the dung basic lead acetate is first formed, which is then converted into basic carbonate, and in five or six weeks the lead sheet has been converted into white lead which is freed from unaltered lead, lead acetate and other impurities by washing with water. It is then dried in porous vessels or in cakes in the air.

In the *German* or *chamber* process lead plates are placed on horizontal gratings in closed chambers, *A* and *B* (Fig. 267), which are constructed of wood or brickwork. Steam and acetic acid vapour first enter these chambers from a boiler, *D*, heated by the hot gases of a coke furnace, *C*. The steam passes through the tubes, *f* and *g*, and into the pan, *M*, containing acetic acid, which is also heated by the gas from the coke furnace. It thus carries acetic acid vapours with it into the tube, *k*, from whence it enters the top of the chamber, *A*, in which the temperature is maintained at 50° to 60° for 10 to 20 hours. The basic acetate thus formed on the plates is transformed into basic carbonate by gases

[1] The powerful poisonous action of white lead and also of other lead compounds, such as the oxides, acetate, &c., has caused many cases of lead poisoning of workmen employed in industries in which such compounds are used, and therefore laws protecting the workmen from such dangers have been passed in various countries. The symptoms of lead poisoning are anæmia, bright olive-yellow coloration of the skin and of the mucous membranes, wasting of the tissues, dark blue discoloration of the gums, fœtid breath, &c., followed by more serious disturbances, such as lead colic (especially in the case of those who drink alcoholic liquors), cerebro-spinal lead poisoning, and finally delirium, convulsions, coma, paralysis, &c. In France the manufacture and use of white lead were prohibited in December 1906, and its prohibition was reinforced by a new law in 1910. In Germany certain regulations for the arrangement and site of the workshops, form of the pans in which the lead is melted, elimination of dust everywhere, the rejection of delicate workmen or those addicted to alcoholism and tobacco are legislatively prescribed in *Reichgesetzblatt*, May 26, 1903, p. 225, and June 27, 1905, p. 555, in which it is also prescribed that all the workpeople shall bathe every day, change their clothes, not partake of eatables in the workshops, &c. In Italy little or nothing has been done. In 1910 a large hospital for the treatment of industrial diseases was opened in Milan and in this establishment lead poisoning has been studied and cured by special methods. The Italian section of the International Association for the Legal Protection of Workpeople presented to the International Congress at Lugano at the end of September 1910 a special memoir on the use of white lead in painting, and it will perhaps be consequently possible to arrange some form of international convention or legislation. In Vienna in 1902 there were 125 well-marked and undoubted cases of lead poisoning amongst painters.

containing much CO_2, which pass in from the coke furnace. The operation lasts several days, and the white lead is then removed from the unaltered lead with necessary precautions in closed rooms provided with fans. The crude white lead is worked up to a paste with water in order to separate lead acetate and unaltered lead, and is powdered whilst still moist, or sometimes when dry, in an ordinary flour mill, then passed through sieves and dried in the air or in drying chambers at a gentle heat.

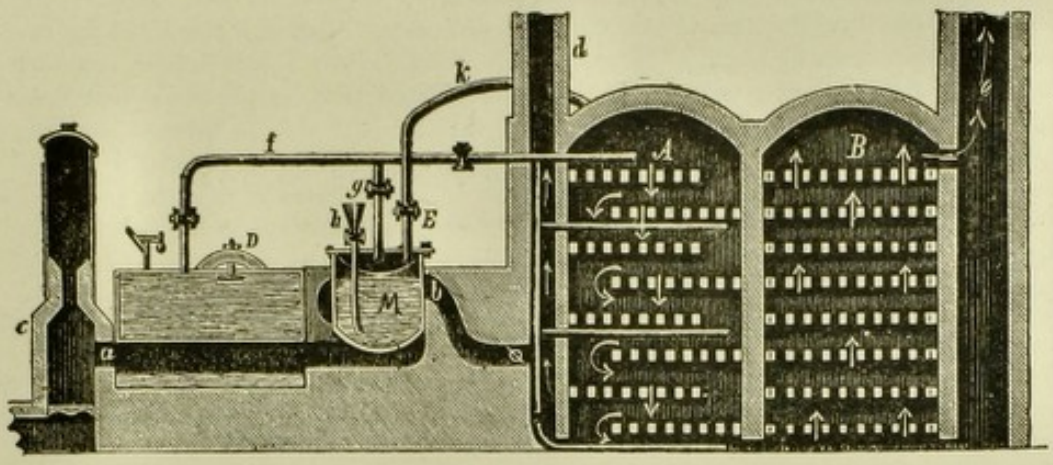


Fig. 267.

According to the *French process*, which was applied by Thénard in a large works at Clichy, litharge is dissolved in acetic acid in the vat, X (Fig. 268), provided with a stirrer, V'; by means of the pump, V, the basic lead acetate which is formed is passed into the vessel, T, which is provided with a stirrer. Carbon dioxide passes into this from the gasometer, a, through the tube, U, until the basic lead acetate is transformed into basic carbonate and neutral lead acetate. The whole mass is then discharged into the large vat, b, where the white lead is allowed to settle from the solution of the neutral lead acetate, which is recovered and withdrawn by the pump, c d, and returned into the vat, X, where

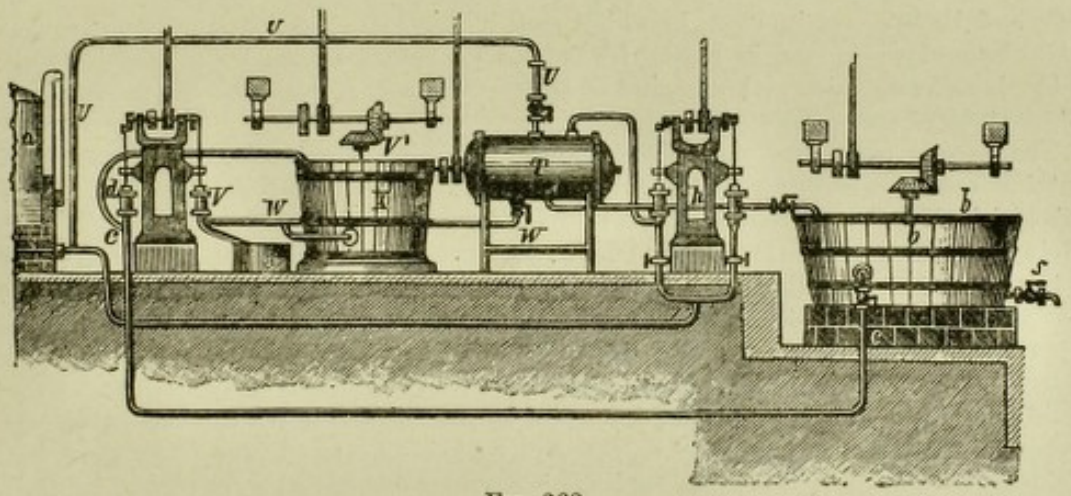


Fig. 268.

it is reconverted into the basic acetate by means of fresh lead oxide without further consumption of acetic acid. The white lead deposited in b is stirred up with water, discharged through the tube, S, and passed into a filter press where it is washed and is then dried and ground.

A rapid process using a similar arrangement is that proposed by Wültze in 1904 (Ger. Pats. 173,105, 174,024, 181,399) in which granulated zinc is treated with acetic acid and lead acetate in a current of air and then with CO_2 under pressure from a coke-fed producer. The solution of the lead is rapid, and in a few hours white lead is precipitated with complete regeneration of the lead acetate, which is used in turn to dissolve new lead without further consumption of acetic acid. A works in Austria and another in Germany use this rapid and economical process.

The process of L. Falk (1909) appears to be more rational and economical and has already been applied in a Russian works. By this process 100 kilos of neutral lead carbonate, for example (obtained from basic lead acetate by the action of CO_2 until the reaction is weakly acid), are worked to a paste with 19 parts of water, 1 per cent. of lead acetate (which acts as a catalyst), and 40·5 kilos of lead oxide. The whole is stirred in the cold with addition of water until the paste gradually ets and hardens. After 3 to 4 hours the operation is finished and the famous *Russian white lead* is obtained which corresponds to the formula, $5PbCO_3.2Pb(OH)_2.PbO$, containing 87·45 per cent. of PbO, 10·78 per cent. of CO_2, and 1·76 per cent. of H_2O.

According to Bronner's process, freshly precipitated lead sulphate is heated to 70° with NaOH and basic lead sulphate is thus formed :

$$3PbSO_4 + 2NaOH = 2PbSO_4.Pb(OH)_2 + Na_2SO_4 ;$$

on then heating with a solution of sodium carbonate, white lead is precipitated :

$$2PbSO_4.Pb(OH)_2 + 2Na_2CO_3 = 2PbCO_3.Pb(OH)_2 + 2Na_2SO_4.$$

In America they start with finely divided lead, obtained by impinging a jet of steam against small holes from which molten lead issues. This "lead sand" is treated with dilute acetic acid in a vat for 7 days, and air, CO_2, and a little steam are simultaneously passed in. The unaltered lead is then separated from the white lead by levigation (Mild's process, which is an improvement of U.S. Pat. 785,023 of 1905 by H. Rowley).

For some years attempts have been made to produce white lead by an *electrolytic process* from a feebly alkaline (1½ per cent.) solution of a mixture of sodium chlorate, 80 parts, and Na_2CO_3, 20 parts. Soft lead is used as an anode and hard lead as a cathode. The potential difference is 2 volts, and the current density 0·5 amp. per square metre surface of the electrodes.

STATISTICS AND PRICES. The production of white lead in Italy in 1905 was 5010 tons, in 1906 4670 tons, in 1907 4376 tons, and in 1908 4645 tons of the value of £96,000. The imports were 79 tons in 1905, 156 tons in 1906, 315 tons in 1907, 590 tons in 1908, and 546 tons in 1909 of the value of £12,640. The exports were 247 tons in 1905, 214 tons in 1906, 157 tons in 1907, 113 tons in 1908, and 129 tons in 1909 of the value of £3008. Germany exported 16,478 tons of white lead in 1905 at £16 per ton, 13,733 tons in 1908, and 10,607 tons in 1909, in which year it imported 2890 tons. Russia consumed 30,000 tons of white lead in 1909. In the United States all the white lead is produced by two large companies with a capital of £6,000,000 each, and in 1903 the production was 113,000 tons of the value of £2,600,000.

The *price of white lead* varies rather much according to its purity, because it often contains considerable quantities of barium sulphate. The price of the pure product varies with the price of lead, and thus in Germany it was sold at £18 16*s.* per ton in 1900, £18 in 1905, and £22 in 1907. In Italy, where white lead enjoys a protective tariff of £3 4*s.* per ton, the following prices held on the trucks at Genoa : £23 4*s.* in 1900, £16 16*s.* in 1902, £15 8*s.* in 1904, £24 in 1906, £27 4*s.* in 1907, £22 in 1908, £18 16*s.* in 1909, and £18 8*s.* in 1910.

LEAD SULPHIDE : PbS. This is found naturally as *galena* (*see above*), and may also be obtained in the form of a black precipitate by passing H_2S into a solution of a lead salt. Even minimal traces of lead may be detected by this extremely delicate reaction as they produce a brown coloration. The sulphide is oxidised to $PbSO_4$ by HNO_3 and by H_2O_2.

FIFTH GROUP

BISMUTH : Bi, 208

This element is a member of the same group as arsenic and antimony in the periodic system, but on account of its high atomic weight it has no non-metallic characters and may be considered as a metal as it forms no gaseous hydrogen derivative and its oxide has basic characteristics.

Bismuth is found naturally both in the native state and as *Bismuthine*, Bi_2S_3, and also in the form of oxide. In order to extract the bismuth the ores are first roasted and then smelted with addition of iron, which acts as a sulphurising agent, of fluxes to

eliminate the gangue, and of carbon to reduce the oxide to metal. The bismuth is then freed from traces of other less fusible metals, such as Ni, Co, Ag, Pb, Fe, by liquation and the last traces of impurities are eliminated by allowing the molten bismuth to run over inclined iron plates, during which process the foreign metals are oxidised and eliminated. It is finally melted with KNO_3 or Na_2CO_3 and $KClO_3$.

The pure metal has a lustrous appearance like antimony, but may be distinguished by its reddish reflex. It crystallises readily and is very brittle. It has a specific gravity of 9·8, melts at 268°, and distils at about 1600°. It is not altered in cold air, but on heating it forms the oxide, Bi_2O_3. It is readily soluble in HNO_3 with which it forms the nitrate. It does not dissolve in cold HCl or H_2SO_4, but on heating with H_2SO_4, SO_2 is evolved and the sulphate is formed.

It also combines readily with the halogens. The soluble salts form insoluble basic precipitates when their solutions are diluted with much water, thus behaving similarly to antimony, but basic bismuth salts do not dissolve in tartaric acid.

Bismuth forms *easily fusible alloys* which are suitable for the reproduction of woodcuts, for fusible valves and wires, &c. **Wood's Metal**, consisting of 3 parts of cadmium + 4 of Sn + 8 of Pb + 5 of Bi, melts at 68° ; **Rose's Metal**, consisting of 9 parts of Bi + 8 of Pb + 3 of Sn, melts at 79° ; **Newton's Alloy** (8 of Bi + 5 of Pb + 3 of Sn) melts at 94·5° ; and **Lipowitz's Alloy** (15 of Bi + 8 of Pb + 8 of Sn + 3 of Cd) melts at 70° and softens at 60°.[1]

By suitably varying the proportions of these various metals, alloys of various melting-points may be obtained so that safety-valves for steam boilers may be prepared as is shown in the following Table :

Bi	Pb	Zn	Melting-point.	Steam pressure	Bi	Pb	Zn	Melting-point	Steam pressure
Parts	Parts	Parts	Degrees	Atmospheres	Parts	Parts	Parts	Degrees	Atmospheres
8	5	3	100	1	8	16	12	146	4
8	8	4	113·3	1½	8	22	24	154	5
8	8	3	123	2	8	32	36	160	6
8	10	8	130	2½	8	32	28	166	7
8	12	8	132	3	8	30	24	172	8
8	19	14	143	3½					

Easily fusible alloys cost from 12*s.* to 16*s.* per kilo.

Until 1880 bismuth was almost exclusively produced in Germany and Austria ; of late years the greater portion has been produced in Bolivia and Australia. In 1860 the total

[1] **Theory of the Melting-Point of Alloys.** In the more common alloys the melting-point is usually lower than the arithmetic mean of that of its components. The metals which are present in a molten alloy often separate on solidification in the form of mixed crystals or may form true chemical combinations. By the aid of thermodynamics the melting-point of an alloy may be calculated in advance by considering it as a dilute solution, but only in those cases in which the components do not form mixed crystals or undergo chemical combination. In the case, for example, of an alloy mainly consisting of molten tin as solvent, the metals which do not form mixed crystals or chemical combinations are Ag, Pb, Cd, Bi, Zn, Tl, &c. If the alloy consists of 99 atoms of tin (the melting-point and solidifying-point of which is 232°) with 1 atom of another metal, then the lowering of the solidifying point is given by the general formula, $\frac{0{\cdot}02T^2}{Q.M}$, where T indicates the absolute temperature, and Q the latent heat of fusion of tin.

In the case of tin as a solvent, $T = 273 + 232 = 505$, and $Q = 14{\cdot}25$, and the lowering of the melting-point by 1 atom of another metal is 3°. In the case of an alloy prepared in the proportions of 96·2 atoms of tin and 3·8 atoms of silver, the temperature of solidification, that is, the point at which the first crystals of the solvent tin commence to separate, will be $232° - (3 \times 3{\cdot}8) = 220{\cdot}6°$, whilst in practice it is found to be 221°. This rule is, however, only true for concentrations up to about 5 per cent. of the dissolved atoms, that is, for dilute solutions. One can understand that as the crystals of the solvent gradually separate, the solution which remains melted is more concentrated, and thus the solidifying point continues to descend until a certain limit is reached. If an alloy is made containing 95·6 atoms of lead (melting-point 328°) with 4·4 atoms of silver, the temperature of solidification or of fusion will theoretically be $328 - (4{\cdot}4 \times 5{\cdot}4) = 304{\cdot}2°$, where 5·4 is the atomic lowering of the melting-point referred to the solvent, lead ; in practice the melting-point is found to be 303°. In the case of high concentrations and for ternary alloys, the *eutectic-points* must be considered which have already been studied on pp. 412-413, and when true chemical compounds are formed between the metals in the alloy we have well-determined melting-points which are sometimes higher than the melting-points of the components. Thus an alloy containing 94·5 per cent. of mercury, which melts at - 38·6°, and 5·5 per cent. of sodium, which melts at 97·5°, has a melting-point of 360°, but in this case we have a true chemical combination, $NaHg_2$. Thus also a mixture of Hg and $NaHg_4$ containing 99·1 per cent. of Hg and 0·9 per cent. of Na has a solidifying-point of — 48·2°, which is thus lower than that of pure mercury.

production of bismuth was 6 tons ; it was 40 tons in 1870, 58 tons in 1881, and after this date the Austrian and German production almost entirely ceased, and we find, on the other hand, that in 1907 the United States produced 4 tons and imported 120 tons of the value of £60,000. Bolivia produced bismuth in 1907 to the value of £140,000. The price was 7*s.* 2*d.* per kilo in 1860, £1 4s. in 1870, 16*s.* in 1894, and 10*s.* 5*d.* in 1900. Italy produced 500 kilos of *bismuth salts* in 1905 of the value of £400, and 1500 kilos in 1906 of the value of £760 ; in 1907 Italy imported 5000 kilos and in 1909 3300 kilos, whilst it exported 500 kilos in 1908.

BISMUTH CHLORIDE : $BiCl_3$. This compound is obtained by dissolving bismuth in aqua regia and by heating bismuth in chlorine. It forms a white, crystalline mass which melts at 227° and boils at 447°. It is soluble in little water, and is decomposed by much water forming bismuth oxychloride, BiOCl, which is a white, amorphous substance insoluble in water, but soluble in acids.

BISMUTH SUBOXIDE : BiO. It is probably formed as a dark brown powder on adding an alkaline solution of stannous chloride to a solution of $BiCl_3$.

BISMUTH TRIOXIDE : Bi_2O_3. This is found ready formed in nature and may also be prepared by heating the carbonate, nitrate, or hydroxide. It forms a yellowish, insoluble powder of sp. gr. 8·2, which melts at a red heat forming a brown liquid which solidifies in a crystalline form.

It is used in the manufacture of crystal glass to replace PbO as it increases the refractivity. It costs £2 per kilo.

The **DIOXIDE, BiO_2,** is only slightly known and the **PENTOXIDE, Bi_2O_5,** is a brown powder which is obtained from bismuthic acid at 130° ; on heating alone or with sulphuric acid it evolves oxygen and when heated with HCl forms chlorine and $BiCl_3$, so that it may rather be considered as a peroxide than as an anhydride.

BISMUTH HYDROXIDES. The orthohydroxide, $Bi(OH)_3$, is a white, amorphous powder which has basic properties, and is formed on adding an alkali to a solution of a bismuth salt. It is insoluble in potassium hydroxide and in NH_3 and loses 1 mol. of water at 100°, being transformed into the **Metahydroxide, BiO.OH,** which also has basic properties and forms basic salts, whilst the orthohydroxide forms neutral salts.

BISMUTHIC ACID : $HBiO_3$. On electrolysing a mixture of KOH + KCl + Bi_2O_3 in the heat, potassium bismuthate, $KBiO_3$, is deposited at the anode and has a scarlet colour. At 120° it loses 1 mol. of H_2O and becomes dark ; at higher temperatures it becomes black and evolves oxygen. At 300° it suddenly acquires a brick-red colour, the substance which is formed being an allotropic form of Bi_2O_3.

BISMUTH NITRATE : $Bi(NO_3)_3$. This is obtained crystallised with $5H_2O$ when bismuth is dissolved in nitric acid and the solution then evaporated. It is easily soluble in a little water, especially in presence of HNO_3, whilst with much water (20 parts) a stable basic bismuth nitrate separates on heating, which is known as the **Subnitrate** or as *Magister of Bismuth*, $Bi(NO_3)_2OH + BiNO_3(OH)_2$. This is used medicinally and also in the preparation of cosmetics, but since it becomes yellow in the air and blackens with H_2S, it is being more and more replaced as a cosmetic by zinc oxide which has not these disadvantages.

On dissolving bismuth in H_2SO_4 the **Neutral Sulphate, $Bi_2(SO_4)_3$,** and the **Basic Sulphate, $Bi_2SO_4(OH)_4$,** are formed.

BISMUTH SULPHIDE : Bi_2S_3. This is found in nature as *Bismuthine*, but is also prepared artificially by melting sulphur with bismuth or from a solution of a bismuth salt with H_2S, and then forms a black powder insoluble in water, but soluble in hot dilute HNO_3. It is insoluble in alkali sulphides because it does not form sulpho-salts in the same manner as As and Sb. A disulphide, Bi_2S_2, is also known, consisting of grey crystals which are obtained on melting the two components together.

SIXTH, OR CHROMIUM, GROUP

This includes four elements, **Chromium, Cr** (atomic weight 52); **Molybdenum, Mo**, 96; **Tungsten, W**, 184; and **Uranium, U**, 238·5. The compounds of these metals have certain analogies with those of sulphur, especially in the case of the higher oxides, and just as there is sulphuric anhydride, SO_3, so we also have the oxides, CrO_3, MoO_3, WO_3, and UO_3, which have acid characters and should be considered as true acid anhydrides. The salts have an analogous constitution to the sulphates and are isomeric with them. The strength of these acids diminishes with increase of the atomic weight. The sesquioxides of this group, such as Cr_2O_3, have basic characters and present many analogies with those of Fe, Mn, and Al.

CHROMIUM: Cr, 52

This element is found in nature, especially as **Chrome Iron Ore**, $FeO.Cr_2O_3$, or *chromite*, and in smaller quantity as *crocoisite*, $PbCrO_4$. Pure chromium was first obtained by Moissan in 1894 by reducing Cr_2O_3 with carbon in the electric furnace, but it is still more easily obtained in the pure state to-day by the alumino-thermic process (Goldschmidt, p. 570), by reducing chromium oxide with aluminium powder: $Cr_2O_3 + Al_2 = Al_2O_3 + Cr_2$.

The chromium which was obtained in the past always contained carbon and was not suited to the manufacture of chrome steel. Pure chromium is a grey shining metal which does not alter in the air. It has a specific gravity of 6·8, and only melts in the electric furnace at a temperature much above 2000°. Chromium prepared by the Goldschmidt process behaves as a *passive* metal, that is, it is not attacked by dilute cold HCl or H_2SO_4 nor by HNO_3, even on heating. Chromium obtained in any other manner is very *active*, that is, it evolves H even in the cold with these acids. The other form also becomes active when it is heated with alkalis, dilute acids or solutions of NH_4Cl, so that it may also be used as the cathode of a cell. The E.M.F. of inactive chromium (p. 419) is 0·3 volt, whilst that of active chromium is 1·8 volts. It seems that the passivity of metals is due to a layer of oxygen which covers the outer surface of the metal, and a metal may even become passive in the air, but more easily by the action of HNO_3, $FeCl_3$, H_2O_2, or by employing it as an anode in solutions of KF, KCN, and chromic acid. The following metals may assume the passive state, Fe, Ni, Co, Cr, Mo, W, V, Ru.

Small additions of chromium to certain other metals render them harder and more resistant to various chemical reagents. Before 1898 chromium cost more than £60 per kilo, but since the introduction of the Goldschmidt process the price has gradually fallen to 8*s*. per kilo.

Chromium forms four series of compounds which may be considered to be derived from chromous oxide, CrO, chromic oxide, Cr_2O_3, chromic acid, and perchromic acid respectively. All these compounds have coloured ions.

The **CHROMOUS COMPOUNDS** are the least stable and are obtained by the reduction of chromic compounds, but are very easily oxidised by the air. Thus **Chromous Chloride, $CrCl_2$**, is obtained from Cr and HCl or by reducing chromic chloride, $CrCl_3$, with nascent hydrogen, in the form of a white, crystalline powder which forms a blue solution which vividly absorbs oxygen from the air, during which process its colour is changed to green. Its vapour density at 1600° corresponds to a mixture of $CrCl_2$ and Cr_2Cl_4.

CHROMOUS HYDROXIDE: $Cr(OH)_2$. This is obtained as a yellow precipitate by adding an alkali to a solution of $CrCl_2$.

Chromous salts differ from the chromic salts by forming black **Chromous Sulphide**, CrS, with alkali sulphides.

CHROMIC OXIDE: Cr_2O_3. This is obtained as a green powder by heating ammonium dichromate or chromic anhydride, CrO_3, to redness. When melted with silicates it forms beautiful green-coloured glasses and porcelains. When 1 part of potassium dichromate is

melted with 3 parts of boric acid and the potassium borate then dissolved in water, a beautiful green pigment remains, which is known as *Guignet's green*, or *chrome green*, and is a hydrate of chromic oxide, $Cr_2O(OH)_4$. Italy produced 70 tons of this product in 1905, 100 tons in 1907 of the value of £1800, and 70 tons in 1908 of the value of £420 (?).

CHROMIUM HYDROXIDE : $Cr(OH)_3$. This compound is formed as a gelatinous bluish-grey mass on adding NH_3 to solutions of chromic salts ; it dissolves in NaOH to form a green solution which again separates the hydroxide on boiling. It is clear from this reaction that the hydroxide has weakly acid characters and forms unstable salts with strong bases which are derivatives of the metahydroxide, CrO.OH, and analogous to the *spinelles* which are obtained from Al. These compounds are called *chromites*, so that natural *chrome iron ore* is a chromite of iron : $\begin{matrix}CrO.O\\CrO.O\end{matrix}\!\!>\!Fe$.

Chromium hydroxide acts as a very weak base and only forms salts with strong acids and not with carbonic acid ; thus sodium carbonate precipitates the hydroxide and not the carbonate from chromium salts (p. 573).

CHROMIUM CHLORIDE : $CrCl_3$. This is formed on passing a current of chlorine over heated chromium or over a mixture of Cr_2O_3 and charcoal, and sublimes in lustrous violet crystals. Its vapour density at 1300° corresponds to the formula $CrCl_3$. It is only slightly soluble in water even on heating, but becomes readily soluble in presence of a trace of $CrCl_2$, which acts catalytically, forming a green liquid which deposits green crystals, $CrCl_3.6H_2O$, on concentration, similar to those which are obtained from a solution of $Cr(OH)_3$ in HCl, whilst on dissolving the hydroxide in HCl a basic chloride is formed. Both are used as mordants in calico printing.

CHROMIUM FLUORIDE : $CrF_3 + 4H_2O$. This compound forms a bright green crystalline powder, stable in the air, and readily soluble in water. It is used as a mordant for various alizarine dyestuffs on wool and costs about £60 per ton.

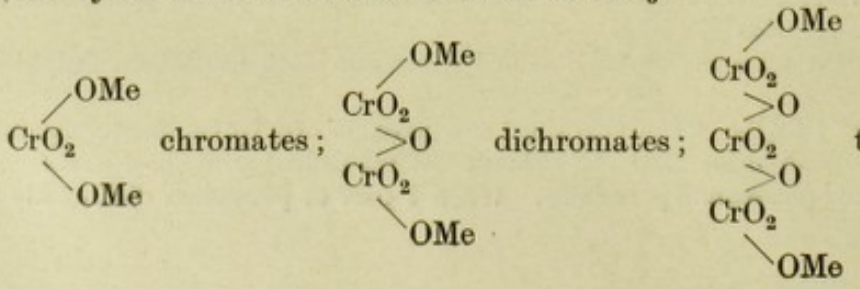
CHROMIUM SULPHATE : $Cr_2(SO_4)_3$. This is obtained on dissolving the hydroxide, $Cr(OH)_3$, in sulphuric acid. The cold aqueous solution has a violet colour but becomes green on heating to 80°. On cooling, the violet colour reappears. Violet-blue crystals containing $16H_2O$ may be obtained from this solution, but on evaporating this green solution a green amorphous residue remains. In the green solution the simple chromium ions are no longer present, but only a more complex ion ; for this reason the green solution does not give the ordinary reactions for chromium salts.

CHROME ALUM : $Cr_2(SO_4)_3.K_2SO_4 + 24H_2O$. This may be prepared in the manner common to all the alums by mixing potassium sulphate with the sulphate of the heavy metal, or more easily by passing SO_2 into a solution of potassium dichromate in presence of H_2SO_4 : $K_2Cr_2O_7 + 3SO_2 + H_2SO_4 = H_2O + Cr_2(SO_4)_3.K_2SO_4$.

From this solution the alum may be obtained in very large octahedra of a bright violet colour. This alum also forms a violet solution in the cold which becomes green on heating to 80° and regains its violet colour on cooling (*see above*).

DERIVATIVES OF CHROMIC ACID

As we have already said, the analogy between chromium and sulphur is especially manifested in the derivatives of chromic acid, but whilst chromic anhydride, CrO_3, corresponding to sulphuric anhydride, is well known, chromic acid, H_2CrO_4, corresponding to H_2SO_4, is not known in the free state, although the corresponding salts, namely, the chromates, which are isomorphous with the sulphates, are well known and have been largely studied. Salts corresponding to polychromic acids are also known, such as the dichromates, trichromates, &c., and are represented by the following constitutional formulæ, where Me indicates a monovalent metal and where the one formula is derived from the other by the addition of one molecule of CrO_3 :



The chromates are yellow and the corresponding acid salts are not known. By the action of acids chromates are transformed into dichromates or polychromates which have a reddish-orange colour, whilst on the contrary polychromates are reconverted by alkalis into chromates, as can easily be seen by the change of colour of the solutions. Chromic acid is a weak acid and its insoluble barium, silver, and other salts are dissolved by strong acids.

CHROMIC ANHYDRIDE : CrO_3 (Chromium Trioxide). This compound is obtained in the form of lustrous red needles by the action of H_2SO_4 on a concentrated solution of potassium or sodium dichromate :

$$K_2Cr_2O_7 + H_2SO_4 = K_2SO_4 + H_2O + 2CrO_3.$$

It is easily soluble in water and when the crystals are pure they are not deliquescent. When heated to 250° it becomes brown, melts, and decomposes, forming oxygen and chromic oxide, $2CrO_3 = Cr_2O_3 + O_3$. It is such an energetic oxidising agent that it sets fire to alcohol when brought into contact with it, and its solution cannot be filtered through filter-paper because the latter is destroyed, and thus this oxidising substance behaves in a very similar manner to a peroxide, evolving oxygen and being transformed into chromic oxide.

