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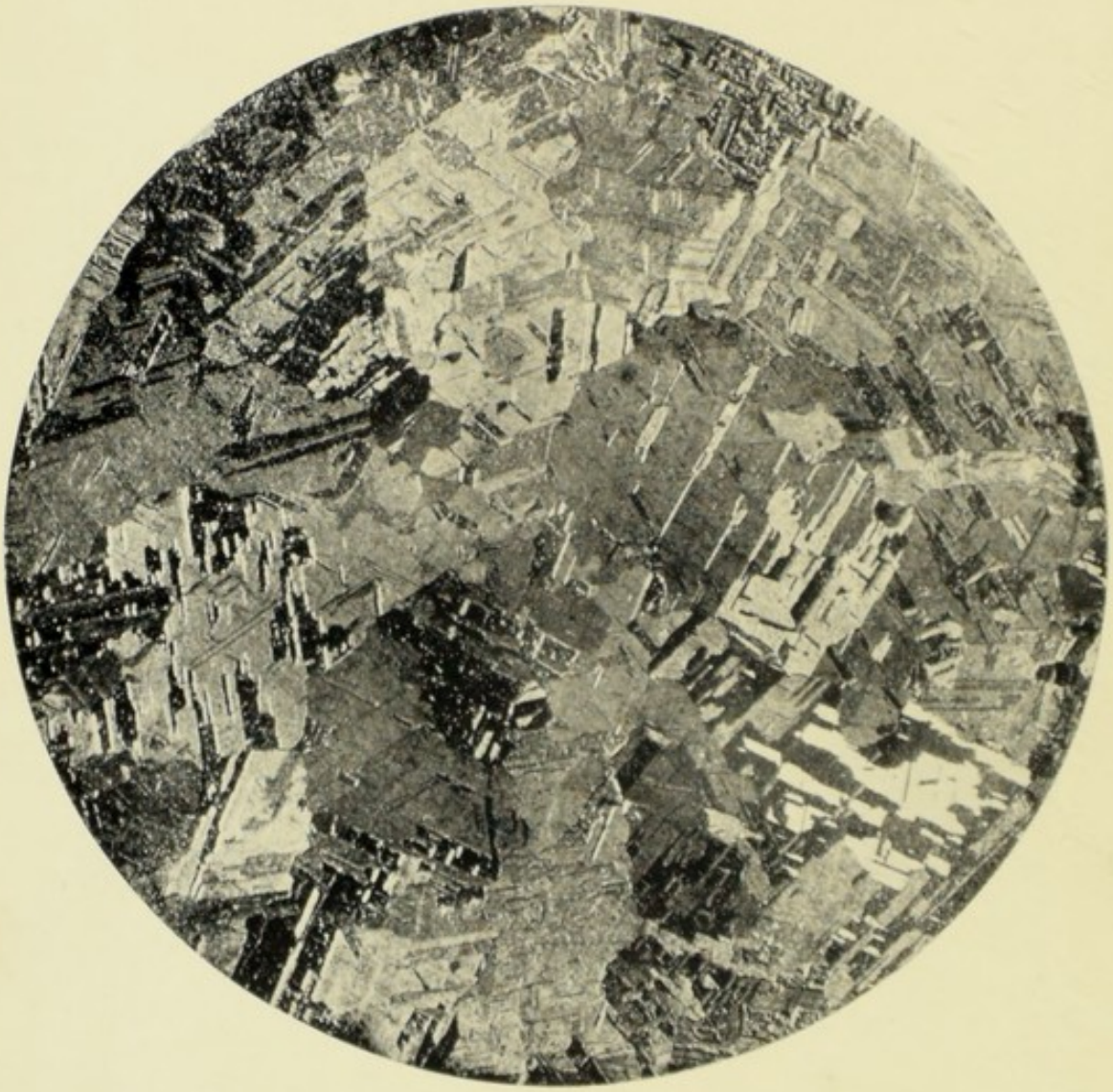

PLATE I.

Pure Copper ($\times 7{\cdot}5$).

SERVICE CHEMISTRY:

BEING

A SHORT MANUAL OF CHEMISTRY

AND ITS APPLICATIONS IN THE NAVAL AND MILITARY SERVICES

BY

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PREFACE TO FIRST AND SECOND EDITIONS.

IN the absence of any text-book dealing with the Chemical treatment of subjects of such paramount importance to the Services as Explosives, Fuel, Drinking Waters, Boiler Incrustation, Corrosion and Fouling of Ships, Spontaneous Ignition of Coal Cargoes, Paints, Ventilation, etc., it became necessary to prepare one for the Officers passing through the Royal Naval College; and in doing so, I have endeavoured to develop in a rational way the main facts of the Science, and the theories which are deduced from them, and have then amplified those portions which touch on Service questions as fully as possible; whilst those parts of the subject which are likely to be of less immediate importance to the readers for whom the book is intended, are condensed as far as is advisable.

Whilst using the title "Service Chemistry," I wish it to be clearly understood that there is but one Chemistry, and that its technical adaptation to any special subject is merely an amplification of the Science in a particular direction, which cannot be properly done without at the same time mastering the general principles of which the technical appli-

cation merely forms a small branch, and that a knowledge of the chief principles and theories of Chemistry is absolutely essential before any useful application of the Science is possible.

The limited time at the disposal of the Officers of both branches of the Service, over and above that required for purely professional work, renders it impossible for them to undertake any such extended course of general study as would justify the subsequent employment of technicalities without full explanation; and I have, therefore, as far as the limits of the book will allow, gone fully into details of manufacture and other subjects generally considered beyond the scope of a chemical manual, as, for instance, in the chapters on Explosives, where the manufacture, proving and keeping of these bodies are treated as fully as the chemistry of their composition and explosion.

In the special portions of the book a large proportion of the matter is original, and the whole work has been carefully brought up to date.

V. B. L.

Royal Naval College, Greenwich,
October, 1895.

PREFACE TO THE THIRD EDITION.

THE great and important advances made in science during the past ten years have necessitated practically the re-writing and re-arranging of the whole work, which has been done with the co-operation of my colleague, Mr J. S. S. Brame. In doing this, alteration has to some extent been made in the general arrangement of the book where experience has shown this to be necessary, whilst in the portions devoted to fuels, explosives, and metallurgy the work has been brought thoroughly up to date, and the authors hope it will be found of value not only to the officers of both branches of the Service, for whom it is primarily intended, but also to the practical engineer.

The authors desire to express their thanks to Mr G. Lorimer for much valued help in correcting the proof-sheets.

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SERVICE CHEMISTRY.

CHAPTER I.

INTRODUCTORY.

Physical and chemical change—Conservation of matter and energy—Elements—Mechanical mixtures and chemical compounds—Analysis and synthesis—The three states of matter—Liquefaction of gases—Refrigeration.

CAREFUL observation shows us that two great methods of change are always at work altering the face of Nature and the forms of matter which are found on the globe.

Physical Change.—We see granite rocks being gradually broken down by the combined action of water and frost, yet the fragments torn from the rock are of the same composition as the rock itself. We know that by cold we can convert water into ice, and by heat into steam; yet the solid ice—the liquid water—and the gaseous steam have all the same composition. We see a coil of platinum wire heated to a temperature at which it acquires the power of giving out light; yet on cooling, the platinum once more loses this property and is found to be in no way changed from the original metal, being chemically identical and no change in weight having taken place. Changes of this kind, in which form and properties only undergo modification, without any alteration in composition, are called *Physical changes*, and the study of this class of phenomena comes under the domain of Physical Science.

Chemical Change.—A second kind of change, however, is at work, in which the alteration affects not only the physical properties of the original mass, but also its composition. A

fallen tree, exposed to air and moisture, gradually rots away and is converted into gases and soil. A candle burns, and the wax of which it is composed disappears. A metal dissolved in an acid loses its metallic properties and remains in solution in the liquid. A piece of magnesium wire, heated in contact with air, emits light, burns away, and at the end of the operation we have a white powder left which is entirely different in form and properties from the metal magnesium. In all these cases a change of weight, as well

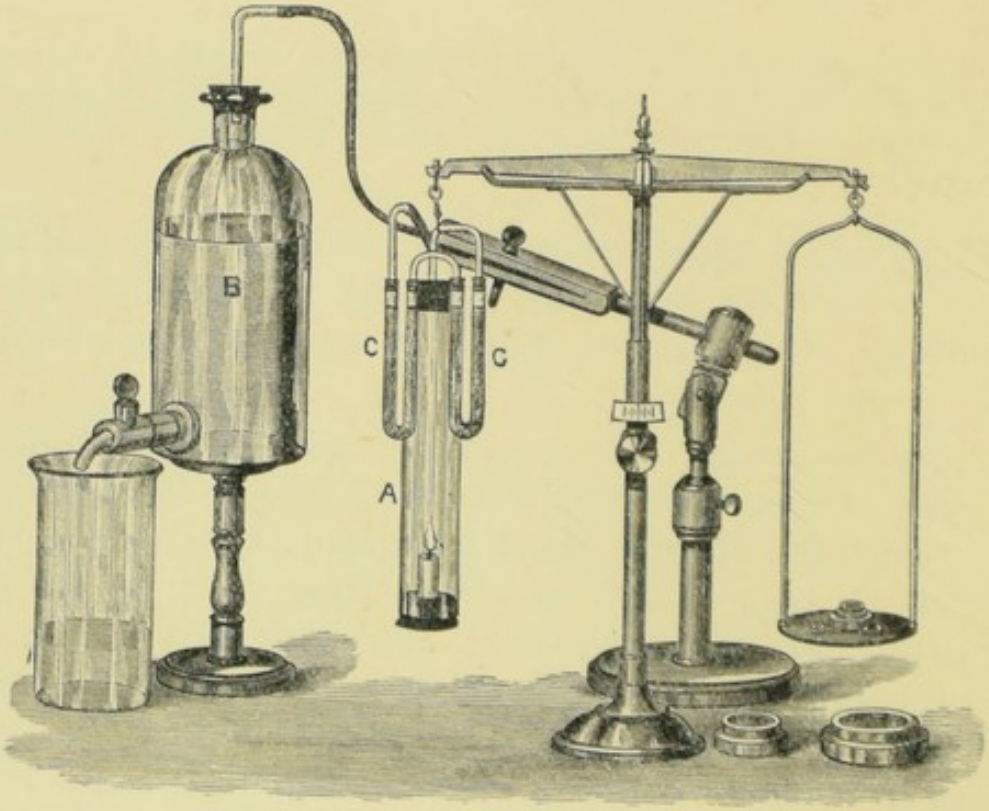


Fig. 1.

as of properties and composition, has taken place; and if we collected and weighed the white powder formed during the combustion of the magnesium wire, it would be found to weigh more than the metal burnt. Changes of this class, in composition as well as properties, are called *Chemical changes*, and the study of the laws which govern and bring about such changes constitute the *Science of Chemistry*.

Conservation of Matter.—In Nature no such thing as loss or creation of matter occurs, although in many cases the

products of the chemical changes taking place, being gaseous, escape our notice, as when a candle burns.

If, instead of allowing the candle to burn in the open air, it had been supported in a glass cylinder (A, Fig. 1) and the products of its combustion had been drawn by means of the aspirator bottle (B) through tubes (C) (C), containing small fragments of sodium hydroxide, which has the power of absorbing carbon dioxide and water vapour (the gaseous compounds formed by the combustion of the wax of the candle), it could be shown that the products formed weighed

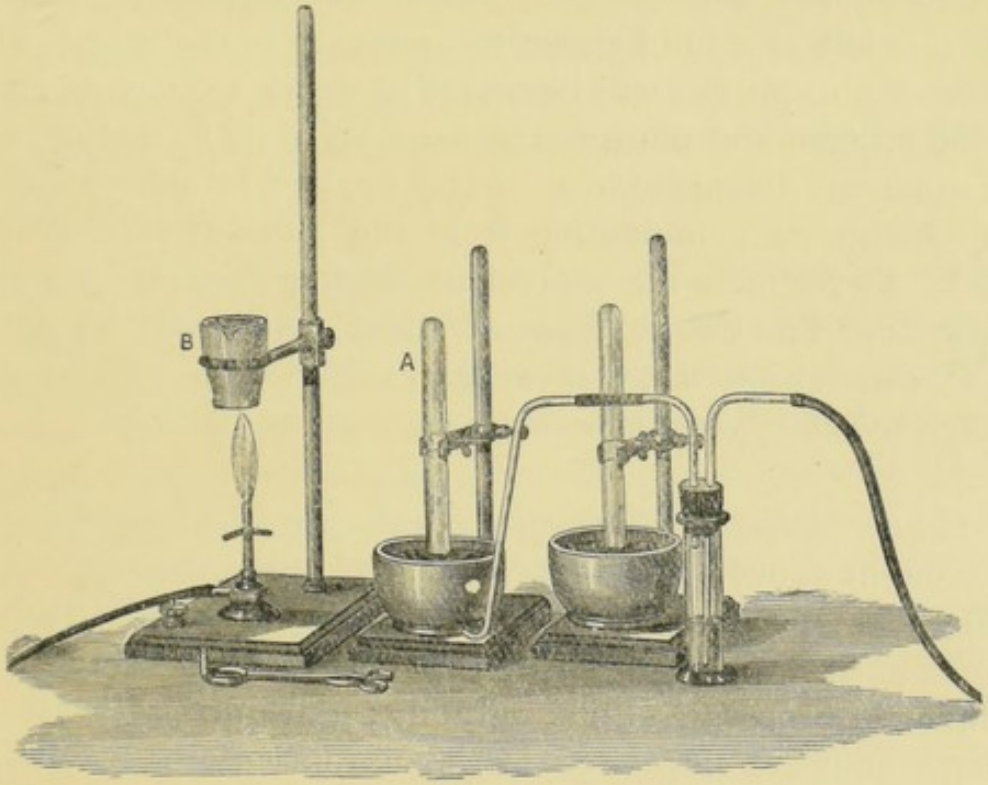


Fig. 2.

more than the wax consumed, by suspending the candle and absorption tubes to one end of a balance, when, instead of losing weight, as might have been expected, from the diminution in size of the candle, the candle and absorption tubes are seen to increase in weight, and this increment is due to the constituents of the wax having entered into chemical combination with one of the constituents of the air, the increase in weight shown by the balance being exactly equal to the loss of weight of the air.

If one of the constituents of the air, called oxygen, be allowed to pass, bubble by bubble, into a tube filled with mercury (A, Fig. 2), the mercury is displaced and the tube fills with the gas, but if it be bubbled up into a second in which a piece of well-dried phosphorus has been passed to the top of the tube, and there melted by holding over it an inverted red-hot fire-clay crucible (B), each bubble of gas as it enters will cause a flash of light and no displacement of the mercury will take place until all action ceases; that is, until all the phosphorus has been converted into a compound of phosphorus and oxygen, called phosphorus pentoxide, which is left as a solid above the mercury in the tube. This oxide of phosphorus will be found to weigh exactly as much as the oxygen and phosphorus used up in its formation, and the apparent disappearance of the oxygen is merely due to the change on combination from the gaseous state to the solid. These facts are embodied in the general principle known as "The Conservation of Mass," which may be stated as follows—"*The mass of matter which takes part in any change, whether physical or chemical, remains unaltered.*"

Causes leading to Chemical Action.—Chemical change may be brought about by several causes, one of the most powerful being heat; but, besides this, mechanical force will often set up chemical action, as when a percussion cap is struck; light, as in processes of photography; galvanic electricity, as when metals are deposited from solutions of their salts by means of a galvanic current; all these being forms of energy which aid or oppose chemical affinity, a force which acts at infinitely small distances, and which in only a few cases causes combination to take place between solids; the liquid or gaseous condition allowing closer contact between the particles of the re-acting bodies.

No chemical change can occur without being accompanied by some physical change, change of temperature being the most usual manifestation.

When chemical combination takes place, heat is generally

evolved, and the amount of heat so given out is generally the equivalent of Chemical and Physical work performed, and is often taken as a measure of the combining energy of the original substances. When such a compound is once more decomposed, heat is again absorbed and remains as latent chemical energy until combination once more takes place. For instance, when the two gases, oxygen and hydrogen, combine, great heat is evolved and water is formed, and in order to once more decompose this water the same quantity of heat or its equivalent in other forms of energy is required.

Conservation of Energy.—Energy, like matter, can be converted from one form into another, but cannot be created or destroyed, a principle known as the "Conservation of Energy."

Elements and Compounds.—If we take a small globule of mercury and warm it gently with strong nitric acid, the mercury dissolves with evolution of a gas which turns reddish-brown in air, and on carefully evaporating the solution, we can crystallise out a colourless salt called mercuric nitrate; on drying these crystals and again heating them, a reddish-brown gas is given off, and a red powder called mercuric oxide is left. This red powder, when placed in a hard glass tube and heated, breaks up into vapour of the metal mercury, which condenses in globules in the cool portion of the tube, whilst a colourless gas called oxygen is evolved, and can be conducted by the leading tube (B) under the surface of water in the pneumatic trough (C) and collected by displacement of water in the cylinder (D). (Fig. 3.)

The question now naturally arises: can we go on decomposing substances in this way to an unlimited extent; further experiment shows us that we cannot. If we take mercury and oxygen and experiment on them, we find that they can be made to combine with other substances to form a large number of compounds, but by no means at present at our

disposal can we sub-divide them into anything but mercury and oxygen.

When, in this way, a substance resists further decomposition, we call it an *Element*, and at present about seventy-eight such substances are known, and of these, as far as we know, all matter is built up. It is by no means unlikely that on the discovery of some new form of energy or method of analysis, we may be able to break up some of these into simpler bodies, and we therefore define an element as "*a substance which by no means at present at our disposal can be decomposed into anything simpler.*"

A list of the elements will be found in the Appendix.

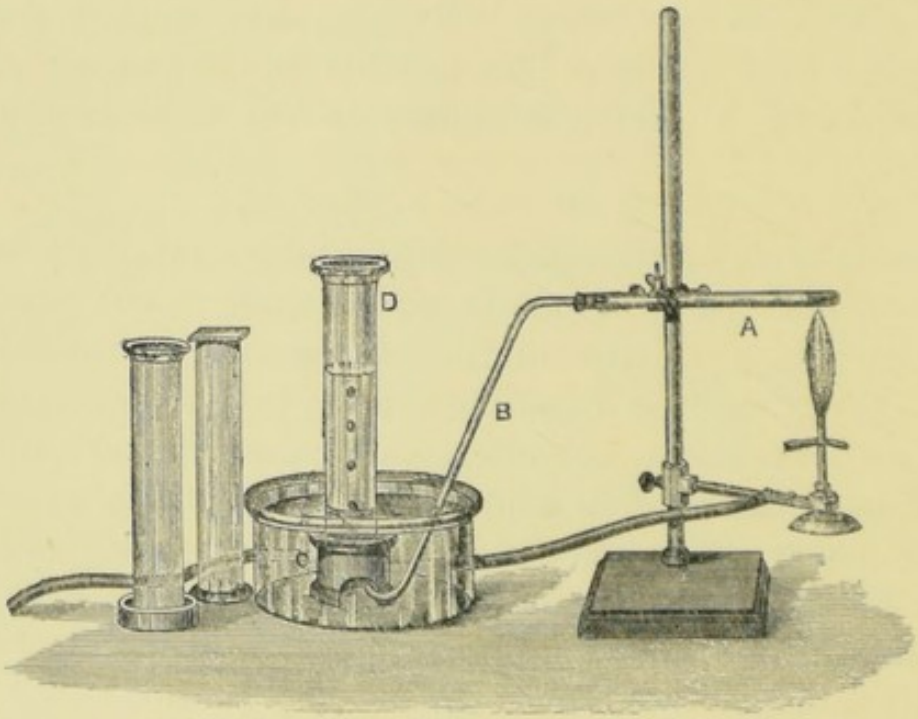


Fig. 3.

The distribution of the elements in Nature is most irregular. Some are found in very large quantities and very widely distributed; whilst others occur in such minute quantities that their properties are scarcely yet known. Indeed, nearly half the elements known at present might be eliminated without, as far as our present knowledge goes, causing any considerable disturbance of the laws of Nature.

The general distribution of the elements is roughly indicated in the following tables:—

COMPOSITION OF AIR.

Nitrogen	76·9	parts by weight.
Oxygen	23·1	„ „
	100·0	

COMPOSITION OF WATER.

Oxygen	88·8	parts by weight.
Hydrogen	11·1	„ „
	99·9	

APPROXIMATE COMPOSITION OF THE CRUST OF THE EARTH.

Oxygen	45·5
Silicon	29·4
Aluminium	8·2
Iron	6·3
Calcium	2·4
Magnesium	1·6
Sodium	2·5
Potassium	2·0
All the other elements	2·1
	100·0

To these elements must be added carbon, which exists in all matter of organic origin, and it is then seen that 99 per cent. of known substances are composed of eleven elements, whilst oxygen alone constitutes upwards of 52 per cent. of earth, air, and water.

Elements combine to form chemical compounds, or more rarely, exist free.

Mechanical Mixtures.—When in mechanical mixture, the distinctive properties of the substances present are retained, although often modified by the properties of the other constituents; but in a chemical compound the properties of the

original factors entirely disappear, and are merged in new characteristics distinctive of the compound formed.

Air is a mechanical mixture, and in air we recognise the properties of the great supporter of life and combustion—oxygen—modified and restrained by the distinctive properties of the other constituent, the inert nitrogen.

Chemical Compounds.—Water, on the other hand, is a chemical compound of oxygen and hydrogen, in which all the properties, chemical and physical, of the constituents have disappeared, and have given place to the distinctive characteristics of water.

If iron filings and finely powdered sulphur be mixed together, a greenish-grey powder is formed, in which, by means of a microscope, the particles of sulphur and iron may be seen lying side by side, and from which the iron and sulphur may be recovered by mechanical means, such as acting upon it by a magnet, which attracts and withdraws the iron, or by throwing it upon water, when the iron sinks. Such a powder is called a mechanical mixture, and has all the properties of the substances composing it.

If some of this mixture be heated a chemical action takes place, and the result is a black homogeneous mass in which no particles of sulphur or iron can be detected by the most powerful microscope: it is only slightly magnetic, and when thrown on water it sinks as a whole, and the iron and sulphur can only be again obtained from it by complicated chemical processes.

The chemical compound so formed has none of the properties of the sulphur or the iron, but has acquired a new set of properties peculiar to itself.

Analysis and Synthesis.—We have seen that by chemical change complex substances may be resolved into simple bodies, and finally reduced to the condition of elements, whilst chemical change also enables us to build up elementary matter into compounds, and these processes can be utilised for revealing the composition of substances. If

we take a body and by chemical means break it up in such a way as to gain an insight into its composition we call it a process of *analysis*, whilst if we have an idea as to what the composition of the body is likely to be, we can often verify the fact by building up the compound from the elements we expect it to contain, a process which is called *synthesis*. For example we can prove that water contains hydrogen and oxygen by passing steam over iron heated to dull redness, when the oxygen remains combined with the iron, and we can collect the hydrogen in a free state. On the other hand by passing a mixture of steam and chlorine through a hot porcelain tube we can decompose the steam with the formation of hydrochloric acid and the liberation of oxygen, the two experiments taken together showing that water contains hydrogen and oxygen, this being an analytical method of arriving at the fact.

Knowing now that oxygen and hydrogen are present in water we can mix these two gases together and explode them by means of an electric spark or flame, when they combine with the formation of water, thus synthetically proving that oxygen and hydrogen alone constitute the substance, and by one or other of such processes the composition of all forms of matter may be arrived at.

The Three States of Matter.—By matter we understand anything that has weight, and it may be either solid, liquid, or gaseous in its nature. These three states of matter are entirely dependent upon temperature. It so happens that at the ordinary air temperature zinc is a solid, water is a liquid, and carbon dioxide is a gas; but if we take water and cool it down below O° C. it becomes a solid, ice, whilst heated above its boiling point (100° C.) it is converted into gaseous steam. In the same way all substances which are not decomposed by heat can be obtained as solids, liquids, or gases.

If we take a bar of zinc at the ordinary air temperature and carefully determine its size, and then heat it, we find that the action of heat is to cause it to increase in bulk, this

increase proceeding at a definite rate until we have raised the temperature to 423° C., when it becomes liquid. If now the liquid be further heated it will be found to still continue to expand until a temperature of 1040° C. is reached, when it boils like water and is converted into the gaseous state.

If we now take the gas carbon dioxide, and having cooled it down to near the freezing point of water bring a pressure of 36 atmospheres (540 lbs. on the square inch) to bear upon it, it is reduced to the liquid state, and in this condition can be kept in steel vessels of sufficient strength to resist the pressure necessary to keep it liquid. On allowing some of this liquid however to escape suddenly into a small box at ordinary atmospheric pressure, it is instantly converted into gas, and in the change from the liquid to the gaseous state takes up so much heat as to produce a degree of cold sufficiently intense to freeze some of the liquid escaping from the vessel into solid carbon dioxide.

From these three experiments it is clear that those bodies which we look upon as solids are simply those which have a melting point above the ordinary temperature, whilst a liquid has its melting point below the ordinary temperature, and a gas its boiling point below the ordinary temperature.

We saw that when the solid zinc was being heated up to the point at which it became liquid, a continuous expansion was taking place, and that the expansion continued until the zinc was converted into vapour, the volume of the vapour being enormously greater than that occupied by the original zinc bar.