ALKALI CHROMATES and DICHROMATES, K_2CrO_4 or Na_2CrO_4 and $K_2Cr_2O_7$ or $Na_2Cr_2O_7$. The alkali chromates are obtained by melting a chromium compound with an alkali carbonate in presence of an oxidising agent such as a nitrate or atmospheric air. Industrially, chrome iron ore is melted in a reverberatory furnace with soda and lime in presence of air :

$$2Cr_2O_4Fe + 4Na_2CO_3 + 4CaO + 7O = Fe_2O_3 + 4CaCO_3 + 4CrO_4Na_2.$$

The melt which is thus formed and which contains sodium chromate mixed with calcium chromate is dissolved in water and a little Na_2CO_3, decanted and the solution then concentrated after acidification with acetic acid until crystallisation commences. The lemon-yellow crystals, which contain no water of crystallisation, are very soluble in water, insoluble in alcohol and show an alkaline reaction. If sodium dichromate is required instead of the chromate, the above-mentioned solution is slightly acidified with sulphuric acid and evaporated until it crystallises. Sodium dichromate is hygroscopic and very soluble in water. In order to obtain **Potassium Dichromate** it suffices to heat the solution of the sodium salt with KCl, when after concentration NaCl readily separates on the bottom of the vessel and $K_2Cr_2O_7$ forms in very fine triclinic crystals on leaden rods suspended in the liquid. These crystals are of an orange-red colour, contain no water of crystallisation, and are not hygroscopic. The compound is somewhat poisonous, and is used in large quantities as a mordant, especially in dyeing wool, also for fireworks and photography and in various chemical industries.

The principal works manufacturing potassium dichromate are in England, which country has almost a monopoly of this product ; the prices have now fallen, however, because in Germany works have arisen which manufacture **Sodium Dichromate**, which is less expensive and can almost always be used instead of the potassium salt, which costs about £30 per ton, whilst sodium dichromate costs about £22. In 1898 800 tons of sodium dichromate and 170 tons of potassium dichromate were produced in Italy ; in 1905 the production was 610 tons of sodium dichromate and 300 tons of potassium dichromate, apart from an importation of 290 tons (in 1908). In 1908 200 tons of potassium dichromate were produced of the value of £7040, and 600 tons of sodium dichromate of the value of £18,240. In 1909 England exported 4700 tons of potassium and sodium dichromates.

Potassium dichromate dissolves in water in the proportion of 1 : 10, and its oxidising action, especially on heating in presence of H_2SO_4, is shown by the following equation :

$$K_2Cr_2O_7 + 4H_2SO_4 = 4H_2O + Cr_2(SO_4)_3.K_2SO_4 + 3O.$$

The chrome alum thus produced, and all reduced chromium salts from various chemical reactions, may be reutilised by submitting them to electrolysis with lead electrodes separated by diaphragms. During the passage of the current chromic acid forms in the anodic space and can be again used as an oxidising agent, whilst H is evolved at the cathode.

Chromates of various other metals are also known, and are used as pigments or for other purposes. **Lead Chromate**, $PbCrO_4$, is much used as a pigment under the name of *chrome yellow*, which is obtained from a soluble lead salt, such as the acetate, with sodium or potassium chromate. On heating, it is a strong oxidising agent for organic substances. **Chrome Red** is a basic lead chromate, $PbCrO_4.Pb(OH)_2$. **Barium Chromate**, $BaCrO_4$, is used as a mineral pigment which is very resistant to atmospheric influences, &c. Many chromates crystallise with $7H_2O$ and are isomorphous with magnesium sulphate.

On distilling a dichromate with NaCl and H_2SO_4, a blood-red liquid distils over of sp. gr. 1·96, which boils at 117°, and consists of **Chromium Oxychloride** or **Chromyl Chloride**, CrO_2Cl_2. It is decomposed by water, forming HCl and CrO_3. A **Monopotassium Chromyl Chloride**, CrO_2ClOK, is also known.

PERCHROMIC ACID. On treating a minimal quantity of a dichromate or chromate with H_2SO_4 and a little hydrogen peroxide, a blue coloration is formed, and on shaking the liquid with ether, washed and free from alcohol, which might contain traces of H_2O_2, the colour passes into the ether and then rapidly disappears. This is probably due to **Perchromic Acid**, $HCrO_5$, which cannot be isolated, but of which an ammonium salt, $NH_4CrO_5 + H_2O$, and a corresponding **Anhydride**, Cr_2O_9, which acts as a peroxide, are known. This reaction with the blue coloration is very sensitive and is used for the detection of traces of chromic acid or of hydrogen peroxide.

MOLYBDENUM : Mo, 69

This is found somewhat rarely in nature in *Wulfenite*, $PbMoO_4$, but more frequently as *Molybdenite*, MoS_2, which is roasted, and the oxide MoO_3, which is thus formed, heated in a current of hydrogen or with charcoal in the electric furnace in order to obtain metallic molybdenum. When thus prepared it is a grey powder which forms a fused mass of silvery appearance and sp. gr. 8·6 at extremely high temperatures. When heated in the air it first forms MoO_2 and then MoO_3. It dissolves in concentrated HNO_3 or H_2SO_4.

In the electric furnace with excess of carbon it forms **Molybdenum Carbide**, Mo_2C.

Molybdenum forms numerous compounds in which it exercises the most varied valencies from 2 to 8. Thus various chlorides, $MoCl_2$, $MoCl_4$, $MoCl_5$, are known and also the oxychlorides, $MoOCl_4$, MoO_2Cl_2, &c. Of the various oxides, Mo_2O_3, MoO_2, and MoO_3, the last is the most important and possesses acid characters, whilst the first is a weak base and the second is neutral. **Molybdic Anhydride**, MoO_3, is insoluble in acids and in water, but dissolves in sodium hydroxide or in NH_3. It is a white substance which becomes yellow on heating, similarly to ZnO.

It forms polyacid salts, $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, &c. One of the commonest and most stable of these salts is **Ammonium Heptamolybdate**, $(NH_3)_6Mo_7O_{24}.4H_2O$, commonly known as **Ammonium Molybdate**. This is soluble in an excess of nitric acid and its solution is a good reagent for the quantitative precipitation of phosphoric acid from soluble phosphates on warming in the form of yellow crystals of the composition $11MoO_3.PO_4(NH_4)_3$. A similar precipitate is produced with arsenates.

In order to detect traces of molybdenum the solution is treated with zinc and H_2SO_4 when a blue coloration is first formed which gradually becomes brown, the former coloration being due to Mo_3O_4, and the latter to Mo_2O_3.

TUNGSTEN : W, 184 (In German, Wolfram)

This element is found in nature in certain minerals which are abundant in North America, namely, *wolframite*, $FeWO_4$, *scheelite*, $CaWO_4$, and *hübnerite*, $MnWO_4$.

The free metal is now obtained by the Goldschmidt process by reducing tungstic acid with aluminium powder and its production is facilitated by the use of liquid air. It has the appearance of lustrous steel, is very hard, melts at extremely high temperatures and has a specific gravity of 19·13 ; when it contains a little carbon its hardness approximates to that of the diamond. It is resistant to the action of the air and fairly resistant

to that of ordinary chemical reagents, being easily dissolved by a mixture of HF + HNO_3 only. It dissolves in pure potassium hydroxide with evolution of H. The addition of small quantities of tungsten to steel renders it exceptionally hard (tungsten steel).

The valency of tungsten varies considerably in its various compounds and thus chlorides containing 3, 4, 5, and 6 atoms of Cl are known. WCl_6, which is obtained from its elements on heating, forms a violet-black crystalline mass which is decomposed by water with formation of **Tungsten Trioxide, WO_3**. This compound is insoluble in water and acids, but dissolves in alkalis forming the **Tungstates** from which acids separate **Tungstic Acid, $WO(OH)_4$**. This acid is capable of undergoing condensation with formation of various polyacids in a similar manner to chromium and molybdenum. With phosphates it forms compounds analogous to those which are obtained with molybdic acid.

Small traces of tungsten are detected by adding stannous chloride to any tungsten salt ; a yellow precipitate of WO_3 is immediately formed, which dissolves in hot HCl, acquiring a strong blue colour as W_2O_5 is formed. Oxychlorides, sulphides, &c., of tungsten are also known. Commercial tungsten containing 95 to 98 per cent. costs £260 per ton and 7000 to 8000 tons are produced annually of strength varying from 37 to 95 per cent. for metallurgical use. It is now used in large quantities in the form of a colloidal solid for the manufacture of the filaments of tungsten lamps, of which the General Electric Company alone manufactured 11,000,000 in 1909, with filaments of a diameter of 0·14 to 0·025 mm. obtained with perforated diamond dies. In 1905 Portugal exported 9 tons of tungsten and 336 tons in 1906.

URANIUM : U, 238.5

This is a heavy metal of a grey appearance similar to that of iron. It has a specific gravity of 18·7 and melts at above 1500°. It was once prepared by the electrolysis of the chloride and by heating this with sodium, but is to-day obtained together with uranium carbide, U_2C_3, by reducing the oxide with carbon in the electric furnace. It is found in combination in nature in the form of the oxide, U_3O_8, in **Uranite** and **Uraninite** (*pitch blende*), together with radio-active substances (p. 121).

When uranium is finely subdivided it slowly decomposes water even at the ordinary temperature. It catches fire at 170°, and fixes nitrogen at 1000°, forming **Uranium Nitride**. Uranium compounds are as poisonous as those of arsenic.

URANOUS OXIDE : UO_2. This compound possesses basic characteristics and in it uranium is tetravalent. It is produced by reducing the trioxide with hydrogen.

Among uranous compounds the **Chloride, UCl_4**, the **Hydroxide, $U(OH)_4$**, &c., are known.

URANIC OXIDE : UO_3 (Uranium Trioxide). This compound has both basic and acid properties simultaneously. Theoretically it corresponds to the hydroxide, $U(OH)_6$, which is not known, but the **Metahydroxide, $UO_2(OH)_2$**, is known and has basic properties, being called uranyl hydroxide, because the divalent group UO_2, **Uranyl**, is found in various other compounds. On heating the metahydroxide, UO_3 is obtained.

A well-known salt of this hydroxide is **Uranyl Nitrate, $UO_2(NO_3)_2 + 6H_2O$**, which forms greenish-yellow crystals which yield UO_3 at 250°. Another salt is **Uranyl Sulphate, $UO_2SO_4 + 6H_2O$**, which forms needle-shaped yellow crystals.

On treating the solution of a uranyl salt with sodium hydroxide, a yellow precipitate of sodium uranate, $U_2O_7Na_2$, is formed which is soluble in acids. It is used technically for the production of a yellow fluorescence in glass.

On heating uranic or uranous oxide, the oxide U_3O_8 is obtained which is found in nature as **Uranite**, and may be considered as the **Uranate of Uranous Oxide, $UO_2.2UO_3$**.

SEVENTH GROUP

MANGANESE: Mn, 55

Whilst in the case of chromium derivatives we find a certain analogy with those of sulphur, in manganese compounds we notice constitutional analogies with certain chlorine derivatives. Thus potassium permanganate, $KMnO_4$, is isomorphous with potassium perchlorate, $KClO_4$, and chlorine heptoxide, Cl_2O_7, has its counterpart in manganese heptoxide, Mn_2O_7. In both cases the manganese is heptavalent. In its more or less red-coloured derivatives, manganese exerts varying valency, being di-, tri-, tetra-, hexa-, or heptavalent, and thus we have manganous compounds, manganic compounds, and salts of manganic and permanganic acids. These compounds show a certain analogy with those of chromium and iron.

Manganese is not found free in nature, but is widely diffused in abundance in its minerals, *Pyrolusite*, MnO_2, *Hausmannite*, Mn_3O_4, *Braunite*, Mn_2O_3, and *Rhodocrosite*, $MnCO_3$ (*spathic manganese ore*).

The metal, which is a grey lustrous substance, is now obtained pure by the Goldschmidt process (p. 570) from a mixture of manganese oxide with powdered Al. It was formerly obtained in a less pure condition from manganese chloride with sodium or from the oxide and carbon in the electric furnace. Whilst it still cost £26 per kilo in 1885, it only costs 16*s.* to-day, whilst the industrial product free from Fe and C costs 6*s.* 5*d.* It is very hard, has a specific gravity of 7·8 to 8, and melts at 1247°. It oxidises readily in the air and dissolves even in weak dilute acids to form manganous salts. In the form of a fine powder it decomposes boiling water. It is much used in metallurgy, and certain derivatives have been tried in Japan as a chemical manure (*see* pp. 302–303). The production of manganese ores in British India in 1893 was 3000 tons and 172,000 tons in 1903. In 1905 Germany imported 263,000 tons of the value of £552,000, and produced 51,463 tons. Italy produced 3050 tons of manganese ores in 1906 and 2750 tons in 1909 of the value of £3644. Japan produced manganese to the value of £4000 in 1904 and of £5200 in 1906.

MANGANOUS OXIDE: MnO. This is obtained as a green powder by reducing the other oxides in hydrogen or by heating the carbonate in the air; but when heated for a long time it is transformed into Mn_3O_4.

MANGANOUS HYDROXIDE: $Mn(OH)_2$. If an alkali hydroxide is added to a solution of a manganous salt free from air, this compound separates as a white mass which readily oxidises in the air and then becomes brown.

The hydroxide is not obtained with NH_3 if NH_4Cl is present in solution, because a complex ion is formed as in the case of magnesium (pp. 100, 526 and 527).

MANGANOUS CHLORIDE: $MnCl_2$. This is formed in large quantities in the manufacture of chlorine (p. 144), and may be obtained in rose-red hygroscopic crystals containing 4 mols. of water of crystallisation. It is sometimes used in dyeing (at £14 per ton), and is reutilised in the manufacture of chlorine.

MANGANOUS SULPHATE: $MnSO_4$. This compound is obtained by dissolving the carbonate in sulphuric acid or by heating manganese dioxide to redness with ferrous sulphate and then extracting with water. It crystallises with 4 to 7 mols. of water and has a fine pink colour; the crystals containing $7H_2O$ are isomorphous with ferrous sulphate. On heating, the last molecule of water is only eliminated at 280°. With alkali sulphates it forms double salts which crystallise with $6H_2O$, and are isomorphous with magnesium sulphate. It is used in dyeing and in painting porcelain. The anhydrous salt costs £18 to £22 per ton.

MANGANOUS SULPHIDE: MnS. This compound is of a pale flesh colour, in which respect it differs from the other sulphides, and since it is soluble in acids it is obtained from manganous salts with alkali sulphides, but not with H_2S.

MANGANOUS CARBONATE : $MnCO_3$. This compound is found in nature as *Rhodochrosite*, $MnCO_3$, and is formed by the action of alkali carbonates on manganous salts. It first separates as a white mass which is oxidised by the air and then becomes brown.

MANGANIC OXIDE : Mn_2O_3 (Sesquioxide). This compound is obtained on heating the other oxides of manganese in a current of oxygen. It is found in nature as *Braunite* ; with H_2SO_4 it forms manganous sulphate and separates MnO_2.

MANGANIC HYDROXIDE : $Mn(OH)_3$. This separates as a brown substance on leaving an ammoniacal solution of a manganous salt exposed to the air. It has very weakly basic properties and its salts are consequently hydrolytically decomposed by water. It is soluble in HCl with which it forms a brown liquid which evolves Cl on heating, and is perhaps transformed into $MnCl_4$.

The **METAHYDROXIDE : $MnO.OH$, $H_2Mn_2O_4$,** or **$Mn_2O_3.H_2O$,** is found in nature as *Manganite*, which forms black crystals.

MANGANOUS-MANGANIC OXIDE : Mn_3O_4 (Mixed Oxide). This oxide is the most stable and is formed when the other oxides are heated for a prolonged period in the air. It is found naturally as *Hausmannite*, Mn_3O_4, and consists of a reddish-brown powder which liberates chlorine on heating with HCl.

MANGANIC SULPHATE : $Mn_2(SO_4)_3$. This compound is obtained on dissolving manganic oxide in H_2SO_4, or a mixture of manganous and manganic sulphates is obtained by treating the mixed oxide, Mn_3O_4, with concentrated H_2SO_4. It dissolves in water with a bright red colour.

MANGANIC PERSULPHATE : $Mn(SO_4)_2$, is prepared by the electrolytic oxidation of manganous sulphate and forms a black substance which can only be obtained in solution in presence of sulphuric acid. It has extraordinary oxidising properties and is used for this purpose in the manufacture of organic products (Fr. Pat. 338,990 of 1903).

MANGANESE DIOXIDE : MnO_2. This is found in nature as a dark mass in the form of *Pyrolusite*, which is the most abundant manganese ore and is used in the manufacture of chlorine. On heating to dark redness it forms $Mn_2O_3 + O$, and at a bright red heat $Mn_3O_4 + O$. It dissolves in cold HCl without evolution of chlorine, but at high temperatures the dark yellow solution of $MnCl_4$ which is thus formed decomposes into Cl_2 and $MnCl_2$. In the section on chlorine (p. 144 *et seq.*) we have described the various processes for regenerating manganese dioxide from various salts, especially from the chloride. We have also explained the tests used in determining the value of manganese dioxide.

The dioxide is readily dissolved by a solution of SO_2 or sodium disulphite and this reaction is utilised for dissolving the dioxide which is deposited on fabrics bleached with potassium permanganate.

The hydroxides $MnO(OH)_2$ and $Mn(OH)_4$ correspond to the dioxide and are obtained by adding a hypochlorite or a permanganate to a solution of a manganous salt.

COMPOUNDS OF MANGANIC AND MANGANOUS ACIDS

The manganates correspond to the formula, $MnO_4X'_2$, and the permanganates to MnO_4X'. When any compound of manganese is fused at a dark red heat with potassium hydroxide or carbonate in presence of an oxidising agent such as KNO_3 or $KClO_3$ a green mass results which is soluble in water and which, after concentration *in vacuo*, separates rhombic prisms of **Potassium Manganate, K_2MnO_4,** which are isomorphous with the chromate and with K_2SO_4.

It is decomposed by water with separation of MnO_2, the solution becoming violet through the formation of potassium permanganate :

$$3K_2MnO_4 + 2H_2O = MnO_2 + 4KOH + 2KMnO_4.$$

Thus a green solution has become violet, hence the name of *mineral chameleon*, whilst it is not altered by alkalis.

The transformation of green manganate into violet permanganate is still more rapid under the action of acids, chlorine, or ozone.

$$K_2MnO_4 + Cl = KMnO_4 + KCl \qquad \text{or}$$

$$3K_2MnO_4 + 2H_2SO_4 = 2KMnO_4 + 2K_2SO_4 + MnO_2 + 2H_2O.$$

On treating violet solutions of permanganates with hot concentrated alkalis green manganate solutions are regenerated.

POTASSIUM PERMANGANATE : $KMnO_4$. This is prepared industrially by mixing 500 kilos of a solution of KOH of sp. gr. 1·44 with 180 kilos of powdered MnO_2 and 105 kilos of $KClO_3$; the whole is boiled, evaporated, and the residue fused in crucibles, heating until it has acquired a pasty consistency. The potassium manganate, K_2MnO_4, which is thus obtained is dissolved by boiling with much water, whilst a current of chlorine, CO_2, or ozone is passed into the liquid. The permanganate separates in the crystalline form from concentrated solutions, even in presence of KOH which is formed during the reaction, and is separated from the dissolved substances in a hydro-extractor. Potassium permanganate forms rhombic crystals, isomorphous with $KClO_4$, of a blackish appearance but a green metallic reflex. It is soluble in 12 parts of water with an intense violet-red colour and the solution is a very strong oxidising agent for both organic and inorganic substances.

The solutions of various permanganates all show the same spectrum, which indicates that they all have the same MnO'_4 ion in common.

In acid solution every 2 mols. of permanganate liberate 5 atoms of oxygen : $2KMnO_4 + 3H_2SO_4 = 2MnSO_4 + K_2SO_4 + 3H_2O + 5O$; and the end of the oxidation of a substance by permanganate is recognised by the permanence of the violet coloration due to the latter, so that no indicators are used, as the colour of manganese sulphate is not perceptible in dilute solution.

In neutral or alkaline solution, only 3 atoms of oxygen are evolved :

$$2KMnO_4 + H_2O = 2MnO_2 + 2KOH + 3O.$$

Permanganate is used for the conservation of wood and for bleaching textile fibres by immersing them for some time in an aqueous solution of $KMnO_4$ and then dissolving the MnO_2 with sodium disulphite. It is also used for purifying various gases, such as CO_2, H, NH_3, &c., and is an energetic disinfecting and oxidising agent. Thus it transforms ferrous salts into ferric salts, nitrous acid into nitric acid, and oxalic acid into CO_2, and reacts with H_2O_2 with liberation of oxygen. Crude potassium permanganate costs £15 4*s.* per ton, and when crystalline £40 per ton.

PERMANGANIC ANHYDRIDE : Mn_2O_7 (Manganese Heptoxide). This compound is obtained as a dark oil on adding very cold concentrated H_2SO_4 to dry $KMnO_4$. It is a powerful oxidising agent which sets fire to paper, alcohol, &c. (*Translator's note.*—This compound is extremely explosive).

EIGHTH GROUP

This is the last group of the periodic system and may be divided into three subsections :

(*a*) **Iron, Fe, 55·85 ; Nickel, Ni, 58·67 ; Cobalt, Co, 58·95.**
(*b*) **Ruthenium, Ru, 101·7 ; Rhodium, Rh, 102·9 ; Palladium, Pd, 106·7.**
(*c*) **Osmium, Os, 190·9 ; Iridium, Ir, 193·1 ; Platinum, Pt, 195.**

(*a*) IRON GROUP

Iron, nickel, and cobalt are distinguished from the other metals by their very pronounced magnetic properties, being attracted by a magnet. Those iron compounds in which the iron is most highly oxidised (*ferric* compounds) are the most stable, whilst in the case of nickel and cobalt the least highly oxidised compounds are the more stable, as in the case of copper and zinc.

IRON : Fe, 55.85

This important metal is only found native in rare instances and in small quantities, whilst it abounds in the native state in stars (the sun, &c.), where a high temperature exists in presence of an atmosphere of glowing hydrogen. It is sometimes found on the earth in the form of *meteorites* (*meteoric iron*),

which occur in blocks up to a weight of 8 or even 15 tons. This iron is not usually homogeneous, but is capable of being worked, does not contain chemically combined carbon, but almost always contains 4 to 10 per cent. of nickel. In Fig. 269 we show a *micrograph* of meteoric iron obtained by Widmanstätten by the method already described on p. 410. In this figure we see regular designs due to crystals of compounds of iron with nickel and with phosphorus.

On the other hand, iron ores are extremely abundant in the earth's crust and consist of the oxides *Magnetite* or *Magnetic Iron Ore*, Fe_3O_4, *Hæmatite*, Fe_2O_3, *Specular Iron Ore* (anhydrous crystalline, Fe_2O_3), and also as *Limonite*, $Fe_2O_3.2H_2O$ and $2Fe_2O_3.H_2O$, *Spathic Iron Ore* or *Siderite*, $FeCO_3$, and *Iron Pyrites*, FeS_2, in which ore it is first necessary to utilise the sulphur. Some iron ores contain much manganese and others contain much titanium. Iron ores are especially abundant in England, the United States, Germany, Luxemburg, Russia, France, Spain, Sweden, Austria, China, &c. In Italy there is not much iron ore, but the most important deposits are those on the island of Elba where *oligist* is abundant, and in Sardinia, where there is hæmatite, and a little spathic iron ore in the Val Trompia and Val Camonica in Lombardy; in the Val d'Aosta there are deposits of magnetite and oligist.

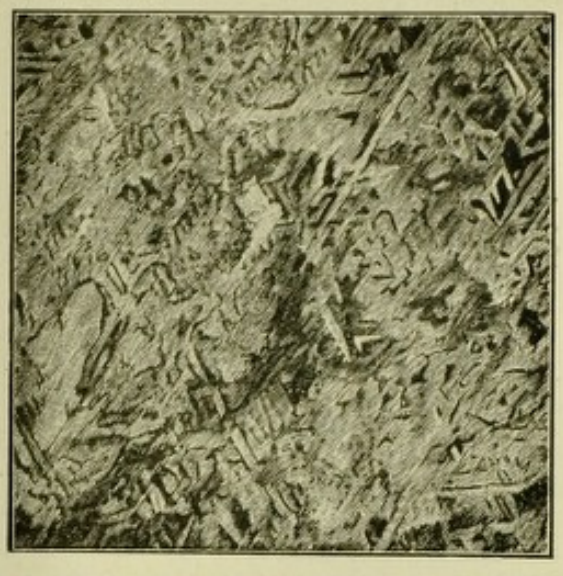


Fig. 269.

PROPERTIES OF IRON. Iron may be obtained chemically pure by reducing pure iron oxide by heating it in a current of hydrogen, or preferably by precipitating Mohr's salt (ferrous ammonium sulphate) with potassium oxalate and igniting the iron oxalate after washing it. The product is then washed with acid and reduced by heating in a current of pure hydrogen. Chemically pure iron has a silvery appearance, a specific gravity of 7·84, and is insoluble in HCl; it melts at about 1510° and expands on solidification.

Pure iron is of no particular importance, but becomes valuable when small quantities of other accompanying elements are present, such as C, Si, Mn, &c. Wrought and cast iron can only be temporarily magnetised, whilst steel can be magnetised in a permanent manner. The metal is not attacked by water free from CO_2, nor even by dry air and still less by alkaline water, whilst, on the other hand, it rusts easily in moist air with formation of ferric hydroxide.

On heating in the air it becomes covered with a scaly layer of Fe_3O_4. It decomposes steam at a red heat with formation of ferroso-ferric oxide, Fe_3O_4, and hydrogen, but the reaction is reversible as this oxide is reduced by hydrogen on heating: $3Fe + 4H_2O \rightleftharpoons Fe_3O_4 + 4H_2$. Iron dissolves in HCl and in H_2SO_4 with evolution of hydrogen, whilst when dissolved in dilute HNO_3, NO is evolved; in concentrated nitric acid it becomes passive (*see* p. 619). Red-hot iron burns in oxygen with production of sparks and of very intense light.

A quality of iron called *neutral iron* is to-day obtained which resists the action of sulphuric and nitric acids at various concentrations, both hot and cold. Its resistance exceeds that of the most highly carbonised iron. The process of manufacture is kept secret.

METALLURGY OF IRON. This is based on the reducing action of carbon at high temperatures by which comparatively infusible iron is liberated from the oxides; this then dissolves carbon at high temperatures, becoming readily liquefied and forming cast iron, whilst the greater portion of the carbon is evolved in the form of CO and CO_2, thus:

$$Fe_2O_3 + 2C = 2Fe + CO + CO_2.$$

The impurities are eliminated during smelting by the use of fluxes which form an easily fusible, separable slag.[1]

According to the nature of the ore, but more especially according to the carbon contained in the product and the method by which it is worked, the following varieties of commercial iron may be distinguished, as defined by an International Commission at Philadelphia in 1876.

IRON
- Cast Iron or Pig Iron containing 2·3 to 5 per cent. of C, non-malleable, readily fusible and non-weldable
  - Common *grey cast iron* containing a large portion of its carbon in the uncombined (graphitic) state and a smaller portion in combination.
  - *White cast iron* containing 3 to 5 per cent. of carbon combined as the iron carbides, FeC_4, FeC_3, Fe_3C_2, and 0·2 to 0·5 per cent. of graphitic C.
- Malleable Iron containing 0·02 to 2·3 per cent. C, and fusible with difficulty
  - Fused iron containing 0·05 to 2·3 per cent. of C.
    - If tempered it is *cast steel* (Bessemer and open-hearth steel), containing 0·5 to 2·3 per cent. of C.
    - If non-tempered it is *soft steel* (Bessemer and open-hearth), containing 0·05 to 0·55 per cent. of C.
  - Unfused iron—softened or welded — containing 0·02 to 0·5 per cent. of C.
    - If tempered, *cementation steel* or *puddled steel*, containing 0·2 to 0·5 per cent. of C.
    - If non-tempered, *wrought iron*, worked or puddled, containing 0·02 to 0·2 per cent. of C, which is almost entirely combined.

The ores which are used for the preparation of iron, which contain 30 to 60 per cent. of Fe, are sometimes roasted in heaps or in cupola furnaces in order to remove water, CO_2, As, S, &c., and to break down the compact lumps and oxidise ferrous oxide, which is reduced by carbon with more difficulty than ferric oxide. Poor and rich ores are then *blended* according to the local conditions in order to obtain the maximum yield of iron and the *flux* is added in such a way that the mixture does not contain more than 50 per cent. of iron. The purpose of the flux is to remove the impurities, S, P, Ca, &c., and to then facilitate the fusion of the iron into a homogeneous mass. If the ore contains a gangue rich in calcium and magnesium, quartz and substances containing much silica and alumina are added, whilst if the gangue of the ore contains much silica or alumina, limestone or dolomite is added in order to always obtain, at temperatures close to the melting-point of the iron, a slag of molten silicates which removes all impurities from the molten iron

[1] Iron was not the first metal to be prepared and worked by man as it was not commonly found native, but it followed immediately on copper. It is not clear how it was extracted by the primitive peoples. It is certain that they treated iron ores in a very rudimentary and imperfect manner, and the resulting metal was certainly not very good. They also first treated meteoric iron, and iron objects are known which were made by the ancient Egyptians at least 5000 years B.C., and by the Chinese about 3000 B.C.

Something very analogous to the primitive smelting of iron is still met with on the western coasts of India and amongst certain African tribes. The oxide is reduced with wood charcoal in a kind of cylindrical clay furnace about 1 metre high and 30 cm. wide, or in a kind of hearth excavated in the ground. Air is injected by bellows formed of goat skins and bamboo tubes, but a homogeneous fused mass cannot be obtained. For many centuries the iron produced at Damascus and Toledo was celebrated, because in these places they understood how to prepare the most varied objects from spongy iron by working it with the hammer.

In the Middle Ages the iron industry developed throughout the world, but the process of working was always primitive and the iron was reduced with wood charcoal.

and carries them to the surface, thus also preserving the molten iron from oxidation by the air which is blown into the blast furnace.

The ore is mixed with the flux, and its reduction to free iron is conducted in large cupola furnaces, called *blast furnaces* (Fig. 270), which are about 20 to 30 metres high and have a diameter of 5 to 7 metres. The largest of these furnaces, which are erected in America and are up to 37 metres high, cost £80,000 to £120,000. The mixture of ore and flux is introduced through the upper mouth by pouring it into *f*, and then raising the pipe, *g*, with a lever, so forming a slit through which the mixture falls into the furnace. This mixture is introduced alternately with charges of metallurgical coke (or wood charcoal or sometimes even anthracite). At one time these furnaces were constructed of brickwork of great thickness and with a wide base, entirely of refractory materials. The internal shape was that of two truncated cones, united by a wider base. To-day they are somewhat simplified as they are built with comparatively thin fireclay walls tightly held together and enclosed by iron plates.[1] The shape of the furnace is generally that indicated in the Figure. In the space above *c* (the *stack*) *drying* occurs at a temperature of about 400° ; the *reduction* of the ore occurs at a temperature of 1000° to 2000° below and 400° above. At the widest point, *d*, called the *belly* of the furnace, the iron commences to soften and to absorb carbon. *Carbonisation* occurs in the conical part, *b*, called the *boshes*, where the temperature rises from 1200° to 1600°, and the iron absorbs carbon and gradually becomes more fusible, finally collecting as a liquid covered with molten slag in the cylindrical zone, *a*, called the *hearth*. Below *a* the fusion of the iron is complete, as the temperature rises to 1800°, and at that point a strong blast of air passes into the furnace from several tuyères, *e*, at a height of half a metre above the floor, causing the combustion of the carbon, so that the temperature in this zone rises to 2600°. The lower part of the hearth forms the *crucible* in which the liquid cast iron collects, covered by molten slag, which protects it from oxidation. The slag is discharged by the mouth, *r*, whilst the cast iron is discharged through the opening, *g*. The main body of the furnace and its walls rest on plates of cast iron circularly arranged and supported by numerous large cast-iron pillars, *n*.

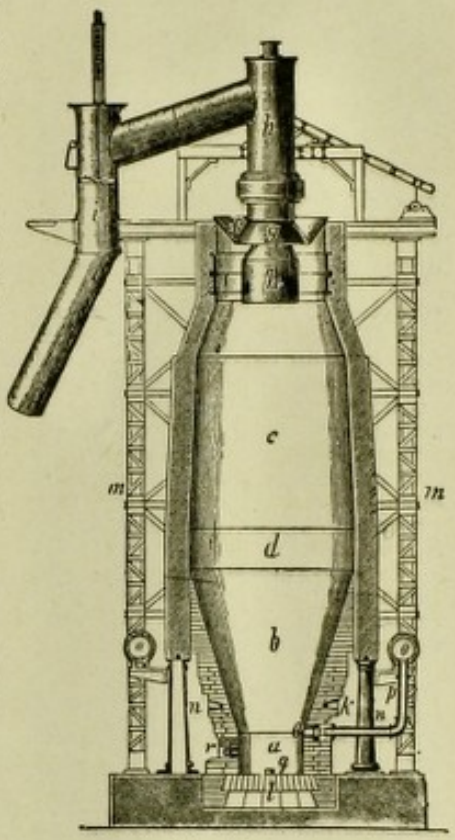


FIG. 270.

The blast furnace is started by first heating the empty furnace by burning coke in it and then gradually charging in the ore and coke as described above. When work has once

[1] A true revolution in the smelting of iron was started at the beginning of the thirteenth century by a modification of the system of heating the ore. In Franconia and in Siegerland (Prussia) the first *blast furnaces* were then erected in which the heat was better utilised by surrounding the whole mass of ore and fuel by a form of brickwork cupola, and driving the blowers which injected air by means of water wheels. We then see the smelting of iron migrate from the top of the mountains towards the valleys in order to utilise water-power, but these blast furnaces led from the commencement to many surprises which seriously embarrassed the metallurgists of that time. The higher temperature and the absorption of carbon by the iron no longer led to a pasty and spongy product which was easily worked with a hammer, but to a product which was liquid at a red heat and which could no longer be wrought after solidification as it was very fragile and could not be welded. *Cast iron* was thus produced, involuntarily, for the first time. It was, however, soon found that after further treatment the cast iron again became malleable and similar to the iron which had been prepared in the past, but of better quality. In 1500 the new process was carried out in blast furnaces which reached a height of 4 to 5 metres, and in addition to work in wrought iron, cast-iron articles of the most varied kinds were also produced and were used for artistic and industrial purposes.

Germany with its great forest wealth maintained itself at the head of Europe during several centuries in iron production, but no important innovations were introduced into this industry until the eighteenth century. Attempts were made in England in 1729, and before that in Belgium in 1627, to replace wood charcoal by coal and to smelt the ore in reverberatory furnaces with coke specially prepared in a species of oven, but did not lead to practical results. All the same in 1619 Dud Dudley worked for several years with coal and was able to sell the iron produced at £4 per ton, whilst that prepared with wood charcoal cost £6 to £6 8*s*.

In America the production of iron in blast furnaces commenced in 1750 and developed considerably during the eighteenth century, but the most fantastic prophet could not have foreseen the immense development of the iron industry in the United States to-day.

In England the development of the iron industry was closely connected with the possibility of replacing wood

been gradually started—a process which requires some weeks—it continues uninterruptedly for several years. A certain quantity of burnt pyrites is now used, together with the ordinary iron ore.[1]

The carbon dioxide which is formed by the combustion of the carbon in the air which is supplied by the blowers is converted into CO on passing through the layers of hot carbon, and this acts on the layers of ore through which it passes and removes oxygen from the iron oxide, again forming CO_2 together with spongy metallic iron. The same reactions alternate and are repeated in each layer. At the upper mouth of the furnace the *blast furnace gases* escape. These were once burnt in the air and lost, but are to-day utilised as they contain much CO and have considerable calorific power. In order to utilise them they are conveyed by large iron pipes, *h* and *i* (Fig. 270), of 1·5 to 2 metres diameter to the *regenerator* for the blast (Fig. 271), and also to the boilers of the steam-engines, which yield the necessary mechanical energy for the works. To-day however these gases are preferably utilised directly in gas motors, as in order to obtain 1 h.p. less than 4 cu. metres are required in this way, whilst in order to obtain the same amount of energy from a steam-engine 22 cu. metres are necessary. In 1895 Thwaite and Gardener at Glasgow and Cockerill in Belgium first used gas motors of 12 h.p., but to-day the best results are obtained with 1200 h.p. gas-engines. In 1902 more than 200,000 h.p. were thus utilised in Europe. At Portoferraio in the works of the *Società Alti Forni Elba*, about 4000 h.p. were produced in 1908 from the blast-furnace gases in 1300 h.p. engines.[2] The Indiana Steel Company at Gary has 16 blast furnaces of which 45 per cent. of the gases are used for the production of 200,000 h.p. For some years it has been found advantageous to inject

charcoal by coal. The first unsuccessful attempts in this direction did not discourage British enterprise, and in 1740 A. Darby and R. Ford succeeded in replacing wood charcoal in the blast furnace by coke prepared from coal, thus increasing the daily output of each furnace considerably. The old furnaces, working with wood charcoal, were increased in size to a height of 12, 15, and even 19 metres in order to compete with the new process, but the maximum production never exceeded 1 ton per day, whilst in a coke furnace in 1800 4 tons of iron per day were produced in certain cases, and the consumption of coke was about 2 tons per ton of iron produced, whilst the consumption of wood charcoal was double and even sometimes four times that amount. The output of the blast furnaces was still further increased by improvements in the blast. Instead of leather bellows more powerful wooden bellows were employed, and then, on the introduction of the steam-engine, cylindrical blowers were proposed by Smeaton in 1768, by which means even the charcoal furnaces were able to raise their production from 300 tons in 1740 to 550 tons in 1788.

On the continent of Europe the first blast furnace using coke appeared in 1767, but was not immediately successful. In England, however, there were more than 161 blast furnaces in 1805 of which only 2 still used wood charcoal, and at that period England over-ran all the world's markets and remained for many years at the head of iron producing and consuming countries.

This pre-eminence did not, however, remain uncontested, and a serious difficulty for England arose from the first in the refining of the cast iron, that is, in its transformation into wrought iron by repeated heating with wood charcoal. Attempts made in 1780 to refine the cast iron with coal did not yield good results, but in 1783 Cort patented a refining furnace which raised hopes of the solution of this problem. In 1784 the first puddling furnace was actually proposed simultaneously by B. Onions and by Cort; the cast iron was charged into a reverberatory furnace with a sand-covered hearth and heated with stirring in presence of air until gas was evolved; the stirring was continued until the atmospheric oxygen gradually removed the carbon from the cast iron in the form of carbon monoxide and dioxide, so that the mass was converted into lumps of wrought iron.

This process was jealously kept secret, but in 1800 the first drawings of puddling furnaces were gradually acquired by other countries, although the predominance of England had already been established.

[1] In the past this could not be used as it contained 4 per cent. and even more of sulphur. The St. Gobain Company, near Vienna, in 1873 attempted desulphurisation in Perret's multiple hearth furnace, using alternate hearths for pyrites and for burnt pyrites.

Burnt pyrites may now be obtained (if it does not contain zinc or lead) with 2 per cent. of sulphur in the case of lumps or 1 per cent. in the case of smalls, and is well suited for the production of iron. Since 1902 the English ironmasters reject pyrites containing more than 2 per cent. of sulphur, whilst in Germany it is rejected if it contains more than 1½ per cent.

But powdered pyrites obstructs the blast furnace and attempts have, therefore, been made to form it into briquettes with the help of tar, peat, and limestone, which latter removes the sulphur. In other cases it is worked to a paste with lime and converted into briquettes, which, after drying, are suitable for smelting. In any case these materials very soon become pulverised at the high temperature of the blast furnace and under the strong compression of the material resting on them, and therefore cause much trouble. Attempts have, therefore, been made to work up the burnt pyrites with clay and sodium silicate (7 per cent.), baking the briquettes in gas furnaces in order to harden them, after which they can advantageously be used in the furnace.

Charges for blast furnaces are used containing 12 to 25 per cent. of burnt pyrites, 30 to 35 per cent. of limestone, and 40 to 50 per cent. of iron ore. Cast iron is thus obtained containing 0·02 to 0·09 per cent. of sulphur and as much as 3 to 4 per cent. of silicon.

[2] The company which owns the blast furnaces, foundry and steel works at Piombino employs about 3000 workmen and annually treats 100,000 tons of iron ore from the island of Elba, which costs 8*s*. 10*d*. per ton at the mine. With a new blast furnace they also treat calcareous iron ore from Campiglia. The blast-furnace gases are used to heat the blast of the furnaces, and also to drive three large gas engines to produce electrical energy, which may also be produced by a reserve gas producer. The blast furnace produces pig iron for the foundry and consumes 950 kilos of coke per ton (1000 kilos) of cast iron. The new blast furnace, which has only been working for a short time, is able to turn out 200 tons of cast iron per 24 hours. A regenerative open-hearth furnace has also been projected capable of producing up to 300 tons of steel per day. The slag from the blast furnaces is partially used in the manufacture of cement and it is intended to granulate it and convert it into bricks. The first

previously dried gas into the blast furnace; but in case this is not used in gas motors it is necessary to dry the air before injecting it into the furnace. Apart from suitable admixture of the ore with the necessary quantity of flux, the nature of the fuel is of importance. Wood charcoal was once used, but was too dear and was then advantageously replaced by coke which, being harder, allows much larger furnaces to be used, which to-day turn out 770 tons of iron per 24 hours in America, whilst in the first blast furnaces the production was only 3 to 4 tons. For certain ores a blast furnace yielding 100 tons of cast iron per day requires 95 tons of coke and 56 tons of limestone and produces about 85 tons of *blast-furnace slag*, the composition and utilisation of which have been described on p. 597. For the production of 1 kilo of cast iron 4460 Cals. are required and by using the dry-air blast a temperature is maintained which is about 200° higher, considerable quantities of fuel being thus saved, with increase of output.

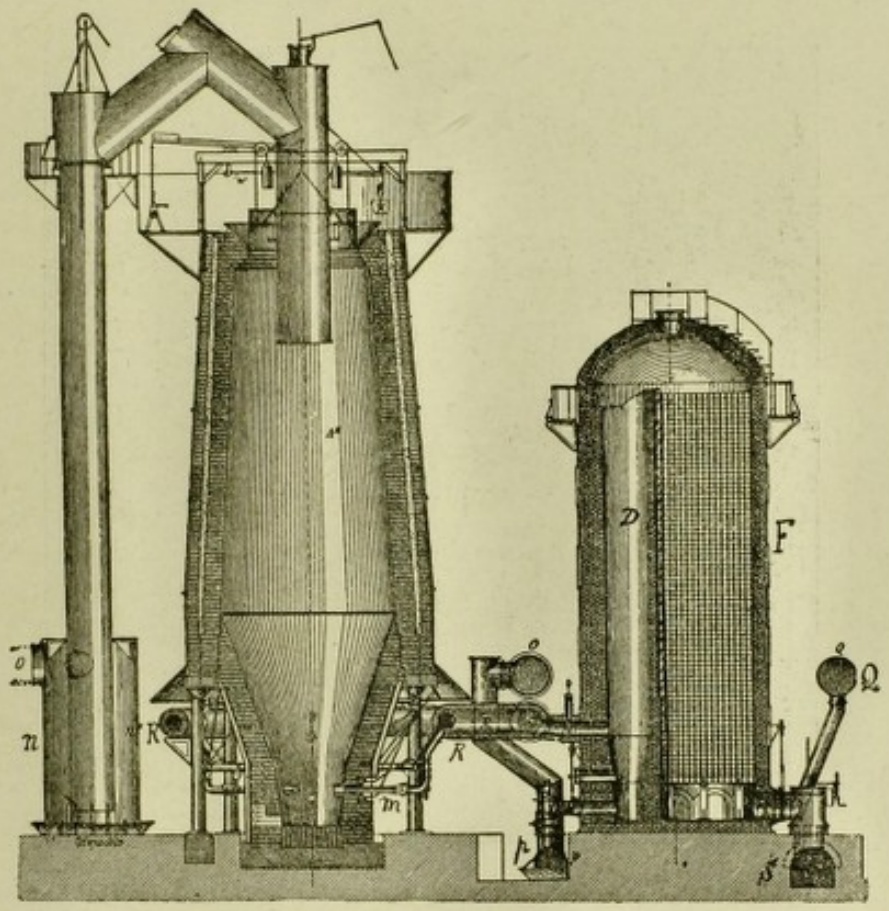


FIG. 271.

A great improvement was effected by the use of strongly compressed and preheated air in the blast. In this way the process was rendered more rapid and the results were improved. The blast-furnace gases are used for preheating the blast. These contain about 25 to 30 per cent. by weight of CO, 7 to 15 per cent. of CO_2, 52 to 58 per cent. of N, 0·4 to 0·8 per cent. of O, 7 to 9 per cent. of H, 2 to 3 per cent. of CH_4, and also 5 per cent. of steam. These gases have a calorific power which varies between 900 and 1500 Cals. per cubic metre.

A blast furnace of the type already cited, yielding 100 tons of cast iron per day, produces 250 cu. metres of gas per minute and utilises about the same quantity of air in the blast. The blast-furnace gases have a temperature of 250° to 300°. When these gases escape from the blast furnace they deposit their dust in an iron cylinder, *n* (Fig. 271), and then pass through the horizontal tubes, *o*, into *p*, which leads to the bottom of a cylindrical *Siemens regenerator* (pp. 367 and 501), *F*, as devised by Cowper (*Cowper's stove*). This is 15 to

coke ovens were not supplied with arrangements for recovery of the distillation products, but their heat was utilised for the production of steam and power for the blowing engines of the blast furnace. They are now using new coke ovens on the system of C. Otto & Co., in which the by-products are recovered and the excess of gas is used for the production of electrical energy.

20 metres high, and has a diameter of 6 to 8 metres.[1] The inside of the regenerator contains very numerous clay cylinders of which there may be as many as 500, with a heating surface of about 5000 sq. metres, and thus the gases burn together with air which enters through the large flue, *D*, and then descend along the small passages between the cylinders, heating them strongly and finally escaping to the chimney through the flue, *S*. This furnace is heated to 900° to 1000° in one hour and the gases are then burnt in a similar neighbouring furnace, whilst cold air enters the first furnace, passing in through the tube, *o*, from the compressor and being heated to 600° to 800°. The hot air then passes through the well-insulated pipe, *R*, from which it is distributed to various pipes which lead it to the tuyères, *m*, inside the blast furnace. With this arrangement the temperature inside the blast furnace is 20 per cent. higher than it was before hot blasts were used. Cowper's stove has extended rapidly throughout Europe since 1865 and has led to great economy of coke as the quantity used fell from 3 tons to 1 ton. A further economy of 5 to 10 per cent. of

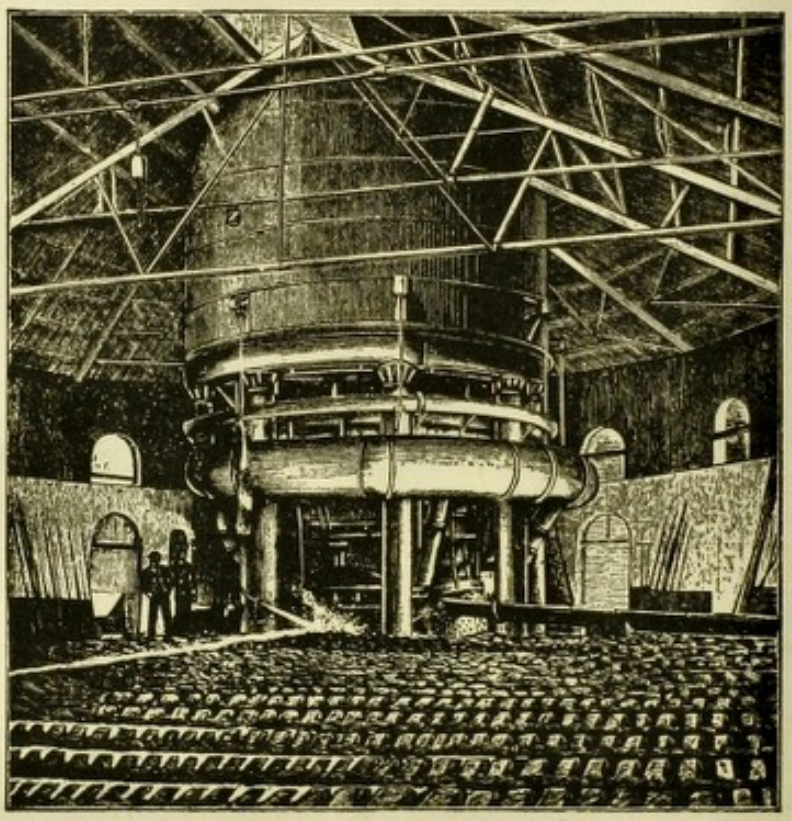


Fig. 272.

coke and a 10 per cent. increase of production has been achieved by previously drying the air of the blast.

The molten cast iron is usually discharged from the furnace in the evening and in the morning, allowing it to flow whilst red hot into channels formed of earth, and directing the molten iron into numerous moulds also of earth, which are lined with sand. The cast iron is thus obtained in bars (*pigs*) ready for further treatment. Fig. 272 shows the lower part of a blast furnace at the moment when the iron is discharged. In 1902 there were 93 blast furnaces in France (122 in 1906, but only 111 active in 1907, 150 in 1908, of which 106 were working, and produced 11,000 tons of cast iron daily);[2] there were 26 in Belgium,

[1] There have been many improvements of the various tube systems for preheating the blast, for instance, the bundles of tubes called *Calder* tubes arranged in a suitable furnace as devised by Neilson, and those proposed by Faber du Faur in 1831 and placed in the upper mouth of the blast furnace, which are heated by the gases which escape at that point. This latter system of tubes was for a long period known as the Wasseralfinger system from the name of the works in Würtemberg in which it was first applied, but the system devised by Alfred Cowper is the most important of all, namely, the system of applying the principle of Siemens regenerator furnaces as stated above.

[2] At the beginning of the nineteenth century in England wood charcoal had everywhere been replaced by coke from coal, and in 1837 G. Crane applied anthracite successfully, as had already been done in America, and obtained the first ton of cast iron by means of hot air, but on the continent of Europe improvements were introduced more slowly. In France there was only a single blast furnace using coke until 1818 at Creusot, but another was then erected at St. Etienne. In Belgium until 1812 the greatest impulse was given to the industry by John Cockerill

343 in England, 139 in Sweden, 11 in Italy, 14 in Canada, and 266 in the United States, in which country 340 furnaces were working in 1906.

For many years it was believed that the abundance of CO_2 in blast-furnace gases was caused by incomplete reaction between the iron oxide and the CO. The height of the furnaces, the temperature conditions and the pressure were all varied, but in vain. It is not actually possible to improve matters in this respect, because the reaction,

$$Fe_2O_3 + 3CO \rightleftarrows 2Fe + 3CO_2,$$

is reversible, and is subject to the laws of chemical equilibrium.

The relation between the CO and CO_2 cannot therefore be appreciably modified, which is also true for the reason that there is no alteration of volume during the reaction as 3 vols. of CO form 3 vols. of CO_2, and thus the relationship between the CO and CO_2 is independent of the pressure and constant for a given temperature (p. 390). Also, since but little heat is evolved during this reaction, the relationship is only altered to a minimal extent by variations of the temperature, and the complete reduction of the Fe_2O_3 is only partially due to the action of the CO. Nothing, therefore, remains but to utilise the gases formed in the blast furnace as completely as possible, and as a matter of fact these now constitute an important source of energy.

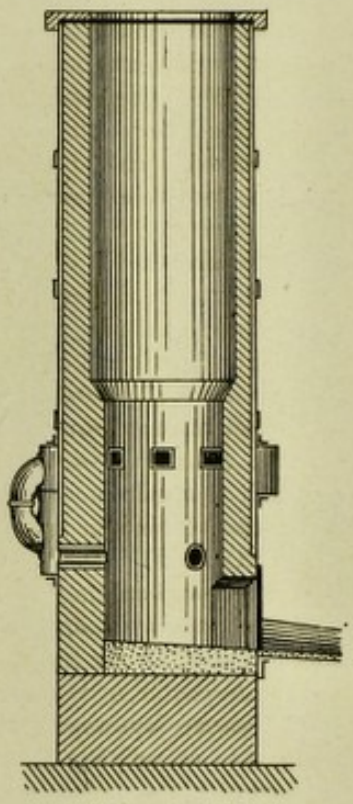


Fig. 273.

The various qualities of commercial cast iron are prepared by remelting the crude pig iron.

Small *foundries* obtain their cast iron from scrap iron which they charge into a furnace mixed with coal. This furnace is small, cylindrical, and vertical with an internal lining of fire clay (Fig. 273); it is called a *cupola furnace* and air is injected below. Such cast iron from blast furnaces as is not immediately transformed into steel is also remelted and refined in cupola furnaces, being mixed with cast-iron scrap, coke, and 2 to 3 per cent. of lime according to the quantity of silica which it contains; a more homogeneous casting is thus obtained, which is harder and has a finer grain. *Malleable castings* are obtained by heating the castings obtained in the cupola for three or four days in furnaces until they become coated with iron oxide, thus producing slight decarbonisation at the surface. In producing iron castings it is necessary to allow for the coefficient of expansion of the cast iron, which is $\frac{1}{162,000}$ of its length for each degree, and when a casting solidifies, about $\frac{1}{100}$ linear shrinkage is allowed. The density of grey or black cast iron is 7, and that of white cast iron 7·5.

Cast iron is sometimes tempered, for instance, by immersing it in oil whilst hot, and it then becomes less brittle.

The value of cast iron which is to be used for the manufacture of steel depends considerably on its contents of silicon and manganese, because if these are present

at Seraing, near Liége, by the use of coke and of puddling furnaces, and in 1823 he constructed a blast furnace using coke, about 15 metres high, which produced 10 tons of cast iron daily to the admiration of the whole of Europe. In 1838 there were already 32 blast furnaces in Belgium. In Germany in 1837 90 per cent. of the iron was still produced with wood charcoal, 75 per cent. in 1850, 30 per cent. in 1860, and then after 1870 coke was used everywhere. In Austria the first coke blast furnace was constructed in 1821. The first blast furnace in America was erected by Germans in 1809, and in 1811 there were already ten of them; the replacement of wood charcoal by anthracite was tried with complete success in 1830 by Geissenhainer who used powerful English cylindrical blowers.

In 1837 the use of bituminous coal was tried with good results, but the use of coke only slowly extended after 1841. Scandinavia alone, with its enormous forests, has continued until to-day to work with wood charcoal.

A great improvement in iron smelting, apart from improvements in the construction of the furnaces, which are now built partly of brickwork and partly of iron, was carried out by J. Neilson in 1829, who proposed the use of a hot blast. He succeeded in this way in doubling the output of the same furnace, and whilst 8 tons of coke were used to obtain 1 ton of iron with a cold blast, the consumption fell to 5 tons with a blast at 150°, and to about 3 tons at a temperature of 300°.

in large quantity a higher temperature is obtained in the converter and purification is easier.

By remelting in cupola furnaces either white or grey cast iron can be obtained at will by cooling more or less rapidly. The difference between the two qualities is indicated in the Table on p. 628. Metallurgical coke is added in the cupola to the extent of about 130 kilos per ton of cast iron obtained. The cupola is heated from the commencement and an air blast is then used at 30 to 40 cm. pressure.

White cast iron is sometimes so hard that it cannot be scratched even by the hardest steel. When grey cast iron is rapidly cooled it is converted into white cast iron ; conversely white cast iron, which is more difficult to melt, is transformed into grey cast iron if slowly cooled.

Grey cast iron has a grey lustrous aspect with granular structure and fracture, is not malleable, melts easily, and passes directly from the solid to the liquid state at 1200° to 1300° ; it cannot therefore be welded, whilst white cast iron remains pasty before melting at 1100° to 1200°. Cast iron containing 10 to 20 per cent. of Mn is called *spiegeleisen*.

Cast iron containing much sulphur (more than 0·3 per cent.) is of inferior quality, and in order to prevent the sulphur from the coke from passing into the iron in the blast furnace, Reusch (1902) proposed to render the slag more liquid by the addition of a little manganese ore—0·5 to 1 per cent.—but Wedemeyer (1904) maintains that desulphurised cast iron is not obtained even when 5 per cent. is added.

A *malleable cast iron* or decarbonisation of castings to a depth of 2 cm. may be obtained, according to Ger. Pat. 213, 950 of 1908, by immersing the castings in molten sodium hydroxide at a temperature of 1100°.

According to Orthey (1907) cast iron with a maximum resistance to tension and minimum resistance to bending should contain 20 to 25 per cent. of its total carbon in the form of carbide, 0·5 per cent. of manganese, 0·2 to 0·5 per cent. of phosphorus, 1 to 1·5 per cent. of silicon and 0·06 to 0·15 per cent. of sulphur, according to the thickness of the casting ; a very pliable cast iron which has very little resistance to tension should, on the other hand, contain, according to the thickness of the casting, from 1·4 to 2 per cent. of silicon and minimal quantities of manganese, phosphorus and sulphur ; good pliability and fair resistance to tension are obtained in castings of intermediate composition.

WROUGHT IRON. Other qualities of iron and steel are obtained from crude pig iron by decarbonising it to a greater or less extent. At one time wrought iron was obtained in the Catalan manner by the direct action of wood charcoal on the ore under the action of an air blast.

White cast iron is more suitable than the grey variety for the preparation of wrought iron, because combined carbon is more easily eliminated than graphitic carbon. The decarbonisation or refining may be carried out in various ways ; in the *finery* or *open hearth* by dropping the molten cast iron through a current of air and then passing an air blast into the molten mass. The temperature is considerably raised by the combustion of the carbon contained in the cast iron and decarbonisation is completed on the floor of the crucible with formation of a considerable amount of slag which is rich in iron.

At a very high temperature the greater part of the fused slag is easily separated and when refining is finished the last residues of slag are eliminated by removing the lumps of semi-molten iron from the furnace and hammering them ; at every blow of the hammer portions of the remaining slag are beaten out of the iron. From 100 kilos of crude pig iron about 75 kilos of wrought iron are obtained.

This iron, when of the best quality, is very dear, and therefore since 1784 the refining of cast iron by *puddling* was started in England. This operation is conducted in reverberatory furnaces with hearths covered with slag from a previous operation. The cast iron is continuously stirred as it gradually softens in order to bring it into intimate contact with the air and eliminate the carbon. It is heated by the direct flame of a coal furnace, and fluxes are added if necessary so that a slag rich in iron is obtained until decarbonisation is complete. At the end of the operation lumps of pasty iron are obtained, because whilst cast iron readily liquefies the wrought iron gradually becomes pasty, and these are then hammered in order to eliminate the last traces of slag. Puddling conducted in this manner is a very lengthy operation lasting several days and is very exhausting and dangerous for the workmen, and also very difficult. Attempts have, therefore, been made to render the operation more automatic and to effect an economy of fuel.

Since 1871 the problem may be said to have been solved by means of Danks' rotary furnace (Fig. 274). The fireplace is similar to those of the usual furnaces and the cylinder —where the cast iron is melted—is formed of cast-iron plates and lined internally with refractory materials (hæmatite and bauxite). The cylinder revolves on pulleys and is turned by cog-wheels. Each charge, which consists of 35 tons of cast iron, may be introduced in the liquid state as it is discharged from the blast furnace ; 50 per cent. of fusible slag is then added in order to refine the product.

When puddling is conducted in this manner it lasts from 1 to 2 hours, and the final lumps of pasty iron are first hammered with the usual hammer and then transformed into sheets, wires, rods, &c., or directly into steel. Pernot furnaces with a circular revolving hearth were used later and their output was double that of the Danks' furnace.