In the same way when water is boiled it is converted into steam, the vapour so formed occupying about 1700 times the volume of the water taken. Roughly a cubic inch of water forms a cubic foot of steam. This enormous increase in volume may be explained in one of three ways: either the cubic inch of water is stretched under the influence of heat, like a piece of indiarubber, until it assumes the dimensions of the cubic foot, or the cubic inch of water is built up of an innumerable host of small particles which, when heated,

undergo individual expansion, which mounts up to the enormously increased volume, or else this multitude of small particles do not themselves expand, but under the influence of heat tend to repel each other, and by spacing themselves further apart give the increase in volume.

If the first or second theory be correct, then every part of the cubic foot of steam would be perfectly homogeneous, and without condensing some of the steam it would be impossible for any other vapour to find room in the space so occupied, whilst experiment shows us that one vapour acts as a vacuum to another, so that other vapours can occupy the space already filled with water vapour: a phenomenon which can only be explained on the assumption that the vapours do not completely fill the space they occupy, although equally distributed through it: that is, they are built up of particles, which by the action of heat become widely separated from each other, thus leaving spaces within which the particles of other vapours may find place.

We have seen that the three states of matter are merely dependent upon temperature and pressure, and it is clear therefore that if the vapours and gases consist of particles, then we must assume that liquids and solids also are built up in the same way, an assumption entirely borne out by experiment.

In the solid state, these particles, each of which has the same properties as the mass of which it is a part, are held together by the force of "cohesion," a force which varies with the nature of the substance; so that when a solid is heated, the particles tend to separate, but in different substances they do so to a different extent; as the stronger the force of cohesion existing between the particles, the greater is the work the heat has to do in separating them; at a certain temperature the particles are so far asunder that the force of cohesion is weakened to a certain extent, and the particles become free to move around each other, *i.e.*, they assume the liquid state; continue the heating, the distances between the particles grow greater and greater until a point is reached at

which cohesion exerts no influence, the particles move independently of each other, and we have the gaseous state.

In the solid and liquid states various substances expand unequally for an equal increment of temperature, while in the gaseous state all substances behave alike, an equal increment of temperature producing in each case an equal increase in volume, because cohesion has ceased to act between the particles.

The Liquefaction of Gases.—The fact that all gases could be converted into the liquid state has only lately received complete confirmation, but as early as 1823 Faraday succeeded in liquefying such gases as chlorine, carbon dioxide, sulphur dioxide, nitrogen monoxide, and ammonia, but up to about 1877 it was supposed that there were six permanent gases, *i.e.*, gases which could not be liquefied, these being hydrogen, nitrogen, oxygen, carbon monoxide, nitrogen dioxide, and marsh gas, but in that year Cailletet and Pictet succeeded independently in obtaining oxygen as a liquid haze in a glass tube, and as a liquid jet. Six years later Olszewski and Wroblewski obtained oxygen as a static liquid that could be experimented with, and in January 1884 the latter observer succeeded in obtaining a haze of hydrogen, whilst in May 1898 Sir James Dewar obtained hydrogen as a static liquid.

In Faraday's experiments on the liquefaction of gases he used the combination of cold and pressure to convert the gas into a liquid, but the lowering of temperature that can be obtained by a mixture of ice and salt was the greatest cold he had at his disposal.

Critical Point.—In 1869 Andrews showed that with every gas there is a particular temperature below which it can be liquefied by pressure, but above which it is impossible to liquefy it: this temperature is called *the critical point*, and in the gases liquefied by Faraday the critical points were above the temperature given by his freezing mixture, whilst

those gases which resisted liquefaction by pressure had a critical point below this temperature.

Gas	Critical temperature °C.
Sulphur dioxide	155·4
Chlorine	141·0
Ammonia	130·0
Hydrochloric acid	52·3
Acetylene	37·0
Nitrogen monoxide	35·4
Carbon dioxide	31·9
Ethylene	10·1
Methane	- 99·0
Oxygen	- 113·0
Carbon monoxide	- 140·0
Nitrogen	- 146·0

When a gas that has been liquefied by pressure is again allowed to become gaseous, the change from the liquid to the gaseous state takes up and renders latent a large amount of heat, and in so doing can be made to cool bodies in contact with it to a very low temperature. For instance the critical point of carbon dioxide being 31·9° C., the gas can readily be liquefied by pressure, and can be kept in the liquid state in a strong steel cylinder: if now the liquid be driven out into a vessel at atmospheric pressure, it is rapidly again converted into gas and lowers the temperature of bodies in contact with it to - 80° C. This is far below the critical point of the gas ethylene, so that if this gas is compressed to a sufficient extent in a cylinder cooled by boiling liquid carbon dioxide, the ethylene in turn becomes a liquid, which, when it boils at atmospheric pressure, gives a temperature of - 100° C., but if the conversion into the gaseous state is hastened by allowing it to gasify into a vacuum the temperature is lowered to - 140° C. At - 140° C. oxygen can be liquefied by pressure, and on allowing liquid oxygen to boil at reduced pressure a temperature of - 205° C. is reached,

a point at which air liquefies by merely coming in contact with the cooled surface.

Cooling hydrogen down to this temperature under a pressure of 180 atmospheres and allowing the gas to escape from a fine nozzle into a vacuum vessel also cooled to the same temperature, Sir James Dewar liquefied hydrogen in considerable quantities.

The reduction of temperature consequent upon the expansion of a gas when released from a high pressure, can be utilised to further cool another quantity of compressed gas, which on being released from pressure in turn gives a still greater degree of cold, and this may be continued until a lowering of temperature sufficiently great to liquefy air can be obtained. This principle is utilised in the forms of apparatus devised by Linde and Hampson respectively, and which are now utilised for making liquid air on a commercial scale.

Refrigerating Machines.—The principles involved in the beautiful series of researches that have led to the liquefaction of all gases, have also received most useful application in the reduction of temperature necessary for the production of artificial ice and cold storage, both on land and sea.

The refrigerating machines by which the necessary lowering of temperature can be obtained can be arranged in three classes:—

1. Those in which air is compressed by powerful compressing pumps with evolution of heat, which is absorbed by passing the air through a coil cooled by water. The compressed air is then allowed to flow into an expansion cylinder, and in expanding takes up and renders latent as much heat as it gave out on compression, and thus cooled several degrees below the freezing point it enters the refrigerating chamber, from which an equivalent volume of air is then withdrawn to the compressing pump.

2. The second class of refrigerating machines depend for their action upon the alternate liquefaction and gasification of an easily condensable gas like ammonia, carbon dioxide, or sulphur dioxide. On a large scale the lowering of temperature caused by the evaporation of the liquefied gas is utilised to cool brine several degrees below the freezing point of water, the cold brine being then made to circulate through a system of pipes in the refrigerating chamber.
3. The third class of machines depends upon the easy condensability of gaseous ammonia to the liquid state, and the fact that after the liquid has done the work of cooling during its gasification the gas is absorbed with enormous rapidity by cold water, and can be again driven out from this solution by heat.

CHAPTER II.

THEORETICAL.

Laws of chemical combination, constant proportion and multiple proportion—The atomic theory—Law of gaseous volumes—Avogadro's hypothesis—Influence of temperature and pressure on gases—The kinetic theory—Atomic and molecular weights—Symbols—Valency—Formulæ ; empirical, molecular, graphic and constitutional.

LAW of Constant Proportion.—Although the nature of many chemical substances has been known from very early times, little advance was possible in the study of the science until chemists introduced quantitative methods, and even then owing to necessarily crude apparatus, unsatisfactory measuring and weighing appliances, and impure materials, the results were often contradictory. Thus the very fundamental law of the constant proportion in which elements combine in any given compound was the subject of keen controversy for years, and it was only finally established by Proust in 1806.

If we take the compound copper oxide we may readily prepare this either by simply heating the metal in air, when it combines with oxygen, or we may act on the copper with nitric acid, so forming copper nitrate, which on further heating gives off brown fumes, leaving a black residue of copper oxide. Whichever method is adopted we always find that for the same weight of copper employed we obtain the same weight of copper oxide. This is found true for every compound, no matter by what means it may be obtained : or if the compound is capable of being broken down into simpler compounds or its elements themselves, we always get the same weight of each constituent from a definite weight of the compound. These facts led Proust to state the general Law of Constant Proportions, that "The same body is invariably composed of the same elements united in the same proportion."

Law of Multiple Proportion.—Many elements are known, however, which combine together in more than one proportion. Carbon for example unites with oxygen forming two gases, carbon monoxide and carbon dioxide. If we make careful determinations of the amount of each element present in the two gases, we shall find they are present in the following ratios:—

	Parts of oxygen with one part of carbon.	Parts of carbon with one part of oxygen.
Carbon monoxide ...	1·33	0·75
Carbon dioxide ...	2·67	0·375

A simple relationship is at once apparent, for in each case we have a simple multiple of the lowest amount. From the above case and others, Dalton (1803-1808) was led to enunciate the following Law of Multiple Proportions:

> "When an element unites with another element in different proportions, the higher proportions are invariably simple multiples of the lower."

The Atomic Theory.—Dalton was not content to simply state the law but sought some theory which should explain these well-established facts, and he was led to adopt an idea of the Greek philosophers, who held that matter was made up of small indivisible particles or atoms. Clearly if these particles have a definite weight, we can best imagine a chemical combination as involving the successive addition of particle after particle up to a certain limit depending on the elements concerned, and this hypothesis is the only satisfactory one proposed so far which will account for the simple multiples found when the weights of elements combining in more than one proportion are considered, and it is also in full agreement with the constant composition of each compound. For example, by whatever method we prepare it, copper oxide may be regarded as being composed of one atom of copper united with one atom of oxygen, and carbon monoxide as one atom of carbon with one atom of

oxygen, whilst in carbon dioxide we have one atom of carbon united with two atoms of oxygen.

The atom may be defined as the smallest portion of matter capable of entering into a chemical compound. Although either mechanically or chemically we are unable to subdivide the atom, yet there is reason for believing that the atom is really complex in its nature.

It follows that the atoms of each particular element must be exactly alike in their power of taking part in any chemical change, and each must have a definite weight peculiar to itself, but since the atoms are exceedingly minute we have no means of ascertaining their exact weight, although we can ascribe to them relative weights as compared with one suitable element taken as a standard. The methods of ascertaining these relative weights will be referred to later.

Molecules.—We have on the other hand another class of particles to which matter can be reduced by physical means, but which we are unable to further reduce without bringing about a chemical change, and these are termed molecules. The molecule of any compound substance will consist of an aggregation of the constituent atoms of the elements which go to form it. If we break down this complex molecule we cause a rearrangement of the atoms; in other words bring about a chemical change. *The best definition of a molecule is that it is the smallest particle of an element or compound which can exist in a free state.*

The molecules of most elements consist as we shall see of at least two atoms, sometimes, however, more than two are present, and in certain cases only one.

Law of Gaseous Volumes.—In addition to the important relationship in the weight of elements entering into combination, Gay Lussac and Humboldt (1805) showed that there also exists an equally important relationship between the volumes, and what is of still greater importance, in the case of gases, a very close relationship is found between the volumes and the weights entering into any combination.

The following table illustrates the simple ratios of the volumes of different gases when they combine, and the volume of the products when gaseous:—

2 vols. of hydrogen + 1 vol. of oxygen = 2 vols. of water (vapour).

2 vols. of carbon monoxide + 1 vol. of oxygen = 2 vols. of carbon dioxide.

1 vol. of hydrogen + 1 vol. of chlorine = 2 vols. of hydrochloric acid.

Whilst on decomposition:—

2 vols. of nitrogen monoxide = 2 vols. of nitrogen + 1 vol. of oxygen.

2 vols. of nitrogen dioxide = 1 vol. of nitrogen + 1 vol. of oxygen.

2 vols. of ammonia = 1 vol. of nitrogen + 3 vols. of hydrogen.

We may now consider in conjunction with these the weights of the interacting bodies and the products, taking as a suitable example the two oxides of nitrogen.

	Composition of nitrogen monoxide.		Composition of nitrogen dioxide.	
	By weight.	By vol.	By weight.	By vol.
Nitrogen	7	2	7	2
Oxygen	4	1	8	2

It will be seen that nitrogen dioxide contains just twice as much oxygen by weight and by volume as nitrogen monoxide for the same weight and volume of nitrogen in each. In other words, when the number of atoms present has doubled, the volume has also doubled, hence there must be a very simple relationship between the volumes of gases and the number of atoms in these volumes. This relationship was first pointed out by Avogadro (1811), and although as originally stated it refers to atoms, for reasons we need not discuss here it is now stated in the following form:—

> "Equal volumes of gases under the same conditions of temperature and pressure contain the same number of molecules."

Influence of Temperature and Pressure on Gases.—If Avogadro's hypothesis is correct, and the molecules of a gas have no action on each other, we should expect to find that all gases exhibit certain similarities in their physical properties, and it has long been known that within certain limits all gases expand equally under the influence of heat or alteration in pressure.

Boyle (1662) showed that the volume of any gas varies inversely to the pressure: thus doubling the pressure halves the volume, or reducing the pressure by one half doubles the volume. Many gases obey this law almost exactly, but some show considerable deviation under high pressures.

That the rate of expansion for all gases was the same for the same rise of temperature was first shown by Charles, and it is found that for every rise of 1° C. the volume is increased $\frac{1}{273}$ of the original, so that if we raise the temperature of any gas from 0° to 273° C., we double its volume, the pressure of course being kept constant. Theoretically then if we measured a litre of gas at 0° C., and the temperature could be reduced to - 273° C., the gas would cease to occupy any space, but this is a condition impossible to conceive, and there is no doubt but that at such a low temperature every gas would be condensed to the liquid condition and cease to obey Charles' law.

This temperature of - 273° C. is therefore taken as the *absolute zero.* A gas at 0° C. will therefore be at 273 on the absolute scale, or generally to arrive at the absolute temperature we must add 273 to each degree Centigrade. 10° C. will therefore equal 283 absolute, and - 10° C. will equal 263 absolute.

From a knowledge of these facts we are enabled to calculate the volume of any gas under any conditions of temperature and pressure. For change of temperature, if we let

v = old volume
v^1 = new volume
t = old temperature
t^1 = new temperature

then $v^1 = \frac{v \times (273 + t^1)}{273 + t}$.

The atmospheric pressure is measured by the barometer, in which a column of mercury is supported in a tube by the weight of the superincumbent air, and the normal height of mercury so supported is 30 inches, which approximately corresponds to 760 m.m., and as we express the barometric pressure in millimeters, it is evident that we can calculate the increase or decrease in volume due to barometric disturbance by a direct proportion.

Suppose a given volume of gas to be measured at a time when the barometer stood at 755 m.m., and that the pressure was increased to 768 m.m., the volume would decrease in the ratio of 768 to 755, or in other words:

$$\text{New vol.} = \frac{\text{old vol.} \times 755.}{768}$$

These variations in volume, due to change of temperature and pressure, have made it necessary to fix a standard temperature and pressure at which all gases shall be measured, and for all scientific purposes 0° C. and a barometric pressure equal to 760 m.m. of mercury have been adopted, and called the "normal" temperature and pressure.

Now it is evident that it would be practically impossible to secure these conditions, so that the usual method adopted is to measure the gas under ordinary circumstances, and having noted the temperature and pressure, to calculate what would be the volume under *normal* conditions of temperature and pressure, and this is done by the formula:

$$\frac{v\,p}{t} = \frac{v^1\,p^1,}{t^1}$$

where—

v = original volume.
p = observed pressure.
t = observed temperature in $(273 + °C.)$
v^1 = required volume.
p^1 = normal pressure.
t^1 = normal temp. $(273 + 0°$ C.)

This formula is adapted for any calculation as to change in volume, etc., by using v^1, p^1, and t^1, as may be required.

The Kinetic Theory.—It has already been shown that a gas must be regarded as a number of individual particles, the molecules, separated from each other by space into which different other gaseous molecules may penetrate.

According to the Kinetic Theory the molecules of any gas are in constant motion and proceed in straight lines until they meet other molecules or the sides of the containing vessel, when they change their course or rebound. The rapidity with which the particles move in the same gas is very variable, owing to these frequent collisions, but the mean speed can be calculated and is dependent on the temperature. A certain small volume of gas will therefore evenly distribute itself throughout a great space, and for this reason a slight escape of coal gas can be smelt several feet away from the leak. When the molecules strike the containing walls they develop pressure on those walls, and if we reduce the space we confine the same number of molecules in a smaller space, hence they strike the walls more frequently in unit time and give a greater pressure (Boyle's Law).

Further let us consider a definite volume of gas in a closed chamber. If we heat the gas we know that we cause an increase of pressure on the containing walls, and this increase can only be due to increased velocity of the molecules, for the energy with which they strike is due to their mass and their velocity, and heat has no effect on the mass; moreover, any individual molecule must strike the walls more often. It can be shown from the laws of energy that all gases should expand at the same rate for equal rises of temperature (Charles' Law).

In the case of very light molecules these must have a greater velocity than heavier molecules, for under similar conditions the pressure on the walls is the same, therefore to give the same striking blow they must travel faster and hit the walls more frequently. Imagine now a very small hole in the walls of the vessel. In a given time a far greater number of light molecules would be likely to pass through the hole than heavy ones. In other words a light gas will

escape under such circumstances far more rapidly than a heavy one, a fact we shall see fully established when dealing with gaseous diffusion.

The Kinetic Theory is in agreement with the behaviour of gases under the Laws of Boyle and Charles, also with Avogadro's hypothesis, and further it easily explains the Law of Graham for the diffusion of gases; hence we may assume that the idea embodied in it of the nature of a gas is not far removed from the truth.

Atomic and Molecular Weight.—It has been pointed out that we can by no possible means obtain the actual weight of the atoms, but we can by suitable methods ascertain the relative weights in which they enter into combination if some suitable element be taken as a standard.

If Avogadro's hypothesis is correct, then the weights of equal volumes of different gases under the same conditions of temperature and pressure will be the relative weights of the molecules themselves, so that if a substance, whether elementary or compound, exists as a gas or is easily converted into one, we can by suitable methods obtain the molecular weight.

Density.—When dealing with gases, by directly weighing a known volume and comparing its weight with that of the same volume of our standard gas we obtain its relative density, and as hydrogen is the lightest gas known, this was taken as unity. At 0° C. and 760 m.m. pressure 1 cubic centimeter of hydrogen will weigh 0·0000896 gram.

In the case of liquids or solids easily vaporised we may take a known weight of the substance and find out the exact volume it occupies as vapour under known conditions of temperature and pressure; then if the volume so obtained is reduced to standard conditions, direct comparison can be made with the standard gas. Such densities are termed "*vapour densities.*" Thus the vapour density of water as compared with hydrogen is 9, that is, the molecule of water (as vapour) is 9 times as heavy as the molecule of hydrogen.

It is obviously desirable that the molecular weight of a compound shall be the sum of the atomic weights of its constituent atoms, but atomic weights are all referred to the atom of the standard gas. It becomes necessary, therefore, to prove the number of atoms present in either the molecule of hydrogen or oxygen, for with densities all numbers refer to the molecule.

Complex Nature of the Hydrogen Molecule.—If we take (say) 1 litre of hydrogen and 1 litre of chlorine, we find they combine to form 2 litres of hydrochloric acid gas. Or again, we may take 2 litres of hydrochloric acid gas and introduce into it metallic sodium, when we shall find the volume diminishes until it is just one half of the original volume, and the residual gas is hydrogen. Hence:

$$\left.\begin{matrix}\text{Hydrogen}\\ \text{1 vol.}\end{matrix}\right\} + \left\{\begin{matrix}\text{Chlorine}\\ \text{1 vol.}\end{matrix}\right. = \left\{\begin{matrix}\text{Hydrochloric Acid.}\\ \text{2 vols.}\end{matrix}\right.$$

We know from Avogadro's hypothesis that these volumes of hydrogen and chlorine contain the same number of molecules, and the two volumes of hydrochloric acid twice the number of molecules. What the number actually is we have no means of ascertaining, but we may assume any number we please, as it will in no way affect our deductions. Let us say unit volume contains 1000 molecules, then in the 2 unit volumes of hydrochloric acid there are 2000 molecules. But each molecule consists of hydrogen and of chlorine, otherwise it would not be hydrochloric acid, so that there must be 2000 atoms of hydrogen and 2000 atoms of chlorine in our 2 volumes. Clearly then the 1000 molecules of both hydrogen and chlorine contained 2000 atoms, or in other words the molecule of either gas contains 2 atoms.

By a similar course of reasoning in the case of 2 volumes of hydrogen combining with 1 volume of oxygen to form 2 volumes of water vapour, we can show that the molecule of oxygen also contains two atoms.

The atomic weight of hydrogen being taken as unity, its molecular weight must be 2 but the density of hydrogen has unfortunately been taken as unity in comparing densities, therefore the molecular weight of any gas will equal its density × 2. For example, the density of oxygen is 16, hence its molecular weight is 32, but as the molecule contains 2 atoms, the atomic weight is the same as the density, and this is true for any elementary gas the molecule of which contains 2 atoms.

It has been already shown that the atomic weight of a gaseous element is the ratio of its weight volume for volume compared with hydrogen as unity, and that the molecular weight of gas, elementary or compound, is its weight, volume for volume, compared with hydrogen as 2. If now we take a definite weight of hydrogen as representing an imaginary atom and determine the volume which this weight represents, we can establish a relation between weight and volume which will be true for all gases. The gram being the unit of weight in all scientific work, we choose 1 gram of hydrogen as the imaginary hydrogen atom, and on measuring the volume of 1 gram of hydrogen under normal conditions of temperature and pressure (0° C. and 760 m.m.), we find that it occupies 11·16 litres, and this volume we take as our *atom volume.*

In the same way 2 grams of hydrogen occupy 2 (11·16) litres, or 22·32 litres, and this we take as our imaginary molecule measure for gaseous elements and compounds; and can now formulate the two following laws:—

1. If the atomic weight in grams of any gaseous element be taken, this weight of gas will occupy a volume of 11·16 litres at 0° C. and 760 m.m. pressure.
2. If the molecular weight in grams (*gram molecular weight*) of any gaseous element or compound be taken, this weight of gas will occupy a volume of 22·32 litres (*gram molecular volume*) at 0° C. and 760 m.m. pressure.

For example, 1 gram of hydrogen, 14 grams of nitrogen, 35·5 grams of chlorine all occupy 11·16 litres, and 2 grams of hydrogen, 44 grams of carbon dioxide, 17 grams of ammonia, all occupy 22·32 litres.

We may therefore define the molecular weight of any gas as that weight of the gas in grams which will occupy 22·32 litres at 0° C. and 760 m.m. pressure.

The above simple rules are of great service in making calculations involving gas volumes, for having written the correct equation for any reaction instead of putting in molecular weights, we can greatly simplify things by putting in molecular volumes.

Atomic Weight of Non-Volatile Elements.—Few of the elements can actually be gasified, therefore other methods than finding the density must be adopted. Many, however, give gaseous compounds or compounds easily gasified, and as we have seen, the molecular weight is the sum of the atomic weights, we can from the composition and molecular weight readily ascertain the atomic weight of any element in the compound. Carbon for example is non-volatile except at the temperature of the electric arc, yet it forms numerous gaseous compounds, of which the following four with hydrogen may be selected, the composition being determined by analysis, and the molecular weight from the density.

	Weight of carbon per cent.	Molecular weight.	Weight of carbon in the gram molecular weight.
Methane	75·0	16	12
Ethane	80·0	30	24
Propane	81·8	44	36
Butane	82·8	58	48

In the molecule of any carbon compound we never find less than 12 parts of carbon, and this may therefore be assumed to be the smallest proportion in which it can enter into combination as compared with hydrogen, hence its atomic weight = 12.

In addition to determining molecular weights from densities we are able to determine them by the effect dissolved substances exert in different solutions, such as their influence on the boiling point, freezing point, and electric conductivity, and as the number of compounds capable of being dissolved is much greater than those for which we can directly determine the vapour density, the method of determining the atomic weights from the density and composition is much more generally applicable than formerly.

Atomic Weight from the Equivalent.—By the analysis of a substance alone we can only determine the ratio in which the elements in it combine and not the atomic weights, for many elements enter into combination in several proportions. This ratio is termed the *equivalent* of the elements in respect to each other. If we take hydrogen as the standard, then the equivalent of any element is that weight of it which will combine with or replace 1 part by weight of hydrogen. In water for example, there are 8 parts by weight of oxygen to 1 part by weight of hydrogen; these numbers are therefore the equivalents of the two elements, and if we find the equivalent of any element from its oxide as compared with oxygen, then the equivalent as compared with hydrogen will be just 8 times this value.

As a matter of fact the number of hydrogen compounds is comparatively small, whilst those of oxygen are very numerous, and mainly for this reason oxygen is a more convenient standard for atomic weights than hydrogen, and it has been agreed at an International Congress to make oxygen the standard instead of hydrogen, the atomic weight of oxygen being taken as 16.

The application of the equivalent to the determination of atomic weights will best be followed from an example. Iron forms two oxides, having respectively the following composition :—

	a	*b*
Iron	77·77	70·00
Oxygen	22·23	30·00
	100·00	100·00

Their equivalents are therefore:—

$$\overset{a}{\frac{77{\cdot}77 \times 8}{22{\cdot}23}} = 28 \qquad \overset{b}{\frac{70{\cdot}00 \times 8}{30{\cdot}00}} = 18{\cdot}66$$

The atomic weight of iron must be some simple multiple of these equivalents, and we are able to arrive at this multiple by a determination of the specific heat of the metal.