The refining of pig iron is conducted still more rapidly and perfectly in Bessemer converters which are also used for the production of steel, their output being very large. Whilst puddling in the primitive puddling furnace lasted several days or even entire weeks for the conversion of a few tons, 10 tons of iron are now decarbonised in the Bessemer converters in 15 to 20 minutes (*see below*), the iron containing less than 0·25 per cent. of Si, 0·2 per cent. of sulphur and 0·5 per cent. of phosphorus.

STEEL is distinguished from cast and wrought iron by the quantity of carbon which it contains, which is 0·2 to 2·3 per cent., preferably from 0·5 to 1·5 per cent., and by its property of acquiring a *temper*, that is, of becoming greatly hardened and losing its elasticity when it is heated to about 900° and rapidly cooled in water, oil, &c.[1] Steel differs from cast iron by its capability of being welded on to itself when heated. It has a very fine grain which is the finer the better the quality. Its structure becomes apparent on immersing steel in HCl. It is more or less hard and more or less elastic according to its composition and the way in which it has been treated. It melts more easily than wrought iron, at 1300° to 1800°. Its hardness is diminished on heating it for a long time, and on varying the temperature it assumes various colours from reddish-yellow to iridescent blue (soft steel, watch springs, knife blades, &c.).

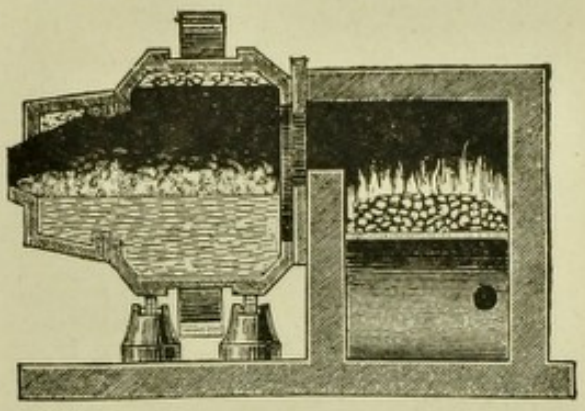


Fig. 274.

Steel obtained directly from the ore is not much used. Almost all steel is to-day prepared by the Bessemer process, which was started in 1855 and became general much later. Since this process became known, the Martin (open-hearth) process and various others have been introduced, which we will briefly describe.[2] A good steel contains less than 0·07 per cent. of sulphur and less than 0·12 per cent. of phosphorus.

MANUFACTURE OF STEEL AND MOLTEN OR HOMOGENEOUS WROUGHT IRON by the Bessemer process. The greatest advance in the metallurgy of iron was achieved by the invention of Henry Bessemer of Sheffield in 1855, who produced enormous quantities of iron and steel rapidly and perfectly in his *converter* (*see below*). In the Bessemer process

[1] The theory of tempering is not yet complete and various hypotheses have been proposed in order to explain this phenomenon. It is probable that the action of the liquid in which the hot steel is immersed is due to a more or less rapid supply of oxygen and other more or less reducing gases which penetrate the steel to a greater or less extent, transforming the *cementite* (iron carbide) into *ferrite* and separating carbon.

[2] In ancient times and until the Middle Ages, the preparation of steel was very dependent on chance and it could not be obtained with certainty as required. Agricola in 1550 and Biringuccio describe the reliable preparation of steel by cementing wrought iron in a bath of molten cast iron obtained directly from the ore, by heating, stirring, and adding wrought iron until the cast iron itself became pasty and refined, and the whole mass was thus converted into steel. In this process there was, however, much loss, which sometimes exceeded 50 per cent. of the metal which was treated. In the eighteenth century another process for preparing steel was perfected, namely, the true *cementation* process. In this process the wrought iron was converted into steel by heating it in presence of powdered charcoal until it softened and then treating it in such a manner that it absorbed the exact quantity of carbon which was required. This process was already used in Piedmont in the seventeenth century and afterwards in England, and was carefully studied and perfected by Réaumur in France in the eighteenth century by preparing suitable cementing powders and constructing suitable furnaces in order to assure a successful result for each operation. In 1740 Huntsman discovered a method of obtaining cast, refined, homogeneous steel in a single operation by heating welded or cemented steel with pure coke in fireclay crucibles in furnaces in an air blast. This process was kept secret until the commencement of the nineteenth century and *cast steel* was only supplied by England.

a strong blast of compressed air is forced through the molten cast iron contained in a pear-shaped iron receiver (*converter*, Fig. 275) lined internally with siliceous fireclay. A very high temperature is maintained not only by the decarbonisation of the cast iron, that is, by the combustion of the carbon, but more especially by the combustion of the silicon which is always contained in cast iron and is supplied by the converter lining. The silicon, manganese, and a part of the phosphorus are eliminated in the form of slag, whilst the decarbonised iron remains as a liquid and therefore forms a very homogeneous product. The Bessemer converter, which is 5 metres high, has a capacity of 10 tons of cast iron. It can be revolved on two pivots by means of the cog-wheel, *H*, which is actuated by a hydraulic piston, *I*, and thus when the operation is finished the converter can be inverted in order to discharge the iron or molten steel. At the base of the apparatus an internally perforated box, *M*, is held by hydraulic pressure and subdivides a powerful jet of compressed air which passes in through the tube, *E*, at the right and then enters through the tube, *D*, supplied with a regulating valve.

The converter is charged with molten cast iron by inclining it at a suitable angle and is then turned into an erect position. A jet of air is then immediately passed through the liquid metal. Through combustion of the Si, Fe, Mn, C, and P the temperature is greatly

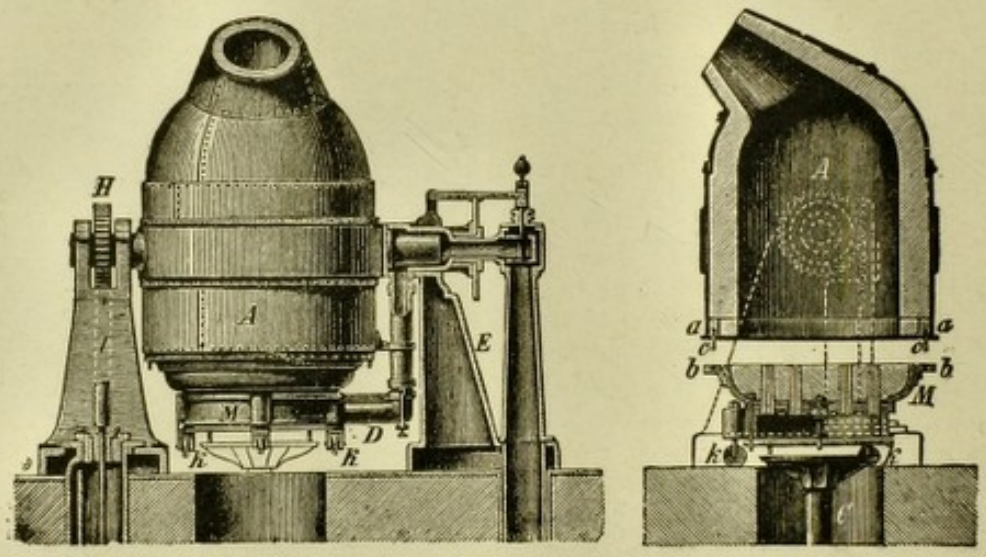


Fig. 275.

raised, and for the first 3 or 4 minutes sparks only escape at the mouth and are followed by a small and finally by a large flame accompanied by sparks, explosions, and brown smoke. The flame (Fig. 276) is continuously observed in order to note its character. After 7 or 8 minutes the flame becomes brighter, the explosions diminish, and to the spectra of sodium and potassium which characterise the first period the spectrum of carbon monoxide is added during the second period, which lasts for 8 to 10 minutes. This carbon monoxide is formed from the ferrous oxide and carbon in the iron. After all heaving motion of the liquid iron has ceased and the flame has become brighter but smaller, all the green spectral lines of CO disappear and a continuous spectrum is obtained, whilst many sparks are still ejected. This is a sign that the carbon has been entirely oxidised. This third period, which is the period of refining, lasts from 8 to 10 minutes. Decarbonisation is then complete and the operation is finished. If molten wrought iron with less than 0·6 per cent. of carbon is required, nothing further is needed but to pour the contents of the converter into suitable moulds. If, on the other hand, steel is required, a given quantity of manganiferous cast iron (spiegeleisen) and other iron containing a definite percentage of carbon (or even a definite quantity of coke) is then added to the molten mass which is stirred for a few minutes by means of the air blast, after which the steel is ready to be poured into suitable moulds.

40 to 60 charges, each of which weighs 10 to 20 tons, can be treated per 24 hours in each converter. It is thus clear that enormous quantities of iron and steel can be produced in a short time with a few Bessemer converters.

From the earliest days of the application of the Bessemer process it had been found

that many forms of cast iron, and especially those containing much phosphorus, were not suitable for this decarbonisation, and formed a faulty and unserviceable iron because the phosphorus did not burn and did not pass into the slag, although it is an element which burns easily, but remained unaltered in the iron. This curious fact was studied by Snelus in 1872 and explained by Thomas and Gilchrist in 1878. Thomas and Gilchrist showed that the phosphorus could not be transformed or separated in the slag as calcium phosphate, because the internal lining of the converters contained much silica, and therefore rendered the metallic bath markedly acid, so that the acid phosphates or phosphoric acid which were formed were easily reduced by the iron; therefore this finally contained all the phosphorus.

Having thus explained the reason for this phenomenon, Thomas and Gilchrist introduced the replacement of the acid lining of the converter by a *basic lining* composed of powdered magnesia and dolomite worked to a paste with a little tar and compressed, and added if necessary to each charge 10 to 15 per cent. of quicklime and flux, calculated on the weight of cast iron containing 2 to 3 per cent. of phosphorus. In this way all the phosphorus separates in the form of calcium phosphate in the slag, which is so rich in phosphates that after being finely powdered it forms an excellent chemical manure which is able to advantageously compete with superphosphates. In 1907 2,600,000 tons of *basic slag* were produced (*see* pp. 509–519).

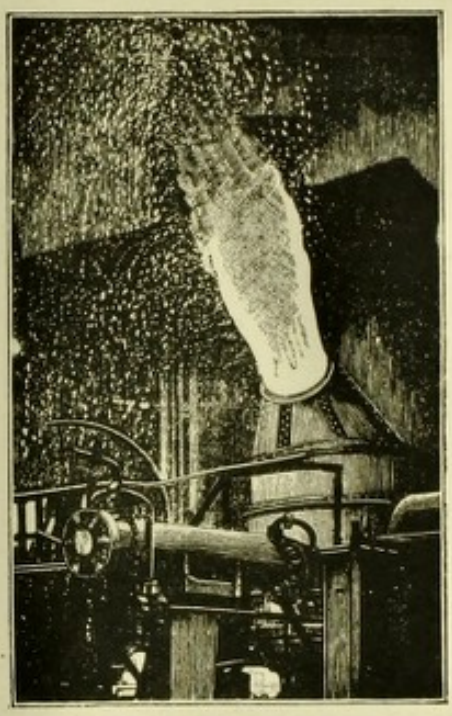


FIG. 276.

Treatment by the basic process is conducted in the same manner as by the acid process and dephosphorisation occurs in 4 or 5 minutes during the last period when the flame has almost or quite disappeared. By suitably inclining the converter the slag alone is poured into iron trucks and a calculated quantity of iron containing a known percentage of carbon is then added to the remaining metal in order to obtain steel in the usual manner. When this is thoroughly molten it is poured into moulds (*ingots*) in which it solidifies. The world's production of steel by the Thomas-Gilchrist process was only 3000 tons in 1879, but rose to 1,000,000 tons in 1885, and in 1895 it had reached 4,000,000 tons, of which about one-half was produced in Germany. By the basic process cast irons containing 2 to 3 per cent. of phosphorus are treated, whilst by the acid process cast iron containing 2 to 3 per cent. of SiO_2 may be employed.

OPEN-HEARTH STEEL (MARTIN STEEL). In 1865 the brothers Martin prepared steel by melting about 75 per cent. of cast iron in a reverberatory furnace with the necessary quantity of wrought iron to obtain exactly the required amount of carbon. The *Martin* or *open-hearth* process was considerably improved by the use of *Siemens'* regenerative furnaces (p. 500), as with their help the temperature of molten iron was easily obtained, whilst without them the production of this temperature was very difficult. In the original Martin process, an acid (siliceous) hearth was used, but a basic lining was afterwards employed, with addition of lime if necessary, and in this way a phosphatic slag similar to that obtained by the Thomas-Gilchrist process is produced.

Each charge consists of 10 to 20 tons and in certain cases even 50 tons, and the process lasts from 8 to 10 hours. Steel and more especially wrought iron of superior quality to that obtained by the puddling process are obtained.

The open-hearth process also presents the advantage that old iron and steel scrap may be employed, and is also suited to the direct production of steel from the ore by starting, for instance, from 60 per cent. of cast iron, 20 per cent. of scrap iron, and 20 per cent. of ore.

In Fig. 277 a modern type of open-hearth furnace with the corresponding Siemens regenerator is shown in section. The path of the hot gases and the recovery of the heat

are exactly analogous to the arrangements in glass-melting furnaces, described on p. 500. Open-hearth furnaces have recently been successfully heated by means of blast-furnace gases mixed with tar. A tilting furnace (Talbot) has also been used with advantage for separating the slag and discharging one-third of the molten product which is then reutilised with fresh cast iron and ore.

Whilst in 1886, in the United States, 91 per cent. of the steel was produced by the Bessemer process and 9 per cent. by the open-hearth process, in 1902 the proportions were 65 per cent. by the former and 38 per cent. by the latter. In England in 1866 the proportions of Bessemer and open-hearth steel were 69·5 per cent. to 30·5 per cent., whilst in 1895 they were 47 per cent. to 53 per cent. In Germany in 1902 69·5 per cent. of Bessemer steel and 30·5 per cent. of open-hearth steel were produced.

CAST STEEL or **CRUCIBLE STEEL.** This is a steel of very high quality which is used for heavy guns, turrets, tyres and axles of wheels, &c., and is obtained by melting open-hearth or Bessemer steel or mixtures of other steels in refractory crucibles in furnaces similar to glass furnaces. The molten steel is then poured into moulds to form ingots.

CEMENTATION STEEL. This is obtained by heating bars of good, malleable iron uninterruptedly, whilst packed in nitrogenous matter or wood charcoal.

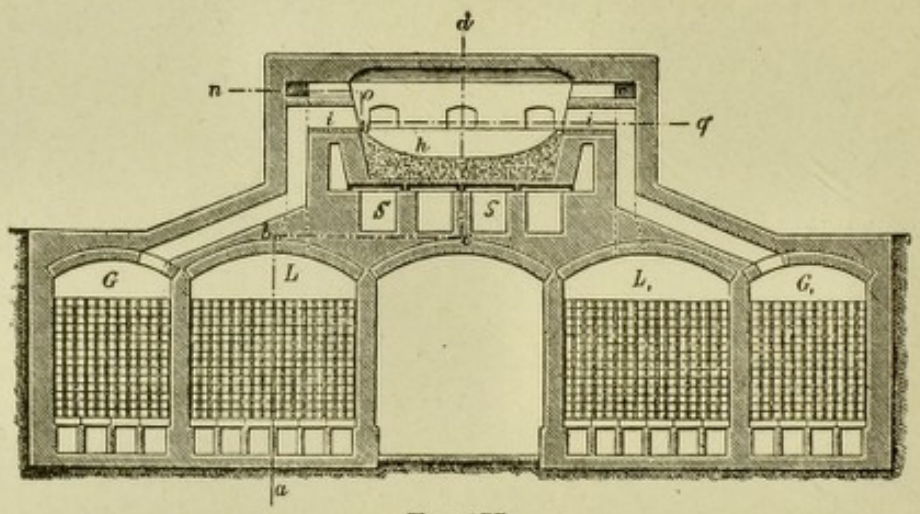


FIG. 277.

Large bundles of these iron bars, weighing 10 to 12 tons, are covered with wood charcoal and packed into furnaces heated to a bright red heat by direct flame for 8 to 10 days. As the carbon penetrates slowly into the outer layers of the bars cementation steel is obtained, but its composition is not very homogeneous. The cooling lasts from 4 to 5 days.

The production of cementation steel by means of calcium cyanamide has now been proposed.

ELECTRICAL PROCESSES. Electrically produced steel has the advantages of being very pure and of high tenacity even when it contains one-third more carbon than ordinary steel. It also contains no blow-holes and has a very high contraction and limit of fusion.

The various electrical furnaces for steel production may be grouped under the following heads. (1) Those in which the mass is melted by heating the outside of the containing vessel: The *Girod furnace* is of this type. It uses a current of 60 volts, produces a very pure steel and costs about £800 for a capacity of 10 tons in 24 hours; a Girod plant commenced work at Ugine in 1910 which utilises 22,000 h.p. for the production of 50 tons of steel per day. (2) Furnaces in which the mass is melted by means of the resistance which the iron itself offers to the passage of the electric current and the corresponding development of heat; the *Gin furnace* is of this type and was applied at Plettenberg, but the working results are not known. The *Keller furnace* is also of this type and has been installed at Livet where cast iron and steel are produced by its means directly from the ore. For the production of 100 tons of steel per day 9750 h.p. are required at the furnace electrodes. (3) Furnaces in which smelting is effected by the heat produced by induction

currents through the mass to be melted: these were proposed by Ferranti and applied at the works of Schneider at Creusot in France, but the *Kjellin furnace* (U.S. Pat. 682,088) has been still more successful, and finally yielded the best technical and economical results, having been worked at Gysing in Sweden since 1901. (4) Melting is produced by the heat of the electric arc: the *Stassano process* belongs to this group. This process was tried very often at first on a small scale and finally on a large scale at Darfo in the province of Brescia, but without practical results, and later at Turin with greater hope of success after various modifications had been introduced into the process. Stassano mixed rich iron ore directly with coal and suitable fluxes in specially contrived electric furnaces, where he produced an electric arc 1 metre long, not through the mass but round its surface, by means of an alternating current of 2000 amps. at 70 volts. The practical results were not good. To-day he works directly with cast iron and the process appears to give better results, but cannot compete with the open-hearth process.

The *Héroult process*, which has been advantageously adopted since 1901 in certain French works, has been more successful; in this process the molten cast iron as it proceeds from the blast furnace is at once submitted to the action of the electric current between two large carbon electrodes. The necessary electrical energy may be produced from the gases of the same blast furnace, by which means a h.p.-hour costs less than 0·2*d.* and the steel has a value of about £4 per ton. In 1906 a plant was also erected in the United States. A Héroult furnace for the production of 10 tons of steel per twenty-four hours costs about £1200.

A mixture of cast and wrought iron in suitable proportions is treated without carbon electrodes in a furnace in which the molten steel replaces the secondary coil of an ordinary transformer, the current intensity being higher and the voltage lower. The results which have so far been obtained on a very large scale are satisfactory and the steel costs less than by other processes if a constant supply of energy costs less than £2 per h.p.-year. The firm of Krupp actually prepared considerable quantities of steel by this process in 1906. It appears that the cost of production of 1 ton of steel by the basic open-hearth process is £3 16*s.* to £4; by the acid open-hearth process £4 4*s.* to £4 8*s.*, and by the Kjellin process only £3 12*s.*, the consumption of energy being 830 to 1040 kw.-hours per ton of steel, whilst by the Héroult process it is 720 to 1100 kw.-hours, or 3400 kw.-hours for the production of 1 ton of cast iron from the ore.

In 1909 77 electric steel furnaces were working throughout the world, of which 19 were of the Héroult type, 14 of the Kjellin type, 10 of the Stassano type, &c.

USES AND PROPERTIES OF VARIOUS TYPES OF STEEL. Steel is to-day used for the preparation of the most varied articles; for armour-plates of ships, for large and small parts of machinery, for guns, rails, needles, watch springs, &c.; altogether the working of steel presents a marvellous example of the increased values which this metal so truly indispensable to mankind acquires. Whilst ordinary iron is only worth £2 to £2 8*s.* per ton, when transformed, for example, into watch springs it acquires a value of about £80,000 per ton, that is 5 times the value of an equal weight of gold. Iron is no longer the only comparatively useful metal, but it is the one which when treated by man is able to acquire the highest degree of value. The nature of iron and steel may not only be modified by physical and mechanical treatment, by puddling and melting at the most varied degrees of temperature, but also by its chemical composition and by the addition of small traces of other substances which alter the properties of iron very greatly. Tungsten, molybdenum, chromium (1 per cent.), manganese (up to 8 per cent.), &c., increase the hardness of steel considerably and render it suitable for special purposes. *Manganese* acts as a species of antidote against the bad effects of phosphorus and sulphur; *nickel*—up to 6 per cent.—renders it tougher and more resistant to shock. We have already seen how even traces of impurities such as phosphorus, sulphur, and more especially of combined nitrogen, modify the nature of iron and steel to such an extent as to render it unserviceable for practical use if they exceed 0·2 per cent. of sulphur, or 0·1 per cent. of phosphorus. *Vanadium* (0·5 per cent.) and *chromium* (up to 1 per cent.) increase the resistance to fracture and to tension (from 34 to 61 kilos). In perlitic steels containing up to 1 per cent of *nickel-vanadium*, the breaking strain is increased, whilst above 1 per cent. it is diminished the same may be said of *mangano-vanadium* and of *siliceous steels*, but brittleness in a direction perpendicular to the lamination is not corrected. *Vanadium* for steel-working purposes costs £2 8*s.* per kilo. Excessive quantities of carbon and manganese render steel very

brittle. *Tungsten*—6 to 9 per cent.—(and more particularly if 5 to 6 per cent. of *chromium* is also added) maintains the hardness of steel even at a high temperature (*rapid tool steel*).

Molybdenum (4 to 5 per cent.) also yields rapid tool steels, but these are less valuable than the tungsten steels as they are more brittle. *Titanium* steel containing not more than 1·5 per cent. is very compact and has a fine grain. *Silicon* renders steel hard and fragile, and if 5 to 15 per cent. is added, it can only be worked in the cold but not on heating.

The steels which offer the greatest resistance to shock are those which contain 0·25 to 0·30 per cent. of carbon and a high percentage of nickel (up to 32 per cent.) or of manganese ; they possess, however, very little elasticity. They are very hard, and if they contain 2 per cent. of chromium become still harder ; they are worked with an emery wheel, for example, in the manufacture of valves for petrol motors and buffers for railway waggons, which are subjected to continual shocks. Hard steels with a very fine grain and very susceptible to high temperatures are obtained by the addition of minimal quantities of vanadium (0·2 to 0·6 per cent.) or even better if chromium and nickel are also added. They are thus very suitable for parts of machinery which are subjected to shocks and to rapid velocity changes, such as the cogs of automobiles, shafts of pulleys, &c. Silicon steels are very elastic and offer great resistance to tension. Steels containing 0·3 per cent. of carbon and 5 to 6 per cent. of nickel are the most suitable for tempering and if they also contain manganese and chromium they become slightly tempered even in the air (*self-tempered steels*). Steels for armour-plate, for large projectiles and for transmission shafts containing 6 per cent. of nickel and 0·2 per cent. of vanadium, are tempered in water, or if they contain, for example, 4 per cent. of nickel and 1 per cent. of chromium, also in oil. Steels which contain more than 0·35 per cent. of carbon have to be reheated after tempering as they otherwise remain too brittle and they thus acquire great elasticity and resistance to fracture.

FIG. 278.

a. Wrought iron. *b*. Soft steel. *c*. Tool steel. *d*. Chrome tungsten steel. *e*. Manganese steel. *f*. Rapid tool steel.

The various types of steel may be recognised without chemical analysis by the *form of the sparks* which they produce when heated to redness and hammered in a powerful current of air or when exposed to the action of an emery-wheel revolving at high speed. In this latter case by varying the pressure or nature of the emery-wheel, the colour and luminous effect of the sparks are modified, but their characteristic formation does not change. In Fig. 278 the bundles of sparks from various types of steel are shown. *a* represents the sparks from forged wrought iron, consisting of a bundle of straight lines more luminous in the centre than at the extremities and without ramifications or stars. *b* and *c* show those from soft steel and tool steel respectively, and the presence of more or less carbon is shown by the formation of a number of larger or smaller luminous stars formed of short rectilinear ramifications which are further ramified in turn in the case of steels containing much carbon, *c*. Chrome tungsten steel for high speed tools forms very short sparks with stars of a dark colour, because both tungsten and molybdenum only become red hot at very high temperatures. Thinner dark red rays are also observed and thicker rays of a brick-red colour. These latter are completely absent in steel containing tungsten only. The spark bundle from manganese steel, *e*, is characteristic. The rays show few sparks, but these are very highly ramified, so that they almost resemble leaves of which the

extremities are united by luminous spheres. High-speed chrome steels show long sparks, large in the middle, and of a dark red colour with a few stars. Nickel steel shows a similar effect to ordinary steels, *b* and *c*.

FERROSILICON. This may be considered as a true alloy of iron and silicon with traces of carbon, and is used, as is also **ferromanganese** containing 30 to 80 per cent. of Mn, for purifying molten iron. Both of these substances are now almost exclusively prepared in electric furnaces, starting from iron ores with addition of coke and of manganese ores in the case of ferromanganese and spiegeleisen (Ger. Pat. 147,311) or of quartz in the case of ferrosilicon. This latter is obtained by reducing the powdered siliceous slag from the open-hearth and Bessemer processes in the electric furnace (U.S. Pat. 712,925), or it may also be obtained from burnt pyrites in presence of silica. Ferro-silicon is poisonous because it evolves PH_3, AsH_3, and SiH_4 from its impurities in presence of moisture ; it has also been known to cause explosions.

Ferromanganese costs from £16 to £24 per ton according to the percentage of manganese. Ferrosilicon containing 10 per cent. of Si costs up to £160 per ton, and when it contains 20 per cent. of Si, it costs more than £180 ; in 1909 a European syndicate was constituted regulating the production and prices. England imports 4000 tons per annum.

MICROGRAPHY OF IRON AND STEEL

The initial work of Sorby in 1867, who first evolved a method of studying a polished section of a metal micrographically, as had already been very successfully achieved in petrography, was quickly followed by other special studies by Martens and Wedding on wrought and cast iron, and in 1883 and 1894 by the important work of Osmond and Werth on steel. After that time metallographic studies increased in number and were notably added to by Guillemin (alloys of copper, bronze, and brass), Charpy (brass and anti-friction metal), and more particularly by H. Le Chatelier, who brought physico-chemical speculations to bear on these studies and showed their full industrial importance. The microscopic examination of the carefully prepared and highly illuminated surface is undertaken, not by transmitted but by reflected light, assisted by microphotography, a suitable camera being added to the microscope. The etching of the polished surface is carried out by the process indicated on p. 410, but more especially to-day by means of certain solutions which colour one or other of the components of the wrought or cast iron or steel in a characteristic manner.

The theoretical researches of Rooseboom on solid solutions have found brilliant practical application in the study of alloys and of more or less highly carbonised iron. On p. 412 *et seq.* we have already studied the phenomena which occur when a metallic alloy is slowly cooled, and have also explained graphically the meaning of the absolute and relative eutectic points by determining the chemical and microscopic composition of the substances which separate at these points. The micrographic examination of wrought and cast iron and steel has led to the study and identification of substances which are characteristic of the various types of steel, &c.

In the alloys of iron and carbon (wrought and cast iron and steel) one or more of the following substances have been found micrographically according to their quality, **Ferrite, Graphite, Cementite, Perlite, Martensite, Austenite,** &c., the properties of which we will discuss later.

If chemically pure (electrolytic) iron is melted and then allowed to cool slowly the cooling curve will show a break at about 1600° and then descend again regularly until there is another break at 890°, and finally a further break at a temperature of 770°. These two last points are indicated in the diagram (Fig. 279) by the letters *G* and *M*. At *G* the iron suddenly changes its thermo-electric properties, and above *M* the iron is non-magnetic, whilst it is magnetic below that temperature.

By means of the same criteria which were used in producing the diagram of the metallic alloy on p. 412, one may also follow that of Fig. 279, which refers to the various alloys of iron and carbon ; on the axis of the abscissæ percentages of carbon are indicated, and on the axis of the ordinates the temperatures corresponding to various eutectic points. The name of the substance which separates in the various zones during gradual cooling is written in the diagram with variation of the types of steel or cast iron and various contents of carbon. In the case of a steel containing 0·35 per cent. of carbon the points *G* and *M* coincide at *O*, and with increase of the carbon this *double point* or critical point is lowered along the line

OS down to 0·86 per cent. of carbon. Steel containing less carbon solidified at higher temperatures mainly separates *martensite*. Again, as the carbon rises from 0·86 to 2 per cent. the critical point is found along the line *SE* and there is also separation of cementite. The gradual transformations which may be caused follow in the order: austenite → martensite → troostite → sorbite → perlite, although Kurbatow (1909) has shown that austenite passes on the contrary through troostite into sorbite, &c.