If we take the amount of heat required to raise a unit weight of water through 1° C., and call it 1, then the amount of heat required to heat the same weight of other substances through 1° C. will be less than 1, and this fraction is called the specific heat.

Dulong and Petit discovered that if the weights of the solid elements be taken proportional to their atomic weights, the same amount of heat will be required in every case to raise them through the same interval of temperature. The atoms of the elements have all the same capacity for heat. For example, 208 grams of lead require as much heat to raise through 1° C. as 63 grams of copper. Clearly then—

Atomic weight × Specific heat = Constant (Atomic heat).

And this constant is found by experiment to be about 6·4, and

$$\text{Atomic weight} = \frac{6{\cdot}4}{\text{Specific heat}}.$$

This number is only approximately true, but it enables us to accurately determine the atomic weight, having first found the equivalent. Thus in the case of iron, for which we have already given the equivalent, the specific heat is found to be 0·1138, and $\frac{6{\cdot}4}{0{\cdot}1138} = 56{\cdot}2$. This is practically 2×28, and $3 \times 18{\cdot}66$, and hence 56 is taken as the atomic weight of iron.

Symbols.—It is a matter of great convenience to chemists to have a recognised system of symbols for the different elements, in order that chemical reactions may be expressed in a simple and convenient manner. Generally the first letter of the name of an element is selected; for example,

C represents carbon, but as there are other elements commencing with C, chlorine, calcium, cobalt, and copper, in these cases we must select some two letters from the name to indicate the element, thus Cl for chlorine, Ca for calcium, Co for cobalt, and for copper the first two letters of the Latin "cuprum." A complete list of the symbols will be found in the Table of Atomic Weights in the Appendix.

When dealing with a compound, we may write the symbols for the constituent atoms in some well-defined order. The compound which sodium (Na) forms with chlorine (Cl) being written NaCl.

Not only does the symbol indicate the elements under consideration, but each time the symbol is written it indicates an atom of the element, and therefore each symbol has a definite numerical value. The formula above given, NaCl, for example, indicates that one atom of sodium, or 23 parts by weight combines with one atom of chlorine, or 35·5 parts by weight, to produce $23 + 35{\cdot}5 = 58{\cdot}5$ parts by weight of common salt (NaCl). In many chemical compounds we have the occurrence of one or more elements several times, and although we may write the symbol each time for each atom present, as HHSOOOO for sulphuric acid, such a proceeding is inconvenient, and we therefore express the same thing by writing H_2SO_4, the number after a symbol only referring to the immediately preceding symbol. Should the number be placed before or after a bracket, it multiplies the whole of the symbols and the corresponding weights of the elements in the bracket. Thus $Ca(HO)_2$ or Ca2(HO) both indicate 2 atoms of hydrogen or 2 parts by weight and 2 atoms of oxygen or 32 parts by weight. A numeral placed before a whole formula similarly multiplies all the symbols written immediately after it, thus $2H_2SO_4$ indicates two molecules of sulphuric acid, or 2 (98) parts by weight.

If we know the composition of the substance we cause to undergo chemical change and also that of the resulting products, we can express the change entirely by symbols,

thus sulphuric acid and zinc react forming the gas hydrogen and the solid substance zinc sulphate. This may be expressed as follows:

Zinc		Sulphuric acid		Zinc sulphate		Hydrogen
Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2
		$2 + 32 + 64$		$65 + 32 + 64$		
65	+	98	=	161	+	2
parts by weight		parts by weight		parts by weight		parts by weight (or 22·32 litres).

Since in any chemical change no loss of matter occurs and there is no change of mass, the weights of the bodies involved in any reaction must exactly equal the weights of the products of that reaction. It does not follow, however, that an equation in which the weights are arithmetically correct is also chemically correct, for in order to write a chemical reaction in this way, we must know that such a reaction does actually take place, and we must also know the composition of the resulting products.

It is the invariable custom to put the formulæ for the reacting substances on the left, and those for the products on the right, having the sign = between them, this latter being best regarded as "produces" rather than as "equals." Certain chemical reactions, however, proceed in one way under certain conditions, but in the opposite way under different conditions, that is, they are *reversible reactions.* Calcium carbonate on heating gives off carbon dioxide and leaves lime, but under other conditions lime combines with carbon dioxide, forming calcium carbonate once more. Such a reaction is most conveniently written:

$$CaCO_3 \rightleftharpoons CO_2 + CaO.$$

Valency or Atomicity.—Although we may have arrived at a satisfactory value for the atomic weight of an element, we are still ignorant of the combining capacity of the element: in other words, does one atom of an element always combine with one atom of any other element, or

are multiples involved? We find on experimenting, that different elements exhibit quite different powers of combination. Hydrogen, for example, combines atom for atom with chlorine to form hydrochloric acid, or 2 atoms of hydrogen with 1 of oxygen to form water, or 3 atoms with nitrogen to form ammonia, or 4 atoms with 1 of carbon to form methane. Clearly for each element there must be some definite *atom-fixing power or valency*, and for convenience we again refer to hydrogen as unity, since no element has a lower atom-fixing power. Beginning with the last of the above elements, we find this value in relation to hydrogen is respectively 4, 3, 2, and 1, and to express this we say that these elements are quadrivalent, trivalent, divalent, and monovalent respectively.

With the oxides of iron already mentioned (p. 27) we have seen that two equivalents are indicated. Now it is impossible for fractions of atoms to take part in a change, therefore the valency of the atom of iron must be variable also. The first oxide has an equivalent of 28, and that of the second 18·66, but the atomic weight of iron is 56. The valency then of iron in each case must therefore be 2 and 3, for then we have $28 \times 2 = 56$, and $18{\cdot}66 \times 3 = 56$. In such cases it is usual to adopt the higher number.

We may regard any chemical compound as composed of two parts called "radicles." These radicles may be either elementary or consist of groups of associated atoms which pass into and out of combination as a whole, the group SO_4 which occurs in all sulphates, NO_3 in all nitrates for example. The radicles have also a definite valency, and before a correct chemical formula can be written for any compound, the valency of the combining parts must be clearly established. As will be seen later, there are good grounds for assuming that all atoms or associated groups of atoms (SO_4 NO_3, etc.) can carry definite electrical charges, and the atom-fixing power always depends upon the relative positive and negative charges of the atoms.

The following table gives a list of the common positive and negative radicles.

	Positive. Kations.		Negative. Anions.	
		MONAD		
	H + Hydrogen		OH − hydroxyl	
Metallic Radicles	Na + Sodium		Cl − chloride	*Acid Radicles*
	K + Potassium		Br − bromide	
	NH_4 + Ammonium		I − iodide	
	Ag + Silver		Fl − fluoride	
	Hg + Mercurous		NO_3 − nitrate	
			ClO_3 − chlorate	
		DYAD		
	Ba + + Barium		SO_4 − − sulphate	
	Sr + + Strontium		SO_3 − − sulphite	
	Ca + + Calcium		S − − sulphide	
	Mg + + Magnesium		CO_3 − − carbonate	
	Zn + + Zinc		(O − − in oxides)	
	Fe + + Ferrous			
	Ni + + Nickel			
	Sn + + Tin			
		TRIAD		
	Bi + + + Bismuth		PO_4 − − − phosphate	
	Fe + + + Ferric			
	Al + + + Aluminium			
		TETRAD		
	C + + + + Carbon			

Hydrogen and hydroxyl are separated from the other radicles, since they behave in quite a distinct manner from the others. The resulting classes of substances which are obtained by the combination of a metallic and acid radicle may be summarised as follows:

Hydrogen	+	Hydroxyl	=	Water
Hydrogen	+	Acid radicle	=	Acid
Metallic radicle	+	Acid radicle	=	Salt
Metallic radicle	+	Hydroxyl	=	Base

If now we desire to write a correct formula for any compound it is essential that the positive and negative

charges assumed in the radicles entering into it shall exactly balance, thus for ferrous sulphate there are two positive charges in the ferrous radicle (Fe^{++}) and two negative charges in the sulphate radicle (SO_4^{--}), hence the correct formula is $Fe^{++}SO_4^{--}$, whilst for ferric sulphate we must write $(Fe^{+++})_2(SO_4^{--})_3$ in order to obtain a balance. Of course, in all ordinary formulæ we omit the indication of the charge, and simply write $FeSO_4$ and $Fe_2(SO_4)_3$.

Empirical and Molecular Formulæ.—From the mere analysis of a compound we are only enabled to ascertain the relative number of atoms present in a given weight, and not the actual number in the molecule. We may therefore write a formula which expresses in the simplest form the number of atoms present, and such a formula is an *empirical* one. For example, carbon forms with hydrogen a compound, which on analysis gives the following percentage composition :—

Carbon	...	...	...	92·3 per cent.
Hydrogen	...	...	...	7·7 ,,

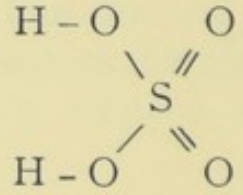
The simplest ratio of the atoms of each element present will be found by dividing the percentage of each element by the atomic weights. Thus, $\frac{92{\cdot}3}{12} = 7{\cdot}7$, and $\frac{7{\cdot}7}{1} = 7{\cdot}7$; in other words, for every one atom of carbon there is one atom of hydrogen, and the empirical formula is CH.

On taking now the density of this gas we find it to be 13, hence its molecular weight is 26; and this can only be possible with 2 atoms of carbon and 2 atoms of hydrogen in the molecule, for then we have the respective weights $24 + 2 = 26$, and the formula which expresses this must be C_2H_2. Such a formula is termed a *molecular formula*, and it expresses the actual number of atoms in the molecule.

Graphic and Constitutional Formulæ.—From the chemical behaviour and the valency of the constituent atoms in a compound we are able to write formulæ which express in a

graphic manner the relative arrangement of the atoms in the molecule. A word of warning is necessary as to the interpretation of such formulæ, for they cannot represent the actual conditions existing in a molecule where the atoms are in constant motion, but such a conventional method of expressing the facts is of great service.

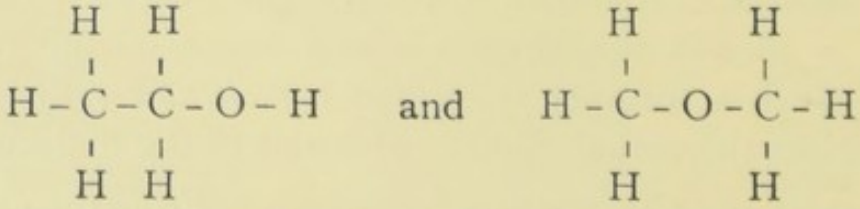
For each atom of hydrogen with which an element is capable of entering into combination we attach a "dash" to the symbol: thus, carbon is a tetrad, uniting with four atoms of hydrogen, which may be expressed $-\overset{|}{\underset{|}{C}}-$ or $C\equiv$. If we wish to write such a formula for sulphuric acid (H_2SO_4), we can only do it in one way which will agree with its properties and the known valency of its constituent atoms—



Such formulæ are termed "*graphic.*"

In organic chemistry many compounds are known which have exactly the same chemical composition but entirely different properties, such bodies being termed "*isomeric.*" Formulæ which express these differences in chemical behaviour thus become necessary. We have for example two compounds, both of which have the molecular formula C_2H_6O, ordinary alcohol being one, but they differ entirely in properties.

Graphic formulæ which express these differences may be written thus—



The same thing may be more shortly expressed by writing respectively—

$CH_3.CH_2.OH$ and $CH_3.O.CH_3$

when we get what is known as a *constitutional formula.*

A constitutional formula not only shows the number of atoms of each element present, but it expresses in a condensed form the characteristic behaviour of the compounds in any chemical reactions in which they take part.

CHAPTER III.

HYDROGEN.

Preparation—Properties—Weight—Effect upon sound—Solubility—Diffusion of gases — Military ballooning — Chemical behaviour of hydrogen.

IT has been shown that water can be decomposed into, or built up from, two gaseous constituents, hydrogen and oxygen, and the properties of these gases will now be considered.

Hydrogen.—This gas is only very rarely found free in Nature, sometimes occurring in the emanations from volcanoes, and in meteorites. Spectroscopic investigations, however, show that it is present in large quantities in the atmosphere of the sun. In combination it forms one-ninth by weight of water, and also occurs in ammonia, sulphuretted hydrogen, and in all animal and vegetable tissues.

Hydrogen was known in the 16th century under the name of "inflammable air," but it was not until 1766 that its properties were fully examined by Cavendish.

Preparation.—The gas is most conveniently prepared for experimental purposes by acting upon dilute sulphuric acid with the metal zinc: for this purpose zinc, which has been granulated by pouring it into water whilst molten, thus increasing the surface, is placed in the two-necked bottle (A, Fig. 4), and water enough to cover the metal is then poured in, sulphuric acid being added a few drops at a time by means of the thistle funnel (B) which passes, gas-tight, through a cork fitting the neck of the bottle, and terminates below the surface of the liquid. The addition of the acid causes an immediate evolution of gas, which is conducted by the leading tube (C) below the surface of water in the pneumatic trough (D), where it can be collected in cylinders by the displacement of water. The first portions of gas

which escape must not be collected, being an explosive mixture of hydrogen and the air which originally filled the generating bottle.

The reaction which takes place may be represented by the equation—

Zinc		Sulphuric acid		Zinc sulphate		Hydrogen
Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2.

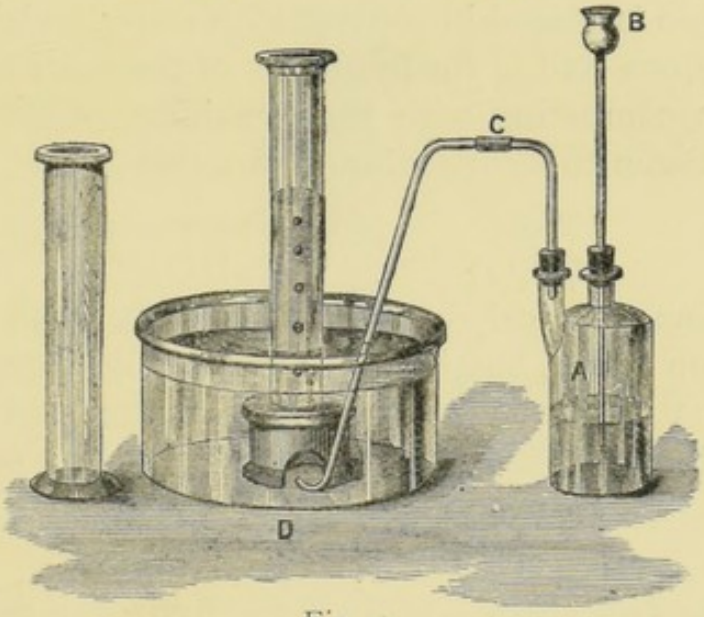


Fig. 4.

In its physical properties hydrogen is most unmistakably non-metallic, but in all its chemical relations with other elements it behaves so like a metal that in considering the reactions in which it takes part we often look upon it as one. In the preparation of hydrogen from zinc and sulphuric acid we have the hydrogen atoms turned out of their combination with the sulphur and the oxygen by the chemically stronger zinc. In the same way we can replace the hydrogen in water by certain other metals, which, combining with the oxygen, set free the gaseous hydrogen. If we pass steam, the vapour of water, over iron heated to a dull red heat, the iron combines with the oxygen, forming an oxide of iron, whilst the hydrogen escapes free. This interchange we may represent by the equation—

Water vapour		Iron		Triferric tetroxide		Hydrogen
$4(H_2O)$	+	$3Fe$	=	Fe_3O_4	+	$4(H_2)$.

This method of obtaining hydrogen is perhaps the cheapest and best when large quantities of the gas are required and purity is not an essential.

Some metals like iron have the property of decomposing water at a red heat; others, like sodium and potassium, break it up at ordinary temperatures; whilst gold and silver are unable to decompose it at all.

If sodium is placed in contact with water a violent action takes place, one-half of the hydrogen of the water is liberated, the sodium combining with the remainder of the hydrogen and the oxygen to form sodium hydroxide—

Sodium		Water		Sodium hydroxide		Hydrogen
Na_2	+	$2(H_2O)$	=	$2(NaHO)$	+	H_2.

The same chemical reaction takes place when potassium is thrown on water, but in this case the heat generated by the combination of the metal with the oxygen and part of the hydrogen is so great that the escaping gas is set on fire.

Potassium		Water		Potassium hydroxide		Hydrogen
K_2	+	$2(H_2O)$	=	$2(KHO)$	+	H_2.

In these two cases only half the hydrogen contained in the water is liberated, but if the sodium hydroxide or potassium hydroxide be again acted upon with excess of sodium or potassium the remaining atom of hydrogen is turned out.

Sodium hydroxide		Sodium		Sodium oxide		Hydrogen
$2(NaHO)$	+	Na_2	=	$2(Na_2O)$	+	H_2.

Properties.—By whichever method prepared, hydrogen, when pure, is a colourless gas, without taste or odour; it has no poisonous action on life, and may be breathed for a few moments, but will destroy life when inhaled for any length of time by excluding the oxygen of the air, required for respiration, from the lungs.

Hydrogen has no action on test papers or lime water; it does not support combustion, but itself burns in contact with oxygen with a non-luminous but intensely hot flame, water being the only product of its combustion.

In burning it produces a greater heat than the same

weight of any other known substance—1 lb. of hydrogen in combining with 8 lbs. of oxygen giving out sufficient heat to raise 34,462 lbs. of water 1° C.

Up to the spring of 1895 hydrogen resisted all attempts to convert it into a liquid, but Professor Olszewski and Sir James Dewar have independently succeeded in liquefying it.

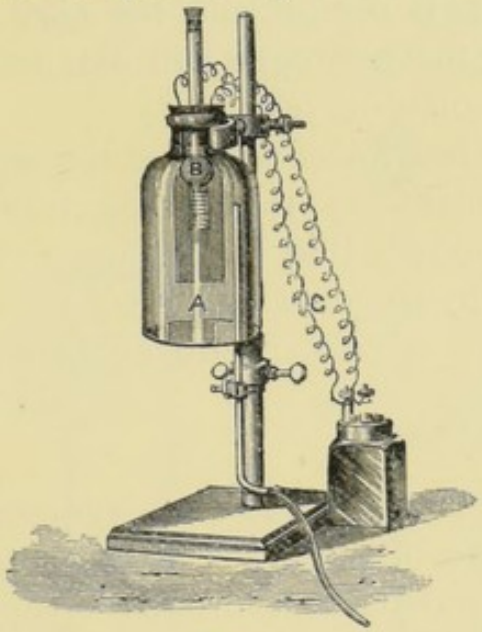


Fig. 5.

At atmospheric pressures liquid hydrogen has a boiling point of—253°, and Dewar has reduced liquid hydrogen to the solid state by the cold produced by its own evaporation.

Hydrogen is the lightest body known, being 14·47 times lighter than air, hence it is taken as the standard with which the weight of all others gases is compared.

Density.—The ratio by weight which a gas bears to an equal volume of hydrogen is called its density ; hence, when we say that the density of oxygen is 16, we mean that any volume of oxygen will weigh 16 times as much as the same volume of hydrogen measured under similar conditions of temperature and pressure.

Effect on Sound.—Sound will travel nearly four times as fast in hydrogen as in air ; but sounds generated in hydrogen are rendered so feeble as to be hardly audible when transmitted to air.

This may be shown by mounting an electric bell (B, Fig. 5) in an open gas jar (A) and while it is ringing, passing in hydrogen gas by the tube (C) from a reservoir of compressed gas. Hydrogen, being so much lighter than air, will collect at the top of the jar and surround the bell, causing the sound to almost entirely disappear; and if now the supply of gas is cut off, and the cork of the exit tube (E) be removed, the hydrogen will escape and the original intensity of the sound be restored.

Temperature has an effect upon the solubility of gases; less being dissolved as the temperature rises, but until lately it was supposed that 100 volumes of water dissolved 1·93 volumes of hydrogen without reference to temperature; this, however, is a mistake, hydrogen behaving in the same way as other gases.

Diffusion.—It is difficult to keep hydrogen for any length of time in a state of purity, as, if the containing vessel is not absolutely gas-tight, hydrogen escapes from it with great rapidity, whilst a small quantity of air finds its way into the residual gas; this is due to a property which gases possess of mingling together so that heavy and light gases tend to become evenly mixed, a property which is of the greatest importance in the economy of Nature.

This action, which is called "diffusion," takes place more slowly in the case of heavy gases than light ones (*see* p. 22), and experiment has shown that the "rate of diffusion" varies with the densities of the gases, the law being that "*Gases diffuse into one another at a rate which is inversely as the square roots of their densities.*" Hence, if a vessel of hydrogen be connected with a vessel of oxygen by means of a pin-hole—the square root of 1 (density of hydrogen) being 1, and the square root of 16 (density of oxygen) being 4—4 volumes of hydrogen will pass through into the oxygen during the first moment of time, whilst only 1 volume of oxygen will pass into the hydrogen, with the result that the pressure will be increased in the vessel con-

taining the oxygen, but will be decreased in that originally containing the hydrogen.

If a tube (A, Fig. 6) be connected with one of wider bore (B), which is closed an inch from the top by a porous plug of plaster of Paris (C) and closed above the plug by an india-rubber cork (D), diffusion through the plug may be shown by filling the tube with hydrogen, standing it in some coloured liquid (E) and removing the cork (D)

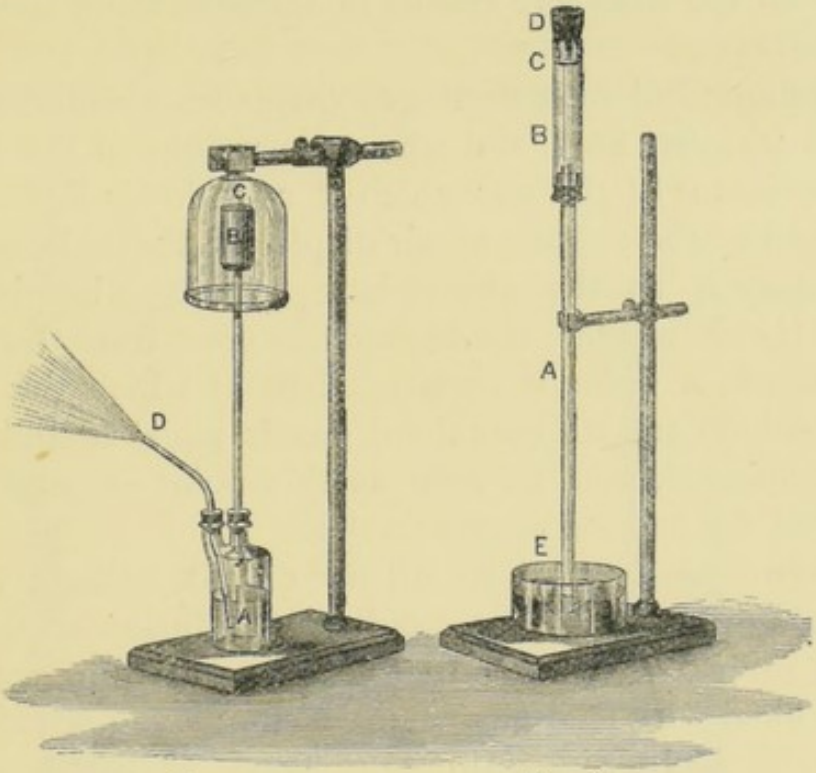


Fig. 6.

Fig. 7.

At once a rise of the liquid in the tube (A) takes place, showing that the hydrogen gas is diffusing out into the air faster than the air diffuses into the hydrogen, with the result that a reduction of pressure takes place in A and B, and water in consequence rises in the tube A. The same thing may be shown in the reverse way by the apparatus shown in Fig. 7. A two-necked bottle (A) is fitted with a tube ending in a porous earthenware vessel (C) such as is used in a galvanic cell. Over this a bell jar (C) containing hydrogen gas is placed, and the hydrogen diffusing in faster than the air can diffuse out, causes an increase of pressure

on the surface of the liquid in A, and drives some of it out from the jet D.

Ballooning.—The great lightness of the gas renders it very valuable for ballooning where a rapid ascent to a great height is desired; but its very lightness is a drawback where an ordinary balloon is wanted to keep afloat for some time, as the rapidity with which the gas diffuses causes it to quickly escape from any cracks or imperfections in the skin of the balloon.

A balloon full of a light gas displaces a volume of air equal to its own bulk, and when the weight of the balloon plus the weight of the gas which it contains is lighter than the weight of the volume of air displaced, the balloon rises; but inasmuch as the atmosphere rapidly diminishes in density (*i.e.*, in weight) the higher one goes from the surface of the earth, a point is soon reached at which the weight of the balloon and its contained gas is equal to the weight of air displaced, and as soon as this point of equilibrium is reached the balloon ceases to rise.

If hydrogen is used to fill an oil-silk balloon it gives great rising power, but the rapidity of diffusion soon brings it down again; whilst, if a long journey is required, a larger balloon filled with coal-gas would be employed, as although coal-gas is about eight times as heavy as hydrogen, still it is lighter than air in the proportions of 8 to 14·47, and the tendency to diffuse is far less.

At the present time great importance attaches to ballooning, from the fact that it is being adopted rapidly and on a very large scale for military and naval purposes.

A regular balloon corps is now attached to the army, and the hydrogen is carried compressed in steel cylinders on a waggon constructed for the purpose; and the balloon when required is filled from these, and is sent up with a rope attached to it, so that when observations have been made of the enemy's whereabouts it can be again drawn down, emptied, and packed away. For ordinary purposes

balloons are made of varnished silk; but the leakage from this would be too great if hydrogen were used, and the military balloons are now all made of a double and sometimes treble thickness of gold-beater's skin.

The hydrogen used in the military balloons is now all made by electrolysis of water, and its purity is so great that a lifting value of 71 pounds per 1000 cubic feet can be obtained. This enables a balloon of only 5000 cubic feet capacity to be used, which will lift the car containing an ordinary-sized man with the necessary apparatus, whilst the gas for filling it is contained in forty tubes weighing half a ton.

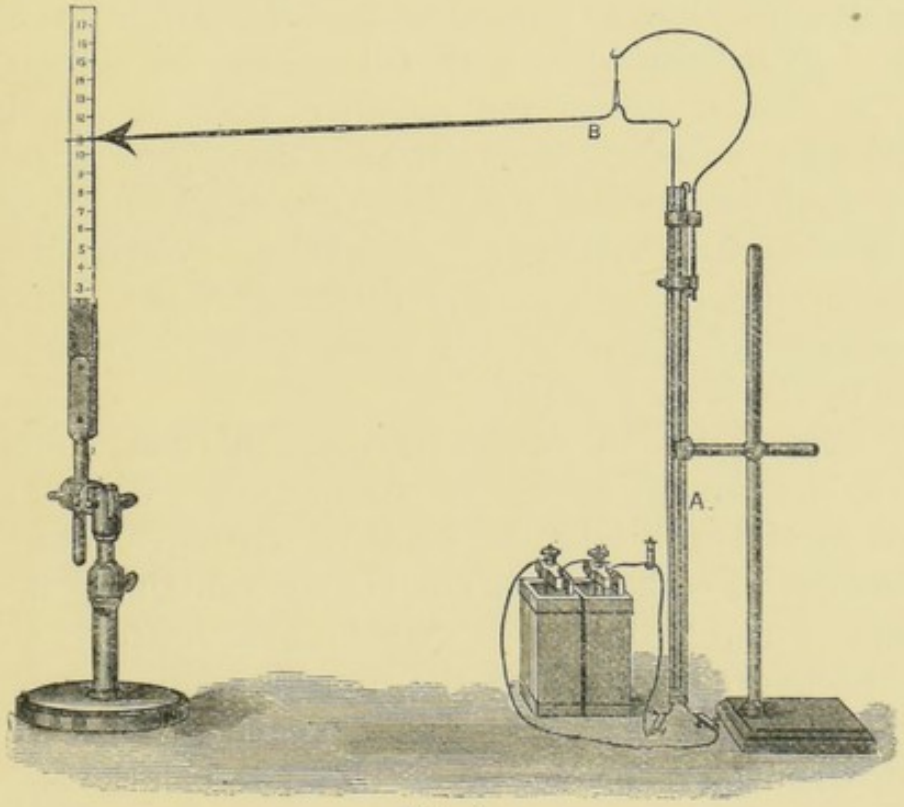


Fig. 8.

Chemical Behaviour.—Although the physical properties of hydrogen and its condition in the solid state are opposed to the idea of its possessing metallic properties, yet its chemical behaviour is such that it is often theoretically looked upon as being the vapour of a metal.

In the first place, when we decompose a solution of a

metallic salt by means of a galvanic current, we always find that the metal is liberated at the negative pole, or where the current leaves the liquid; and on decomposing water, rendered a conductor of electricity by addition of a few drops of sulphuric acid, we find that the hydrogen is liberated at the negative pole, that is, at the pole at which metals are always set free. Again, certain metals have the power of absorbing large quantities of hydrogen, and having absorbed it, they are found to have changed their physical properties, which points to the hydrogen having formed an alloy with them. The metal Palladium at ordinary temperatures absorbs no less than 376 times its own bulk of the gas, the alloy so formed being called Hydrogenium.

If a palladium wire, 2 ft. 6 in. long, be so arranged (Fig. 8) that it forms the negative pole in a galvanic circuit, with a large glass tube as a decomposing cell (A) and a platinum wire as the positive pole, on decomposing acidulated water hydrogen gas will be evolved on the surface of the palladium, and being occluded will cause an increase in length of the wire, which will be made visible by the lever arm (B).

Finally, hydrogen, under certain thermal conditions will replace many metals in compounds; whilst, under others, metals will take the place of hydrogen when they are brought in contact with compounds containing it. For instance, when hydrogen is passed over heated oxide of iron, the hydrogen replaces the iron—metallic iron is left and the hydrogen unites with the oxygen to form water—whilst, when zinc is acted upon by hydrochloric acid, the zinc turns out the hydrogen, which escapes free and zinc chloride is the resulting compound.

CHAPTER IV.

Chemistry of the Galvanic Battery.

Heat of chemical action converted into galvanic electricity—"Polarisation"—Arrangements adopted in various cells—Chemical action taking place in the "Daniell"—"Varley-Daniell"—"Menotti-Daniell"—"Leclanché"—"Grove"—"Bunsen"—"Bichromate" and secondary cells—Electrolysis—Electrolytes—Electro-metallurgy—Importance of the electro-chemical relations between metals on ships' bottoms—Muntz metal—Zinc protectors—Zinc sheathing—Mooring vessels.

NO chemical change can take place without being accompanied by a physical change, and the most ordinary physical manifestation accompanying chemical action is change of temperature.

For instance, when we acted upon dilute sulphuric acid with zinc, hydrogen gas was rapidly evolved, zinc sulphate was formed and considerable heat generated. The heat so generated may be used to boil ether or alcohol, and the vapour so generated might be made to do mechanical work, in the same way that the heat generated by burning coal may be made to boil water, and the steam then used for driving an engine—so converting the heat of chemical combination, a form of energy, into mechanical work. In this way one form of energy can be translated into other forms of energy; but, like matter, energy cannot be created or destroyed.

Conversion of Chemical Energy into Electricity.—When zinc decomposes sulphuric acid, energy is developed as heat, the energy being due to the rearrangement of the atoms in the sulphuric acid and the zinc, and by proper arrangements we can convert this heat into electricity.

Instead of taking granulated zinc, take a sheet of zinc

and place it in the dilute acid; the same action as before takes place, hydrogen is generated on the surface of the zinc and the zinc slowly dissolves as zinc sulphate; now place a sheet of copper in the acid but not touching the zinc, the action continues as before ; but now allow the copper to touch the zinc either below or above the surface of the liquid, or connect the two plates of dissimilar metal by a wire, the evolution of hydrogen on the surface of the zinc plate diminishes, and gas now appears on the copper plate.

If the plates be weighed before and after the action the weight of the copper plate will be found to be unchanged, whilst the zinc will have lost weight, and on testing the acid it will be found to contain large quantities of zinc sulphate in solution, showing that the zinc has continued to dissolve although the hydrogen has been coming off on the copper plate. If the wire which connects the two plates when in the acid solution be now examined, it will be found to possess properties it did not before, and if cut in the centre and one end be placed above the tongue and the other end under the tongue, a peculiar sensation and strong metallic taste will be experienced ; whilst if several such couples of zinc and copper be placed in vessels full of dilute acid, and the zinc of one be connected with the copper of the next, and so on, the two terminals being as before connected with a wire, a strong galvanic current will be found to be flowing through the wire, and if the wire be held over and parallel to a magnetic needle, the needle will be deflected and will tend to stand at right-angles to the wire, instead of pointing North and South. The current so produced, however, will soon diminish in strength, and will eventually cease.

If we examine the thermal conditions existing in the interior of the cell, we find that although we get heat given off by the solution of zinc in sulphuric acid under ordinary conditions, yet, when the zinc is dissolved in contact with a copper plate and a galvanic current is produced, the generation of heat diminishes in the cell, although the zinc dissolves more rapidly, that is, the heat which is generated by the

chemical action is converted into another form of energy, viz., electricity, and will again be converted into heat wherever resistance occurs.

All our batteries are dependent upon some such action as the solution of zinc in sulphuric acid for the production of electricity, and the chief differences in the forms of the batteries used consist of devices for maintenance of the current.

We have seen that commercial zinc placed in diluted sulphuric acid rapidly dissolves under ordinary circumstances; but if we use perfectly pure zinc and perfectly pure diluted sulphuric acid, no solution of the zinc or other action takes place until the second metal is introduced and brought in contact with it; hence it is evident that the purer the zinc and the purer the acid, the smaller the quantity that will be used up in the intervals when the battery is not in action. Perfectly pure zinc is not easy to obtain, but if we rub a clean surface of the metal with mercury the mercury dissolves the pure zinc and forms what we call an amalgam, and in this way only the pure metal is presented to the action of the acid, and the minimum amount is used up when the battery is not at work, all local action being done away with.

Polarisation.—We saw that when a galvanic current was produced by a sheet of zinc and a sheet of copper immersed in dilute sulphuric acid, that the current rapidly diminished in strength—a result partly due to the hydrogen liberated collecting on the copper or platinum plate and so opposing more and more resistance to the current, and also to the hydrogen setting up a counter electro-motive force; and in all forms of battery in ordinary use various devices are adopted to prevent this so-called "Polarisation of the plate."

The hydrogen acts in three ways in weakening the current: (1) being a non-conductor of electricity, the more hydrogen there is present, the more will the available surface of the copper or platinum be reduced in size, and therefore the smaller will be the acting surface; (2) the

freshly liberated (nascent) hydrogen deposited on the surface of the copper being electro-positive to zinc, will set up a current in the reverse direction of the original one; (3) when much zinc sulphate is present in the solution, the nascent hydrogen tends to decompose it and a deposit of zinc is formed on the copper, so that we practically have two plates of zinc opposing each other instead of a plate of zinc and a plate of copper.

The usual method employed for getting rid of the hydrogen is to surround the copper or platinum plate with some substance with which the hydrogen can combine and so prevent its deposition.

"*Daniell*" *Cells.*—In the "Daniell" and the "Varley-Daniell" this is done by separating the cell into two parts by a porous partition, placing in one the zinc and dilute sulphuric acid, and in the other the copper in a saturated solution of copper sulphate; the two liquids meet in the pores of the partition, but otherwise only mingle very slowly. The zinc is dissolved by sulphuric acid with formation of zinc sulphate, and nascent hydrogen coming off at the copper plate, being evolved in presence of copper sulphate, reduces it, forming sulphuric acid and depositing pure copper on the copper plate, the deposit tending rather to increase the current than otherwise.

In this way the current is rendered much more constant, but in spite of the porous partition, whether formed of unglazed earthenware or fearnought, there will always be a tendency on the part of the copper sulphate solution and zinc sulphate to mingle; and when the copper sulphate reaches the zinc plate, then copper is deposited on the zinc and at once weakens the current.

The current generated in a Daniell's cell is rarely as strong for the first few minutes as that generated by a single liquid cell, as the decomposition of the copper sulphate by the nascent hydrogen uses up a certain amount of chemical energy, and tends to create a current

in the opposite direction, so that it is only the difference between the two forces that we can utilise as a current; the various forms of the Daniell cell are therefore used where a continuous but not very strong current is required.

The "Menotti-Daniell," used for testing purposes, consists of an ebonite or glazed earthenware vessel, at the bottom of which is a tray of copper half-an-inch deep, filled with crystals of copper sulphate, above which is placed a diaphragm of fearnought, and on the top of this a layer of sawdust; the whole is moistened with water, and a slab of zinc is placed on the top of the sawdust and has connected to it a wire, a second insulated wire being in connection with the copper tray at the bottom of the cell.

In this case, the oxygen of the water molecule combines with the zinc, forming zinc oxide, and a rearrangement of the molecules takes place throughout the mass until the copper sulphate is reached; here the liberated hydrogen reduces the copper sulphate with formation of hydrogen sulphate and deposition of copper on the copper vessel, whilst the liberated sulphuric acid diffuses through the sawdust and dissolves the zinc oxide on the zinc plate which would otherwise tend to decrease the current; this action again tends to reproduce water, and so the action continues.

Leclanché Cell.—In the "Leclanché" cell we have the copper plate replaced by a block of dense carbon — the form used being that obtained from gas retorts, where the heat has caused some of the hydrocarbons present to be decomposed with deposition of carbon, the deposit being especially hard and dense; this carbon plate is surrounded with manganese dioxide (MnO_2), which is found native as the mineral dioxide "Pyrolusite," and this is rendered a better conductor of electricity especially after it has been in use by mixing with it small pieces of carbon. The carbon plate, surrounded by the mixture of

pyrolusite and carbon, is now placed in a porous vessel or bag made of porous material such as canvas or flannel, this standing in an outer cell containing a saturated solution of sal-ammoniac or ammonium chloride, in which the zinc plate is immersed.

When not in circuit, that is, when there is no connection between the zinc and carbon plate, the zinc is unacted upon, but, directly connection is made, the ammonium chloride is decomposed, zinc chloride is formed, ammonia gas and hydrogen are liberated, the hydrogen appearing as before at the carbon plate; here, however, it meets with the pyrolusite, and combines with some of its oxygen, forming a lower oxide of manganese and water.

This water then dissolves up some more crystals of the ammonium chloride, an excess of which is present, and so the strength of the solution is maintained. The advantages of the Leclanché cell are, that there is no waste of material when not in use, as the zinc and ammonium chloride do not react until the circuit is closed, and that a solid being employed to absorb the hydrogen, no mixing of liquids takes place.

The manganese dioxide gives up its oxygen so slowly that when short circuited for a time it acts almost like a single liquid cell and the carbon is quickly polarised, whilst zinc oxy-chloride and a compound of zinc, chlorine, and ammonia, having the formula $ZnCl_2\ 2NH_3$, are formed, which quickly weaken the current.

For intermittent work, however, it is one of the best and most lasting of the forms of battery, although not constant.

The current required for firing fuses is considerable, and few batteries of convenient form will give it for any length of time, but for a moment the Leclanché battery is sufficiently powerful, and it will fire the fuses as rapidly as would ever be required in actual practice, and is therefore adopted for firing purposes.

For Service use, the Leclanché is made up in sets of

six cells, called "Ship's firing battery," which is used for firing the guns; three-cell boat batteries are used for firing outrigger torpedoes, and ten-cell batteries are used for firing submarine mines and countermines.

In the form of cells used for these purposes internal resistance is, as far as possible, reduced by exposing a large surface of zinc and carbon in each cell, and using a partition of fearnought between the mixture of carbon and pyrolusite and the ammonium chloride solution containing the zinc.

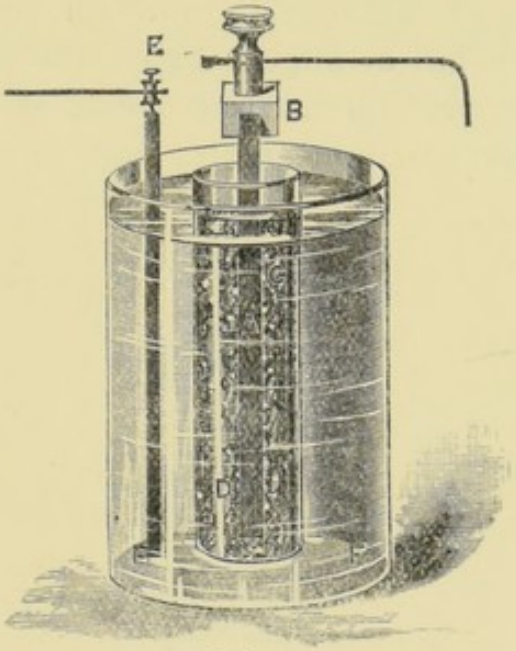


Fig. 9.

In the Leclanché cell (Fig. 9) A is the carbon plate on to which is cast the lead connection and binding screw (B); D is the mixture of pyrolusite and carbon surrounding the carbon plate; and E the zinc plate immersed in the saturated ammonium chloride solution (F), the fearnought partition being replaced by the porous cell (C).

In one form of Leclanché the carbon and manganese dioxide are cast into blocks or sticks, and these are fixed to the carbon plate by elastic bands, the whole being kept from contact with the zinc by having a piece of coarse sacking wound round it.

Grove's Cell.—Grove's cell depends upon the solution of zinc in sulphuric acid to generate the current, whilst the negative metal present is platinum, and the liberated hydrogen is oxidised to water by strong nitric acid.

A U-shaped zinc plate (Fig. 10) is immersed in dilute sulphuric acid contained in an ebonite or earthenware vessel, and inside the zinc is placed a porous earthenware pot containing strong nitric acid, in which is the platinum plate.

The zinc dissolves in the dilute sulphuric acid, forming zinc sulphate and hydrogen; and on the circuit being completed, the usual arrangement of the molecules takes place throughout the liquid, the molecule of hydrogen being liberated on the platinum plate, and in presence of the

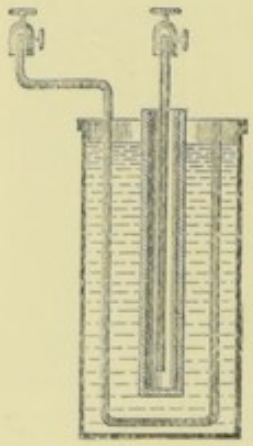


Fig. 10.

nitric acid which oxidises it forming water, whilst the acid is itself reduced with evolution of nitrous fumes. The reactions taking place may be represented as—

Zinc		Sulphuric acid		Zinc sulphate		Hydrogen.
Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2

and

Hydrogen		Nitric acid		Water		Nitrous acid.
H_2	+	HNO_3	=	H_2O	+	HNO_2.

The nitrous acid becoming concentrated breaks up into—

Nitrous acid		Nitrogen trioxide		Water.
$2(HNO_2)$	=	N_2O_3	+	H_2O.

The nitrogen trioxide forms the red fumes escaping after the battery has been some time at work, and is further oxidised by the oxygen of the air into nitrogen tetroxide, which also is a reddish-brown gas.

Nitrogen trioxide		Oxygen		Nitrogen tetroxide.
$2(N_2O_3)$	+	O_2	=	$4(NO_2)$.

Some authorities prefer to express the reaction as at once forming the tetroxide.

Nitric acid		Hydrogen		Water		Nitrogen tetroxide.
$2(HNO_3)$	+	H_2	=	$2(H_2O)$	+	$2NO_2$.

Nitrous acid has a green colour, which can be readily noticed in the acid after use, whilst the gaseous oxides may

Fig. 11.

be seen escaping as red fumes above the battery, and have a highly corrosive action, rendering the use of this form of cell, in a confined space, for any length of time very objectionable. It has a very high electro-motive force and small internal resistance, so that a very strong current can be obtained from it; but, on account of the fumes and the initial expense of the platinum, it is only used when a very powerful current is wanted for a short time.

In "Bunsen's" cell the same construction and liquids are used, but the platinum is replaced by carbon.

Bichromate Cell.—The Bichromate battery is a single liquid cell in which zinc is acted on by dilute sulphuric acid,

and the hydrogen generated is oxidised to water by chromic acid, the negative element being formed by carbon plates.

A very ordinary form of this battery is shown at Fig. 11, in which the zinc plate can be drawn up above the surface of the liquid when the cell is not in use, whilst the carbon plates, not being acted on, remain stationary.

The cell is charged with potassium bichromate and sulphuric acid, which react upon each other, forming potassium sulphate and chromic acid—

Potassium bichromate		Sulphuric acid		Water		Chromic acid		Potassium sulphate.
$K_2Cr_2O_7$	+	H_2SO_4	+	H_2O	=	$2(H_2CrO_4)$	+	K_2SO_4.

On lowering the zinc into the mixture in solution and completing the circuit, hydrogen is evolved, thus—

Zinc		Sulphuric acid		Zinc sulphate		Hydrogen.
Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2

and the hydrogen liberated on the carbon plates is then attacked by the chromic acid which is reduced, and in presence of sulphuric acid forms chromium sulphate and water—

Chromic acid		Sulphuric acid		Hydrogen	Chromium sulphate		Water.
$2(H_2CrO_4)$	+	$3(H_2SO_4)$	+	$3H_2$	=	$Cr_2(SO_4)_3$	+ $8(H_2O)$

the chromium sulphate and potassium sulphate so formed crystallising together when the cell is exhausted, as chrome alum, $K_2SO_4.Cr_2(SO_4)_3$.

Secondary or Reversible Batteries.

Gas Battery.—When water is decomposed in a voltameter with platinum electrodes, and the battery is taken away and the wires connected with a galvanometer in circuit, the electrodes being in contact with the oxygen and hydrogen, the gases gradually recombine and a galvanic current will once more flow through the wires, but in an opposite direction to the direct current formed by the battery; and such a source of electricity is called a gas battery.

Storage Cells.—In the same way, if a strong current be passed through slightly acidulated water, between two lead

plates, one lead plate becomes oxidised on the surface and coated with a brown powder known as peroxide of lead or lead dioxide (PbO_2); if now the battery be removed and the two electrodes be connected by a wire, a current in the reverse direction is produced and one-half the oxygen from the lead dioxide appears on the other lead plate, coating it with litharge or lead monoxide (PbO), so that both plates are now coated with lead monoxide and are alike, and the current ceases.

In practice, the plates are made of cast lead in the form of grids, the holes being about $\frac{1}{4}$-inch square, and one plate has the holes filled with a paste of lead monoxide (PbO) and dilute sulphuric acid, whilst the other has the holes filled with red lead (Pb_3O_4); these plates are then placed in a vessel of dilute sulphuric acid and connected to a dynamo or other generator of electricity, and a current passed from the red lead (Pb_3O_4) plate to the lead monoxide (PbO) plate. The lead monoxide is reduced to spongy metallic lead, whilst the red lead is oxidised to lead peroxide.

The plates so prepared are arranged alternately in a vessel and are kept apart by india-rubber plugs, the vessel being filled with dilute sulphuric acid (sp. grav. 1·15), and on connecting them a current is set up. Before discharging we find lead dioxide (PbO_2) at one plate and metallic lead at the other, both in presence of sulphuric acid. After action we have lead sulphate ($PbSO_4$) and water (H_2O) formed—both plates having become coated with lead monoxide (PbO), which has then been converted by the sulphuric acid into lead sulphate ($PbSO_4$). The action is a reversible one, and may be expressed by the equation—

Lead		Lead peroxide		Sulphuric acid		Lead sulphate		Water.
Pb	+	PbO_2	+	$2H_2SO_4$	$\rightleftharpoons$	$2PbSO_4$	+	$2H_2O$.

In all the cells mentioned it is found that the current generated flows from the metal which is acted upon, and which is called the positive metal, through the liquid of the cell to the metal unacted upon and called the negative

metal, and then back to the positive metal by the wire connecting the plates outside the cell; and if we break the conducting wire the two ends are called poles, the negative pole being the end connected with the positive metal and the positive pole the one connected with the negative metal of the cell. If these two poles be now dipped into any solution which will conduct electricity, the current (if sufficiently powerful) in passing through the liquid will set up chemical decomposition.

Electrolysis.—If two platinum plates, each connected with one pole of a galvanic cell, be brought into a vessel containing pure water, no current is found to pass, and we find that the solution of certain substances, such as sugar, still leaves the water a non-conductor of electricity. On the other hand, if such substances as the acids, hydroxides or salts, be added to the water, we find that it readily permits of the passage of the current, and certain well-marked changes take place, such as the evolution of gas at the surface of the platinum plates.

Any solution which permits of the passage of an electric current is termed an *electrolyte*, and the change brought about *electrolysis*.

Ionisation.—Physical phenomena point to the conclusion that all these substances, which in a state of solution (or rendered liquid by fusion) become electrolytes, are in a state of dissociation, that is, the constituent elements or groups of elements which go to form the molecule have separated into a simpler form, termed *ions*, each of which carries a strong electrical charge, which may be either positive or negative. On now bringing into such a solution the platinum plates in connection with a cell, one of which is positively charged (called the *anode*) and the other negatively (called the *kathode*), it follows that the positive plate will attract the negatively charged ions, and repel those carrying a positive charge, and the reverse will of course be true with the negative plate. Those negative

ions which travel to the anode are spoken of as *anions*, and those positive ions which travel to the kathode as *kations*.

When the positively charged kation touches the negatively charged kathode it loses its charge, and similarly the anions are discharged, and the discharging of the anions and kations proceeds at the same rate, so that those remaining in solution are always equivalent to each other. The ions of hydrogen and the metals are positively charged (kations), whilst oxygen and the acid radicles are negatively charged (anions).

A point of great importance is that, so long as the ion exists, it carries its electrical charge and is incapable of acting on the solvent, but the moment it is discharged it is free to enter into new associations, either escaping free or decomposing the solvent. Thus, in a solution of salt we have free sodium ions and free chlorine ions, but the sodium does not react in its customary manner until the ion has been discharged, when the atom, or it may be molecule, of sodium attacks the water with liberation of hydrogen, the net result being therefore on the electrolysis of such a solution that hydrogen is set free at one plate and chlorine at the other.

The electrolysis of potassium sulphate solution may be taken as a typical one where these secondary charges take place. The net result of the electrolysis is simply the liberation of hydrogen and oxygen, which is brought about by the potassium kation being attracted to the negative plate (kathode) where it loses its charge, immediately attacking the water with the formation of potassium hydroxide and the liberation of hydrogen which escapes. Similarly, the negative anion SO_4 discharges at the anode, and reacts with the water, forming sulphuric acid and setting free oxygen.