In the system *iron-carbon* there is separation of graphite independently of the presence of other substances, such as silicon, &c. It is only formed if at least 2 per cent. of carbon is present in the system and to a still greater extent if it approaches 4·3 per cent. The most favourable condition for the separation of graphite is the prolongation of the

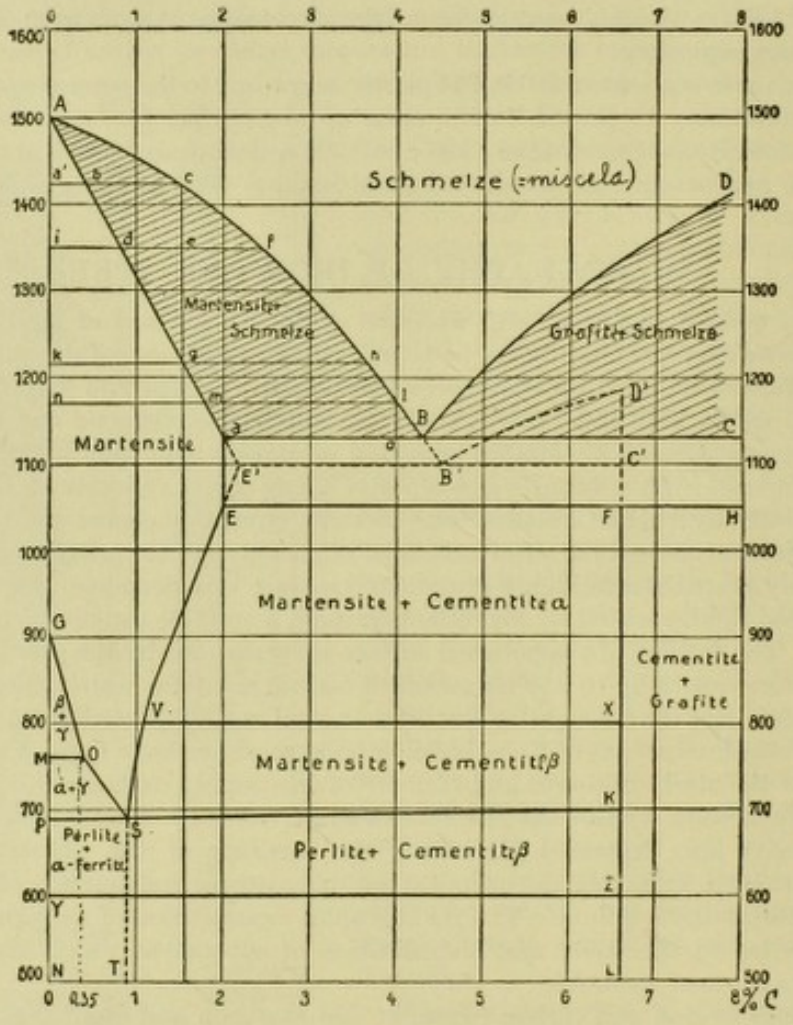


Fig. 279.

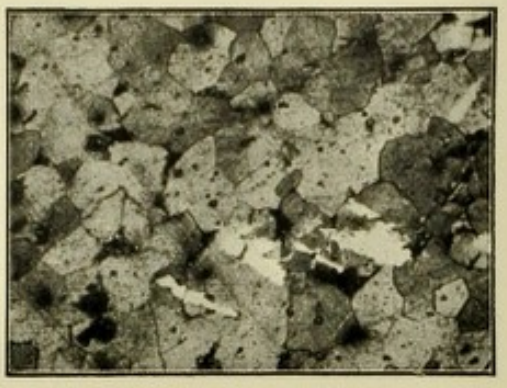
interval of solidification at 1130°. Silicon facilitates the formation of graphite by prolonging the duration of this eutectic point; manganese, on the other hand, abbreviates it.

But the rest of the diagram is only explained by the considerations which follow.

(1) FERRITE. Under this denomination pure iron free from carbon (*α* iron) is understood. This product does not exist commercially, but is found, for example, in hypo-eutectic steels, that is, steels which contain less than 0·85 per cent. of carbon (irons containing nickel, silicon, and vanadium in solution are also incorrectly called *ferrites*). Ferrite appears under the microscope in the form of polygonal faces produced from cubical crystals, by treating with tincture of iodine or better still with picric acid in 5 per cent. alcoholic solution or sodium picrate (solution in boiling water of 25 per cent. of sodium hydroxide and 2 per cent. of picric acid) (Plate II, Fig. *a*). On treating an exceptionally soft steel with a solution of 4 per cent. of nitric acid in amyl alcohol, if polygons of ferrite with well-defined contours appear they are a sign that the steel is brittle.

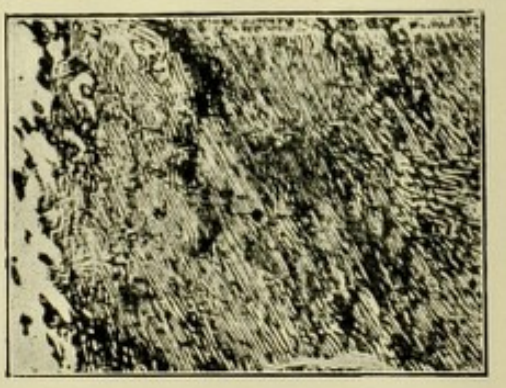
(2) GRAPHITE. This is evident without further treatment in the form of large, irregular, black veins. It is found in grey cast iron (Plate II, Fig. *b*), in which the cementite

PLATE II

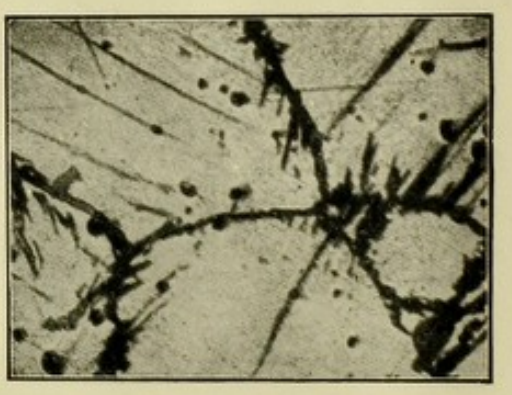


(*a*) Ordinary wrought iron; light-coloured polyhedra of *ferrite* predominate; traces of *perlite* (black spots) and small round black patches of slag. Magnification, 300 diams. Treated with picric acid.

(*b*) Grey cast iron; *cementite* (white portion); *perlite* (predominant laminated mass); *graphite* (black veins). Magnification, 500 diams.



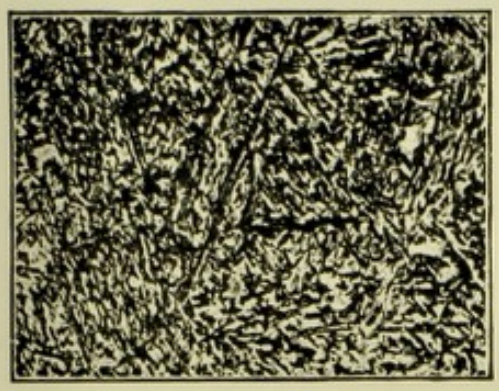
(*c*) Hypereutectic steel; *cementite* (white striations) surrounded by laminated *perlite*. Magnification, 500 diams. Treated with picric acid.



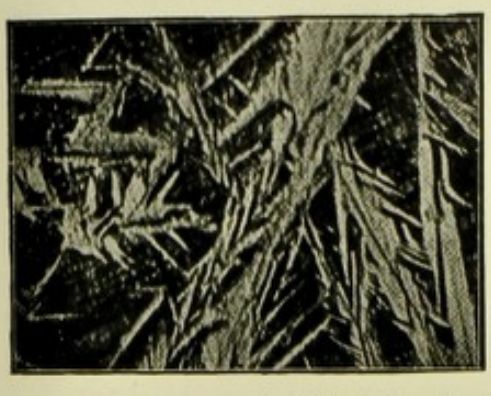
(*d*) Hypereutectic steel; *cementite* (black striations). Magnification, 500 diams.

(*e*) Hypoeutectic steel; *perlite* in black laminæ, *ferrite*, light coloured. Magnification, 750 diams.

(*f*) Eutectic steel; lamellar *perlite*.



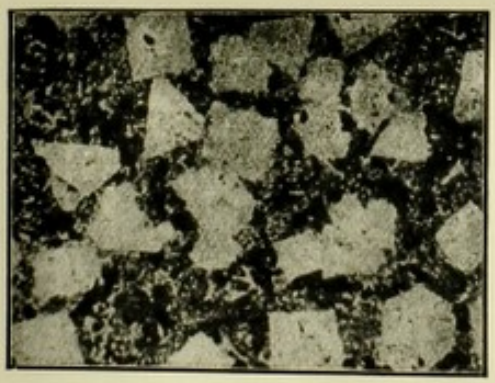
(*g*) Quickly quenched tool steel; *martensite* (dark needles). Magnification, 200 diams.



(*h*) Highly tempered tool steel, rich in carbon; *martensite* (white needles); *austenite* (dark, almost formless mass).

(*i*) *Troostite* (black); *martensite* (grey needles); *austenite* (white mass). Treated with picric acid for five minutes.

(*l*) White cast iron; *cementite* (bright); *sorbite* (dark). Magnification, 500 diams. Treated with picric acid.



(*m*) Anti-friction metal (Pb, Sn, and Sb) for heavy loads. Magnification, 50 diams.

(*n*) Anti-friction metal for light loads. Magnification, 50 diams. Treated with hydrochloric acid.

forms white spots and bands, the perlite small black bands and the graphite large black veins. It is also seen in certain silicon and vanadium steels.

(3) **CEMENTITE : Fe_3C (or Iron Carbide)** (and perhaps other carbides in addition). This is formed abundantly during the cementation of steel and is the hardest component of annealed steel. In general it is only found free in hypereutectic steels containing more than 0·85 per cent. of C.

On treatment with picric acid, cementite is not coloured (Table II, Fig. *c*, where there are white bands of cementite and black plates of perlite). If, on the contrary, it is treated with an alkaline solution of sodium picrate, cementite acquires an appearance of brownish-black striations (Plate II, Fig. *d*).

(4) **PERLITE.** This is the eutectic product (pp. 229, 412 and 413) resulting from an alloy of ferrite and cementite, and is thus formed as superposed alternate laminæ of the one and the other. Picric acid or iodine tincture colour perlite, which is, however, only very slightly coloured by sodium picrate. In Fig. *c* we have already seen perlite, and in Plate II, Fig. *e*, we see a *hypoeutectic steel* containing black layers of perlite and the remainder of bright ferrite. In Plate II, Fig. *f*, we see a *eutectic steel* with homogeneous layers and completely composed of perlite.

(5) **MARTENSITE.** This is a solid solution of carbon in iron, and its properties vary with variation of the carbon contents. It forms the characteristic constituent of steel which has been tempered at temperatures a little above the transformation point. It is formed of minute needles which become larger as the steel becomes more eutectic, and is tempered at higher temperatures. These needles only become visible after the action of picric acid for 5 minutes (in 5 seconds there is no colour at all ; dilute hydrochloric acid colours martensite a bright brown, whilst it does not colour *austenite*). In Plate III, Fig. *g*, the black needles of martensite are evident. In Plate III, Fig. *h*, we see martensite as much enlarged colourless needles in a hardened tool steel very rich in carbon. In such cases picric acid does not colour the martensite, whilst the dark, almost formless mass consists of *austenite*, which is not coloured by picric acid in the case of a steel with less carbon, whilst the martensite is coloured.

(6) **AUSTENITE.** This is found as a characteristic constituent of very highly carbonised steels, containing more than 1·1 per cent. of C, which have been reheated for tempering to high temperatures (1000°) and immersed in a very cold tempering bath (under 0°). Austenite forms at the most 70 per cent. of the whole mass in a steel containing 1·65 per cent. of carbon. These steels ordinarily consist of a mixture of austenite and martensite, or rather of a mixture of austenite, troostite, and sorbite. The austenite forms the almost shapeless mass which is comparatively soft, is scratched by a needle, and except in special cases (*see above* 5, Plate III, Fig. *h*) is not coloured by picric acid. In order to obtain a good hardened steel containing much austenite, steel containing 1·8 to 2·2 per cent. of carbon is heated almost to its melting-point and then immersed in mercury at 130°. According to Kurbatow (1909) austenite is probably an iron carbide of composition intermediate between Fe_6C and $Fe_{10}C$.

(7) **TROOSTITE** is the most important constituent of a steel tempered in water during the critical interval, or of a steel tempered at a higher temperature, if an oil-bath is used for tempering, this being less active than water. It is coloured by picric acid even in 5 seconds, forming a black shapeless mass, thus differing from martensite (*see above*). Under the same conditions or after a few seconds' longer exposure, troostite forms grey needles, whilst austenite remains white (Plate III, Fig. *i*). It also acquires a dark colour under the action of nitric acid dissolved in amyl alcohol after 7 to 15 minutes.

(8) **SORBITE.** This is a product intermediate between troostite and perlite. It may be formed from martensite or on tempering steely cast iron. It is easily coloured by picric acid, and in Plate III, Fig. *l* (500 diameters), it is shown together with colourless cementite in a *white cast iron*. According to Kurbatow (1909) sorbite and troostite are solutions of carbon in α- and β-iron.

(9) **TROOSTO-SORBITE** is very similar to troostite.

In 1905 Le Chatelier classified the components of ordinary steels by considering them strictly as solid solutions, following the phase-rule :

(1) The **homogeneous constituents** which are the true phases. These are ferrite, graphite, and cementite. In special steels the ferrite may hold nickel, vanadium, &c., in solution, whilst the cementite may contain other carbides, such as Mn_3C, Cr_2C_3. &c.

(2) **Constituents consisting of eutectic aggregates**: Ferrite-cementite, which is simply perlite.

(3) **Structural constituents**, such as martensite, austenite, troostite, troosto-sorbite, and sorbite. These products are more especially stable at high temperatures, and are formed from the so-called γ-iron at above 900°. By rapid cooling they are in great part dissociated. In general, perlite changes into troostite by way of sorbite.

From these metallographic studies, extremely important practical conclusions may be derived. When perlite and ferrite are found, one can affirm with certainty that the steel contains less than 0·85 per cent. of carbon and with experience one may estimate the carbon contents within 0·1 per cent. Thus also, from the thickness of the ferrite, one may determine whether a steel is very soft, and if the ferrite polyhedra have clear contours, one may be certain that the steel is brittle. Thus also, a steel in which perlite is present in parallel plates and bands is certainly fragile. A steel which has been heated to 900° and then slowly cooled is called a *normal steel*.

If the micrographic examination reveals the presence of perlite and cementite, this is a sign that the steel contains more than 0·85 per cent. of carbon, and with increase of this amount the amount of cementite also increases. If the presence of martensite is observed and neither nickel, manganese, nor chromium is present one may be certain that the steel has been tempered, and from the greater or lesser ease with which it is coloured one may deduce the carbon contents ; so from the greater or lesser size of the needles of martensite one may form an opinion as to whether the tempering has been carried out at the right temperature or at too high a temperature, or if ferrite is present together with the martensite, this is an indication that the steel is *hypoeutectic*, that is, that it has been tempered at too low a temperature. If, on the other hand, cementite is present together with martensite the steel is *hypereutectic*, and a shaft of cementation steel tempered in this manner, and more particularly when it shows free cementite in the form of needles, should be rejected on account of the brittleness of its surface layers. A special steel showing graphite is always brittle.

By means of the same criteria with regard to which we have studied carbon steels micrographically, we may also study *special steels* containing nickel, chromium, manganese, silicon, tungsten, aluminium, cobalt, titanium, &c., and we will always find criteria of great practical importance with respect to the limits of elasticity, the breaking load, brittleness, hardness, resistance to shock, &c.

The applications of micrography to the common metallic alloys are not less important. To what has already been stated on p. 413 *et seq.* on anti-friction metal (Sb, Sn, Pb) we may add that in alloys of lead, tin, and antimony bright, hard, cubic crystals of SbSn, when they are very large as in Plate III, Fig. *m*, and surrounded by a more plastic eutectic mixture are suitable for bearings for heavy loads, and that these may be the greater the larger the surface occupied by these crystals ; on the other hand, in Plate III, Fig. *n*, we see an anti-friction metal in which the crystals, SbSn, have almost disappeared and are extremely small, and this alloy is suitable for bearings for high speeds but light load. The micrographs were etched with hydrochloric acid.

STATISTICS. The past century has been called the iron age on account of the large consumption of this metal for all purposes, especially for mechanical structures. Certain figures will best indicate the importance of this metal, and we will show it by the increase of production of iron and steel, which may be considered as an index of the industrial progress of the individual nations.[1]

[1] In the past England almost held a monopoly in the iron and steel industry, but for several years the lead was taken by Germany ; to-day, however, the United States is at the head of all other countries. The iron industry is centred in enormous works of which we may mention those at Creusot in France with 15,000 workmen, of Cockerill at Seraing in Belgium with 12,000 workmen, which showed a net profit of £214,000 in 1905, the Krupp works in Germany which at Essen alone employ 46,000 workmen with a share capital of £9,000,000, and which showed a net profit in 1906–1907 of £1,200,000, and the works of the Carnegie Steel Company, the first steel trust, which had a capital of £66,000,000, and produced 3,250,000 tons of steel in 1900 showing a profit of £4,800,000.

The United States is at the head, not only with regard to production, but also with regard to the technical perfection of its processes, in spite of the great discoveries in this field of human activity which were made by the Englishmen Cart, Bessemer, Siemens, Mushet, Thomas, Gilchrist, Lowthian-Bell, &c.

A workman in a steel works formerly earned 7½*d*. per ton of the product, whilst to-day he earns ½*d*. per ton, and in this way his total earnings are 20 per cent. larger than formerly with a smaller amount of labour on account of the large daily production by modern machinery. The mean production of an English blast furnace is 220 tons per 24 hours, whilst in the United States it is 600 tons, but the ore worked in England contains 45 to 48 per cent. of iron on the average, whilst that worked in the United States contains 60 to 65 per cent. If it were not for the enormous internal consumption of iron in America, which sometimes obliges its importation from Europe, American competition would be fatal to the European iron industry.

WORLD'S PRODUCTION OF IRON ORE, CAST IRON, AND STEEL

	1850		1880				1901			
	Cast iron	Percentage of world's production	Cast iron	Percentage of world's production	Steel	Percentage of world's production	Cast iron	Percentage of world's production	Steel	Percentage of world's production
	Tons		Tons		Tons		Tons		Tons	
England	2,286,000	53·2	7,875,545	42·5	1,300,000	32·8	7,886,000	19·3	5,800,000	16
Germany	215,659	5·1	2,792,040	14·8	650,000	16·3	7,880,090	19·2	6,394,000	20
France	405,653	9·7	1,725,000	9·4	360,000	9	2,400,240	5·8	1,465,000	4·7
United States	572,893	13·6	3,879,840	21·2	1,000,000	25·2	16,132,400	39·5	13,690,000	44
Austria-Hungary	198,500	4·7	464,000	2·5	120,000	3	1,315,530	3·3	1,142,000	3·6
Russia	204,750	4·8	448,596	2·4	190,090	4·9	2,831,000	6·9	1,815,000	5·7
Belgium	144,452	3·4	608,084	3·2	110,000	2·9	765,400	1·9	526,670	1·8
Sweden	181,156	4·3	405,713	2·2	35,000	0·9	528,375	1·4	350,000	1·2
Italy	30,000 ?	—	20,000 ?	—	3,500	—	16,000	—	123,310	0·4
Spain	32,380	—	85,940	—	—	—	294,120	0·7	122,954	0·4
Other Countries	70,000	0·8	307,000	1·4	40,000	1·0	635,000	1·5	500,000 ?	1·7
Total (approximat.)	4,270,000	—	18,630,000	—	4,000,000	—	40,684,150	—	31,500,000	—

	1906				1908				Iron ores		
	Cast iron	Percentage of world's production	Steel	Percentage of world's production	Cast iron	Percentage of world's production	Steel	Percentage of world's production	1869	1908	Increase of production, 1869–1908
	Tons		Tons		Tons		Tons		Tons	Tons	Per cent.
England	—	—	—	—	9,037,000	15	5,380,000	12	11,509,000	15,031,000	30
Germany	—	—	—	—	11,805,000	20	11,186,000	27	4,084,000	24,225,000	500
France	3,200,000	6	2,500,000	7	3,412,000	5·8	2,713,000	6	2,500,000	10,000,000	300
United States	25,300,000	49	24,000,000	64	26,000,000*	43	26,700,000*	65	5,302,000	43,202,000	750
Austria-Hungary	—	—	—	—	1,770,000	—	1,200,000	—	—	4,500,000	—
Russia	—	—	—	—	2,700,000	—	2,040,000	—	—	6,000,000	—
Belgium	—	—	—	—	1,380,000	—	2,150,000	—	—	320,000	—
Sweden	—	—	—	—	600,000	—	400,000	—	—	4,500,000	—
Italy	45,000	0·08	—	—	112,929	0·18	437,674	—	—	539,120	—
Spain	—	—	—	—	390,000	—	240,000	—	—	9,500,000	—
Other Countries	—	—	—	—	900,000	—	800,000	—	—	2,000,000	—
Total (approximate)	55,000,000	—	37,000,000	—	60,000,000	—	40,000,000	—	—	120,000,000	—

* 1907.

In Italy the manufacture of steel has acquired importance, the principal centres of production being in Liguria, at Terni, in Bresciano, at Arezzo, at Como, in Piedmont, at Milan, &c. ; in 1908 302,500 tons of worked iron were produced of the value of £2,440,000.

Germany and Luxemburg produced 24,444,073 tons of iron ore in 1905.

In France in 1907, and especially in the departments of Meurthe and Moselle and of Meux, 10,000,000 tons of iron ore were mined (compared with 8,500,000 tons in 1906) of the value of £1,880,000, and 2,147,000 tons were exported to Belgium and Germany ; of the total production 418,000 tons consisted of hæmatite.

Italy imported the following quantities :

	1906	1907	1908	1909	
	Tons	Tons	Tons	Tons	£
Wrought iron and steel in plates, bars, and wire .	144,585	188,377	166,659	151,859 at	1,152,776
Crude pig iron and steel ingots . . .	22,782	32,119	43,163	52,547 ,,	294,260
Refined cast iron and ingots	169,956	231,042	254,239	246,730 ,,	937,572
Crude ferrosilicon containing 15 to 75 per cent. Si.	152	196	224	136 ,,	3,164
Iron and steel rails . .	21,066	31,267	31,262	12,894 ,,	82,526
Iron and steel tubes . .	11,683	13,445	14,832	13,351 ,,	212,896
Unfinished wrought and cast iron and steel articles . . .	3,682	6,117	6,839	5,212 ,,	95,176
Tinplate and tinned, copper-plated, or oxidised iron and steel .	12,480	13,544	12,947	13,523 ,,	319,164
Soft steel . . .	690	1,560	1,494	1,390 ,,	30,976
Wrought and cast iron and steel scrap . .	344,977	362,567	326,119	416,353 ,,	1,498,872
Total . .	731,953	880,234	857,778	913,995 ,,	4,627,388

The production of the Italian iron and steel works was 570,000 tons in 1906 and 595,000 tons in 1907 of the value of £5,520,000. The consumption of steel, sheet iron, and other unworked products was 850,736 tons in 1906 and 901,272 tons in 1907. 86 iron and steel works were in operation in 1906 and 85 in 1907 ; 20,700 workmen were employed in these works in 1906 and 24,200 in 1907 ; in 1906 they used 58,827 h.p. and 60,275 h.p. in 1907.

In 1909 France produced 3,632,105 tons of cast iron and 3,069,109 tons of steel.

The world's production of cast iron reached 50,000,000 tons in 1905, of which 23,000,000 tons were produced in the United States, 11,000,000 in Germany, and 9,000,000 in England. The production of steel increased in the same proportion and exceeded 35,000,000 tons. Germany mined 22,000,000 tons of iron ore in 1904. In 1908 Sweden exported 313,000 tons of various qualities of steel.

The price of crude cast iron has only varied slightly, except during exceptional periods of short duration. In 1850 the price in England was about £2 5*s*., in 1880 £2 8*s*., and in 1902 £2 5*s*. per ton. The price rose exceptionally to £4 in 1854, £6 in 1873, and £3 12*s*. in 1900. Nickel steel for armour-plates costs £120 per ton.

In view of the extraordinary consumption of iron it does not seem out of place to consider whether there is any danger of exhaustion of iron ore, but our descendants of the twentieth century may still sleep quietly as a shortage of iron is an eventuality which might perhaps interest the generations of the twenty-first century.

Thus the capacity of the principal deposits existing in various countries has been

calculated as follows, in millions of tons: United States, 10,000 (of which the United States Steel Corporation alone consumes 50,000,000 tons per annum); Germany 3900, France 1500, Russia 1500, Spain 500, Sweden 1000, England 250, Austria-Hungary and other countries 1200. In Norway there are still 150,000,000 tons of ordinary ore and 200,000,000 tons of titaniferous magnetic iron ore, containing 65 per cent. of Fe and 10 to 15 per cent. of titanium, which cannot be successfully treated in blast furnaces up to the present on account of its great infusibility. Pictet has prophesied the use of oxygen in blast furnaces for the treatment of such ores.

FERROUS COMPOUNDS

Iron forms two important classes of compounds. In the *ferrous* compounds, the cation $Fe^{\cdot\cdot}$ is divalent, whilst in the *ferric* compounds the cation $Fe^{\cdot\cdot\cdot}$ is trivalent. Compounds of the former class have generally a greenish colour, whilst those of the latter class are brownish yellow.

Ferrous compounds are obtained on treating iron with acids with exclusion of the air; they are also obtained by reducing ferric compounds.

FERROUS OXIDE: FeO. This is obtained by the action of carbon monoxide on ferric oxide, $Fe_2O_3 + CO = CO_2 + 2FeO$; it forms a blackish powder which is easily oxidised on heating in the air.

FERROUS HYDROXIDE: $Fe(OH)_2$. This is obtained as a greenish gelatinous mass by treating the solution of a ferrous salt with an alkali. It rapidly acquires a brown colour in the air as it is oxidised with formation of ferric hydroxide. It possesses weakly basic properties.

FERROUS CHLORIDE: $FeCl_2$. This compound is formed by the action of hydrochloric acid on an excess of iron and crystallises from the intensely green solution in green monoclinic prisms containing $4H_2O$. When prepared in the anhydrous state by the action of HCl vapour on hot iron it is white and the density of its vapours at 1400° corresponds to the formula $FeCl_2$. It readily forms well-crystallised double salts such as

$$FeCl_2.2KCl.2H_2O.$$

FERROUS SULPHATE: $FeSO_4$. This compound crystallises in large green, monoclinic prisms with $7H_2O$ and is then called *green vitriol* or *iron vitriol*. It is obtained by dissolving iron in dilute H_2SO_4, or preferably by partially roasting iron pyrites, FeS_2, and so transforming it into FeS and then exposing the product to the action of moist air, which transforms it into $FeSO_4$ and H_2SO_4. The resulting ferrous sulphate is extracted with water and the solution poured into wooden vats containing iron turnings in order to saturate the small amount of free H_2SO_4 and to reduce the small amount of ferric sulphate which is mixed with the mass to ferrous sulphate. The solution is then evaporated in presence of iron, decanted from the yellow sediment which is thus formed, consisting of basic ferric sulphate and gypsum, and the green vitriol is then allowed to crystallise. The firm of Schnorf Söhne at Uetikon work up burnt pyrites to a paste with hot sulphuric acid of 60° Bé. as obtained in the Glover tower, and after stirring, and when the reaction is finished, the product is dissolved in water and reduced to ferrous sulphate by the action of iron turnings. The solution is concentrated to 35° to 36° Bé (measured at 90°) and is allowed to cool in the presence of hoop-iron which is suspended in the liquid. Ferrous sulphate is thus obtained in a more economical manner, and the disadvantage of the evolution of hydrogen which occurs on dissolving Fe in H_2SO_4 is avoided. Ferrous sulphate is isodimorphous with the sulphates of the magnetic series and also forms well-crystallised stable double salts, such as Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, which forms green crystals very stable in the air which are used in volumetric analysis.

At 100° ferrous sulphate loses $6H_2O$, whilst the last molecule of water is

evolved at 300°. When exposed to moist air it becomes brown and is transformed into basic ferric sulphate :

$$3FeSO_4 + O + H_2O = Fe_2(SO_4)_3.Fe(OH)_2.$$

100 parts of water at 10° dissolve 60 parts of crystallised ferrous sulphate, whilst at 100° they dissolve about 330 parts.

It is used technically in large quantities for mordanting wool which is to be dyed with logwood black. It is also used as an economic disinfectant and absorbs both H_2S and NH_3; also in the manufacture of black ink, Prussian blue, &c. It costs £2 to £2 16*s*. per ton, and when chemically pure £10 per ton. The Italian production was 1300 tons in 1893, rose to 1497 tons in 1905 and was 1571 tons in 1906 of the value of £2218; in 1908 it was 2100 tons of the value of £3240. The exports were 8 tons in 1907, 108 tons in 1908, and 97 tons in 1909 of the value of £155 12*s*.

FERROUS CARBONATE : $FeCO_3$. This compound is found naturally as *Siderite*, and also dissolved in mineral waters through the action of CO_2, in the form of **Ferrous Dicarbonate, $Fe(CO_3H)_2$**, but separates from such water in the form of insoluble ferric hydroxide on contact with air. The basic carbonate is also formed on adding an alkali carbonate to a solution of a ferrous salt, but is very unstable as the $Fe^{\cdot\cdot}$ ions, being weakly basic, do not yield stable salts with weak acids. It quickly becomes brown in the air, being transformed into $Fe(OH)_3$.

FERROUS PHOSPHATE : $Fe_3(PO_4)_2 + 8H_2O$. This occurs in nature as *Vivianite* in bluish crystals. It is obtained by the action of sodium phosphate on solutions of ferrous salts, as a white amorphous, easily oxidisable powder.

FERROUS SULPHIDE : FeS. On melting iron and sulphur together or even on moistening a mixture of iron filings and flowers of sulphur in the air, a blackish mass of metallic lustre is obtained which consists mainly of FeS and is used in the laboratory for the preparation of hydrogen sulphide by treating it with HCl or H_2SO_4. It is obtained pure as a black precipitate by treating a solution of a ferrous salt with an alkali sulphide, but FeS is readily oxidised in the air and transformed into ferric sulphate. Instead of starting from a ferrous salt a ferric salt may also be used, as it is reduced by the alkali sulphide and then precipitated :

$$2FeCl_3 + (NH_4)_2S = 2FeCl_2 + 2NH_4Cl + S$$
$$FeCl_2 + (NH_4)_2S = 2NH_4Cl + FeS.$$

Italy produced 30 tons of ferrous sulphide in 1905 of the value of £480.

FERRIC COMPOUNDS

These have a brownish-yellow colour and are formed by the oxidation of ferrous salts. They may be easily reduced again to ferrous salts. They contain a trivalent ion, $Fe^{\cdot\cdot\cdot}$, which has weakly basic properties and cannot therefore form salts with weak acids, whilst the salts with strong acids are readily hydrolised in aqueous solution (*see* pp. 106, 222).