Potassium sulphate.

$$\underbrace{K_2SO_4}.$$

KATHODE OR - POLE.			ANODE OR + POLE.		
Potassium		Water	Sulphate radicle		Water
K_2	+	$2(H_2O)$	SO_4	+	H_2O
Potassium hydroxide		Hydrogen	Sulphuric acid		Oxygen
$= 2(KHO)$	+	H_2.	$= H_2SO_4$	+	O.

The production of alkaline potassium hydroxide and sulphuric acid may be shown by dividing a glass cell into two compartments by means of a vegetable parchment diaphragm (B Fig. 12) and filling the cell with a strong solution of potassium sulphate coloured with a freshly prepared decoction of red cabbage, which turns green with alkalis and red with acids. On now putting the platinum electrodes (AA) into the solution, one in each compartment, and passing the current from a five-cell Grove's battery, decomposition occurs and the purple solution turns bright red in the compartment containing the anode, and green in contact with the kathode.

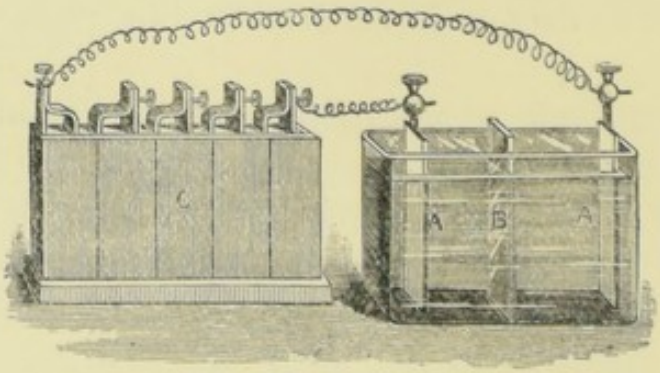


Fig. 12.

Diagrammatic Representation of Changes auring Electrolysis of a Solution of Potassium Sulphate—

I.

The solution is shown in a cell with porous partition down the centre, the liquid being coloured with red cabbage

solution. No current is yet passing, and in the liquid are molecules of K_2SO_4 and free + K ions and $-SO_4$ ions.

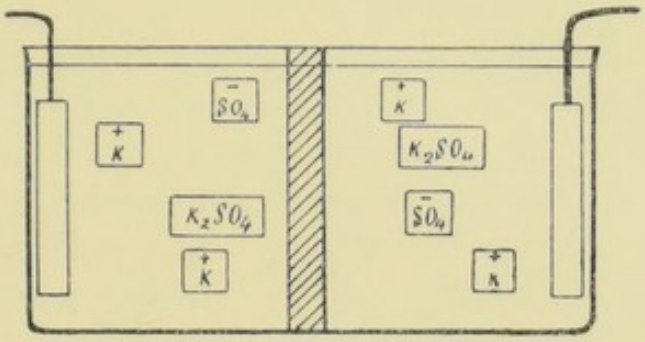


Fig. 13.

II.

The current is now passed through the liquid, the + K ions are repelled by the anode and attracted by the kathode, the reverse occurring with the $-SO_4$ ions. More K_2SO_4 molecules dissociate.

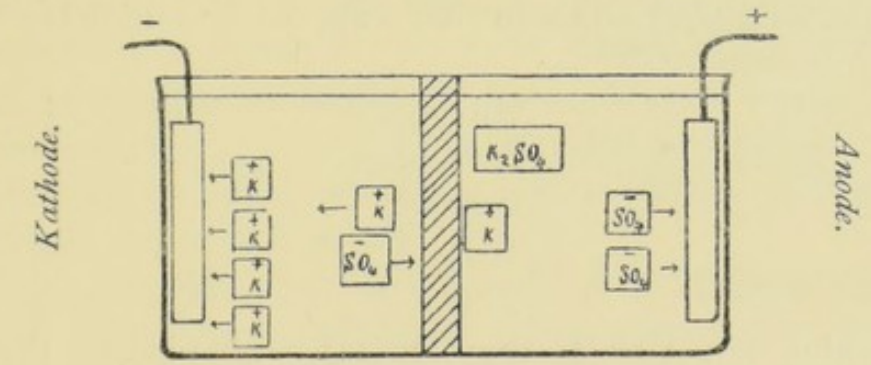


Fig. 14.

III.

On reaching the kathode the + K ions are discharged, becoming atoms which can react as K itself does on water,

liberating H at the kathode, and similarly the discharged SO_4 groups liberate O at the anode.

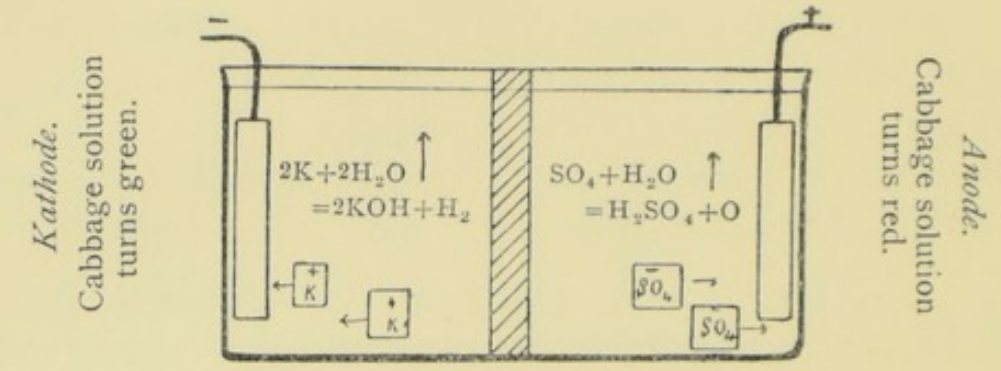


Fig. 15.

Electro-Chemical Series.—Metals may be arranged in a series, the order of which is determined by the power possessed by the metal of depositing other metals from solution, *i.e.*, being electro-positive to the metals preceding it.

Thus mercury will deposit silver from solution, copper will precipitate mercury from its salts. Iron leads to the deposition of copper, zinc will replace iron, and so on.

Arranging the metals in this way, we should have them in the following order:—

Silver,
Mercury,
Copper,
Iron,
Zinc,

and, taking any two of these metals and placing them in contact in a saline solution, we should find that the metal lowest in the list would be electro-positive to the metal above it, and that a galvanic action would be started, in which the electro-positive metal would be vigorously attacked.

Galvanic Action on Ships' Plates.—A great interest attaches to the electro-chemical behaviour of metals upon

each other when excited by various solutions from the bearing this has upon the condition of the bottoms of ships.

Already in the days of wooden vessels this question arose, because copper sheathing was used to protect the timber from fouling, and the attacks of the *Teredo*, a kind of worm which bores its way into wood. The copper acted in preventing fouling by reason of its forming, in contact with the salt water, oxy-chloride of copper, which being poisonous, helped to retard the growth of the germs of certain forms of animal and vegetable life, whilst the wasting of its surface from this cause threw off barnacles and such forms of fouling as obtained hold in spite of the poisonous character of the copper salts.

Protectives.—The copper, however, wasted too rapidly; and, to prevent this, Faraday advised the use of plates of zinc in metallic contact with the copper, the result being that the zinc and copper excited by the salts in the sea water formed a galvanic couple in which zinc was the positive metal, *i.e.*, the metal dissolved; but this retardation of the destruction of the copper defeated its own purpose, as the copper did not waste or, as it is called, "exfoliate" with sufficient rapidity to throw off barnacles and weed; indeed, the current tended to cause the deposition of earthy matters on the copper surface, which formed a surface well adapted to the growth of marine life.

The same idea was also carried out in Muntz's metal, an alloy of copper and zinc, which, while it had the advantage of being able to be rolled hot into sheets, also caused, when in sea water, less waste of the sheathing, but with the saving of metal the fouling at once increased.

With iron and steel ships the same considerations come into play, and great care has to be taken to prevent the skin of the ship from becoming electro-positive to any other substance: for instance, the bearings of the screw shaft and the valves for the escape of waste water, etc., are made of

alloys containing copper; and near these points, where excited by salt water, a strong galvanic action would be set up, attended with rapid destruction of the steel of the shafting, rudder post and plating near these points, because the iron or steel would be electro-positive to the copper alloy, and would be therefore the metal acted upon. In order to prevent this, a zinc protector, consisting of a heavy casting of this metal, is placed round all openings where copper or copper alloys are present, and the zinc being more electro-positive than the iron, places the iron in the electro-negative condition, so that, whilst the iron is unacted upon, the zinc rapidly dissolves.

Many attempts have been made to cover the bottom of iron ships with zinc plates, to prevent corrosion; but, apart from the mechanical difficulties of attachment, it is found that the large surface of metal exposed causes so strong an action that the zinc sheathing wastes too rapidly to make it a practical method.

Protective Compositions.—Many modifications of this idea, such as using very finely-divided zinc as a constituent of protective compositions, have been advocated and tried, with results which will be discussed under the heading of Protective and Antifouling Compositions.

The consideration of the electro-chemical relations of the metals must also be taken into account in the mooring of vessels, as it is evident that the making fast of an iron or steel vessel to a copper-bottomed ship, or even to another iron vessel coated with certain compounds of copper in use as antifouling compositions, would be sufficient, if the connection were made by a steel hawser or even a wet rope, to set up galvanic action at the expense of the iron ship. For the same reason, copper-bottomed vessels should not be made fast to iron piers, or iron or steel ships to piers protected by copper.

Corrosion due to Galvanic Action.—Electrical disturbances and galvanic action, leading to rapid increase in corrosion,

are set up in the plates of a ship by many causes which are but little understood. When plates are riveted together, and the iron of the rivets varies in composition from the iron of the plate, corrosion is often extremely rapid, and either tends to eat away the rivet or enlarge the hole in the plate. Currents also are sometimes set up from one part of a plate to a second portion of the same plate which has undergone a different amount of stress; whilst temperature also adds to these risks, as when a plate of metal is warmed and is in metallic contact with a similar plate which is cooler, a galvanic current is induced at the expense of the heated metal.

The fact that the double bottom plates near the boiler corrode more rapidly than similar plates in other parts of the vessel is undoubted, and the increase in temperature near the boiler is the only factor of difference. It is also to be noted that the plates at the bottom of the cellular spaces which are kept cool by contact with the sea water do not corrode, and cases are not wanting in which parts of a plate, which get locally warmer than other parts, although the difference can only be a few degrees, corrode much more rapidly than the cooler portions.

The double bottom plates and the outer plates of the vessel are in metallic contact by means of stays, and the bilge water will in most cases provide a saline solution through which the current can freely flow, and under these conditions the action of hot moist air upon the plates nearest the boiler sets up a galvanic current with the cold plates in contact with the sea, in which the hot plates play the part of the positive metal, and thus become rapidly corroded.

CHAPTER V.

OXYGEN.

Occurrence—Preparation of oxygen gas—Oxygen obtained from air—Properties of oxygen—Combustion in oxygen—Ozone.

OXYGEN, the second constituent of water, is the most abundant of the elements, and is not only found in air and water, but also constitutes nearly 45 per cent. of the solid crust of the globe.

The fact that a film forms on the surface of many metals when heated in air was known from the earliest times, and in 1774 Priestly, working with mercuric oxide—the film so formed on mercury—found that it could be decomposed at a high temperature into mercury and oxygen, which was thus first prepared and examined, and a little later Lavoisier showed the part it plays in combustion and gave it the name it now bears.

Preparation.—It may be prepared—

1. By heating mercuric oxide, which breaks up into mercury and oxygen.

Mercuric oxide		Mercury	Oxygen.
$2(HgO)$	=	$2Hg$	O_2.

2. By heating "Pyrolusite" (manganese dioxide) in an iron vessel to a high temperature, when it gives off one-third of its oxygen and forms a lower oxide.

Manganese dioxide		Trimanganic tetroxide		Oxygen.
$3(MnO_2)$	=	Mn_3O_4	+	O_2.

Some oxides, like mercuric oxide, give off the whole of their oxygen on heating; others, of which the peroxide of manganese or manganese dioxide may be taken as a type, only give off a portion, whilst the members of a third

class, like potassium or sodium oxide, are not broken up by heat.

3. By passing steam and chlorine through a hot porcelain tube, when the hydrogen and chlorine unite to form hydrochloric acid and oxygen is liberated. On collecting the gases over water the hydrochloric acid is absorbed and only pure oxygen is left.

Steam + Chlorine = Hydrochloric acid + Oxygen

$$2(H_2O) + 2Cl_2 = 4(HCl) + O_2$$

4. By heating potassium chlorate, a compound of potassium, chlorine, and oxygen, when oxygen is liberated and potassium chloride left. The final reaction may be represented by the equation—

Potassium chlorate = Potassium chloride + Oxygen

$$2(KClO_3) = 2(KCl) + 3O_2.$$

This is the usual method adopted for its preparation.

The decomposition may be effected much more rapidly by mixing a little manganese dioxide with the potassium chlorate, which effects the breaking up of the chlorate at a much lower temperature and more rapidly. If the temperature rises much above 300° the gas comes off with great violence, and is often found to contain small traces of chlorine, liberated by the decomposition of some of the potassium chloride.

The relative rates at which the gas is evolved from the chlorate alone, and from chlorate mixed with the manganese dioxide, may be shown by performing the operations side by side (Fig. 16) and collecting the gas formed in two cylinders of equal size (AA). The chlorate is heated in the retort (B) fitted with a delivery tube leading under water in the pneumatic trough, whilst the mixture of chlorate and manganese dioxide is heated in the Florence flask (C), and the gas, before collecting, is washed by passing through water in the two-necked bottle (D).

Preparation from Air.—Oxygen existing free in the atmosphere, one might expect that air would be the cheapest

and best source from which to obtain it; but nitrogen, with which the oxygen in air is diluted, has such feeble affinities for other substances that it is impossible to absorb it so as to leave the oxygen pure, whilst, if oxygen be extracted by chemical means, it forms such strong compounds that it cannot easily again be liberated from them.

As we have already seen, it can be made to combine with mercury, and the oxygen can then be recovered from the mercuric oxide, but this is a tedious and costly process. The best method yet devised for extracting oxygen from air is by heating barium oxide in a current of air; the barium oxide takes up another atom of oxygen, becoming barium dioxide, and this, if heated to a higher temperature than that at which it was formed, gives off its acquired oxygen, becoming barium oxide once more.

Barium peroxide		Barium oxide		Oxygen
$2(BaO_2)$	=	$2(BaO)$	+	O_2.

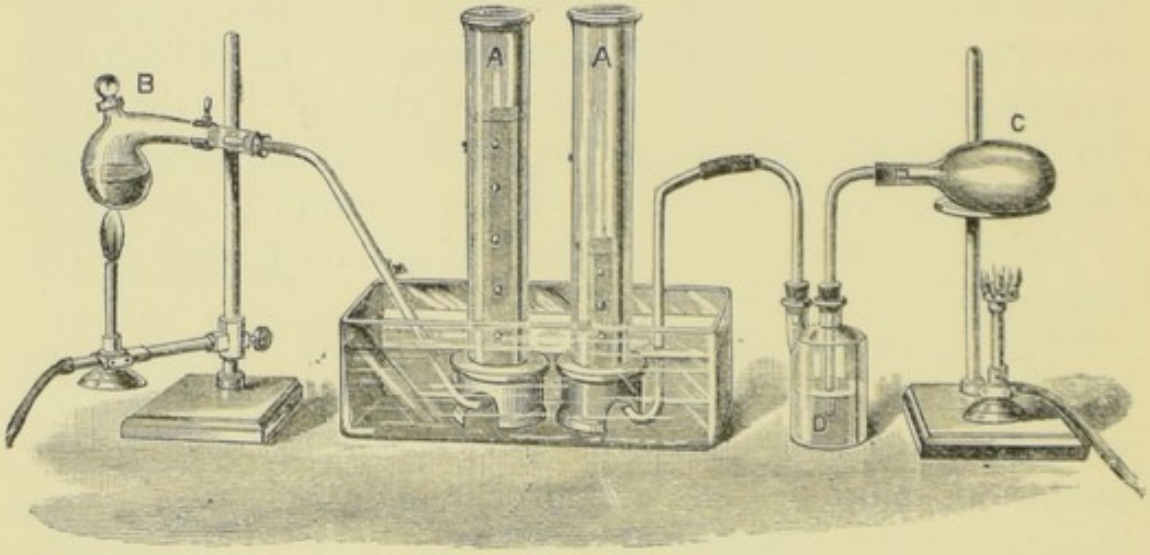


Fig. 16.

It is upon this reaction that the process of Brin Frères, for the production of oxygen on a large scale, is based.

Anhydrous barium oxide is placed in a series of retorts heated to 650° C., whilst air carefully freed from carbon dioxide is passed through them under a pressure of about 10 lb.; the oxygen being absorbed by the barium oxide produces barium peroxide, the flow of air is then stopped

and the pressure is taken off, and a partial vacuum produced, when decomposition takes place, nearly pure oxygen being evolved.

One kilo. of barium oxide will produce nearly fifty litres of oxygen at each operation.

Another process for obtaining oxygen from air depends upon the fact that the oxides of manganese when heated in contact with alkalis and air are able to absorb oxygen, and will give it off again when heated in a current of steam.

Air is now liquefied on the commercial scale by the process introduced by Linde and Hampson of cooling the air to below - 190° C. by compression and dilatation, and, as liquid nitrogen has a lower boiling point than liquid oxygen, the gas first escaping from the liquid air is chiefly nitrogen whilst the latter portions are so rich in oxygen that for all practical purposes it may be looked upon as oxygen.

There are other methods for preparing the gas, but they are of scientific rather than general interest.

Properties.—Oxygen is a colourless, odourless, tasteless gas ; it is 16 times heavier than hydrogen, hence we say its density is 16, and it is only slightly soluble in water—at ordinary temperatures 100 volumes of water dissolve 3 volumes of the gas, but the amount so dissolved depends to a great extent upon the temperature ; at 0° C. 100 vols. water dissolve 4 vols. of gas, whilst at 20° C. they dissolve only 2·8 volumes. Small as this amount is, it plays a most important part in Nature, as it is required for the support of fish life and also tends to destroy any refuse organic matter which may find its way into the water.

All bodies which burn in the air burn with increased brilliancy in oxygen gas.

The gas has no action upon test papers, and does not turn lime water milky.

Liquid Oxygen.—Oxygen can only be condensed to the liquid state by a combination of intense cold and pressure,

a temperature of - 118° C. and a pressure of 50 atmospheres being required for its liquefaction.

Liquid oxygen has a light blue colour, and boils under atmospheric pressure at a temperature of - 183° C.

Detection.—When free, oxygen can be detected—

(*a*) By its power of supporting combustion.

(*b*) By its forming a reddish-brown gas when brought in contact with the colourless gas nitrogen dioxide.

(*c*) By its being absorbed by potassium pyrogallate with formation of a deep brown compound.

Ozone.

At the close of the eighteenth century Van Marum observed a peculiar odour whilst working his great electrical machine at Haarlem; and in 1840 the Swiss chemist, Schönbein, showed that when electric sparks are passed through oxygen, or buildings are struck by lightning, the same odour is observed; and it has been found that the odour is due to a modification of oxygen, to which, on account of its odour, the name of ozone has been given. If ozone be experimented upon, it is found to be identical in chemical composition with oxygen, but physically it is very different, being also much more active in its oxidising properties, and corroding substances upon which oxygen has no effect.

Allotropes. — When elements change their physical properties and activity and yet remain unaltered in composition they are said to be "allotropes," or allotropic modifications, and this allotropism is due to a rearrangement of the particles of which the mass is built up. Thus ozone is said to be an allotropic modification of oxygen. The analogous change of properties in compounds is called "isomerism": for instance, chalk and Iceland spar are both of them calcium carbonate and are chemically the same, although they differ widely in physical properties; hence they are said to be "isomeric."

Preparation.—Oxygen may be made to assume the condition of ozone in several ways—

1. By the passage of silent electric discharges, as when oxygen passes between surfaces charged with opposite electricities.

This may be effected in the apparatus shown in Fig. 17. An inner tube (A), closed at its lower end, is sealed near the upper end into a slightly larger tube (B), the latter being prolonged for some distance below (A) and terminating in a small manometer (D) partly filled with strong sulphuric acid suitably coloured. The tube B is furnished with a stopcock near its junction with the inner tube, and again just above the manometer. Surrounding a portion of these two tubes is a glass cylinder (C). Four platinum electrodes are provided at *pp* and *p'p'*.

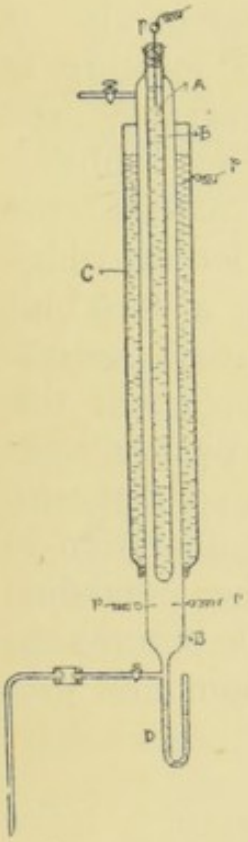


Fig. 17.

The inner tube (A) and outer cylinder (B) are both nearly filled with dilute sulphuric acid, leaving a free gas space between them. Oxygen is slowly bubbled through a wash-bottle containing strong sulphuric acid, and led into the apparatus at the upper tap. On connecting the electrodes (*pp*) with an induction coil, a silent discharge passes between the inner and outer acid tubes, the oxygen in this contracted space being rapidly converted into ozone, which is delivered through a suitable side lead tube fitted to the lower tap with corks.

2. Ozone is formed in contact with substances undergoing slow oxidation in presence of moisture.

This is shown by half covering a freshly scraped stick of phosphorus with water, in the bottom of a large flask, the mouth of which is closed by a glass plate. The phosphorus slowly oxidises at the expense of some of the oxygen of the air, the products dissolving in the water,

whilst a considerable amount of ozone is at the same time formed, and may be detected by the usual tests.

3. When water is decomposed by electrolysis, a certain proportion of the oxygen liberated at the positive pole is converted into ozone.

Detection and Properties.—Ozone may be recognised by its smell, which can be detected when there is only one volume of ozone present in $2\frac{1}{2}$ million volumes of air. It can also be detected by its action upon a mixture of starch and potassium iodide, which is generally used spread upon paper. Ozone has so strong an oxidising action that it breaks up potassium iodide, oxidises the potassium to potassium oxide and liberates iodine, which immediately combines with the starch, forming a deep blue coloured compound. Other bodies beside ozone possess this same power, so that it is well to supplement this test by a second, which consists of red litmus paper dipped in a dilute solution of potassium iodide. In contact with ozone the decomposition of the iodide and liberation of potassium oxide takes place as before, the potassium hydroxide formed with water being a strong alkali, turns the red litmus to blue. This result, taken in conjunction with the other, affords a sure test for ozone.

Potassium iodide		Ozone		Water		Potassium hydroxide		Oxygen		Iodine
$2KI$	+	O_3	+	H_2O	=	$2KOH$	+	O_2	+	I_2.

Ozone will exercise a bleaching action on dilute solutions of indigo, and attacks vulcanised caoutchouc with great rapidity; brought in contact with metallic mercury, it soon tarnishes the surface owing to formation of oxide. It is entirely absorbed by oil of turpentine, and at a temperature of 149° C. ozone is at once re-converted to ordinary oxygen.

Ozone is slightly soluble in water, 1000 volumes of water dissolving about 4·5 volumes of ozone.

On passing ozonised oxygen through a coil, cooled down to −131° C. by surrounding it with boiling oxygen,

ozone can be condensed to an intensely blue liquid having a boiling point of - 106° C.

Although ozone in small quantities is one of the strongest agents in Nature for the destruction and removal of waste organic matter, yet when present in large quantities it is a violent poison, acting as an intense irritant to the eyes and nose, and rapidly proving fatal.

The facts that oxygen can be converted into ozone by the brush discharge, and the ozone so formed reconverted into oxygen by the action of heat, prove conclusively that ozone and oxygen are merely allotropic modifications of the same element.

Occurrence.—It is generally stated that ozone is present in country air and in the air over the sea, but the question has not been definitely settled up to the present, for the effects usually ascribed to this gas may really be due to the presence of small quantities of hydrogen dioxide.

It is supposed that ozone is formed during the evaporation of water, hence an extended surface like the sea is favourable to its formation, and, the sea air containing but few impurities for the ozone to oxidise, the amount present remains fairly constant; in towns, however, where coal is consumed, the air contains sulphur dioxide and also organic impurities, which, being oxidised by the ozone, reduce it to oxygen once more.

Molecular Composition.—When oxygen is converted into ozone, at most one-fifth of the volume present, generally far less, is ozonised, and the formation of ozone is attended with a contraction of volume. This may readily be shown with the apparatus already described (p. 69). If oxygen is allowed to fill the space between the inner and outer tubes, on closing both taps and passing the silent discharge, in the course of a minute or so a considerable contraction will be observed from the movement of the acid in the manometer (D). If now the wires from the induction coil are connected to p' p' and

sparks passed through the gas, the expansion due to the heating and consequent decomposition of the ozone may be demonstrated. We have seen that the density of oxygen on the hydrogen scale is 16, and if we take 12 volumes of oxygen and pass the brush discharge until contraction ceases, we find we have 11 volumes of mixed ozone and oxygen left; on introducing some turpentine into this mixture all the ozone is absorbed, and 9 vols. of oxygen are left, so that 2 vols. of ozone were present and had been produced by 3 vols. of oxygen. Let the 12 vols. of oxygen weigh $12 \times 16 = 192$, then the 9 vols. left will $= 16 \times 9 = 144$, $192 - 144 = 48$, the weight of the 2 vols. of ozone formed, and therefore 1 vol. of ozone $= 24$, or one-third heavier than an equal vol. of oxygen.

It has been shown that the molecule of oxygen contains two atoms and is represented by O_2, and it follows, therefore, from the above experiment that ozone must contain 3 atoms in the molecule and will be represented as O_3, its great tendency to act as an oxidising agent being due to the loose hold it has on the third atom of oxygen which is readily given up to an oxidisable substance. This view of its action is corroborated by the fact that when ozone oxidises a substance no alteration in volume of the gas takes place.

Mercury		2 vols. Ozone		Mercuric oxide		2 vols. Oxygen
Hg	+	O_3	=	HgO	+	O_2.

CHAPTER VI.

OXIDES AND SALTS.

Oxides, acid-forming, basic, and neutral—Salts—Formation—Normal, acid, and basic salts—Decomposition of salts—Nomenclature.

IN any process of ordinary combustion in which the oxygen of the air or oxygen gas alone takes part, we have a process termed *oxidation*. If the substance burning is an element, then the product is termed an *oxide*. All the elements, with the exception of fluorine, combine with oxygen, and even fluorine forms some double salts containing oxygen, such as the oxy-fluoride of phosphorus. If we examine carefully the characters of the different oxides, we shall find they admit of ready classification into three groups.

1. *Acid-forming Oxides.* — If we burn sulphur, phosphorus, or carbon in oxygen, we obtain oxides which on solution in water form *acids*, and these acid-forming oxides are sometimes called *anhydrides*.

Sulphur		Oxygen		Sulphur dioxide or sulphurous anhydride
S	+	O_2	=	SO_2

Phosphorus		Oxygen		Phosphorus pentoxide or phosphoric anhydride
$4P$	+	$5O_2$	=	$2(P_2O_5)$

Carbon		Oxygen		Carbon dioxide or carbonic anhydride
C	+	O_2	=	CO_2

And these combined with water yield the corresponding acids—

Sulphur dioxide		Water		Sulphurous acid
SO_2	+	H_2O	=	H_2SO_3.
Phosphorus pentoxide		Water		Phosphoric acid
P_2O_5	+	$3H_2O$	=	$2(H_3PO_4)$.
Carbon dioxide		Water		Carbonic acid
CO_2	+	H_2O	=	H_2CO_3.

These substances have a strongly acrid taste, and when brought in contact with a blue vegetable colouring matter called litmus turn it red. Lavoisier having observed this fact, supposed that all bodies burnt in oxygen would yield acids as the product of their combustion, hence he gave it the name of oxygen, from the Greek *oxus* (acid) and *gennao* (I produce). If we carefully examine the products of the combustion of various elements in oxygen, we find that *it is only the non-metallic which on combustion yield these strongly acid oxides.*

2. *Basic Oxides.*—On the other hand, we may burn such substances as sodium, zinc, or magnesium in oxygen, when we obtain oxides of a totally different character.

Sodium		Oxygen		Sodium monoxide
Na_2	+	O	=	Na_2O.
Zinc		Oxygen		Zinc oxide
Zn	+	O	=	ZnO.
Magnesium		Oxygen		Magnesium oxide
Mg		O	=	MgO.

These are all known as *basic oxides*, and they have the characteristic property of neutralising acids to form salts. Should the basic oxide dissolve in water, a *hydroxide* results.

Sodium oxide		Sulphuric acid		Sodium sulphate		Water
Na_2O	+	H_2SO_4	=	Na_2SO_4	+	H_2O
Sodium oxide		Water		Sodium hydroxide		
Na_2O	+	H_2O	=	2NaHO		
Sodium hydroxide		Sulphuric acid		Sodium sulphate		Water
2NaHO	+	H_2SO_4	=	Na_2SO_4	+	$2H_2O$.

The solution of a soluble basic oxide (the hydroxide) has exactly opposite properties to the solution of an acid oxide, for it turns red litmus blue, and, as we have seen above, can

exactly neutralise the solution of an acid-forming oxide (an acid).

Many basic oxides cannot combine with water to form the hydroxide—zinc and iron for example; but the hydroxide can be obtained in other ways, and by raising it to a high temperature loses water, leaving behind the basic oxide itself, thus establishing the relationship.

Zinc hydroxide		Zinc oxide		Water
$Zn(HO)_2$	=	ZnO	+	H_2O.

Every element which forms at least one basic oxide is classed by chemists as a metal.

3. *Neutral Oxides.* — Certain oxides exhibit neither acid-forming nor basic properties—in other words they are neutral oxides; but these must be regarded as somewhat exceptional: for example, water H_2O, and nitrogen dioxide NO.

Salts.—We have already seen that the neutralisation of an acid by a basic oxide or hydroxide results in the production of a salt, and further, a salt has been described as resulting from the combination of a metallic radicle with an acid radicle (p. 32).

Formation of salts—

(*a*) In certain cases salts may be formed by the direct union of the elements: thus sodium or copper readily combine with chlorine to produce the respective chlorides.

Sodium		Chlorine		Sodium chloride
Na	+	Cl	=	NaCl.

Copper		Chlorine		Copper chloride
Cu	+	Cl_2	=	$CuCl_2$.

(*b*) By neutralisation of an acid by a base (p. 74).

(*c*) By the replacement of the hydrogen in an acid by a metal.

Zinc		Sulphuric acid		Zinc sulphate		Hydrogen
Zn	+	H_2SO_4	=	$ZnSO_4$	+	H_2.

Zinc		Hydrochloric acid		Zinc chloride		Hydrogen.
Zn	+	2HCl	=	$ZnCl_2$	+	H_2.

Attention must be called here to the fact that when nitric acid is employed no hydrogen is evolved, because, although we may regard it as the first result of the action on the metal, the freshly liberated hydrogen attacks the excess of nitric acid, breaking it down with the liberation of oxides of nitrogen.

Normal, Acid, and Basic Salts.—Normal salts are those in which all the replaceable hydrogen of the acid has been replaced by an equivalent weight of a metal or compound radicle, as—

$ZnSO_4$	...	...	zinc sulphate,
$(NH_4)_2SO_4$	...	...	ammonium sulphate.

It is clear, however, that in the case of a dibasic or tribasic acid all the hydrogen atoms need not be displaced by a metallic radicle in the formation of a salt: thus from phosphoric acid (H_3PO_4) we may have—

Na_3PO_4	...	Normal sodium phosphate,
Na_2HPO_4	...	Disodium hydrogen phosphate,
NaH_2PO_4	...	Monosodium dihydrogen phosphate.

Such salts are termed "acid" salts, but the name is misleading, as it implies that such salts are always acid in their properties (action on litmus); but this is by no means the case, for the neutrality or otherwise of any salt, whether "normal" or "acid," entirely depends on the relative strength of the basic and acidic radicles which go to form it.

A neutral normal salt results from a strong acid and strong base, or weak acid and weak base.

An acid normal salt results from a strong acid and weak base.

An alkaline normal salt results from a weak acid and strong base.

Sodium sulphate (Na_2SO_4), for example, is neutral, copper sulphate ($CuSO_4$) acid, and sodium phosphate (Na_3PO_4) alkaline.

Similarly, what is strictly speaking an *acid salt*—that is,

one still containing replaceable hydrogen—is generally acid in its reaction to litmus, but many are neutral and some even slightly alkaline, this altogether depending on the relative weakness of the acid radicle. Disodium hydrogen phosphate (Na_2HPO_4), for example, has a slightly alkaline reaction.

Basic Salts.—Basic salts are those in which there are present one or more molecules of the normal salt with a certain excess of the base, either oxide or hydroxide. Sometimes they are defined as formed by the union of one metallic radicle with two or more negative radicles, one of which is hydroxyl (OH); but common usage does not altogether agree with this, for the salt HgO, $HgCl_2$ is known as basic mercuric chloride. Two examples may be given of basic salts which agree with the above definition.

$Hg{+}{+}(OH^-)(NO_3^-)$ ... Basic mercuric nitrate.

$2(Pb^{++}CO_3^{--}).Pb^{++}(OH^-)_2$ } Basic lead carbonate (white lead).

Decomposition of Salts.—By far the greater proportion of chemical reactions result from the decomposition or interaction of salts. A large number of salts break up into simple substances by the action of heat alone: thus calcium carbonate splits up, the acid anhydride (CO_2) escaping, and the basic oxide, lime, (CaO) remaining. On the other hand, the sulphates of many metals, barium sulphate for example, may be raised to a very high temperature and suffer no change. Other salts, like sodium chloride, fuse without decomposition.

From the solutions of two soluble salts entirely fresh salts may be formed by a mutual exchange of radicles, thus—

Mercuric chloride		Potassium iodide		Potassium chloride		Mercuric iodide
$HgCl_2$	+	$2KI$	=	$2KCl$	+	HgI_2.

For any pair of salts we can write such an equation, but it does not follow that the chemical change indicated

can really take place. The only general rule we can follow is, that when by such an interaction it is possible for an insoluble salt to result, then such reaction will always take place. The mercuric iodide above is insoluble, and therefore is precipitated. This simple rule is really the basis of all our methods of analysis in which we rely upon the precipitation of definite compounds.

When an acid acts on the salt of another acid, it will always replace more or less of the acid radicle originally present in the salt, and the extent to which it does this is a rough measure of the relative strength of the acids. Thus acetic acid is a very weak acid, and from its salts, the acetates, is very easily displaced by almost any other acid.

It is of great importance, as determining how far one acid may replace another from a salt, to know the conditions under which the reaction will be brought about. Thus sulphuric acid and potassium or sodium nitrate interact, and at the temperature attainable in a glass vessel only one hydrogen atom of the two present in the sulphuric acid can be replaced by the metal:—

Sodium nitrate		Sulphuric acid		Sodium hydrogen sulphate		Nitric acid
$NaNO_3$	+	H_2SO_4	=	$NaHSO_4$	+	HNO_3

whilst, if we can employ a higher temperature, the hydrogen is totally replaced.

Sodium hydrogen sulphate		Sodium nitrate		Sodium sulphate		Nitric acid
$NaHSO_4$	+	$NaNO_3$	=	Na_2SO_4	+	HNO_3.

If the acid liberated can be removed in any way from the vicinity of the interacting bodies, then a strong acid will completely replace a weaker acid from its salts.

Similarly, a powerful base may completely remove a weaker one from combination if the liberated base can escape as gas, or in some other manner.

Calcium hydroxide		Ammonium chloride		Calcium chloride		Water		Ammonia
$Ca(HO)_2$	+	$2NH_4Cl$	=	$CaCl_2$	+	$2H_2O$	+	$2NH_3$.

Nomenclature.—No uniformity of nomenclature exists amongst the older elements, names having been given to them as they were discovered, these old familiar names being in most cases retained. The more recently discovered metallic elements end in *-um*, as calci*um*, sodi*um*, etc.

When two elements combine together, the name of the metal is written first, and the non-metal is given the termination *-ide*, as—

Calcium combines with oxygen to form calcium ox*ide*.

Sodium combines with chlorine to form sodium chlor*ide*.

Lead combines with sulphur to form lead sulph*ide*.

When the same metal forms several distinct compounds with different proportions of the same non-metal, a prefix is added to the non-metal to signify the number of atoms of it present in the molecule.

An atom of lead forms with one atom of oxygen—lead *mono*xide.

An atom of lead forms with two atoms of oxygen—lead *di*oxide.

When the metal and non-metal are present in the ratio of two atoms of the metal to three of the non-metal, we use the prefix *sesqui*—

Fe_2O_3 is iron *sesqui*oxide (or diferric trioxide).

When a metal forms two classes of compounds, one of which corresponds to a lower oxide and the other to a higher, the lower class is distinguished by adding the suffix *-ous* to the metal, whilst the higher class has the termination *-ic*: for instance we have—

Ferrous chloride ($FeCl_2$) and ferric chloride ($FeCl_3$).

Mercurous iodide (HgI) and mercuric iodide (HgI_2).

To be systematic, the acids must be regarded as salts of hydrogen, hence H_2SO_4 is, strictly speaking, hydrogen sulphate, but by common usage we generally revert to an older system of nomenclature and speak of it as sulphuric acid: so with HNO_3, hydrogen nitrate, as nitric acid.

If an acid contains only one other element than hydrogen, we give the prefix *hydro-* and the termination *-ic*, and the salts derived from it end in *-ide*: *e.g.*, HCl *hydro*chlor*ic* acid, NaCl sodium chlor*ide*.

If an acid contains two or more elements other than hydrogen, it either terminates in *-ous* or *-ic*, the former indicating the lower state of oxidation: thus H_2SO_3 sulphur*ous* acid, and H_2SO_4 sulphur*ic* acid. The salts in each case end in *-ite* and *-ate*.

This system of nomenclature may be conveniently summarised as follows:—

Elements present		Acid	Salt
Two only—*hydro*	...	*-ic*	*-ide*
Three or more	...	*-ous*	*-ite*
		-ic	*-ate*

Acids are generally spoken of as mono-, di-, or tri-basic, according to the number of replaceable hydrogen atoms present, which is equivalent to the valency in each case: thus HCl is monobasic, H_2SO_4 dibasic, and H_3PO_4 tribasic.

CHAPTER VII.

COMBUSTION.

The Phlogistic theory—Lavoisier shows combustion to be active chemical combination — Reciprocal combustion — Slow combustion—Decay—Respiration—Spontaneous combustion—Point of ignition—Spontaneous ignition of charcoal, coal, oily rags, hay, etc.—Combustion by combined oxygen.

THE theory of combustion which was generally accepted during the eighteenth century was that every combustible body contained within itself the products of combustion combined with a "something" called Phlogiston, and when the substance was burnt this phlogiston escaped, giving the flame or incandescence of combustion, whilst the products were set free. This theory could not, however, for long stand the test of exact experiment, and as soon as the use of the balance was introduced into scientific research it was found that when any substance underwent combustion the products weighed more than the body did before it was burnt, the reverse of what might have been expected had the "Phlogistic theory" been correct.

The discovery of oxygen, by Priestly, in 1774, enabled Lavoisier, a few years later, to explain the actions which take place when substances burn in air, and it was to him that we owe the first enunciation of the fact that ordinary combustion is the result of vigorous chemical combination between the body burnt and the oxygen of the air, and that the products formed were heavier than the substance consumed, because the air in which the combustion had taken place had lost in weight, owing to the using up of some of its oxygen during the action.

The enunciation of these truths by the great French philosopher was one of the most important steps in the

history of science; but with increase of knowledge it is found necessary to still further widen the views held with regard to combustion.

Reciprocal Combustion.—We must take care not to fall into the error of looking upon those substances which will burn in air or oxygen as the only combustibles, and oxygen as the only supporter of combustion, as these terms are purely relative, and a substance ordinarily looked upon as a combustible may, under altered conditions, become a supporter of combustion. Indeed, a body like coal-gas, which burns in air or oxygen, will support in turn the combustion of air, and it can be experimentally shown that it is just as easy to have a flame of air burning in coal-gas, as under ordinary conditions to have a flame of coal-gas burning in the air.

Again, many cases of combustion will take place without the presence of oxygen or those substances generally looked upon as combustibles, and a metal like antimony can be caused to undergo brilliant combustion by throwing it in a powdered condition into an atmosphere of the gas chlorine, although neither the metal nor the gas answer to our general ideas as to combustible or supporter of combustion.

Definition.—If all cases of combustion are carefully examined, it is found that in them there is a body with certain definite properties of its own, uniting itself with something else to form what are called the products of combustion, which are equal in weight to the sum of the weights of the two bodies uniting, and which have characteristic properties differing from those of the original substances, an action which is termed Chemical combination; and extended experiments show that, in order to obtain a true conception of combustion, it must be looked upon as *the evolution of heat during active chemical combination.*

Rate.—The rapidity with which chemical combination takes place varies to a very great extent with surrounding circumstances, and, inasmuch as heat is rapidly dissipated, it often happens that where a chemical combination is slow

the heat produced by it is got rid of as rapidly as it is generated, so that the temperature of the mass becomes but little raised, and escapes detection by our senses. For instance, if a steel watch-spring is taken, and a small piece of German tinder attached to the end of it is ignited, and plunged into a vessel of oxygen gas, the combustion of the tinder ignites the watch-spring, which burns away in the gas with the greatest brilliancy, and the evolution of heat is sufficient to fuse the metal, the final result being that the watch-spring is converted into a chemical compound of iron and oxygen. If instead of bringing about the combination of the iron and oxygen in a few seconds it were allowed to remain in moist air for two or three months, combination with the oxygen of the air would result, and the metal would rust away; and if the weight of metal had been the same in each case, and the same weight of oxygen had been combined with, exactly the same amount of heat would have been generated in each case, but in the rapid combustion of the metal this heat, being all generated in a few seconds of time, would have made its presence perfectly manifest, whilst when the same action is spread over a long period, as in the rusting of the metal, the heat being dissipated as it is generated escapes our notice.

Effect of State of Division.—In this case the heat generated by the combustion of the iron with oxygen was made manifest by raising the burning metal to a high temperature in the presence of oxygen free from the diluting action of the inert nitrogen which is mixed with it in the air, and so increasing the rapidity of the action, but the same thing can be done by taking the iron in a very finely-powdered condition, so that a very large surface shall be exposed to the action of the oxygen of the air.

The influence which the rapidity of oxidation, owing to fineness of division, has upon temperature may be shown by taking a hard glass tube containing some finely-divided oxide of iron, passing a slow current of dried

hydrogen gas over it, and at the same time heating it. The hydrogen reduces the oxide, forming water, which escapes as steam, whilst the iron is left in the form of a very finely-divided powder, which is allowed to cool in the stream of hydrogen gas; the tube is then sealed up whilst still full of gas, care being taken to admit no air. On opening such a tube (called a *pyrophorus*) and shaking out the finely-divided metal into the air, it is at once oxidised, and the heat generated is sufficient to make it red-hot, the fine state of division affording a very large surface for the oxygen of the air to act upon. If now the same weight of iron be taken in a compact form such as wire, it would take several months, if not years, for air and moisture to convert it into oxide, and the heat generated is spread over so long a period of time that we do not perceive its evolution; but even in this case, if surrounded with a non-conductor, a temperature might be reached which would be perceptible. A case of this kind occurred during the manufacture of one of the Mediterranean telegraph cables, which was enclosed in a strong casing of iron wire and tightly coiled in water tanks, 163 miles of cable being wound in a coil 30 ft. in diameter. Owing to a leak in the tank which contained the cable, the water ran off, leaving the wire casing exposed to air, and the moist metal oxidised so rapidly that sufficient heat was generated to form considerable quantities of vapour, and to give rise to serious fears as to the softening of the insulating material of the core.

Slow Combustion.—Many cases of chemical combination with the oxygen of the air take place in Nature, which are so slow that the heat evolved during the action escapes our senses, and indeed all cases of decay are processes of this kind, and the action is termed *slow combustion.*

A tree left to rot upon the ground gradually disappears in the course of years, being mainly oxidised into gaseous products such as carbon dioxide and water vapour, and

yet scarcely any evolution of heat is observed, although the same amount of heat is generated as if the tree had been cut into logs and burnt.

Respiration, and the Circulation of the Blood.—Another example of slow combustion is found in the carrying on of life by respiration, and the circulation of the blood. The blood is distributed by the arteries, which carry blood from the heart to the body, while the veins bring the blood back to the heart; between the extremities of the arteries and the commencement of the veins we find a minute system of vessels, called the "capillaries," which connect the arteries and the veins. The heart is divided into four chambers, and the blood is brought to the heart by two great veins, one from the lower and the other from the upper extremities; these empty themselves into the right-hand upper chamber; from this it passes into the right-hand lower chamber, whence it passes through a vessel which terminates in the capillaries of the lungs. These capillaries communicate with four large veins which bring the blood back to the left-hand upper chamber of the heart, whence it passes into the left-hand lower chamber, and is forced out into the great artery, which distributes it to the different organs and tissues of the body. In the lungs the blood comes in contact with the inhaled air, admitted to the air-cells of the lungs by the windpipe, and here a great change takes place in the character of the blood; the blood as it comes into the lungs is purple, and is charged with carbon dioxide, but in the air-cells of the lungs this gas passes out from the blood and oxygen passes in by diffusion, and takes its place, whilst the colour of the blood turns from purple to red, and passes back through the heart to the arteries and the system; here in the capillaries the tissues of the body take the oxygen from the blood, replacing it by carbon dioxide, with the result that it again changes to purple, and in this condition returns by the veins to the

heart and lungs, once more to give up carbon dioxide and take in a fresh supply of oxygen. The purple blood is called "venous," or the blood of the veins; the bright scarlet blood is called "arterial."

Whenever we move, some of the tissues of the body are used up, and this waste matter, unless removed, would accumulate and cause death. The tissues consist chiefly of carbon, nitrogen, and hydrogen; and when done with, the oxygenated blood oxidises them, converting the hydrogen into water, which escapes as perspiration, exhaled moisture and urine, whilst the carbon converted into carbon dioxide is brought back to the lungs and discharged with the exhaled air, and it is this process of slow combustion which maintains the heat of our bodies.

Surface Action.—Oxygen is, under some circumstances, induced to combine with another substance by the influence exerted by the surface of a third, which takes no apparent part in the chemical action. If we take a piece of platinum foil, and, having heated it, allow it to cool down somewhat, and then expose it to a stream of hydrogen and air, the platinum again becomes red-hot, and may be kept glowing in the stream of mixed gases for a considerable time. Platinum has the power of attracting to its surface both hydrogen and oxygen; and under these conditions the gases, being in an increased condition of activity, combine, and by the heat of their combination make the platinum red-hot. If platinum in the condition of fine powder (*platinum black*) be employed, the action is even more energetic, the mixed gases being inflamed.

Point of Ignition.—The temperature at which a combustible body enters into rapid combustion with manifestation of incandescence or flame is called its point of ignition.

When the ignition point is below the ordinary temperature, as in the case of zinc methyl, the substance is said to be spontaneously inflammable, because it will take fire on coming in contact with air without the application of heat,

whilst if the ignition point be above the ordinary temperature ignition has to be set up by raising the temperature to the necessary point.

When combustion is in this way started, if the heat evolved by the action raises the temperature above the ignition point of the burning body, combustion continues until the combustible has burned away; but if the heat generated be insufficient to raise the body to its ignition point, the combustion ceases as soon as the external heating is removed.

The combination of nitrogen and oxygen is a good example of this latter class of phenomena, as, although they will combine at the temperature of the electric discharge, the combination does not emit sufficient heat to continue the combustion, and it is upon this that the safety of the atmosphere depends.

All ordinary cases of combustion belong to the first class, and the heat evolved when once the point of ignition is reached carries on the action.

Spontaneous Ignition or Combustion.—During the decay or slow oxidation of combustible bodies heat is generated, and that it is only necessary for this heat to reach a certain point, *i.e.*, the point of ignition, for the little noticeable slow combustion to become ordinary combustion with its manifestation of flame or incandescence, and it is this action to which the term spontaneous combustion has been given.

When the combustible substance has a great affinity for oxygen, and at the same time a low point of ignition, spontaneous combustion will take place with great ease. Indeed, in some cases, such as that of phosphorus, we are obliged to prevent the access of air to the body if we wish to prevent ignition taking place, and we also find that the finer the state of division of the substance the more readily will its spontaneous ignition take place, not because sub-dividing the body in any way lowers the point of ignition, but because the surface exposed

to the oxidising action of the air is so much increased that the heat is generated with greater rapidity than it can be dissipated. If we take a piece of phosphorus and expose it to the action of the air, it almost directly commences to give off white fumes, and if the weather is warm it will in the course of a short space of time even ignite ; in cold weather, however, it may be left until it has nearly all undergone slow oxidation without ignition. If, however, we dissolve it in carbon disulphide and pour some of this liquid upon a piece of blotting paper or linen, the carbon disulphide being highly volatile will all evaporate, and leave the phosphorus in such a fine state of division that it will at once spontaneously ignite.

In practically all of the cases of spontaneous ignition which come under our notice we have the heat evolved during slow combustion kept in by the presence of a mass of non-conducting material, and the heat being unable to escape gradually raises the temperature, the chemical combination becoming more and more rapid as the temperature increases, until we reach the point at which ignition of the mass takes place.

Sometimes also the increase in temperature necessary to bring about spontaneous ignition is partly due to physical actions. If a gas be suddenly compressed, heat is always evolved—a fact prettily shown by the so-called fire syringe, in which the heat evolved by the compression of air is sufficient to ignite a piece of German tinder.

Certain bodies have the power of absorbing many times their own volume of gases, and in doing this they not only give rise to a certain increase in temperature, due to the compression of the absorbed gas upon their surfaces or in their pores, but they also increase the chemical activity of the gas so compressed.