FERRIC OXIDE : F_2O_3 (or **Iron Sesquioxide**). This is found in nature in compact reddish masses in the form of hæmatite or as *oligist*, which is a crystalline anhydride, or as *ochre* which is more or less highly coloured from yellow to red. It is obtained artificially as a bright red powder by heating ferric hydroxide or ferrous sulphate to redness in the air. It is then called *iron red*, *caput mortuum*, or *colcothar*.

It is stable up to the temperature of 1350°, and then loses a little oxygen.

It is abundant in a very impure condition as burnt pyrites (pp. 255, 280).

It is used as a red pigment in paints, and for polishing glass. Its price varies according to its degree of fineness from £6 to £10 per ton.

It is now obtained in various brightly coloured qualities of different shades by heating ordinary iron oxide to redness for several hours mixed with 6 per cent. of sodium chloride in clay crucibles, and then allowing it to cool slowly out of contact with the air. By varying the temperature and the duration of the heating, various shades are obtained from a bright red to a reddish violet.

Of late years various patents have been taken out for the preparation of such iron pigments, Ger. Pat. 143,517, Eng. Pat. 16,338 of 1907, and U.S. Pats. 739,444 and 758,687.

Italy produced 1630 tons of iron oxide in 1908 of the value of £31,160, and 750 tons in 1905. It imported 596 tons in 1905, about 1000 tons in 1907 and 1141 tons in 1908 of the value of £11,400, and 1045 tons in 1909. Italy exported 4577 tons in 1907 and 9691 tons in 1909 of the value of £97,000 (official statistics !). The imports of mineral pigments, both natural and artificial, were 964 tons in 1906 and 982 tons in 1908 of the value of £4680 apart from 1643 tons of umber of the value of £2288. The exports were 3300 tons in 1908 of the value of £13,280. Germany exported 391 tons of mineral pigments in 1905.

FERRIC HYDROXIDE : $Fe(OH)_3$. This is formed as *rust* on iron exposed to moist air, or as a voluminous reddish-brown precipitate on treating a solution of a ferric salt with an alkali. It is best to use NH_3 as the precipitate is then more easily washed. It is insoluble in water and soluble in acids. When freshly precipitated it is soluble in a solution of ferric chloride or acetate and by dialysing this solution a pure colloidal reddish-brown solution of $Fe(OH)_3$ is obtained which is used in medicine. On boiling the hydroxide for some time with water, it is transformed into $Fe_2O(OH)_4$, that is, into a hydroxide which is partially soluble in acids, and which is also found naturally as *limonite*.

Ferric hydroxide is a weak base.

FERROSO-FERRIC OXIDE : Fe_3O_4. This is found naturally as *magnetite* or *magnetic iron ore*, which abounds in Sweden, Norway, and the Ural Mountains. It is formed on burning iron in excess of oxygen or on heating iron in a current of steam or of CO_2. It is sometimes used as a pigment in paints.

FERRIC CHLORIDE : $FeCl_3$. This compound is obtained on passing a current of chlorine into a solution of ferrous chloride, or by oxidising such a solution with HNO_3. It crystallises with various amounts of water from 5 to 15 mols., but on heating it not only loses water but also HCl, similarly to $MgCl_2$, and anhydrous $FeCl_3$ is therefore only obtained by heating iron in a current of dry chlorine. It is soluble in water, alcohol, and ether. The density of its vapours at 400° corresponds to the formula Fe_2Cl_6, whilst at 1000° it corresponds to FeC_3.

Its molecular weight has been determined by the rise of the boiling-point of an ethereal solution.

It is used in the chlorination of copper and silver and as a mordant in dyeing textile fabrics. It is also used for purifying effluent waters. In solution of 40° Bé. it costs about £14 8*s*. per ton. The solid crystalline salt costs £20 per ton.

FERRIC SULPHATE : $Fe_2(SO_4)_3$. This compound is obtained on dissolving ferric oxide in sulphuric acid or by oxidising ferrous sulphate with HNO_3. On evaporation a whitish substance remains which dissolves in water with a brownish-red colour. It is used in dyeing silk and cotton (*see* vol. ii, "Organic Chemistry"). With the alkali sulphates it forms well-crystallised alums such as $K_2SO_4.Fe_2(SO_4)_3.24H_2O$.

FERRIC PHOSPHATE : $FePO_4$. This is a yellowish powder, insoluble in water and acetic acid, which is obtained by precipitating a solution of a ferric salt with sodium phosphate.

IRON DISULPHIDE : FeS_2. This forms *iron pyrites* which is found abundantly in nature in lustrous, yellow, octahedral crystals. It is used for the manufacture of sulphuric acid (*see* p. 255). We may complete the statistics given on p. 255 by the following figures :

The *world's consumption* of pyrites was 300,000 tons in 1860 and 3,000,000 tons in 1905. In 1907 the production of the various countries was : Germany 196,500 tons, England 10,194 tons, United States 247,500 tons, Norway 225,000 tons (of which 30,000 were consumed in the country), Newfoundland 75,000 tons, France 267,000 tons, Portugal 380,000 tons, and Spain 2,700,000 tons (half of which was cupriferous), Canada 47,000 tons, Japan 40,000 tons.

Great Britain consumed 400,000 tons in 1900 and in 1908 imported from Spain alone 769,000 tons, of which 600,000 tons were used in sulphuric acid manufacture.

Germany imported 691,000 tons of pyrites in 1909 and exported 14,565 tons.

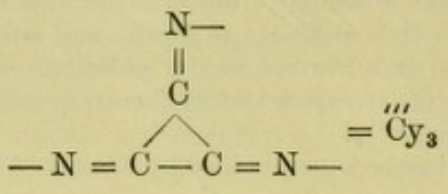
Italy produced 122,350 tons of pyrites in 1906 and 131,720 tons in 1908 of the value of £94,760. The imports into Italy were 11,691 tons in 1907, 16,348 tons in 1908, and 15,062

tons of iron pyrites in 1909 (three-quarters of which were from Spain), whilst in the same years 11,000, 14,200, and 11,110 tons of copper pyrites were imported (nine-tenths of which came from Spain) of the value of £60,000.

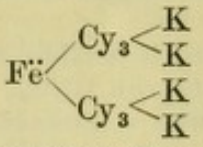
POTASSIUM FERRATE : K_2FeO_4. This compound is formed on heating iron filings with saltpetre or by suspending ferric hydroxide in an alkaline solution through which a current of chlorine is passed. It forms dark red crystals, isomorphous with potassium sulphate and chromate. It is decomposed by water with evolution of oxygen and separation of $Fe(OH)_3$. This compound may be considered as the potassium salt of a hypothetical **Ferric Acid.**

CYANOGEN COMPOUNDS OF IRON

When nitrogenous organic matter is melted with iron and an alkali carbonate iron cyanides are formed. If potassium cyanide is added to the aqueous solution of a ferrous or ferric salt, yellow precipitates of ferrous cyanide, $Fe(CN)_2$, or ferric cyanide, $Fe(CN)_3$, are formed, which are decomposed by the air and dissolve in an excess of KCN, forming the double cyanides, $Fe(CN)_2.4KCN$ and $Fe(CN)_3.3KCN$; these no longer show the ordinary reactions for iron with KOH, H_2S, &c., nor those of ordinary cyanides. It must, therefore, be admitted that they contain complex ions instead of the Fe ion, namely, the tetravalent ferrous anion, $FeCy_2''''$ (where Cy is an abbreviation for cyanogen, CN), which forms **ferrocyanides**, and the trivalent ferric anion, $FeCy_6'''$, which forms **ferricyanides**. On adding concentrated HCl to strong solutions of these salts, the corresponding acids, H_4FeCy_6 and H_3FeCy_6, separate as white powders which become blue in the air. If we imagine a trivalent radical formed of three cyanogen groups :

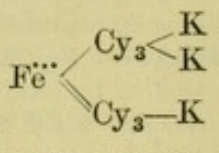


we may imagine potassium ferrocyanide and ferricyanide to be constituted as follows :



Potassium ferrocyanide

and



Potassium ferricyanide

POTASSIUM FERROCYANIDE : K_4FeCy_6 (Yellow Potassium Prussiate). This was once prepared almost exclusively by the addition of dry animal refuse, such as blood, hides, horns, hide parings, &c., and iron turnings to red-hot molten potassium carbonate. Ferrous sulphide was thus formed from the organic sulphur, together with KCN, and on lixiviation a solution of potassium ferrocyanide was formed without further treatment : $6KCN + FeS = K_4FeCy_6 + K_2S$. By concentrating and recrystallising potassium ferrocyanide was obtained in large monoclinic yellow prisms, containing $3H_2O$, which lost their water of crystallisation on heating, then forming a white powder. Now, however, almost all potassium ferrocyanide is prepared from the *spent oxide* which is obtained in abundance during the purification of coal gas and consists of a mixture of sawdust, lime, iron oxide, and sulphur, together with ferrocyanides and sulphocyanides. This mass is first lixiviated with water in order to separate NH_3 and soluble salts. It is then dried, the sulphur extracted with carbon disulphide and the residue mixed with powdered lime. The whole is then heated with steam to 40° to 100° in closed pans so that the ammonia which distils may be utilised, and calcium ferrocyanide is thus obtained in strong aqueous solution. On adding a boiling solution of KCl to this, the almost insoluble double ferrocyanide of calcium and potassium, CaK_2FeCy_6, separates, and on heating this with a solution of K_2CO_3, a solution of potassium ferrocyanide is formed together with insoluble $CaCO_3$.

Potassium ferrocyanide dissolves in 4 parts of cold water or 2 parts of hot water. It is decomposed at a red heat into KCN + FeC_2 (iron carbide). It forms HCN on heating with dilute H_2SO_4. With strong H_2SO_4 it forms CO according to the following equation:

$$K_4FeCy_6 + 6H_2SO_4 + 6H_2O = 3(NH_4)_2SO_4 + 2K_2SO_4 + FeSO_4 + 6CO.$$

If potassium ferrocyanide is added to the solution of a ferric salt, a blue coloration, and then an intensely blue precipitate is formed which is *Prussian blue*, a ferric ferrocyanide:

$$3K_4FeCy_6 + 4FeCl_3 = 12KCl + Fe_4'''(Fe'''Cy_6)_3:$$

this compound is insoluble in acids and is decomposed by alkalis:

$$(FeCy_6)_3Fe_4 + 12KOH = 4Fe(OH)_3 + 3FeCy_6K_4.$$

The formation of Prussian blue is a sensitive reaction for ferric salts.

With copper salts potassium ferrocyanide forms a bright red precipitate of cupric ferrocyanide, insoluble in acids and decomposed by alkalis:

$$K_4FeCy_6 + 2CuSO_4 = 2K_2SO_4 + Cu_2FeCy_6.$$

This reaction is extremely sensitive and serves for the detection of minimal traces of copper salts.

With *ferrous* salts potassium ferrocyanide forms a white precipitate which becomes blue in the air. **Potassium Sulphocyanide, KCNS,** forms a blood-red coloration of ferric sulphocyanide with ferric salts: $3KCNS + FeCl_3 = 3KCl + Fe(CNS)_3$.

Potassium ferrocyanide is not poisonous and is used in the manufacture of explosives, for the preparation of pigments, and in silk dyeing. It costs £52 to £56 per ton. Italy produced 247 tons in 1908 of the value of £2866, and imported 286 tons in 1906 and 293 tons in 1909 of the value of £15,840.

POTASSIUM FERRICYANIDE: K_3FeCy_6 (Red Potassium Prussiate). On passing chlorine into a solution of potassium ferrocyanide this is oxidised and potassium ferricyanide is formed which separates in red rhombic crystals:

$$2K_4FeCy_6 + Cl_2 = 2KCl + 2K_3FeCy_6.$$

On adding a solution of potassium ferricyanide to a solution of a ferrous salt, a bright blue precipitate of ferrous ferricyanide is formed, which is called *Turnbull's blue*. It is a sensitive reaction for ferrous salts, whilst with ferric salts no precipitate is formed:

$$2K_3FeCy_6 + 3FeSO_4 = 3K_2SO_4 + \overset{\cdot\cdot}{Fe_3}\overset{\cdot\cdot\cdot}{Fe_2}Cy_{12}, \text{ that is, } \begin{matrix} FeCy_6{=}Fe \\ \qquad\quad\ \ Fe \\ FeCy_6{=}Fe \end{matrix}$$

This precipitate does not dissolve in acids, but is decomposed by hot alkalis with formation of potassium ferricyanide and ferrous hydroxide which immediately transforms the potassium ferricyanide into potassium ferrocyanide:

(*a*) $$Fe_3Fe_2Cy_{12} + 6KOH = 3Fe(OH)_2 + 2K_3FeCy_6$$

(*b*) $$2K_3FeCy_6 + 3Fe(OH)_2 + 2KOH = 2K_4FeCy_6 + 2Fe(OH)_3 + Fe(OH)_2.$$

Commercial Prussian blue contains large amounts of Turnbull's blue.

Red potassium prussiate is poisonous. It is readily soluble in water, and is also used for the production of pigments, and in dyeing and printing. It costs about £140 per ton.

POTASSIUM PERFERRICYANIDE, $K_2[Fe(CN)_5.H_2O]$ (Black Potassium Prussiate), was prepared pure by Skraup, and its constitution was elucidated by L. Cambi in 1910, by showing its analogies with **Sodium Ferriaquapentacyanide, $Na_2[Fe(CN)_5.H_2O]$,** which was produced by K. A. Hofmann from the nitroprusside. The formation of the perferricyanide by the action of chlorine takes place according to Cambi as follows:

$$[\overset{III}{Fe}(CN)_6]''' + Cl_2 + H_2O = [\overset{III}{Fe}(CN)_5.H_2O]'' + Cl' + CN.Cl.$$

SODIUM NITROPRUSSIDE : $FeCy_5(NO)Na_2.2H_2O$. This is a very sensitive reagent for alkali sulphides and various organic substances because it acquires an intense violet colour ; it is obtained in red crystals from a solution of sodium ferrocyanide with nitric acid.

CALCIUM FERROCYANIDE : $FeCy_6Ca_2$. This compound is obtained in the course of gas manufacture (*see above*) during the preparation of potassium ferrocyanide. It crystallises with $12H_2O$ and already loses $11\frac{1}{2}H_2O$ at 40°. It is used for the preparation of the corresponding potassium salt and of other cyanides (*see above*).

NICKEL : Ni, 58.68

Nickel is sometimes found native in meteorites, but abounds in *Nickeline*, $NiAs_2.NiS_2$, in *Nickel Arsenide*, NiAs, but most abundantly in the form of *Garnierite*, a mixed silicate, $2(Ni.Mg)Si_4O_{13}.2H_2O$, which is found in large quantities in Nova Scotia and in Norway and contains 10 to 20 per cent. of nickel. The nickel is obtained from this silicate by heating it with coke and a basic flux and then puddling in an open-hearth furnace (p. 637) with hot air in order to separate the Fe, Mn, and Si in the form of a slag and obtain free nickel ; magnesium is finally added in order to eliminate all the oxygen, the presence of which is very disadvantageous. In the extraction of nickel from metallic sulphides, the fact is made use of that nickel has more affinity for sulphur than has iron, but less affinity than copper, whilst the affinities of these metals for oxygen are in the reverse order. These ores, which often contain copper and iron, are first roasted and then smelted until a matte is formed containing much nickel. On repeatedly roasting and smelting this then forms crude nickel, the treatment being similar to that of copper (p. 542). The nickel is finally refined in a Bessemer converter (p. 635). A new and important process is that of L. Mond, 1889, which has been used since 1902 in Canada, and by which 400 or 500 tons of ore may be treated daily. The regulus, containing 80 per cent. of nickel, as obtained in the Bessemer converters is then treated in England by the Mond-Lange process, which consists in first reducing the regulus at 300° with water-gas in a tower, and then charging the product into a " volatiliser," into which a current of carbon monoxide at 100° is passed. Nickel tetracarbonyl, $Ni(CO)_4$, is thus formed, which is volatile and passes into the decomposition tower, where at 180° all the nickel is separated of 99·6 per cent. purity. Nickel is also obtained from alloys and from the regulus by electrolytic means, using the alloy itself as an anode in a bath of copper and nickel chlorides and collecting the copper on a copper cathode. The nickel which remains in the concentrated solution is separated from copper, and also from iron, by H_2S. The solution is then electrolysed with an anode of carbon and a cathode of copper on which the nickel collects.

Pure nickel has a silvery appearance, is as ductile as copper, but tougher, and is weakly magnetic. It has a specific gravity of 8·9 and melts at about 1500° to 1600°. It is unalterable in the air and dissolves with difficulty in hydrochloric and sulphuric acids, but easily in nitric acid. It is a constituent of various alloys, as in nickel coinage, which contains 75 per cent. of copper and 25 per cent. of nickel, and *German silver* or *pinchbeck*, which is used in the preparation of electrical resistances on account of its low conductivity and contains 50 per cent. Cu, 25 per cent. Ni, and 25 per cent. Zn (p. 547). It is also much used for nickel-plating [1] (pp. 416 *et seq.*), in the manufacture of many laboratory

[1] **Galvanoplastics and Electro-plating.** In 1805 Brugnatelli already succeeded in gilding silver coinage electrolytically, and in 1836 Elkington in Birmingham attempted to replace the usual method of gilding silver articles in a furnace by the use of baths of gold chloride and potassium dicarbonate, but the gilding obtained in this way was very thin. In 1873 Jakobi at St. Petersburg invented an ingenious process of reproducing medals and artistic objects by producing an exact mould of these by means of wax or plaster and then coating every detail of the surface of these moulds with very fine graphite and thus rendering it electrically conductive. He then suspended the mould from the negative pole (cathode) of an electrolytic bath containing a suitable metallic salt and formed the positive pole of the same metal ; on passing an electric current through this bath the mould became lined with very

utensils, and for other purposes, including the manufacture of nickel-steel armour-plates (p. 639). In a finely divided state it is used as a catalyst, especially in presence of sodium hydroxide.

The world's production of nickel in 1892 was 2968 tons ; it was 9850 tons in 1903 and 14,100 tons in 1907, of which 6500 tons were produced in the United States and Canada and 2600 tons in Germany. In 1909 Germany imported 3745 tons and exported 1625 tons. In 1907 Italy imported 530 tons of nickel and its alloys and 525 tons in 1909 of the value of £72,000. The price was 16*s*. per kilo in 1875, whilst in 1901 it cost less than 3*s*. 4*d*.

NICKEL OXIDES : NiO and Ni_2O_3. These are similar to the oxides of cobalt, although nickel compounds all correspond to **Nickelous Oxide,** in which the nickel is divalent. This oxide is formed on heating the hydroxide or the nitrate and is found in nature in green crystals as *bunsenite* ; **Nickelic Oxide, Ni_2O_3,** is formed by the action of a hypochlorite on a nickel salt, or on gently heating the nitrate or chlorate. It is a black powder which is transformed into NiO on heating.

NICKEL HYDROXIDE, $Ni(OH)_2$, is formed as a green precipitate by the action of KOH on a nickel salt. It dissolves in NH_3 to form a blue solution.

NICKEL CHLORIDE : $NiCl_2$. This is obtained on dissolving nickel in aqua regia. It crystallises from water in green crystals containing $6H_2O$. On heating, these lose water and become yellow. It costs 3*s*. 4*d*. per kilo.

NICKEL SULPHATE : $NiSO_4$. This compound is formed on dissolving nickel or its hydroxide in H_2SO_4. It crystallises at 15° to 20° with $7H_2O$ in bright emerald-green crystals, isomorphous with $MgSO_4$, whilst at higher temperatures it crystallises with $6H_2O$ in bluish-green crystals. At 280° it loses all its water and becomes yellow. It dissolves in 3 parts of water and is often used in nickel-plating. It costs about £48 per ton. Germany produced 220·3 tons in 1905.

NICKEL-AMMONIUM SULPHATE : $NiSO_4.(NH_4)_2SO_4.6H_2O$. If a solution of ammonium sulphate is added to a solution of $NiSO_4$ in water acidified with H_2SO_4, then on concentration green crystals of this double salt separate. It is only slightly soluble in water (2 : 17). This salt is also used for nickel-plating, and costs £40 per ton.

NICKEL SULPHIDE : NiS. This is obtained from soluble salts with alkali sulphides, though not by passing H_2S into acid solutions, because it is soluble in acids ; as obtained from alkali sulphides it does not however dissolve in acids, perhaps because it is polymerised. When freshly precipitated it is soluble in alkali sulphides, but becomes insoluble after a short time.

NICKEL TETRACARBONYL : $Ni(CO)_4$. This compound is now of industrial importance as it is used in the preparation of nickel by the Mond process (*see above*), and is formed on passing CO over powdered nickel. It is a colourless liquid which boils unaltered at 43° and burns with a smoky flame. It is solid at − 25°. Its vapours explode at 60° with separation of Ni and CO.

fine particles of the metal, forming a continuous and compact surface ; the metal forming the anode was gradually dissolved in the bath as fast as it was deposited on the cathode. This method was improved by Spencer of Liverpool and then by Delarive of Paris. In 1840 the latter succeeded in gilding copper and brass articles. Thus galvano-plastic methods were no longer limited to the reproduction of objects, but the art of *electro-plating* was evolved by means of the generalisations introduced and industrially applied by Ruolz in 1842, so that the most varied metals could be covered with layers of any desired thickness of another metal. It was at this period and by utilising this process that the celebrated firm of Christofle was started in Paris and the firm of Elkington Bros. in Birmingham in 1844. These enterprises were quickly followed by numerous others of a similar character in various countries.

In 1843 Böttger had already perfected the process of platinising by employing a bath of ammonium chloro-platinate and ammonia. In 1878 he proposed the use of a bath of ammonium chloroplatinate and sodium citrate, which is still used to-day. The first industrial form of nickel-plating is also due to Böttger who succeeded in 1843 in devising a process by the use of a bath of the double sulphate of ammonium and nickel. This bath was improved by Planzan in 1875 by the addition of citric acid, and still further by Weston in 1879 who obtained perfectly white, homogeneous nickel deposits by replacing the citric acid by boric acid. In 1897 Förster succeeded in preparing thick nickel deposits from hot baths of nickel sulphate.

The electrolytic deposition of iron presented remarkable difficulties and the attempts of Böttger and of Ryhiner did not lead to practical results, whilst, on the other hand, great hopes were awakened by the work of Feuquières in 1867 and still more by that of Lenk in 1869, who used a bath of magnesium sulphate and iron sulphate in presence of basic magnesium carbonate.

Attempts were also made by Ruolz and by Jakobi to obtain metallic alloys electrolytically by the use of baths containing mixtures of various metallic cyanides, but they were without industrial results. The process has only become important and practical since 1895, when Yordis replaced the cyanides by lactates, that is by solutions of the metals in lactic acid.

NICKEL CYANIDE, $Ni(CN)_2$, is formed as a green precipitate when KCN is added to a solution of a nickel salt, but it is easily soluble in an excess of KCN with which it forms **Potassium Nickelocyanide**, K_2NiCy_4, which is unstable and is decomposed by HCl.

COBALT : Co, 58.97

This metal is less abundant and less used than nickel. It is found in nature, especially in *Cobaltine*, $CoAs_2.CoS_2$, and in *Smaltine*, $CoAs_2$. It is extracted in the same way as nickel, and is often found in company with it. In order to separate cobalt from solutions of nickel they are treated with potassium nitrite, by which means the cobalt only is precipitated. The metal is also obtained by reducing the oxide, Co_3O_4, with charcoal or hydrogen.

The pure metal is lustrous, with a reddish reflex. It has a specific gravity of 8·5, does not alter in the air and is less magnetic than iron. It melts at about 1600° and by the addition of very small amounts of Mg it may be obtained in compact and very hard masses. It dissolves slowly in HCl or H_2SO_4, whilst it dissolves immediately in HNO_3, forming cobalt nitrate. It costs £1 8*s*. to £1 12*s*. per kilo.

The more ordinary cobalt compounds contain a divalent cation $Co^{\cdot\cdot}$ and correspond to cobaltous oxide, CoO ; the other derivatives correspond to cobaltic oxide, Co_2O_3. Ionised cobaltous salts are red, whilst when not ionised they are blue. A solution of $CoCl_2$ is red because it is highly ionised, whilst if HCl is added the ionisation is diminished and it becomes blue. Sympathetic inks may thus be prepared, as when used for writing on red paper the characters cannot be seen, whilst they become blue on heating the paper.

The value of the cobalt ores mined in Canada, which have been the subject of much financial speculation, amounted to about £1,520,000 in 1906.

COBALTOUS OXIDE : CoO. This is a brown powder which is formed on heating the hydroxide or carbonate out of contact with the air.

Cobalt Enamels are alkali silicates coloured blue by CoO or in other colours due to mixtures of cobalt oxide with other oxides such as ZnO, &c.

COBALTOUS HYDROXIDE : $Co(OH)_2$. This is obtained as a red precipitate by the action of KOH on cobaltous salts in the absence of air, as in presence of air it is easily oxidised.

COBALTOUS CHLORIDE : $CoCl_2$. When cobalt is dissolved in hydrochloric acid, crystals of $CoCl_2 + 6H_2O$ of a bright red colour separate from the solution. On heating, these lose water and become blue.

COBALT SULPHATE, $CoSO_4$, is analogous to nickel sulphate. It forms dark red monoclinic crystals containing $7H_2O$, isomorphous with $FeSO_4$, and also forms double salts with alkali sulphides, such as $K_2SO_4.CoSO_4.6H_2O$.

COBALT NITRATE, $Co(NO_3)_2$, crystallises with $6H_2O$ in bright red prisms very soluble in water, which are hygroscopic.

COBALT SILICATE has an intense blue colour and is used in the preparation of coloured glass and enamels, whilst when powdered it is used in painting. By heating alumina to a white heat for some time with a cobalt salt, *Thenard's blue* is obtained, which is of various shades of blue according to the proportions of Co and Al which are present.

COBALTIC OXIDE : Co_2O_3. This is a black powder which is formed on calcining cobalt nitrate at a moderate temperature. At higher temperatures it is transformed into **Cobaltous-Cobaltic Oxide**, Co_3O_4, and if the temperature is raised still further CoO remains.

On treating Co_2O_3 with hydrochloric or sulphuric acids the corresponding cobaltic salts are not formed, but the cobaltous compounds are produced with evolution of oxygen, chlorine, &c. **Cobalt Alums** may, however, be obtained by dissolving this oxide in cold dilute sulphuric acid and then adding alkali sulphates.

POTASSIUM COBALTICYANIDE : $[CoCy_6K_3$. This compound crystallises in colourless rhombic prisms which have a constitution corresponding to that of red potassium prussiate.

COBALTIPOTASSIUM NITRITE : $Co(NO_2)_3.3KNO_2.1\frac{1}{2}H_2O$. This is obtained in the form of somewhat insoluble yellow crystals by adding potassium nitrite and acetic

acid to a cobaltous salt. It is used for separating nickel from cobalt, as on increasing the number of potassium ions it becomes almost insoluble.

COMPLEX AMMONIUM SALTS. On adding ammonia to cobaltous salts until the precipitate which is first formed is redissolved a solution is obtained which absorbs oxygen from the air, and if to this an acid corresponding to the cobaltous salt which has been employed is added, a brick-red crystalline powder separates which is known as a salt of *roseocobalt*. Thus, according to the salt employed, roseocobaltic chloride, $CoCl_3(NH_3)_5.H_2O$, or roseocobaltic nitrate, $Co(NO_3)_3(NH_3)_5.H_2O$, is obtained. If these roseocobaltic salts are heated with a little acid they acquire a purple-violet colour forming salts of **Purpureocobalt**‘ such as $CoCl_3(NH_3)_5$ or $Co(NO_3)_3.(NH_3)_5$.

If ammonium chloride and an oxidising agent are added to an ammoniacal solution of cobalt chloride, reddish-yellow crystals of $CoCl_3(NH_3)_6$ separate, which are soluble in cold water ; compounds of this type are called *luteocobalt* salts. By suitably varying the groups with other acid radicals, such as NO_2, &c., **Croceocobalt, Flavocobalt,** and **Xanthocobalt** salts are formed.

Platinum, chromium, and copper also form similar compounds to those just described, but differing according to the valencies of these metals. In compounds containing the **Hexammino** group, $(NH_3)_6$, a portion of the molecules of the NH_3 may be replaced by water molecules or a portion of the ammonia may simply be eliminated ; there are thus five series of salts in which X indicates the acid radical : **Hexamminocobalt** salts or **Luteocobalt** salts, $CoX_3(NH_3)_6$, **Pentamminocobalt** salts or **Purpureocobalt** salts, $CoX_3(NH_3)_5$, **Tetramminocobalt** or **Praseocobalt** salts, $CoX_3(NH_3)_4$, and **Triammino-cobalt** salts, $CoX_3(NH_3)_3$.

These salts do not show the ordinary reactions for cobalt and ammonia and we must, therefore, suppose them to contain complex ions. They are more or less ionised by water ; thus, for example, all the chlorine may be removed from luteocobalt chloride, $CoCl_3(NH_3)_6$, by means of silver nitrate, from which we may infer that the three atoms of chlorine form the anions and that the trivalent cation will be formed by the group $Co(NH_3)_6^{\cdots}$, so that we have a quaternary electrolyte with three anions and one associated cation. When 1 mol. of ammonia is eliminated, 1 atom of chlorine loses its property of being ionised ; therefore the solution conducts the current less well and only 2 atoms of chlorine are separated by silver nitrate, that is, a ternary electrolyte is formed. On eliminating a further molecule of NH_3 the conductivity is still further diminished and only a single atom of chlorine remains ionised, so that we now have a binary electrolyte. If, finally, a third molecule of ammonia is removed we obtain triamminocobalt chloride, $Co(NH_3)_3Cl_3$, which is no longer ionised and therefore no longer conducts the electric current.