Spontaneous Ignition of Charcoal.—Carbon is one of those substances which possess to an extraordinary degree the power of attracting and condensing gases upon their surface,

this power varying with the state of division of the particular form of carbon used. The charcoal obtained from dense forms of wood, such as box, exhibit this property to a high degree, one cubic inch of such charcoal absorbing, according to Saussure—

Ammonia gas	90	cubic inches.
Sulphuretted hydrogen ...	55	„ „
Carbon monoxide	35	„ „
Ethylene	35	„ „
Oxygen	9·25	„ „
Nitrogen	6·5	„ „

This absorption is very rapid at first, but gradually decreases, and is moreover influenced very much by temperature. It is at first purely mechanical, and itself causes a rise of temperature, which in the case of charcoal formed in closed retorts, as in preparing alder, willow, and dogwood charcoal for powder-making, would produce spontaneous ignition if it were not placed in sealed cooling vessels for some days before exposure to air. The rate of absorption varies with the amount of surface exposed, and therefore able to take part in this condensing action, so that, when charcoal is finely powdered, the exposed surface being much greater, absorption becomes more rapid, and rise of temperature at once takes place. If, after it has been made, charcoal is kept for a day out of contact with air, and is then ground down into a powder, it will frequently fire after exposure to the air for thirty-six hours, whilst a heap of charcoal powder of 100 bushels or more will nearly always ignite. It is for this reason that in making the charcoal for powder it is always kept after burning for three or four days in air-tight cylinders before picking over, and ten days to a fortnight before it is ground.

There are several very interesting points with regard to the spontaneous combustion of charcoal, which call for more attention than has yet been devoted to it. It is self-evident that the more porous a body is the greater amount of exposed

surface will be available for the condensation of gases, and the great power which charcoal has of absorption is undoubtedly due to its great porosity. Now the temperature at which wood can be carbonised varies very considerably, and wood will begin to char, that is to say, will begin to be converted into charcoal at temperatures very little above that of boiling water, and in the manufacture of some of the newer kinds of gunpowder the charcoal is formed by heating with superheated steam.

Charcoal formed at this low temperature, however, still contains large quantities of hydrogen and hydrocarbons, and is not nearly so porous as charcoal made at a high temperature, and although the diminution in porosity makes it less susceptible to spontaneous combustion, due to the heat produced by the condensation of gases, yet another cause which tends still more to dangerous rise of temperature comes into play.

When a substance condenses oxygen upon its surface from the atmosphere, the gas is in a very chemically active condition, and will set up chemical combination with considerable rapidity.

If now charcoal be burnt at a high temperature the carbon is in a dense condition, and resists to a considerable extent the setting up of chemical action by the oxygen condensed and absorbed in its pores, but if it has been formed at a low temperature this condensed oxygen will rapidly act upon the hydrocarbons and hydrogen still remaining in the mass, and will raise in this way the temperature to a dangerous point, and it is more than probable that very many unexplained fires have been brought about by beams and woodwork becoming charred in contact with flues and heating-pipes.

It has been experimentally determined that when wood has been charred at 500° it will take fire spontaneously when the temperature is raised in the presence of air to 680°, and that when wood has been carbonised at 260° a temperature of 340° only is required for its spontaneous ignition.

If a beam is in contact during the winter months with a heated flue, or even steam pipes, it becomes carbonised upon its surface, and during the summer, when the flue or pipe is probably not at work, it absorbs air and moisture, and during the next winter it again becomes heated and further carbonised, whilst the moisture and air are driven out, leaving the pores in a condition eminently adapted for the absorption of more air as soon as the temperature is allowed to fall, and in many cases sufficient heat is generated to cause the charred mass to smoulder, and, when air is freely admitted to it, to burst into flame.

In the case of charcoal burnt at a high temperature it may be taken that the cause of heating is almost entirely physical, whilst in the low burnt charcoal it becomes chemical as well as physical, and it is this chemical action which is the most dangerous, and acts in most cases of spontaneous combustion.

Coal.—The spontaneous ignition of coal has been the cause of an enormous number of serious accidents, and the earliest theory as to its cause was that it was due to the heat given out during the oxidation of the pyrites or "coal brasses," which are compounds of sulphur and iron, and are present in varying quantities in nearly all coal. This idea has held its ground up to the present time, in spite of the researches of Dr Richters, who twenty years ago showed that the explanation was an erroneous one; and even earlier, in 1864, Dr Percy pointed out that the cause of spontaneous ignition was probably the oxidation of the coal, and that the pyrites had but little to do with it.

Action of Pyrites.—Pyrites is found in coal in several different forms, sometimes as a dark powder, closely resembling coal itself, and in larger quantities in thin golden-looking layers in the cleavage of the coal, whilst sometimes it is found in masses and veins of considerable size. These masses, however, are very heavy, and are carefully picked out from the coal, and utilised in various manu-

factures. The yellow pyrites, and even the dark varieties when in the crystalling form, remain practically unaltered even after long exposure to moist air; but the amorphous and finely-divided portions will oxidise and effloresce with great rapidity, and it is during this oxidation that the heat is supposed to be generated.

Some coals that are liable to spontaneous ignition only contain 0·8 per cent. of pyrites, and if we imagine this to be concentrated in one spot instead of being spread over the whole mass, and to be oxidised in a few hours, the temperature would rise only a few degrees, and under ordinary circumstances this rise in temperature would be practically inappreciable.

The oxidation of masses of pyrites, under certain conditions, gives rise to the formation of ferrous sulphate and sulphur dioxide, with liberation of sulphur, and one might easily imagine that this free sulphur, which has an igniting point of 250° C., would play an important part in the action by lowering the point of ignition. This, however, could only happen with large masses of pyrites undergoing oxidation; and with the small amount of pyrites present in coal, supposing air were present in sufficient quantity to oxidise it, the sulphur formed would be converted into sulphur dioxide at temperatures as low as 60° C. This oxidation of sulphur at low temperatures is an action not generally known, but it takes place with considerable rapidity. The only way in which pyrites can assist the spontaneous ignition of coal is that when it oxidises it helps the general rise of temperature, and by swelling splits up the coal, thus exposing fresh surfaces to the action of the atmospheric oxygen.

Igniting Point of Coal.—The igniting points of different kinds of coal vary considerably—

Cannel coal	ignites at	668° F.	= 370° C.
Hartlepool coal	„ „	766° F.	= 408° C.
Lignite coal	„ „	842° F.	= 450° C.
Welsh steam coal	„ „	870° F.	= 477° C.

So that it is impossible for the small trace of pyrites scattered through a large mass of coal, and slowly undergoing oxidation, to raise the temperature to the necessary degree.

When coal is heating a distinctive and penetrating odour is evolved, which is the same as that noticed when wood is scorched, and the gases produced consist of nitrogen, water vapour, carbon dioxide, carbon monoxide, hydrocarbons of the paraffin series, and sulphuretted hydrogen, the presence of the latter gas showing, beyond doubt, that oxidation of the sulphur has little or nothing to do with the action.

Ever since coal has been generally adopted as a fuel it has been recognised that great care was necessary in the storing and shipment of masses exceeeding 1000 tons, and, if the coal has been stored wet or in a broken state, firing or heating of the mass has frequently taken place. Much inconvenience and loss has been caused by this on shore, but the real danger has occurred during shipment, and, owing to this, many a vessel has been lost with all hands, without any record of the calamity reaching shore.

Owing to the greater facility for treating the coal when it becomes heated on shore in coal stores and gas works, absolute ignition only rarely takes place, and it is from evidence obtained in the case of coal cargoes that we learn most as to the causes which lead to it.

Coal is a substance of purely vegetable origin, formed out of contact with air by long exposure to heat and pressure, from the woody fibre and resinous constituents of a monster vegetation which flourished long before the earth was inhabited by man. Coal, therefore, may be looked upon as a form of charcoal, which, having been formed at a temperature lower than that of the charcoal burner's heap and under great pressure, is very dense, and still contains a quantity of these constituents which, in the ordinary burning, are driven off as wood naphtha, tar, etc., and these bodies consist of compounds containing essentially carbon

and hydrogen, together with a little oxygen and nitrogen, and form the volatile matter and hydrocarbons of the coal. Coal also contains, besides these, certain mineral bodies which were present in the fibre and sap of the original wood, and these form the ash which is left behind on the coal being burnt. These mineral substances consist almost entirely of gypsum or sulphate of lime, silica, and alumina, together with some oxide of iron which gives the colour to the reddish-brown ash of many coals, and which has been formed by the decomposition of the pyrites in the original coal.

The mineral constituents of coal, other than the pyrites, are the only ones that play no part in the phenomena attending the heating and spontaneous ignition of coal, and we must, therefore, regard the actions which take place when the carbon, hydrocarbon, and pyrites in freshly-won coal come in contact with air and moisture.

Absorptive Power of Coal.—Certain kinds of coal exhibit the same power of absorbing gases which charcoal has, although to a less degree. The absorptive power of new coal due to this surface attraction varies, but the least absorbent will take up one and a quarter times its own volume of oxygen, whilst some coals absorb more than three times their volume of the gas, which gives rise to an increase in temperature, and tends to accelerate the action which is going on, but is rarely sufficient to bring about spontaneous ignition, only about one-third the amount of oxygen being absorbed by coal that is taken up by charcoal, and the action being much slower, tends to prevent the temperature reaching the high ignition point of the coal.

All coal contains a certain proportion of hydrogen combined with carbon, and these, together with the nitrogen and oxygen, form the volatile matter in the coal. The amount of this volatile matter varies greatly, anthracite containing the smallest quantity, and cannel and shale the

largest. When the carbon of the coal absorbs oxygen the compressed gas becomes chemically very active, and soon commences to combine with the carbon and hydrogen of the bituminous portions, converting them into carbon dioxide and water vapour. As the temperature rises so this chemical activity increases, so that the heat generated by the absorption of the oxygen causes it to rapidly enter into chemical combination. This kind of chemical combination—oxidation—is always accompanied by heat, and this further rise of temperature helps the rapidity of oxidation, so that the temperature rises steadily; and this taking place in a large mass of coal, which from physical causes is an admirable non-conductor, it will often cause such heating of the mass that if sufficient air can pass into the heap in order to continue the action, the igniting point of the coal will be reached.

It has been suggested that very bituminous coals, such as cannel and shale, are liable to spontaneous ignition from the fact that heavy oils would exude from them on a rise of temperature, and that these, by oxidising, might produce rapid heating. Experiment, however, shows that this is not the case, and that the heavy mineral oils have a decided effect in retarding heating.

Actions leading to Ignition. — We can now trace the actions which culminate in ignition. As soon as the coal is brought to bank, absorption of oxygen commences, but, except under rare conditions, the coal does not heat to any great extent, as the exposed surface is comparatively small, and the size of the masses allows of the air having free access to all parts, so keeping down the temperature. After the coal has been screened, and the large pieces of pyrites picked out, it is put in trucks. Here it begins to get broken up, owing to the many joltings and shuntings, and so offers a larger surface to the action of the air. When it has arrived at the ship it is further broken up by being shot down the tips or shoots, and more harm is done at this than

at any other period, for the coal is broken by reason of the distance it has to fall, and, as it has to bear the impact of every succeeding load falling upon it, it rapidly becomes slack, so that the under part of the shipload is a dense mass of small coal, which soon rises in temperature by reason of the large surface exposed to the air and the consequent absorption of oxygen. This sets up chemical combination between the oxygen absorbed by the coal and the hydrocarbons, and in some cases culminates in combustion.

Influence of Mass.—It is found that the mass of coal exercises a most important action in the liability to spontaneous combustion, as although with 500 tons of coal to the cargo the cases of spontaneous combustion amount to only about $\frac{1}{4}$ of a per cent., when the bulk is increased to 2000 tons cases of spontaneous combustion rise to 9 per cent., this being due to the fact that the larger the cargo the more non-conducting material will there be to keep in the heat, and also to the fact that the breaking up of the coal and the exposing fresh surfaces will of course increase with increase in mass, and it is also found that coal cargoes sent to European ports rarely undergo spontaneous combustion, whilst the number of cases rises to a startling extent in shipments made to Asia, Africa, and America. This result is partly due to the length of time the cargo is in the vessel, the absorption and oxidation being a comparatively slow process, but the main cause is the increase of heat in the tropics, which causes the action to become more rapid ; and if statistics had been taken, most of the ships would have been found to have developed active combustion somewhere about the neighbourhood of the Cape, the action fostered in the tropics having raised the temperature to the igniting point by that time.

Moisture has a most remarkable effect upon the spontaneous ignition of coal. The absorption of oxygen is at first retarded by external wetting, but after a time the presence of moisture accelerates the action of the absorbed

oxygen upon the coal, and so causes a serious increase of heat. The researches of Cowper, Baker, Dixon, and others have of late years so fully shown the important part which moisture plays in actions of this kind, that it is now recognised as a most important factor.

In order to prevent the spontaneous ignition of large masses of coal, it is manifest that every precaution should be taken during loading or storing to prevent crushing of the coal, and on no account must a large accumulation of small coal be allowed. Where possible the depth of coal in the store should not exceed 6 to 8 ft., and under no conditions must steam-pipes or flues be allowed so near the mass of coal as to give rise to any increase of temperature.

Professor Threlfall has advocated the wetting of coal cargoes as a preventative for spontaneous ignition, and if 15 per cent. or over of water were added to the cargo it would probably prove efficacious, but the increase in weight, or rather reduction in the amount of coal the ship could carry, would prove a serious drawback, whilst the addition of a smaller quantity of water or only partial treatment of the cargo would be an active danger.

Spontaneous Ignition of Oily Rags.—Perhaps the commonest case of spontaneous combustion is to be found in the ignition of oily waste or greasy cotton rags. Nearly all vegetable and animal oils have the power of slowly absorbing oxygen, and in some of them this goes on with considerable rapidity, with conversion of the oil into a resin—a property which gives them the power of drying and causes a considerable rise of temperature. A mass of oil, however, only exposes a very small surface to the oxidising influence of the air, but when such oil comes to be spread upon any non-conducting fabric, the oxidation is very rapid, and the non-conducting power of the fibre of the fabric prevents the rapid dispersion of the heat, with the result that even a small quantity of such oily substance will readily inflame.

There are plenty of well-authenticated cases in which even

a handful of oily cotton waste, which has been used for polishing furniture, has ignited when thrown on one side, and caused most disastrous fires. Some years ago, Mr Galletly read a most valuable paper before the Chemical Section of the British Association, in which he showed that the liability of oils to produce spontaneous combustion was in proportion to their tendency to dry. If a substance like cotton waste be rendered oily with anything except the mineral oils, it acquires the power of taking up oxygen from the air, and this gives rise to heat. The oxidation is slow at ordinary temperatures, and, accordingly, it may be some time before the increase of temperature becomes manifest; but when this point is reached the action proceeds with great rapidity, and the point of ignition is reached in a very short time, and then the mass bursts into flame. If the oily matter be placed in a warm position at first, spontaneous ignition may take place within a few hours, or even minutes. Galletly found that oily cotton at ordinary temperatures took some days to heat and ignite, whilst if placed in a chamber warmed to 130° to170° F. (54° to 76° C.), the cotton, greasy with boiled linseed, ignited in 1 hour 15 minutes, and olive oil on cotton in five hours; and in a chamber heated to 180° to 200° F. (82° to 93° C.), olive oil on cotton ignited in two hours.

Cases of spontaneous combustion due to this cause have been more abundant than from any other, and cases are even on record where serious fires have resulted from sparrows using oily waste in the construction of their nests. In all well-regulated workshops, the orders against allowing any accumulation of oily waste are very stringent, and the most reasonable precaution to be taken is that all oily material when done with should be thrown into a metal vessel containing water, or which, at any rate, can be either emptied of waste or filled with water at night. If a sheet of cotton be hanging in a warm room and is splashed with oil, a hole will often be found charred in the fabric by the next morning; whilst if a few drops of a drying oil be allowed to fall

on powdered charcoal or lamp-black, ignition is almost certain to follow in a few hours.

Hay.—Another common case of spontaneous ignition is that of haystacks, which have been made up before the grass has been thoroughly dried; this being due to the sap left in the vegetable fibre undergoing fermentation, which, being a process of oxidation, gives rise to heat. The heat is kept in by the surrounding hay, which is an admirable non-conductor of heat, and gradually increases until the ignition point of the mass is reached, when the stack bursts into flame. In some cases, the action does not go as far as this, and we often see the inside of a haystack charred to an almost black colour, showing that the action has stopped but little short of the point required to give active combustion; this being probably due to the stack having been very closely built and the access of air to the centre being small, and in some cases when such a rick is cut, the air coming in contact with the central portion causes active ignition. If hay has once been properly dried, and then becomes wetted with rain, spontaneous ignition hardly ever takes place, although the hay becomes mouldy, and it is evident that the action which leads to ignition of the hay is fermentation of the sap.

Combustion by Combined Oxygen.—In very many cases oxidation can be effected by "combined oxygen," that is to say, certain compounds which contain large quantities of oxygen are capable of giving it up to readily oxidisable substances with which they are brought in contact, the conditions being such that chemical action can take place. For instance, potassium chlorate, as we have seen, holds large quantities of oxygen in such loose combination that merely heating it above the temperature at which it fuses is sufficient to drive it off. If now we throw any oxidisable substance upon the surface of fused potassium chlorate, we find that it burns with great vigour at the expense of the oxygen of the chlorate.

Again, potassium permanganate, a body rich in oxygen

when mixed with strong sulphuric acid, has the power of giving oxygen to all substances which can take it up, and will even oxidise substances which do not combine with oxygen under ordinary conditions.

This property is of enormous importance in the manufacture of explosives, as it enables us in a small space to supply combustible bodies with others which are capable of supplying sufficient oxygen for their combustion. In gunpowder the charcoal and sulphur are readily combustible, whilst the potassium nitrate yields the oxygen necessary to support their combustion.

CHAPTER VIII.

WATER AND ITS PROPERTIES.

Water—Composition of water by volume and weight—Physical properties of water—Latent heat—Specific heat—Change of volume during change of state—Boiling point of water—Spheroidal state—Solution—Water of crystallisation—Water of hydration—Circulation of water in Nature.

A LITTLE more than one hundred years ago Cavendish showed, that when oxygen and hydrogen were mixed together in the proportions of two vols. of hydrogen to one of oxygen and the mixture exploded, water, and nothing but water was formed. Since that time the composition of water has been investigated by many chemists, whose results confirm the experimental facts arrived at by Cavendish, and explained by Lavoisier during the years 1781-83.

Whenever hydrogen or any substance containing hydrogen, such as coal, wood, fat, etc., burns in air or oxygen, water is produced, and by the decomposition of water the gases, oxygen and hydrogen, can once more be obtained.

Composition of Water by Volume.—The proportions of hydrogen and oxygen in water can be accurately determined by eudiometric synthesis. For this purpose we take a strong, accurately graduated glass tube (A, Fig. 18), open at one end and closed at the other, whilst through the closed end two platinum wires are fused, which terminate one-third of an inch apart inside the tube, and which can be connected with the poles of an induction coil (B) connected with the battery (C).

The tube is first filled with water, and is then inverted mouth downwards in a trough, also filled with water; hydrogen gas is then allowed to enter, and the volume it

occupies is read off (say 100 volumes); oxygen is next passed in and the volume of mixed gases is noted (say 175). The tube is then pressed down upon a piece of flat india-rubber placed under the water, in order to prevent the sudden expansion due to heat (when combination takes place) blowing any of the gases out of the tube. An electric spark is now passed through the mixed gases by means of the platinum wires fused through the glass. A flash is seen to pass down the tube, showing that combina-

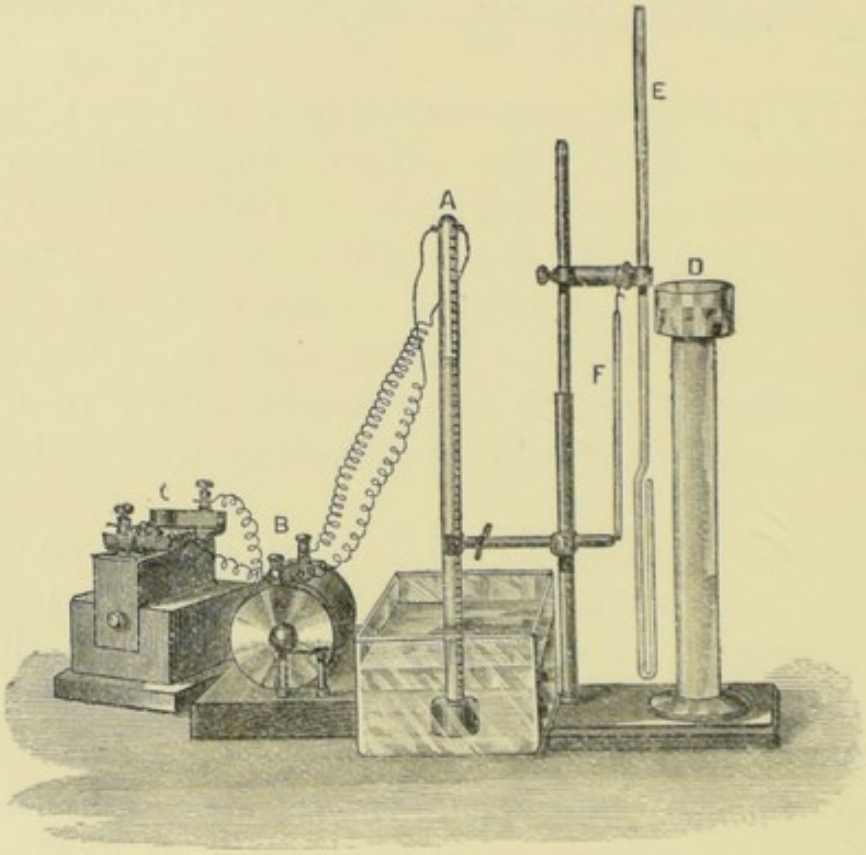


Fig. 18.

tion has taken place; and the water formed is deposited as dew on the sides of the tube and only occupies about $\frac{1}{2000}$ part of the bulk of the gases forming it. When the eudiometer is raised from the india-rubber pad the water rises in the tube and only 25 volumes of gas remain, and this is found to be pure oxygen.

Now the oxygen originally added was 175—100 or 75 volumes, 25 of which remain unused.

Thus we see that 100 volumes of hydrogen require exactly 50 volumes of oxygen for their complete combus-

tion. In reading the quantities of gases contained in the eudiometer it is necessary to sink the tube in water until the level of the water inside the tube is the same as that on the outside, and this is done in the well (D).

Having thus proved that two volumes of hydrogen combine with one volume of oxygen to form water, we can repeat the experiment, using, however, a different shaped eudiometer and jacketing it with a glass tube

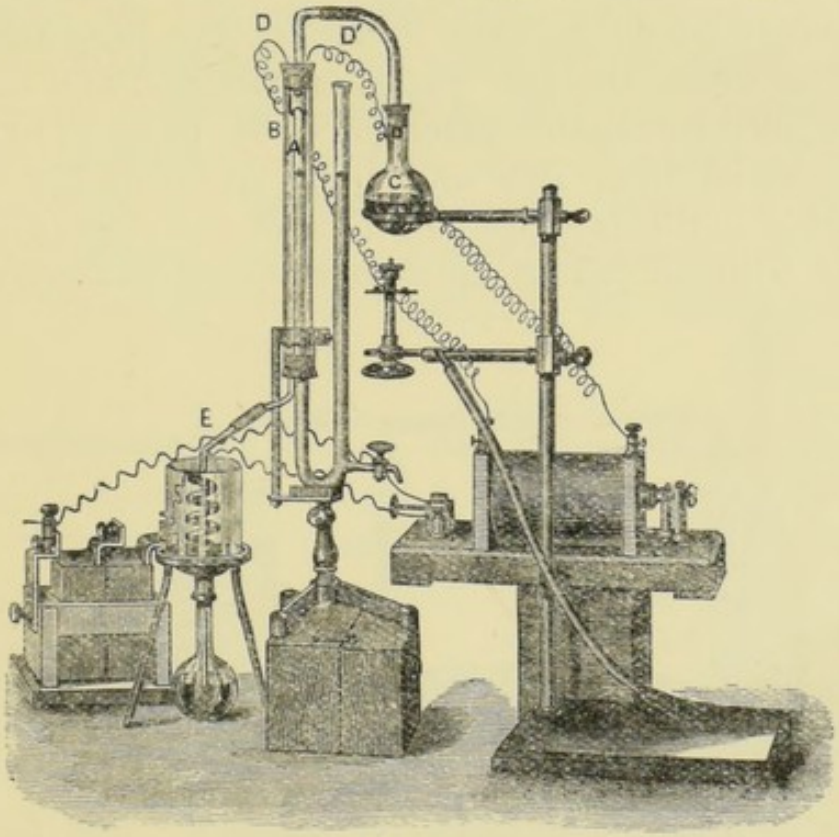


Fig. 19.

through which the vapour of some liquid having a higher boiling point than water can be passed, so as to keep the water formed in the condition of steam. (Fig. 19.)

To do this the eudiometer (A) is surrounded by a wide glass tube (B); exactly two volumes of hydrogen and one of oxygen are placed in the eudiometer over mercury, and amyl alcohol (fusel oil), which boils at 128° C., is then vaporised in the flask (C), and passing through the outer tube (B), is condensed in the worm (E). This heats the gases and mercury in the eudiometer to a temperature

several degrees above the boiling point of water, and if a spark is now passed through the mixed gases, a contraction exactly equal to one-third of the volume takes place, that is to say, the three atom volumes, in combining to form a molecule, have contracted to the volume occupied by two atom volumes of hydrogen.