By placing the dissociated anion, X, within square brackets, we obtain the four following general formulæ, in which Me represents the fundamental metal, Co, Pt, Fe, &c., around which the other groups are attached, the number of which (*co-ordination number of* Werner) attains a maximum of 6 (Co = 6 ; C = 4 ; N = 4 ; B = 4, &c.), whilst the other groups or ionised atoms are indirectly united to the fundamental metal :

$$[Me(NH_3)_6]X_3 ; \quad [Me(NH_3)_5X]X_2 ; \quad [Me(NH_3)_4X_2]X ; \quad [Me(NH_3)_3X_3].$$

If we now commence to increase the number of negative groups or atoms (Cl, NO_3, Cy, OH, &c.) at the expense of the NH_3 groups, we obtain new negative complexes the valency of which is given by the number of new groups which are introduced ; thus we have, for example, tetramminocobalti-potassium nitrite, $[Co(NH_3)_2(NO_2)_4]'K$, and we might also obtain the compound, $[Co(NH_3)(NO_2)_5]''K_2$, which has not yet been prepared, and finally we might obtain the compound $[Co(NO_2)_6]'''K_3$, which is **Cobalti-potassium Nitrite**, which is well known and which may be compared with potassium ferricyanide, $Fe'''Cy_6K_3$. None of these compounds show the reactions of the NO_2 residue because it is not ionised and is united directly to the fundamental metal Co. When the metal is divalent we obtain compounds of the type $Me''(NH_3)_6X_2$ (where Me indicates the divalent metal) which correspond to the compound $[Me''Cy_6]''''X_4$, if NH_3 is replaced by various other groups such as cyanogen. A well-defined salt corresponding to this group of compounds is potassium ferrocyanide, $Fe''Cy_6K_4$.

Light was thrown on the constitution of these very numerous complex compounds of cobalt, platinum, &c., by the work of Werner and of his pupils, especially Miolati. The

number of these compounds which are now known is about 2000, and until lately it had not been possible to interpret their constitution in any rational manner.

For example, two isomeric compounds, $Pt(NH_3)_4SO_4(OH)_2$, are known, of which, although they have the same atomic composition and the same molecular weight, the one behaves as a strong base and gives no reaction for the SO_4'' ion in aqueous solution (no precipitate with $BaCl_2$), whilst the other behaves as a neutral salt and precipitates $BaSO_4$ with $BaCl_2$. The former is thus a hydroxide of **Sulphotetramminoplatinum** of the following constitution $[SO_4Pt(NH_3)_4](OH)_2$, whilst the latter is a sulphate of dihydroxyltetramminoplatinum, $[(OH)_2Pt(NH_3)_4]SO_4$.

The crystallised hexamminic salts in which several molecules of ammonia are replaced by 1 to 6 molecules of water are also interesting. In some of these the molecular conductivity is only slightly influenced (Jörgensen), for instance, $[Co(NH_3)_4(H_2O)_2]Br_3$, $[Co(NH_3)_5H_2O]Br_3$, and $[Co(NH_3)_6]Br_3$, whilst in others one acid residue ceases to be ionised for each molecule of water which is introduced, and in others again for each molecule of water which is introduced one acid residue is ionised, and is placed outside the square brackets in the following formulæ, which show the 3 hydrates of trichlorotriamminocobalt $[Co(NH_3)_3Cl_3]$:

$[Co(NH_3)_3(H_2O)Cl_2]Cl$;	$[Co(NH_3)_3(H_2O)_2Cl]Cl_2$;	$[Co(NH_3)_3(H_2O)_3]Cl_3$
Dichloroaquotriammino cobalt chloride	Chlorodiaquotetrammino cobalt dichloride	Triaquotriammino cobalt trichloride

In these *aquo salts* we also find cases of *isomerism of hydration* to which various colorations correspond, and their constitution is explained by stereochemical considerations which are developed in the second volume of this work (" Organic Chemistry "). Complex salts of this character are also known which contain several fundamental and stable condensed nuclei which are not broken up either by ionisation or by spontaneous hydrolysis.

(*b* and *c*) PLATINUM GROUP

This is divided into two sub-groups :

Light Metals

	Ruthenium, Ru	Rhodium, Rh	Palladium, Pd
Atomic weight .	101·7	102·9	106·7
Specific gravity .	12·26	12·1	11·9

Heavy Metals

	Osmium, Os	Iridium, Ir	Platinum, Pt
Atomic weight .	190·9	193·1	195
Specific gravity .	22·4	22·38	21·45

The valency of these elements varies considerably ; thus in osmium it varies from 2 to 8 and in palladium from 1 to 4.

These metals are found naturally in the native state only, generally mixed with others, in the island of Sumatra, California, Australia, the Ural Mountains, &c., and frequently together with iron and gold. The complete separation of these metals from one another is difficult because their salts have many properties in common and the impurities of the one and the other further complicate the processes of extraction and separation.

Generally speaking, by the action of aqua regia on a mixture of these minerals, a mixture of the chlorides, $PtCl_4$, $IrCl_4$, $RhCl_2$, and $PdCl_3$, is obtained, which on heating with NaOH forms $IrCl_3$ (from the $IrCl_4$) and sodium hypochlorite (which forms the chloride with alcohol). On then adding ammonium chloride ammonium chloroplatinate, $(NH_4)_2PtCl_6$, separates and yields spongy platinum on heating, whilst the chlorides of palladium and rhodium do not form insoluble double salts like platinum and are separated on further concentration. From the final mother liquors the other metals are precipitated by iron turnings.

RUTHENIUM : Ru, 101.7

This is a brittle metal, very infusible (melting at about 2000°), and only dissolves slowly in aqua regia, being transformed into the chloride, $RuCl_3$, although if the ruthenium is alloyed with a little platinum it is much more easily dissolved. It forms several oxides, RuO, Ru_2O_3, RuO_2, and RuO_4 (peroxide) and several chlorides, $RuCl_2$, $RuCl_3$, and $RuCl_4$.

A compound is also known which has a certain similarity with potassium manganate, namely **Potassium Rutheniate**, $K_2RuO_4.H_2O$, which is formed on melting ruthenium with potassium nitrate and potassium hydroxide. From the bright orange-coloured aqueous solution obtained from this melt black crystals separate. When a current of chlorine is passed through this solution it carries with it the volatile **Tetroxide**, RuO_4, which condenses on cooling in golden-yellow crystals. With dilute acids it forms **Potassium Per-Rutheniate**, $KRuO_4$, which is analogous to $KMnO_4$, and forms intensely green solutions.

RHODIUM : Rh, 102.9

This element was discovered in 1803 by Wollaston who prepared it from the **Chloropurpureorhodium Chloride**, $Rh(NH_3)_5Cl_3$ (*see* p. 655). It has the appearance and ductility of silver and a specific gravity of 12·1. When pure it is not even attacked by aqua regia but becomes soluble in that mixture when alloyed with platinum. When heated in the air it forms the oxide, RhO, and another oxide, Rh_2O_3, is also known, which forms salts with acids. It has the property of absorbing considerable quantities of hydrogen. On heating in a current of chlorine it forms the dark red **Trichloride**, $RhCl_3$, which forms double salts, and its sulphate also forms **Alums** with alkali sulphates. Rhodium is rare and very dear, costing 12*s.* per gramme. It is now used in the construction of extremely sensitive *electrical pyrometers*, which may be used up to a temperature of 1600°. These pyrometers are constructed of two wires, one of platinum about 0·6 mm. thick and 150 cms. long, and the other of platinum alloyed with 10 per cent. of rhodium. The two wires are melted together at one extremity and thus form an element which, when connected at the two other extremities with a galvanometer, gives rise to a feeble current as the temperature is raised (an E.M.F. of 0·001 volt for each 100°). The E.M.F. which is produced is exactly proportional to the temperature and is indicated by the galvanometer with an error not exceeding 5° at 1000°. The galvanometer may also be placed at a long distance from the source of heat by connecting it to the pyrometer by ordinary electric leads, and it is thus possible to control the course of temperature changes in a furnace at any moment even from a distance.

PALLADIUM : Pd, 106.7

This element is found in nature alloyed with gold or in certain ores with selenium. It has a silvery appearance, a specific gravity of 11·8, and a melting-point of 1700°.

It is dissolved by strong concentrated boiling acids. On heating it first forms an oxide which decomposes at still higher temperatures. The most significant and characteristic property of palladium is that of absorbing in the cold, but after to heating to redness, 370 times its own volume of hydrogen gas and 800 volumes at 100° when it is finely divided (palladium sponge). If palladium foil is used as a cathode in the electrolytic decomposition of water it is capable of absorbing 960 volumes of H, which it evolves completely on heating *in vacuo*. Hydrogen so absorbed by palladium has very energetic reducing properties ; it reduces ferric to ferrous salts, and transforms Cl into HCl ; its action appears to be based on a catalytic phenomenon. Palladium forms a chemical compound, Pd_2H, with hydrogen, which has a constant dissociation tension and is capable of dissolving a further amount of hydrogen until an alloy, Pd_3H_2, is formed (*see* " Hydrogen," p. 127).

Palladium costs about 4*s.* per gramme.

In its compounds palladium is sometimes divalent and sometimes tetravalent ; it is divalent in its more stable compounds.

It forms **PALLADIOUS IODIDE**, PdI_2, in the form of insoluble black crystals by the

action of palladious chloride on KI. This reaction is used for the separation of iodine from Cl and Br because these latter form soluble palladium compounds.

PALLADIOUS CHLORIDE, $PdCl_2$, is obtained by evaporating a solution of palladium in aqua regia and forms brownish-red crystals containing $2H_2O$. Its solution is used for the qualitative and quantitative determination of CO.

PALLADIC CHLORIDE, $PdCl_4$, is not known in the free state because it immediately decomposes into $PdCl_2 + Cl_2$. It is, however, known in the form of rather insoluble double salts, such as K_2PdCl_6 and $(NH_4)_2PdCl_6$.

OSMIUM : Os, 190.9

This element has the highest specific gravity of all the metals, namely 22·48, and excepting chromium it has the highest melting-point, about 2500°. When massive it is not dissolved even by aqua regia, whilst when finely divided it dissolves in various mineral acids.

Before 1900 osmium cost 4*s*. per gramme, but it is now used in an electric lamp and the price has risen to 8*s*. per gramme, as it is only found in very small quantities in nature. (*Translator's note.*—Various metals are now known to have a still higher melting-point than osmium.)

OSMIUM OXIDES. Various oxides are known, namely OsO, Os_2O_3, and OsO_2, but the most important is OsO_4, which is formed on heating powdered osmium in the air or in steam, or also by treating osmium with HNO_3, aqua regia, or moist chlorine. It forms a colourless, crystalline mass which sublimes in needles, melts easily and boils at about 100°. The vapours have an irritating smell and are highly poisonous. This oxide is commercially known as *osmic acid*, but its aqueous solution shows neutral reaction and it does not form salts. It is used in microscopy as it easily separates osmium as a black powder when reduced by organic matter. It was employed by Auer for the new incandescent *osmium lamp*. This electric lamp was prepared with filaments obtained by squirting a paste formed of an adhesive substance mixed with osmium oxide through a very fine hole. These filaments were used instead of carbon filaments in an ordinary evacuated electric lamp, and on passing the current the oxide was reduced to metallic osmium which resisted the highest temperatures *in vacuo*. Such lamps show the advantage that for an equal time (1000 hours) and equal consumption of electrical energy, they produce a quantity of light almost double that of the ordinary incandescent lamp, but they can only be used on low-voltage circuits (50 volts or preferably 25 volts), although they are now also adapted to ordinary circuits at 120 volts by means of a distributor which divides the current into three portions at 40 volts each.

The glass bulb of this lamp does not blacken even after prolonged use, and it can therefore be used at maximum efficiency to the end. The temperature of the filament does not exceed 1450°, whilst that of the carbon filament is as much as 1600°. The advantage obtained is therefore due to the more intense light emitted by the osmium filament.

In 1893 the first important experiments on this lamp were conducted, and a great future was prophesied for it. It is, however, possible that an insufficient amount of osmium will be found on the earth's surface to satisfy the demand.

The oxide now costs 5*s*. 7*d*. per gramme.

(*Translator's note.*—The osmium lamp is now obsolete, having been replaced by other metallic-filament lamps.)

POTASSIUM OSMIATE, K_2OsO_4. On melting osmium with potassium hydroxide and potassium nitrate, this compound is obtained in a similar manner to the corresponding ruthenium compound. It crystallises in violet octahedra, containing $2H_2O$.

Several chlorides are known, such as $OsCl_3$ and $OsCl_4$, which are similar to the corresponding ruthenium chlorides.

IRIDIUM : Ir, 193.1

This element melts at a slightly lower temperature than ruthenium. It is separated from admixture with osmium by heating it in the air so that the osmium is volatilised as oxide. In the compact state it is not dissolved even by aqua regia, and its resistance to chemical reagents is also communicated to other metals with which it is alloyed, such as osmium and platinum. It is, therefore, used in the manufacture of crucibles, capsules, and other chemical apparatus, alloyed with 90 per cent. of platinum. In the massive state it is brittle in the cold and has a specific gravity of 22·42. In the spongy state its specific gravity is 15·8.

Two chlorides, $IrCl_3$ and $IrCl_4$, and their double salts, $IrCl_3.3KCl.3H_2O$—which is soluble in water—and $IrCl_4.2KCl$—which is insoluble—are known.

$IrCl_4$ is black and dissolves in water with a bright red colour.

The oxide, Ir_2O_3, forms salts and also an alum.

PLATINUM : Pt, 195

This metal is almost entirely obtained as small granules in sandy deposits in the Ural Mountains. On levigation this sand leaves a crude residue containing 75 to 80 per cent. of platinum and small quantities of other metals of the platinum group. The extraction and separation of the platinum is carried out by the methods already described above, but whilst the sands from the Ural Mountains once contained up to 12 grms. and more of platinum per ton, platinum-bearing sands are now treated which only contain 3 grms.

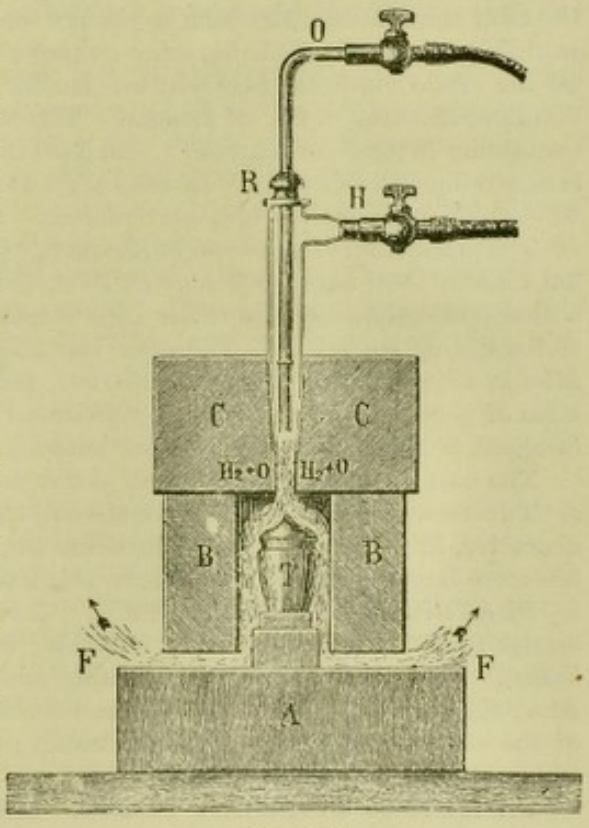


Fig. 280.

The *platinum sponge* which is obtained is converted into massive platinum by melting it in a refractory crucible arranged in a simple furnace which is heated by the oxy-hydrogen flame, as is seen in Fig. 280 (*see also* pp. 175–176). The platinum which is thus melted at a high temperature is cast into bars of 3 to 5 kilos each, which are then hammered or drawn into sheets and thin wires for various commercial purposes ; the wires may be as thin as 0·0001 mm. diameter.

The platinum thus prepared almost always contains iridium which does not, however, depreciate its value. Its separation is not an easy matter, but after melting and slowly cooling, the platinum may be dissolved in aqua regia, leaving part of the unaltered iridium behind in a crystalline form. **Ammonium Platino-chloride**, $(NH_4)_2PtCl_6$, may be precipitated from the solution with NH_4Cl, and on heating to redness leaves *platinum sponge*, whilst from the solution a fine black powder separates through the action of reducing agents, which is called *platinum black*.

Pure platinum has a silvery appearance and is less hard and a poorer conductor of electricity and heat than copper.

It is one of the *noble metals* which are not altered by the air even on heating. In the cold it is very resistant to all chemical reagents, except aqua regia. On heating it is, however, attacked by the alkali hydroxides, by phosphorus, cyanides, sulphides, and the halogens ; with Ag, Au, Sn, Sb, As, Cu, Pb, and Bi it forms easily fusible alloys. In order to avoid accidents in the laboratory, these substances should not, therefore, be heated in platinum apparatus.

At a white heat it softens and may then be welded on to itself by continuous hammering. It is very ductile and malleable and may be drawn into very thin wires and foil. It has a specific gravity of 21·48. At about 1760° it commences to melt and absorbs much oxygen at that temperature which is again liberated in the cold (spitting) as in the case of silver (pp. 409 and 556).

Platinum has been very largely used for the preparation of scientific and industrial apparatus since 1851, as after the studies of Deville in 1852 and Debray in 1857 this metal could be more easily purified, and worked and welded into any desired shape by the aid of the oxy-hydrogen flame.

Finely divided platinum (*platinum black*) absorbs considerable quantities of gases, such as H, O, CO, which are again liberated at a red heat. Sheets of red-hot platinum allow hydrogen but not other gases to diffuse through them.

Colloidal Solutions of Platinum (*see* p. 105) are obtained by passing an electric arc between two platinum electrodes under water. The particles of platinum are so fine that they pass through a filter.

The colloidal solution is black and is an active catalytic agent, even in very minute traces. It loses its catalytic properties, however, through the action of time and of heating and also through that of poisons, such as hydrocyanic acid or corrosive sublimate.

STATISTICS AND PRICES. Platinum is almost entirely produced in Russia, in the Ural Mountains, amounting to about 6 tons per annum, which is 95 per cent. of the total world's production. This industry employs 15,000 to 20,000 workmen, and up to 1890 all the crude platinum obtained in Russia or elsewhere was acquired by the firm of Johnson, Matthey & Co. of London. This firm monopolised the refining of the product, containing 75 to 85 per cent. of Pt, and fixed the price. A considerable quantity of platinum is now refined in Germany. In 1899 a syndicate was formed, with headquarters at Paris, which monopolised the world's production. In 1905 this amounted to 7 tons.

The production of platinum in Russia in 1840 was 1·5 tons and in 1860 0·99 tons. It was 2·9 tons in 1880 and 7·306 tons in 1903, but these official statistics are lower than the actual production, because it has been calculated that about 25 per cent. of the metal is stolen during treatment. The price was £35 per kilo in 1860, £48 in 1880, £40 in 1887, £100 in 1890, £240 in 1906, £200 in 1907, £160 in 1908, and about £140 in 1909. A few kilos of platinum are also annually produced in Canada, the United States and Australia (altogether about 50 to 60 kilos per annum).

The cost of refining platinum is to-day estimated at about £2 per kilo.

Two series of platinum compounds are known, *platinous* compounds of slightly basic character, in which platinum is divalent, and *platinic* compounds of acid character which are more important and in which the platinum is tetravalent.

PLATINOUS CHLORIDE : $PtCl_2$. This compound is obtained on heating platinum sponge to 250° in presence of dry chlorine, or on heating chloroplatinic acid to 200° (*see below*). It forms a greenish-grey powder, insoluble in water and soluble in strong HCl. At a red heat it is converted into platinum and it forms soluble double salts with the chlorides of the alkali metals, such as $PtCl_2.2NaCl$; these may be considered as derivatives of **Chloroplatinous Acid, H_2PtCl_4.**

PLATINOUS CYANIDE : $Pt(CN)_2$. This compound has little importance in itself, but the double cyanides, which have a bright colour and strong and varied dichroism are interesting. **Potassium Platinocyanide, $K_2PtCy_4.4H_2O$,** forms yellow rhombic prisms with a blue reflex. **Barium Platinocyanide, $BaPtCy_4.4H_2O$,** forms yellow monoclinic crystals which when viewed in various directions appear violet-blue or greenish-yellow, and are used for the production of screens which render *Röntgen-rays* visible.

PLATINIC CHLORIDE : $PtCl_4$ (Platinum Tetrachloride). This compound is obtained on heating platinum with aqua regia. On then evaporating in presence of excess of HCl, brownish-red deliquescent crystals of **Chloroplatinic Acid, $H_2PtCl_6 + 6H_2O$,** remain which are ordinarily called **Platinum Chloride.** It is a reagent which is used in chemical analysis as it serves for the quantitative separation of K, NH_4, Cs, and Rb as yellow, crystalline precipitates which are almost insoluble in water and insoluble in alcohol, such as K_2PtCl_6, whilst the corresponding sodium salt is soluble in both water and alcohol. Chloroplatinic acid contains a complexion, $PtCl_6''$, and thus on electrolysing its aqueous solution, $PtCl_6$ separates at the anode. **Platinum Trichloride, $PtCl_3$,** is also known.

On treating a solution of H_2PtCl_6 with KOH and then with acetic acid, **Platinum Hydroxide, $Pt(OH)_4$**, separates. This compound is partly of basic and partly of acid character. Thus it is dissolved both by acids, excepting acetic acid, and by strong bases. These latter form salts corresponding to a hypothetical **Platinic Acid, $H_2Pt(OH)_6$**.

Numerous complex platinum compounds are known analogous to those of cobalt which we have already studied (p. 655), and the platinammonium compounds are of special importance, such as **Platinodiammonium Chloride, $Pt(NH_3)_4Cl_2.H_2O$**, known as *Magnus' Green Salt*, which is obtained from cold solutions of $PtCl_2$ by adding ammonia and then heating until the compound in question separates from the green solution, whilst **Platosemidiammonium Chloride, $Pt(NH_3)_2Cl_2$**, remains in solution.

The corresponding bromides, iodides, and nitrates are also known.

In 1909 L. Wöhler obtained and identified **Platinum Oxide, PtO_3**, with certainty.

PERIODIC SYSTEM OF THE ELEMENTS

If we take a comprehensive view of all the substances which we have studied, and which we have already divided into groups with respect to their valency, we will now be able to find a reason for this classification, and we will further be able to assemble certain regularities which unite the elements into individual groups and the groups with one another.

We have many times observed how certain laws which regulate matter refer rather to the molecules themselves individually than to the nature of the atoms or elements of which they are composed ; such are the physical laws which regulate gases and which lead us among other things to the determination of molecular weights, and many laws which refer to solutions also depend exclusively on the number of ions and not on their nature. On the other hand, many properties of the elements are a function of their atomic weights, and thus we find that the specific gravity of the halogens, the alkali metals and other groups of elements increases with increase of the atomic weight. The colour of these same halogens is a function of the atomic weight and its intensity varies from yellow to violet black with rise of the atomic weight from fluorine to iodine. The affinity of the halogens for hydrogen and for oxygen is also evidently a function of their atomic weight ; we find the maximum affinity for hydrogen in the case of fluorine, whilst its affinity for iodine is least ; on the other hand, the affinity for oxygen increases in the reverse direction.

Such regularities are found to a still greater extent in connection with the basic characters of the hydroxides of the alkali and alkali earth metals and in their affinity for water, basicity, and general chemical activity, which increases in each individual group with increase of the atomic weight, and so on. If we wish to ignore any atomic hypothesis on the nature of matter, these relations between weights and properties do not cease to exist, because that which we now call atomic weight is no other than the *simple weight* of each element, as it is called by Mendelejew, which enters as such or in a multiple quantity to form the molecules of simple or compound substances. That is a relative quantity which is exactly determined apart from any presupposed atomistic hypothesis by means of isodimorphism, specific heat, &c. ; it is also the quantity which we may derive from the combining weights deduced directly from analysis and which led Dalton to his law of multiple proportions. If we now collect all the elements in a given order or system regulated by the atomic weights of these elements themselves, we can include in a single comprehensive view the more important general laws regulating the relations which exist between the more marked physical and chemical properties of these elements and their grouping, and we can also predict the existence of new substances which have not yet been discovered. We can explain the reason for certain exceptions, for certain gaps, which are encountered in this harmonious and graduated grouping of the individual elements and groups, and we may also introduce new laws which permit us to attain a larger and wider horizon which will be gradually conquered through the continuous progress of science.

In 1817 already, and still further in 1829, Döbereiner already divided the elements which presented the closest analogy with one another into *triads*, in each of which the differences of the atomic weights of the elements remained almost constant, such as Cl, Br, and I and Ca, Ba, Sr. In 1862 Chancourtois and more especially Newlands in 1864, grouped all the elements into columns of increasing atomic weight and then divided them into

several groups of 7 each, because after 7 elements the eighth differed greatly in its properties and resembled on the other hand the first of the previous group. The *law of octaves* was thus discovered. It was also found that the properties of each element of the preceding and succeeding groups which occupied the same progressive position, and the elements which occupied, for example, the third position in each group were similar.

In 1859 Mendelejew and Lothar Meyer almost simultaneously discovered a complete system, according to which the various physical and chemical properties of all the elements were reduced to periodic functions of the atomic weight or atomic volume of the elements themselves, thus forming a natural grouping of the simple substances into several families or periods in which the analogy between the physical and chemical properties is periodically reproduced in each group of 7 elements (small period) up to chlorine (atomic weight 35·4), and then the periods are increased up to 17 elements, which may be arranged in two series as is indicated in the Table on the following page, in which the atomic weights are rounded off. We have thus the *large periods* in which a progressive analogy is found in the first series of 7 elements which are then followed by 3 elements (for example, Fe, Co, and Ni), similar to one another but differing from the first series, and separating it from the second series formed of 7 other elements. In the second large series the three intermediate elements are ruthenium, rhodium, and palladium. Then follows a period with many gaps due to still undiscovered elements and then a further large period which is somewhat incomplete, in which the three intermediate elements uniting Series 9 and 10 are represented by osmium, iridium, and platinum.

In the vertical columns the elements are found divided into other groups each of which embraces elements which have the same valency in their hydrogen and halogen compounds or in their oxygen compounds, and thus from Groups I to Group VII, the valency of the atoms with respect to oxygen increases from 1 to 7, whilst with respect to hydrogen it increases from 1 to 4 (from Na, K to C, Si, &c.), and then descends again to 1 in the case of fluorine. In the zero group (O) we find the 5 new gases discovered in the atmosphere which possess zero valency as they do not combine with any other substances. In Group VIII we find 3 triads of elements which, as we have seen, cannot be included in the other groups and which therefore together form a special group, in which we find so many analogies in the properties of the individual elements as fully to justify this division. Thus all have a very high melting-point and also a high specific gravity and consequently low atomic volume. Certain members behave as octavalent elements (OsO_4 and RuO_4) and form cyanides with complex ions.

On arranging the even series below Series 1 in such a manner that the odd series are displaced horizontally to the left, vertical columns result which contain various sub-groups of superposed elements which have more or less marked analogy with one another such as K, Rb, Cs, and then Li, Na, Cu, Ag, Au, which all behave as monovalent elements. Then we have the two sub-groups (Ca, Sr, Ba) and (Be, Mg, Zn, Cd, Hg) and again (Sc, Y, La, Yb) and (B, Al, Ga, In, Tl), &c.

Each series starts with the most electropositive (metallic) element and ends with the most electronegative (non-metallic) element ; thus the vertical Column I includes the most positive metals and the vertical Column VII includes the most negative non-metals (halogens). In respect to their derivatives, we pass gradually in each horizontal series from the most basic compounds (alkali hydroxides) to the most acid compounds.

Various regularities are found on comparing the atomic weights of the elements of each series with the specific gravities and atomic volumes of the elements themselves or of their derivatives, such as the oxides, denoting in each case by " atomic volume " the number of cubic centimetres occupied by a gramme-atom of the element in the solid or liquid state. This is obtained by dividing the atomic weight by the specific gravity. In Series 2 the specific gravity rises up to Al and then descends towards chlorine (liquid) ; on the other hand the atomic volume diminishes from sodium to aluminium and then rises to liquid chlorine.

With the aid of the periodic system of the elements substances may be classified although they themselves or their constituent elements have not been completely studied. Thus, for example, uncertainty formerly existed as to which formula was to be attributed to glucinum oxide—whether GlO or Gl_2O_3—and which atomic weight to assign to glucinum, because the volatile chloride was not then known and its molecular weight could not therefore be determined directly ; on account of the analogies of glucinum with magnesium

Group and Valency	O	I	II	III	IV	V	VI	VII	VIII		
Type of the hydrogen or halogen compounds . (X = halogen or H) (M = element)	—	MX	MX_2	MX_3	MX_4	MX_3	MX_2	MX	—	—	—
Type of the oxygen compounds . .	—	M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_4	MO_2	MO
Period I . . . Series 1	He 4	Li 7	Gl 9	B 11	C 12	N 14	O 16	F 19	—	—	—
II . . . 2	Ne 20	Na 23	Mg 24	Al 27	Si 28	P 31	S 32	Cl 35·4	—	—	—
III . . . 3	A 39·9	K 39·2	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Ni 59	Co 59
4	—	Cu 63	Zn 65	Ga 70	Ge 72	As 75	Se 79	Br 80	—	—	—
IV . . . 5	Kr 82	Rb 85	Sr 87	Y 89	Zr 90	Cb 94	Mo 96	—	Ru 102	Rh 103	Pd 106
6	—	Ag 108	Cd 112	In 114	Sn 118	Sb 120	Te 127·6	I 126·5	—	—	—
V . . . 7	X 128	Cs 133	Ba 137	La 138	Ce 140	(Pr 140) (Nd 144)	—	Sa 150	—	—	—
8	—	—	—	—	—	—	—	—	—	—	—
VI . . . 9	—	—	—	Yb 173	—	Ta 183	W 184	—	Os 191	Ir 193	Pt 195
10	—	Au 197	Hg 200	Tl 204	Pb 207	Bi 208	—	—	—	—	—
11	—	—	—	—	Th 232	—	U 239	—	—	—	—

and aluminium, the selection of its atomic weight was not easy. The analysis of the oxide showed 9·4 parts of glucinum to 16 parts of oxygen, and if the formula GlO were attributed to the oxide, glucinum would have an atomic weight of 9·4, whilst if the oxide were Gl_2O_3, its atomic weight would be 14·1. On the other hand, glucinum oxide has somewhat marked basic properties, and thus approaches boron or to a still greater degree, lithium. With an atomic weight of 14·1 and an oxide, Gl_2O_3, the position of glucinum in the periodic system would be between oxygen and nitrogen, the oxides of which are of acid character, whilst if it had an atomic weight of 8·4 and an oxide, GlO, it would be found between lithium and boron, and in fact, this is the position which may best be assigned to it. This position was later confirmed by the vapour density of glucinum chloride. It has been found possible to classify indium and other elements in the same manner, thus establishing or correcting their atomic weights with certainty.

The most exact experiments of recent years have always fully confirmed all deductions from the periodic system of the elements and although it has been necessary to displace more than a few items of this grouping (*see* Table, p. 663), and although the periodic system may not always be in harmony with all the laws of modern chemistry, its positive basis remains assured and will some day find a rigorous mathematical explanation. In the same way that the discovery of the planet Neptune was prophesied by Leverrier at Paris in 1846 and by Adams in England, by mathematical calculations, thus constituting an astronomical triumph, the discoveries of scandium, gallium, and germanium in recent years were not less surprising and marvellous. In 1869 already, Mendelejew, by studying the gaps which remained unfilled in his classification, had established that in the third series, below boron, and at the side of titanium, there should be found an element which he called *ekaboron*, and which was then actually discovered and called scandium. In the fourth series, corresponding to aluminium and silicon there should have been *eka-aluminium* of atomic weight 69 and *ekasilicon* of atomic weight 73 ; in 1875 Lecoq de Boisbaudran actually discovered gallium of atomic weight 70, corresponding to eka-aluminium, and in 1866, C. Winkler discovered germanium of atomic weight 72·5, which corresponded to the ekasilicon of Mendelejew. The correspondence of the properties of germanium with those of ekasilicon, described in advance by the founder of the periodic system in 1871, was still more surprising. Mendelejew had assigned to ekasilicon a specific gravity of 5·5 and an atomic volume of 13 ; to the corresponding oxide he assigned a specific gravity of 4·7 and to the chloride a specific gravity of 1·7. Fifteen years later C. Winkler found the specific gravity of germanium to be 5·47, its atomic volume to be 13·1, the specific gravity of the oxide to be 4·603 and that of the chloride to be 1·887. As will be seen the prophecy was fulfilled with mathematical accuracy.

The periodic system, by indicating the intimate connection between the atomic weights and other properties of the elements, thus showing that the properties are a function of the atomic weights, became a most important contribution to the hypothesis of the *unity of matter* (p. 119), a hypothesis which represents the most advanced side of that to which the powers of the greatest geniuses are directed. The discoveries made by means of the spectroscope and of radio-active substances (p. 121) have again accentuated and justified these hopes, and perhaps in the near future the hopes of to-day will be realised and be the prelude to a new era of progress and of conquest in theoretical and practical fields.

APPENDIX

ADDITION TO THE SECTION ON THE TREATMENT OF WATER FOR INDUSTRIAL PURPOSES (p. 218). The Bérenger-Stingl process, using lime and soda, which was described on p. 219, although it is the most commonly used and yields fairly good results is still incomplete and in a measure inexact, because the permanent hardness, that is the hardness which does not disappear on boiling followed by filtration of the water, is not due to gypsum alone, but also to nitrates and chlorides of magnesium which are not eliminated by the same quantities and not always even with the identical reagents which are used for eliminating gypsum, although this latter may be the principal factor of the permanent hardness. In fact, whilst gypsum is eliminated as less soluble calcium carbonate by means of sodium carbonate, magnesium chloride and sulphate cannot be separated in the form of carbonate because this latter is still somewhat soluble, but are better separated in the form of magnesium hydroxide, $Mg(OH)_2$, which is less soluble. Again, whilst magnesium chloride is eliminated in the form of hydroxide by means of sodium hydroxide [$MgCl + 2NaOH = 2NaCl + Mg(OH)_2$], or calcium hydroxide [$MgCl_2 + Ca(OH)_2 = CaCl_2 + Mg(OH)_2$], magnesium sulphate is better eliminated by means of barium hydroxide, with which it forms two insoluble salts [$MgSO_4 + Ba(OH)_2 = BaSO_4 + Mg(OH)_2$].

Thus, when basing treatment of the permanent hardness of water on the number of degrees resulting from the volumetric test with soap solution, no account is taken of the above-mentioned facts, and the treatment is thus incomplete. Another small cause of error in the ordinary treatment of water consists in not allowing for the free carbon dioxide which is always in solution, which may however be determined analytically, but which escapes in the determination of hardness by means of a titrated soap solution, which in practice actually absorbs a very small quantity of calcium hydroxide, which separates in the form of insoluble calcium carbonate, $CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$.

For all these reasons the method of calculating the quantity of reagents to be added to the water, based on the temporary and permanent hardness, sometimes gives incorrect results which may be rather costly.

On the other hand, the methods proposed by Wehrenfenning, Blacher, and Hundeshagen of establishing the *equivalent hardness* of individual salts in the water in respect to individual reagents which are used in its treatment, are more rational and fully justified.

When these equivalents of hardness are once established, it becomes possible to establish general formula which permit the quantities of various reagents which may be necessary to produce the best and most rational treatment of the water to be calculated in any particular case.

An analysis of water which is to be purified should indicate the following kinds of hardness which may be represented by symbols in the necessary calculations ; hardness in French degrees corresponding to all the calcium salts expressed as $CaCO_3$ (symbol C_{ca}) ; ditto, for the magnesium salts expressed as $CaCO_3 (= D_{mg})$; ditto for dicarbonates $(= D_{di})$; ditto for free carbon dioxide expressed as $CaCO_3$ (D_{CO_2}) ; ditto for sulphates expressed as $CaCO_3$ $(= D_{SO_3})$. In order then to calculate the quantities of the various reagents which are necessary to soften the water, the following equivalents are used, that is, the following quantities of reagents corresponding to 1° of hardness per cubic metre of the water : *calcium hydroxide*, 7·4 grms. (that is 5·700 litres of clear, saturated lime-water) ; *sodium carbonate*, 10·6 grms. ; *barium chloride*, 20·6 grms. ; *barium carbonate*, 19·6 grms. ; *barium hydroxide*, 17 grms.

Various *general formulæ* were then proposed (by Kalmann in 1890, Pfeifer in 1895 and 1902, and Thiele and Flade in 1906, &c.) for directly calculating the quantities of reagents to be added to water on the basis of analysis ; but one of the most complete and rational formulæ is that proposed by Hundeshagen in 1907, which we will illustrate by various

examples. We will suppose a water to have the following degrees of hardness: D_{ca} 17°, D_{mg} 9·5°, D_{di} 18°, D_{co_2} 2·6°, D_{so_3} 7·7°; if this is treated by the lime-soda process, the following two formulæ are used:

I. 7·4 ($D_{mg} + D_{di} + D_{co_2}$), that is 7·4 (9·5 + 18 + 2·6) = 223 grms. of $Ca(OH)_2$ or 172 litres of clear lime-water.

II. 10·6 ($D_{ca} + D_{mg} - D_{di}$), that is 10·6 (17 + 9·5 − 18) = 90 grms. of sodium carbonate.

One cubic metre of this water will therefore require for treatment 90 grms. of soda and 172 litres of lime water.

If we wish to treat the water by the barium chloride and lime process, the Formula I. remains the same and Formula II. becomes 20·6 D_{so_3}, that is 20·6 × 7·7 = 158·6 grms. of barium chloride.

If we wish to treat it by the barium carbonate and lime process (*see below*) Formula I. remains unaltered, that is 172 litres of lime water are used, and Formula II. becomes 19·6 Dso_3, that is 19·6 × 7·7 = 151 grms. of barium carbonate.

In the first case the reagents for the purification of 1 cu. metre of water cost about 0·15*d.*, whilst in the second case they cost about 0·3*d.*, and in the third case about 0·2*d.* It will be noted that it is necessary to use chemically precipitated barium carbonate and not the powdered natural product (witherite).

The purification of water by the lime and soda process, even if applied with the help of rational conceptions on equivalents of hardness, still presents a weak side if sulphates are to be eliminated which produce permanent hardness and the corresponding boiler incrustations. Thus, if sodium carbonate is adopted in eliminating calcium sulphate, we have: $CaSO_4 + Co_3Na_2 = CaCO_3 + SO_4Na_2$, and calcium carbonate is separated (not entirely, because the reaction is reversible), but in place of the gypsum an equally large quantity of sodium sulphate remains in solution which does not form incrustations because it is very soluble, but gradually remains in the water as it evaporates and accumulates in the boiler, forming solutions which continuously become more concentrated and lead to greater consumption of fuel and to corrosion of the metallic joints, and thus render it necessary for all the water contained in the boiler to be occasionally emptied.

The ideal process of purification would be one which eliminated all the salts which produce incrustations from the water without any other salts remaining in solution.

The processes of purification by means of barium salts arose through such considerations; barium chloride proposed by F. Kuhlmann in 1841 was an improvement, as it *completely* separates the sulphates, because the reaction is one which is only reversible to a minimal extent, but it leaves soluble calcium chloride in solution, $CaSO_4 + BaCl_2 = BaSO_4 + CaCl_2$. The *barium hydroxide* process which was already proposed by Parker in 1825 would have been more rational, but was only applied later. This allows the permanent and temporary hardness to be completely eliminated without introducing other soluble salts into the purified water:

$$CaSO_4 + (CO_3H)_2Ca + Ba(OH)_2 = BaSO_4 + 2CaCO_3 + 2H_2O.$$

This truly ideal reaction (independently of the fact that this baryta purification process is slightly dearer than the lime and soda process) presupposed, in common with the barium chloride process, that the water contained the same amounts of permanent and temporary hardness, but this is obviously infrequent in practical cases, and in cases in which there is more permanent hardness a solution of calcium hydroxide still remains,

$$CaSO_4 + Ba(OH)_2 = BaSO_4 + Ca(OH)_2.$$

Of recent years a proposal has therefore been reconsidered which was already made by E. Würtz in 1859 to use a single reagent, *barium carbonate*, which in spite of repeated practical attempts up to that time had led to continuous failures.

Barium carbonate is almost insoluble in water (0·007 per cent.) and when finely divided and employed in considerable excess it almost completely separates all the calcium and magnesium salts which produce temporary and permanent hardness, especially if used together with a little calcium hydroxide in cases in which the water contains much dicarbonates, thus:

$$CaSO_4 + Ca(CO_3H)_2 + BaCO_3 + Ca(OH)_2 = 2H_2O + 3CaCO_3 + BaSO_4.$$

Thus on adding an excess of barium carbonate to the water, that which does not react remains undissolved and its reactive power gradually increases, whilst it unites with the deposit of precipitated salts.

In 1902 and succeeding years the firm of H. Reisert of Cologne patented various forms of automatic apparatus with special arrangements for periodically removing the excess of finely divided barium carbonate introduced into the apparatus in sufficient quantities to last for two or three months.

Barium carbonate treatment costs less than treatment with soda, because the molecular weight of the latter is higher and more is therefore consumed, and permits purified water to be obtained containing not more than 4° of hardness, even from very hard water. Calcium chloride, which however is rarely found in water and does not form incrustations, is not precipitated by barium carbonate.

The Gans process, which not only serves to soften water but also to free it from manganese and iron, has recently attracted great interest. In 1907 Gans showed that on passing water through a layer of powdered *artificial sodium zeolith*, that is of a silico-aluminate of sodium, prepared by melting together quartz sand, kaolin, and soda, all the lime and magnesia in the water are absorbed by the zeolith in the form of insoluble salts, whilst soda is given up to the water. Thus the water loses all its temporary and permanent hardness.

Various artificial zeoliths are placed on the market by the firm of J. D. Riedel, of Berlin, under the name of *permutite*. The natural zeolith only gives a minimal purifying effect. When the artificial zeolith has been exhausted by use, that is when all its alkali has beer replaced by lime, magnesia, iron, &c., it is reactivated by passing a solution of sodium chloride through it. It then reabsorbs sodium, whilst calcium, iron, &c., are liberated as chlorides.

THE ELIMINATION OF IRON FROM FERRUGINOUS WATERS (*see* p. 221). All waters contain iron in combination, but they are not all ferruginous. Those only may be considered to be ferruginous which separate the iron in the form of ferric hydroxide when they are brought into contact with air for some minutes or hours or when they are heated. Such waters contain more than 0·35 mgrms. of iron oxide per litre.

It was first believed that all that was necessary in order to immediately separate the iron from such water was to aerate it strongly and then clarify it (Salbach 1868, Auklam 1880, Wingen 1882); thus in 1890 Oesten proposed to allow water to fall from a height in the form of a shower in very fine spray, and in many cases obtained splendid results. In other cases, however, this treatment was incomplete, however much the water was aerated, and it always remained yellowish and opalescent. The iron was not always present in the same form of chemical combination and it therefore became necessary to study the various forms in which the iron was present in water more closely.

If the water runs over the surface of soils rich in iron-containing minerals, these are not actually dissolved or only in negligible quantities; even if it already contains iron salts dissolved, they are readily separated under such conditions. On the other hand, if this water passes through surface layers of the soil which contain much carbon dioxide, partly provided by the air and partly by organic matter decomposing in the soil, the water on penetrating into deeper strata, out of contact with the air, and meeting with deposits of minerals containing iron, will dissolve relatively large amounts of iron with ease up to 100 mgrms. of iron per litre in the form of iron dicarbonate, and if there is also decomposing organic matter in these deep strata, such as peat, &c., more complex iron compounds will be formed containing organic acids (humic acids) and accompanied by hydrogen sulphide and ammonia from the decomposition of the albumenoids contained in such organic matter. In these deposits there is sometimes very considerable microbic activity and production of carbon dioxide, and under these conditions *siderophilic algæ*, such as *Crenothrix*, *Chlamydothrix*, and *Gallionella*, &c., often develop abundantly even in the iron mains and contribute notably by their anaerobic vitality to the attack on iron minerals and iron, then giving up the iron which they assimilate to the water in the form of soluble salts.

Thus during the action of air on such ferruginous water as contains iron in the state of organic combination, the oxygen of the air must oxidise the organic matter before it can cause the separation of the iron, and it is thus comprehensible how the separation of the iron does not always immediately take place through simple aeration.

In 1891 Pifke proposed to pass the aerated water over layers of coke or flint, thus causing the rapid separation and precipitation of the iron, which was transformed by the action of the air into ferric hydroxide in a state of colloidal suspension.

In 1898 Dunbar and Kryck made the interesting observation that the action of the coke or pebbles increased with the increase of the layer of hydrated ferric oxide, which is deposited on them. This iron oxide acts in fact as a kind of catalyst, absorbing oxygen from the air and simultaneously giving it up to the oxidisable matter in the water holding iron in various compounds.

Kröhnke actually obtained a greater activity of the coke from the commencement of the purification by previously depositing ferric hydroxide on it by means of a preliminary soaking of the coke in ferric chloride and calcium hydroxide. The iron hydroxide thus sub-divided enormously increased the surface of contact with the colloidal hydroxide suspended in the water and caused its separation by a true catalytic action.

About 10 grms. of ferric chloride, followed by 50 to 100 grms. of calcium oxide, previously slaked in water, may also be first added directly to each cubic metre of the water, but during deposition the alkaline precipitate, $Fe(OH)_3$, which is formed, not only causes the separation of the dissolved iron salts, but also a portion of the calcium carbonate, and carries down organic matter, colouring-matters, &c., so that after filtration through sand a clear and colourless water results.

In 1900 Schindowsky showed that all the iron may be separated from water under any conditions by adding a sufficient excess of air, and then in 1904–1908 Bock, Deniss, and Jacobi, Halvor Breda and Darapsky devised very simple and convenient *closed sand-filters*, sometimes consisting of a simple iron tube inserted in the pipes which lead to the tank, into which the water to be purified is injected under pressure, together with an excess of air, sometimes up to 40 per cent. of the volume of the water ; the velocity of the water is then suitably regulated in accordance with the surface of the filtering mass and the quantity of injected air. In this way not only is the iron separated, but also the siderophilic algæ (*see above*), which would otherwise flourish and multiply in the tanks and mains, thus causing obstruction.

Mertens (1904 and 1907) aerates the water by centrifugation.

MANGANIFEROUS WATERS are frequently found. Some years ago the water from the aqueduct at Breslau suddenly became very manganiferous through the presence of $MnSO_4$; this water became brown in the air and formed brown deposits. Manganese and iron may be separated from ferruginous waters either by aeration or more advantageously by means of *permutite* (*see above*) by passing it through filters containing a layer of 60 to 80 cms. of *artificial zeolith*, containing dispersed manganese and formed by Gans' process by first melting a calcium silico-aluminate with $MnCl_2$, the manganese radical of which is then transformed into Mn_2O_7 by treatment with sodium or calcium permanganate ; then the MnO of the manganous compounds in the water is oxidised by the Mn_2O_7 and separates in the form of insoluble MnO_2 which is retained by the filter. When the Mn_2O_7 has given off all its active oxygen the filter is exhausted, but may be reactivated by regenerating the Mn_2O_7 by solutions of sodium or calcium permanganate. This purification costs from 0·3*d.* to 0·5*d.* per cubic metre of water. The separation of the iron is affected by the same zeolith which separates the manganese.

APPENDIX TO ENGLISH EDITION

ERRATA

P. 106, line 37. *Insert*: Colloids also have the property of *adsorbing* liquids, such as water or salt solutions, in quantities not directly proportional to the concentration of the dissolved substance, and of persistently retaining the adsorbed substance, without combining with it chemically; thus both the adsorbing and the adsorbed substances retain their fundamental properties. Under certain circumstances the process is reversible. The soil retains large quantities of fertilising salts by means of the adsorptive capacity of its colloidal components and weighted silk similarly retains large quantities of inorganic matter.

P. 122, line 32. *Insert*: The emanation from radium is called **Niton**, and its atomic weight has been found to be 222·4.

P. 140, line 10, *for* " 57 " *read* " 5·7."

P. 140, line 18 from foot, *for* ($Cl.8H_2O$) *read* ($Cl_2.8H_2O$).

P. 167, line 15, *for* Balard in 1900 *read* Balard in 1830.

P. 319, line 7 from foot, *for* 140° *read* 625°.

P. 340, line 18 from foot. *Insert*: In recent years the Uebel process for the continuous production of nitric acid has proved very successful. This is based on the preparation of monosodium disulphate by heating the ordinary disulphate to 260° and over with sulphuric acid of 60° Bé.; water is evolved and monosodium disulphate remains. This reacts with sodium nitrate at 200° to form sodium disulphate and very strong (95 per cent.) nitric acid:

(1) $NaHSO_4 + H_2SO_4 + xH_2O = NaH_3(SO_4)_2 + xH_2O$.
(2) $NaH_3(SO_4)_2 + NaNO_2 = HNO_3 + 2NaHSO_4$

In practice the fused monosodium disulphate, together with the corresponding quantity of nitric acid, is alternately passed into one or other of two parallel, horizontal cylindrical retorts which are maintained at 200°. The pure concentrated nitric acid which is formed at this temperature is collected separately and the fused disulphate is alternately discharged into a single cylindrical pan below, the temperature of which is maintained at 280°–300°; the remaining nitric acid is here evolved in a more dilute form and is collected; a certain quantity of the remaining disulphate is rejected and the rest passes into an underlying pan in which it is treated with sulphuric acid of 60° Bé. at 300°; it then loses water and the fused mass of monosodium disulphate which is produced is conveyed to the upper cylindrical retort in which the reaction with sodium nitrate again takes place.

P. 446, line 12 from foot, for 60 cu. metres *read* 6000 cu. metres.

P. 514, line 15 from foot, *for* " In some works the superphosphate is already discharged after twenty-four to thirty-six hours . . . " *read* " The chambers are now usually discharged after six to ten hours . . ."

ADDITIONAL STATISTICS

The production of BROMINE in the United States was 500 tons in 1909 and less than 400 tons in 1910.

The United States imported 585,000 lbs. of CRUDE IODINE in 1910, of the value of £226,400, and 423,000 lbs. in 1911 of the value of £168,400.

The United States consumed 269,000 short tons of HYDROCHLORIC ACID in 1900 and 377,000 short tons in 1905.

Germany produced 450,000 tons of 30 per cent. HYDROCHLORIC ACID in 1910.

The United States imported the following quantities of SULPHUR : 28,647 tons in 1910 and 24,250 tons in 1911 of the value of £87,400, and exported 30,742 tons in 1910 and 28,103 tons in 1911 of the value of £109,000. England imported 21,000 tons of sulphur in 1911, of the value of £107,136.

In 1910 the United States produced 1,200,000 tons of SULPHURIC ACID, calculated at 100 per cent.; England produced 1,000,000 tons.

The United States produced 1617 short tons of ANTIMONY in 1909 and 1598 short tons in 1910 ; England imported 7326 tons in 1909 and 9905 tons of the value of £175,205 in 1910.

The United States produced 65,000 tons of NITRIC ACID in 1910 ; Germany produced about 110,000 tons in the same year.

The United States produced 1250 tons of WHITE ARSENIC (arsenious oxide) in 1910, and 3000 tons in 1911. They imported 4000 tons of the value of £50,400 in 1910, and 2500 tons of the value of £32,000 in 1911.

In 1911 the Acheson Graphite Co. produced 6000 tons of ARTIFICIAL GRAPHITE, of which England imported 16,645 tons in 1909, and 16,386 tons, of the value of £222,249 in 1910. The United States imported 22,600 tons of GRAPHITE in 1910, and 18,500 tons, of the value of £299,200, in 1911.

England imported 20,300 tons of BORACITE and CALCIUM BORATE in 1911, of the value of £176,556.

The United States consumed STASSFURT POTASH SALTS of the value of £840,000 in 1900, £2,440,000 in 1910, and £3,040,000 in 1911.

The United States imported 190,000 tons of POTASSIUM CHLORIDE in 1910, and 250,000 tons, of the value of £1,530,400, in 1911.

The production of POTASSIUM NITRATE in India is now only 21,000 tons, of which England imported 11,200 tons, of the value of £218,304, in 1911. The United States imported 5000 tons of CRUDE POTASSIUM NITRATE in 1910, and 3600 tons, of the value of £53,000, in 1911.

The United States imported 41,000 tons of POTASSIUM SULPHATE io 1910, and 58,000 tons, of the value of £445,600, in 1911.

England exported 7300 tons of POTASSIUM CYANIDE in 1909, and 7800 tons, of the value of £633,329, in 1910.

Russia produced 2,484,700 tons of SODIUM CHLORIDE in 1909. England produced 1,818,500 tons in 1909 ; 2,050,630 tons of the value of £581,504, in 1910, and exported 515,443 tons in 1909 ; 562,810 tons in 1910, and 604,630 tons, of the value of £487,280, in 1911. The United States imported 143,000 tons in 1910, and 138,000 tons, of the value of £75,600, in 1911, the United States production being about 4,000,000 tons, of the value of £1,580,068, in 1910.

England imported 90,207 tons of SODIUM NITRATE in 1909, 126,500 tons in 1910, and 128,500 tons in 1911. The United States imported 529,000 tons in 1910, and 545,000 tons, of the value of £3,362,800, in 1911.

England exported 35,000 tons of SODIUM SULPHATE in 1909, 58,000 tons in 1910, and 58,400 tons in 1911, of the value of £108,635.

England exported 101,000 tons of SODIUM CARBONATE in 1909 and 140,000 tons in 1910.

England exported 229,500 tons of Sodium Dicarbonate in 1910, and 260,000 tons, of the value of £130,909, in 1911.

England exported 7700 tons of Ammonium Chloride, of the value of £186,956, in 1911.

The United States produced 116,000 short tons of Ammonium Sulphate in 1910, about 127,000 short tons in 1911, and imported 92,300 short tons in 1910 and 94,600 short tons, of the value of £1,013,200, in 1911. England exported 283,610 tons in 1910, and 291,883 tons in 1911, of the value of £3,830,096.

England exported 3300 tons of Ammonium Carbonate in 1909, and 3750 tons, of the value of £115,393, in 1910.

England produced 11,811,122 tons of Limestone in 1909 and 12,512,736 tons, of the value of £1,296,169, in 1910. The United States produced 3,500,000 tons of Quicklime, of the value of £2,800,000.

The United States produced 46,670 tons of Calcium Fluoride in 1908 and 45,800 tons in 1909. England produced 42,483 tons in 1909, and 61,621 tons, valued at £20,678, in 1910.

In Norway 12,600 tons of Calcium Nitrate were produced from the atmosphere in 1909 and 13,531 tons in 1910.

England produced 239,000 tons of Gypsum in 1909, and 255,560 tons, of the value of £98,242 in 1910. The United States produced 2,050,000 short tons in 1910 and 2,150,000 short tons, of the value of £1,200,000, in 1911.

England imported 11,800 tons of Calcium Carbide in 1909, and 13,000 tons, of the value of £133,282, in 1910. The United States exported 12,000 tons in 1910, and 13,500 tons, of the value of £165,600, in 1911.

England imported 34,417 tons of Guano in 1908, 20,321 tons in 1909, 20,395 tons in 1910, and 34,124 tons, of the value of £193,000, in 1911.

England imported 39,031 tons of Bones, calcined and uncalcined, in 1909, 44,505 tons in 1910, and 45.876 tons, of the value of £226,174, in 1911.

England imported 451,807 tons of Phosphorite in 1909, 455,593 tons in 1910, and 493,413 tons, of the value of £779,706, in 1911. The United States exported 1,083,000 tons in 1910, and 1,246,500 tons, of the value of £1,847,000 in 1911.

Australia consumed 12,000 tons of various Fertilisers twelve years ago ; it now produces 100,000 tons, and imports a further 160,000 tons. England produced about 1,000,000 tons in 1910 and exported 141,422 tons in 1909, 152,512 tons in 1910, and 159,353 tons, of the value of £393,602, in 1911. The United States consumed 2,000,000 tons of Superphosphates in 1910. France produced 1,600,000 tons in 1909, of which 227,840 tons were exported. Japan produced 350,000 tons of Superphosphate in 1910.

England exported 218,813 tons of Basic Slag in 1909, 231,277 tons in 1910, and 195,950 tons, of the value of £195,500, in 1911.

The United States produced 80,000 tons of Barium Sulphate in 1906, 150,000 tons in 1907, and 54,000 tons in 1908.

The United States produced 67,945 short tons of Baryta in 1909, and 42,975 short tons in 1910. England imported 40,000 tons in 1909, 40,800 tons in 1910, and 46,500 tons in 1911, in which year it exported 8420 tons.

The United States produced 277,065 short tons of Zinc in 1910, and 292,700 short tons in 1911. England imported 102,576 tons in 1909, 121,117 tons in 1910, of the value of £2,781,220, and 115,228 tons in 1911.

England imported 1500 tons of Mercury in 1909, and 1550 tons, of the value of £401,000, in 1910.

England imported 156,920 tons of Copper in 1910, and 166,131 tons in 1911. It exported 83,740 tons in 1910 and 75,353 tons in 1911. The United States produced 450,000 tons in 1910, and 460,000 tons in 1911.

The United States produced 12,000 tons of Copper Sulphate in 1910, and 15,000 tons in 1911, and exported 3500 tons in 1911, of the value of £63,800. England exported 42,706 tons in 1910 and 79,831 tons, of the value of £1,509,000, in 1911.

The United States produced 7700 tons of Alum in 1908, 8500 tons in 1909, and 8250 tons in 1910, of the value of £60,000.

The United States produced 90,000 tons of Aluminium Sulphate in 1908, 105,000 tons in 1909, and 115,000 tons, of the value of £500,000, in 1910. England exported 11,125 tons in 1909 and 13,000 tons, of the value of £56,525, in 1910.

Denmark produced 115,000 barrels of Cement in 1889, 1,560,000 barrels in 1908, of which 380,000 were exported, and 2,600,000 barrels in 1910. England exported 598,253 barrels in 1909, and 753,817 barrels, of the value of £1,062,345, in 1910. The United States produced 77,785,000 barrels in 1910 and imported 58,462 barrels in 1910, and 32,760 barrels in 1911; they exported 2,476,000 barrels in 1910 and 3,135,000 barrels in 1911, of the value of £926,400.

England imported 41,752 tons of Tin in 1909, 46,285 tons in 1910, of the value of £7,159,782, and 45,906 tons in 1911, and evaporated 11,194 tons (unworked) in 1909, and 12,377 tons in 1910.

The United States produced 393,704 short tons of Lead in 1910 and 402,281 short tons in 1911. England imported 207,660 tons in 1909, 218,936 tons in 1910, of the value of £2,834,000, and 213,704 tons in 1911; it exported 46,906 tons in 1909 and 45,576 tons in 1911.

England imported 15,850 tons of White Lead in 1909, 14,435 tons in 1910, and 16,750 tons, of the value of £283,747, in 1911; it exported to the value of £367,647 in 1909, £401,900 in 1910, and £422,636 in 1911.

England exported 4725 tons of Sodium and Potassium Dichromates in 1909, 5250 tons in 1910, and 4300 tons, of the value of £119,751, in 1911.

The world's production of Ferrosilicon in 1910 was 30,000 tons, of which one half was consumed in the United States.

The United States produced 350,000 tons of Ferromanganese in 1910, and imported 140,000 tons.

Germany produced 25,000,000 tons of Iron Ore in 1909, of the value of £4,800,000. The United States produced 53,000,000 tons in 1909, 54,200,000 tons in 1910, and 41,816,470 tons in 1911. England produced 14,800,000 tons in 1909, and 15,226,000 tons in 1910, of the value of £4,022,269.

In 1910 England produced 10,547,000 tons of Cast Iron, the United States 27,737,000 tons, Germany 14,794,000 tons, France 4,001,000 tons; Russia, 3,040,000 tons; Austria-Hungary, 1,991,000 tons, and Belgium 1,804,000 tons.

In 1910 England produced 3500 tons of Nickel, and Germany 4500 tons. The United States produced 11,000 tons in 1909 and 12,000 tons in 1910. The world's production was 17,310 tons in 1909 and 20,100 tons, of the value of £3,300,000, in 1910.

Russia produced 1742 kilos. of Platinum in 1908 and 5442 kilos. in 1910. The United States imported platinum to the value of £664,200 in 1910 and £964,600 in 1911. England imported to the value of £96,926 in 1909 and 175,516 in 1910.

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