Composition by Weight. — Knowing that the atoms of oxygen are sixteen times heavier than the atoms of hydrogen, it would be easy to deduce the proportions by weight in which the two elements combine, and this can be also experimentally determined by passing hydrogen gas generated from zinc and dilute sulphuric acid in the generating bottle (A, Fig. 20), through the tube (B), which is filled with anhydrous calcium chloride, and which will

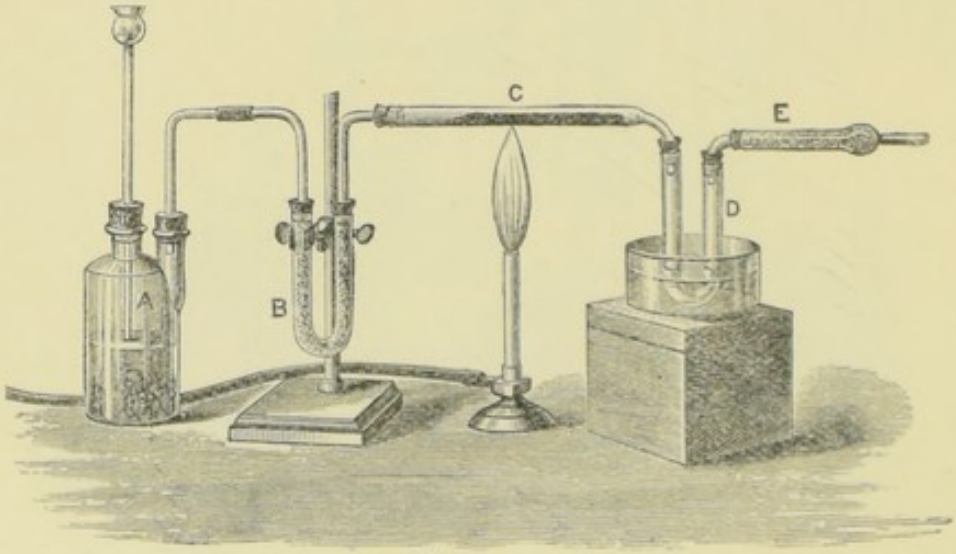


Fig. 20.

absorb any moisture the gas may contain. The dried hydrogen now passes over heated oxide of copper in the tube (C), and reduces it to metallic copper, combining with the oxygen and forming steam, which passes on and condenses in the U tube (D), which is kept cool by standing in a vessel of water, whilst any moisture which escapes condensation is taken up by the chloride of calcium tube (E).

Hydrogen		Copper oxide		Copper		Water.
H_2	+	CuO	=	Cu	+	H_2O.

If the tube containing the copper oxide be weighed before the experiment, and again after the experiment is finished, the loss of weight will represent the oxygen taken up by the hydrogen to form water, whilst the increase of weight in the vessels arranged to condense the steam will give the weight of water formed. For instance, suppose the tube containing the copper oxide, before the experiment, weighs 179·5 grams, and after the experiment only 163·5 grams, the loss in weight representing oxgyen used up by the hydrogen to form water is 16 grams; and if we weigh our condensing tubes we find we have collected 18 grams of water — therefore, this 18 grams of water must consist of 16 grams of oxygen combined with 2 grams of hydrogen; or, in other words, one-ninth of the weight of water is due to hydrogen and eight-ninths to oxygen.

Decomposition of Water.—If we take water, and, having converted it into steam, pass it over iron heated to dull redness, we find that it is broken up into its constituents, the oxygen remaining combined with the iron, whilst hydrogen comes off free and may be collected by suitable arrangements. Iron is not the only metal which will do this; indeed, certain metals, like sodium and potassium, will decompose water at ordinary temperatures, whilst magnesium only requires a temperature of 100° C. to effect the decomposition. The fact that we can obtain hydrogen gas from steam proves that hydrogen is one of the constituents of water; and we also find that if a mixture of steam and chlorine be passed through a heated porcelain tube, the steam is decomposed, the hydrogen and chlorine uniting to form hydrochloric acid whilst oxygen is liberated.

This is best done by generating chlorine gas by gently warming a mixture of hydrochloric acid and black oxide of manganese in the flask (A, Fig. 21), and leading the liberated chlorine through water in the retort (B) which is

kept just at the boiling point by a water bath; the chlorine so saturated with water vapour is then passed through a porcelain tube (C) heated to dull redness in the gas furnace—a larger heating surface being obtained by filling the tube with pieces of broken porcelain or glass. Under the influence of heat chlorine decomposes water vapour, and the resulting oxygen and hydrochloric acid, together with any chlorine or steam which may have been in excess, pass on; and if they are led into water in the

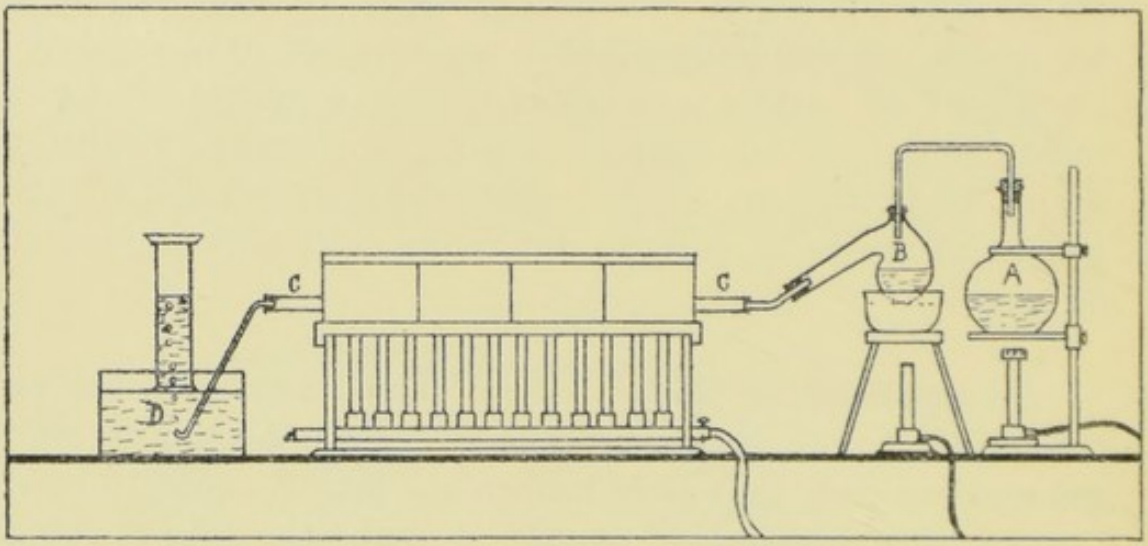


Fig. 21.

pneumatic trough (D) and collected by displacement of water in the cylinder, the chlorine and hydrochloric acid, being soluble, will be absorbed by the water, any steam will be condensed, and nothing but oxygen will remain.

Electrolysis of Water.—By passing a galvanic current through water acidulated with a few drops of sulphuric acid the water can be decomposed, the oxygen being liberated at the pole at which the current enters the liquid, and the hydrogen at the pole at which it leaves, and by using an apparatus of the kind shown in Fig. 22, the gases can be collected separately; and we find that under certain experimental conditions we always obtain two volumes of hydrogen and one of oxygen.

Properties of Water.—In masses pure water has a blue colour, but a very small percentage of impurities imparts to it a greenish tint. Water is practically incompressible, a pressure of 30,000 lbs. only compressing 14 volumes into 13. The weight of water at 4° C. is taken as the unit of comparison for solids and liquids, so that when iron is said to have a specific gravity of 7·8, it means that a given bulk of water is taken as weighing 1 at 4° C., and that the same bulk of iron would weigh 7·8. One gallon of water weighs 70,000 grains, or 10 lb. English, and a litre of water weighs 1,000 grams, or 1*c.c.* = 1 gram.

Water as a Solvent.—As a neutral solvent water is unsurpassed, and it dissolves all gases to a greater or less degree. If no chemical action takes place between the gas

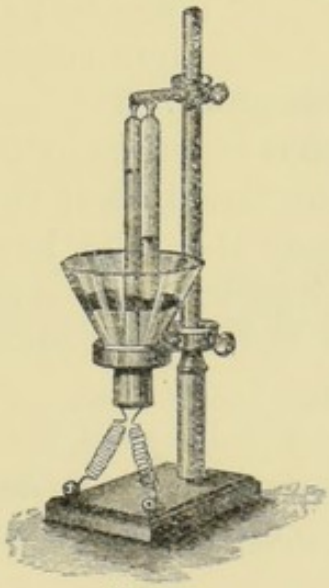


Fig. 22.

and the water the amount absorbed depends upon—(1) the nature of the gas; (2) the temperature of the water; and (3) the pressure under which the absorption is effected.

1. Some gases are much more soluble than others; a given volume of water at 0° C. will dissolve 1,149 times its own volume of ammonia gas, but only ·019 of hydrogen.
2. The cooler the liquid the more gas will it dissolve.

3. The volume of the gas absorbed varies directly as the pressure; that is to say, at all pressures the water absorbs the same volume of gas, since the volume of the gas itself varies inversely as the pressure.

This is taken advantage of in the manufacture of aërated waters. Carbon dioxide gas is absorbed by water under pressure, the amount dissolved depending upon the pressure; this pressure is then kept constant by the bottle being corked and wired, but when the cork is removed the liquid is now under ordinary atmospheric pressure, and can only hold in solution the volume of gas corresponding to that particular pressure, the excess escaping and causing the effervescence.

The solution of solids, like the solution of gases, depends largely upon the nature of the solid; one litre of water will dissolve 0·14 grams of strontium sulphate and nearly 1,000 grams of magnesium sulphate.

The rate of solution is increased by the fineness of division and by agitation of the liquid, as, if the liquid be quite still, the layer of water next the solid becomes saturated, and being therefore denser protects the remainder, solution only proceeding by liquid diffusion, a process infinitely slower than gaseous diffusion.

The solubility of a salt, as a rule, increases with the temperature of the water, but strontium sulphate and lime are exceptions, being more soluble in cold than hot water.

Water of Crystallisation.—When a point is reached at which no more of the solid can be dissolved, the liquid is said to be saturated, and if allowed to stand so that the water can cool or evaporate, the solid will again separate out—often in the crystalline form, and this form is in many cases due to water held in a feeble state of combination, and called *water of crystallisation.* For instance, sodium carbonate crystallises with ten molecules of water of crystallisation, and these crystals when exposed to air

effloresce, that is, give off some of their water, and crumble down to a white powder.

The solution of a solid in water is generally accompanied by a lowering of temperature, caused by the conversion of sensible into latent heat, when the substance passes from the solid into the liquid state, and in the same way when the substance crystallises the heat so rendered latent reappears.

Water of Hydration.—In the cases of some oxides and anhydrous salts, solution is accompanied by a rise in temperature, and this is caused by the water forming a definite combination, heat being generated by chemical action. When many oxides of the metals are brought in contact with water they combine with it, forming a body called a hydroxide.

Calcium oxide		Water		Calcium hydroxide.
CaO	+	H_2O	=	$Ca(HO)_2$.
Sodium oxide				Sodium hydroxide.
Na_2O	+	H_2O	=	2(Na HO).
Potassium oxide				Potassium hydroxide.
K_2O	+	H_2O	=	2(KHO).

The water which so combines with the metallic oxide to form a hydroxide is called *water of hydration.*

Water exists in Nature in three forms: as ice, water, and steam. Below 0° C. it exists as ice, from 0° to 100° C. as water, and above that temperature as steam.

The relations of water to temperature are amongst the most wonderful and important of its properties; it is indeed the great climate-maker; the presence or absence of water making an incalculable difference in the ranges of temperature to be found in different countries.

Water has the power of absorbing more heat in order to raise it through any given range of temperature than any other known substance, and the result is that it can absorb a very large amount of heat, without itself undergoing any very great increase in temperature.

Specific Heat of Water.—The amount of heat required to raise a unit weight of water one degree is called its specific heat, and water being taken as unity, the specific heats of various substances are all less than 1. For instance—

SPECIFIC HEATS OF SOLIDS AND LIQUIDS.

Alcohol	0·615	Copper ...	0·095
Ether	0·516	Silver ...	0·057
Sulphuric acid ...	0·333	Mercury ...	0·033
Carbon	0·241	Tin	0·056
Sulphur	0·202	Gold ...	0·032

—so that a given weight of alcohol could be raised 1° in temperature by 0·6 of the heat required to raise an equal weight of water the same degree, whilst one pound of mercury would only take 0·033 the heat required by a pound of water.

The result of this great capacity for heat is, that as the summer sun beats down upon large masses of water heat is slowly absorbed, and stored up without the water itself becoming unduly heated, and then as summer slowly gives way to winter and the temperature falls, this store of heat is again slowly given off, checking the too sudden inroads of cold, and tempering the climate, as one cubic yard of water in cooling down 1° C. warms 12,300 cubic yards of air through one degree.

Latent Heat of Water.—If we take a vessel containing ice and place a thermometer in it, the mercury falls to 0° C.; if now a flame be placed under the vessel, no rise of temperature is observed until every particle of ice is melted. The heat so used up in melting the ice is said to be rendered latent; and it has been found by experiment that in passing from the solid to the liquid state a given weight of ice renders latent as much heat as would raise the same weight of water from 0° C. to 79° C. The latent heat of water is therefore said to be 79 thermal units—a thermal unit meaning the quantity of heat required

to raise a unit weight of water one degree Centigrade. When water freezes, this amount of heat is again given out.

Heat is absorbed when a solid becomes a liquid or a liquid becomes a gas, and the heat is again developed as sensible heat when the reverse changes take place; and it is upon this principle that many freezing mixtures and other devices for lowering the temperature are devised.

Point of Maximum Density.—Nearly all bodies contract when cooled and expand when heated, but between certain temperatures water is an exception to this rule. If we take water at its boiling point and gradually cool it, we find it contracts with regularity until it reaches a temperature of 4° C.; at this point it begins to expand, and continues to do so until at 0° C. it is converted into ice, when a sudden and still greater expansion takes place. Hence we say that the point of maximum density of water is 4° C., because a given bulk of water will weigh more at this temperature than at any other. Although the amount of expansion, from 4° C. to 0° C., is very small, yet it exerts a great influence upon our climate. When water expands it becomes lighter; hence the water cooler than 4° C. always remains on the surface of a pond or lake, and the surface freezing first protects the water below it from the cold. If water continued to contract on cooling, all water would be converted into solid masses of ice, which would not entirely melt in the hottest summer, a condition which would not only render our climate far colder but would destroy all aquatic life. With the conversion of the water into ice, a sudden and much greater expansion occurs, and ten gallons of water form eleven gallons of ice.

Bursting of Water Pipes by Frost.—The sudden expansion due to the conversion of water into ice is a frequent cause of the bursting of water-pipes during severe frost. Pipes are left full of water and often under pressure, and when the water freezes, the sudden expansion bursts the pipe at its weakest point. The damage, however, is only discovered

when the thaw comes, and the ice melting allows the outrush of the water. Leaden water-pipes are made perfectly cylindrical in order to give them the greatest carrying capacity; but if they were made oval instead of round, when the water froze it would by its expansion make the tube cylindrical, and so make room for the surplus.

Latent Heat of Steam.—When water is heated to 100° C. under normal barometric conditions, it commences to boil, and as long as the steam generated is allowed to freely escape, no further rise in temperature takes place, the whole of the additional heat being rendered latent in converting the liquid into a gas.

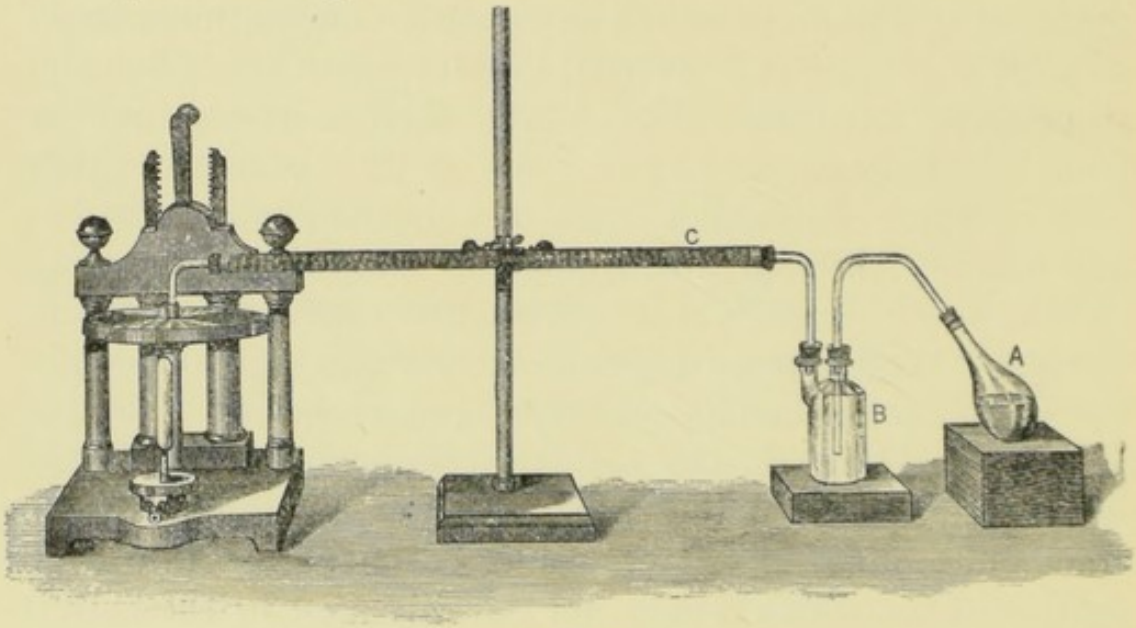


Fig. 23.

The latent heat of steam is said to be 536 thermal units, because if we take 100 grams of water at 0° C. and pass steam into it, 18·6 grams of steam will be condensed before the mass is heated to 100° C. Now, 18·6 is to 100 as 1 to 5·36, so that a unit weight of steam in condensing gives out enough heat to raise 5·36 units of water from 0° C. to 100° C., or 536 unit weights of water from 0° to 1° C.

Boiling Point.—Water boils when the tension of its vapour is equal to the superincumbent atmospheric pressure; therefore, at the top of a mountain, where the atmospheric

pressure is less than at the sea level, water boils below 100° C., but at the bottom of a deep mine, where the pressure of the atmosphere is greater, water has to be heated above 100° C. before it is converted into steam.

This may be shown by warming water to about 80° to 90° C. in a flask (A, Fig. 23.) and attaching it to an air pump; an empty bottle (B) and a long tube filled with calcium chloride (C) being interposed in order to condense and absorb water vapour and so prevent any reaching the air pump. On giving a few strokes of the air pump, the pressure is reduced on the surface of the water in the flask and the water boils briskly. This principle is applied in the sugar-maker's vacuum pan, in which water is boiled off from the saccharine syrup at temperatures far below the boiling point in air; and also in "Papin's digestors," where, by increasing the pressure, the boiling point is raised.

The effect of raising the pressure is well shown in high-pressure boilers, and in the following table the boiling point is given for various pressures expressed in atmospheres (1 atmosphere = 15 lbs. on the square inch).

Pressure in atmospheres.	Boiling-point in degrees Centigrade.	Pressure in atmospheres.	Boiling-point in degrees Centigrade.
1	100	12	190·0
1·5	112·2	14	197·2
2	121·4	16	203·6
3	135·1	18	209·4
4	145·4	20	214·7
5	153·1	25	226·3
6	160·2	30	236·2
7	166·5	35	244·8
8	172·1	40	252·5
10	181·6	45	265·9

Spheroidal State.—When water is thrown upon a heated silver dish it is seen to assume a spheroidal form and does not boil, although the plate or dish is heated very far above its ordinary boiling point. If the dish be now allowed to cool, at a certain point the water suddenly bursts into violent

ebullition and is converted into steam. This spheroidal form is due to the generation of a cushion of steam between the water and the heated surface which prevents the water coming in contact with it, so that it only slowly evaporates away; but on allowing the temperature to fall, a point is reached when the heat is no longer sufficient to rapidly generate the steam.

This has been shown by Perkins to hold good in the case of boilers, so that if a boiler has been allowed to run dry and the plates have been highly heated, on the entrance of feed-water the first portions assume the spheroidal state, but as more water is added and the plates are gradually cooled, contact takes place with formation of enough steam, in many cases, to cause explosion.

Tension of Aqueous Vapour.—Although water does not boil until the tension of its vapour is equal to the pressure of the atmosphere upon its surface, yet we find that even at temperatures below the freezing point it slowly evaporates, as is shown by the gradual evaporation of water left exposed to air in a saucer, and even by the gradual disappearance of snow. This used to be explained as being due to the air having the power of taking up water; but it can be shown that air has nothing to do with it, as water will evaporate just as well into a vacuum, the property being due to the elastic force or tension of the aqueous vapour.

If a few drops of water be passed up into the Torricellian vacuum of a mercury barometer, the mercury falls to a certain extent, and the higher the temperature the greater will be the depression, until at 100° C. the mercury inside the tube will stand level with the mercury outside—that is to say, at 100° C. the tension of the aqueous vapour is equal to the atmospheric pressure, and it is therefore at this particular temperature that boiling commences.

The fact, however, that even at ordinary temperatures water above the mercury column causes a depression, shows that it has a certain tendency to volatilize, and it is this

power which causes it to evaporate at all temperatures. When water boiled and was converted into steam, we saw that a large amount of heat was rendered latent, *i.e.*, disappeared as sensible heat, because it was doing the work of keeping the particles of water in a state of vapour ; and, no matter how low the temperature may be at which water is converted into vapour, it takes up and renders heat latent.

Cooling by Evaporation.—This may be very beautifully shown by what is called "Wollaston's Cryophorus," which consists of a broad tube with a bulb at each end, one of which is partly filled with water, the space above the water being a vacuum as far as air is concerned, only containing water vapour ; if the upper bulb be surrounded with a freezing mixture, it condenses some of the vapour, and the water in the lower bulb at once commences to evaporate, and thus supply more vapour to take the place of that which had been condensed ; and if the water in the lower bulb be surrounded with cotton wool, to prevent its obtaining heat from the air, so much is abstracted from the water that it is quickly frozen.

The Circulation of Water.—It is evident that as evaporation is dependent on the tension of the aqueous vapour, and as this increases with the temperature, the warmer it is the more rapid will evaporation be, so that in tropical climates water vaporises with great rapidity from the surface of the sea, and the water vapour being lighter than air forms an ascending current, and fresh air from the north and south is drawn in to take its place; whilst in order to replace these supplies, the ascending air divides and forms an upper current which flows back from the equator overhead in the opposite direction to that which the lower current is taking. If the earth were stationary these currents would flow due north and south, but the earth revolves on its axis once in the twenty-four hours, and as the circumference of the globe is 24,900 miles at the equator, it is evident

that anything relatively stationary there is moving with the earth at more than 1000 miles an hour, and although the air nearest the earth moves with the earth, still there is a certain amount of friction which deflects these currents from due north and south, and gives them a north or south-easterly direction.

As the warm moist air ascends from the surface of the sea it rapidly expands, because the greater the altitude the less will be the pressure of the superincumbent air above it, and as the pressure falls, so does the volume of the moist air expand. We have seen that expansion in gases always means absorption of heat, so that the ascending current of air cools by its own increase in bulk, and at first does so at the rate of about 1° for every 183 feet rise. Had the air contained the largest possible amount of water vapour which could have evaporated at the particular temperature at which it commenced to rise, a very small increase in altitude would have been sufficient to cause some of it to condense; but air is never quite saturated, so that it is some time before this fall in temperature begins to affect the water vapour, and by the time vapour begins to condense as cloud, it is probably being rapidly borne away north and south by the great overhead currents.

As soon as the water vapour commences to condense, the latent heat of the vapour is liberated, and checks any further condensation until this new supply of heat is used up.

The Formation of Cloud.—In the higher regions the vapour meets currents of air cooler than itself, or it may come in contact with the tops of mountain ranges, any of which causes by rapid cooling cause deposition of some of the water vapour, and this forms very minute particles, which, being unable to overcome the friction of the air, are kept floating as clouds until something causes them to coalesce into larger drops, which fall back to the earth as rain. When this condensation of water vapour happens near the surface of the earth, the result is mist, fog and dew. There are three

distinct forms of cloud, the "Cirrus," the "Cumulus," and the "Stratus."

The little flecks of delicate cloud which are always seen at the greatest height are the Cirrus, then we have the bold rounded masses of white cloud which are the Cumulus, and finally the horizontal sheets of cloud nearest the earth, which we call the Stratus. These forms often run into one another, and are known as "Cirro-stratus," "Cirro-cumulus," and "Cumulo-stratus"; this latter is the densest form of cloud and includes what is known as the "Nimbus"—the heavy black thunder cloud.

Snow, Hail and Rain.—When the temperature of the upper regions of air is below the freezing point, the moisture, as it condenses, freezes and descends as snow, which, if examined under the microscope, is seen to be composed of most exquisitely formed crystals; whilst if the rain drops after they are formed pass through a region of air below the freezing point, we have the formation of hail.

When the little particles of water of which the clouds are formed condense and fall as rain, in their passage through the air they dissolve some of the more soluble gases with which they come in contact, such for instance as ammonia, traces of nitric acid, small quantities of oxygen and carbon dioxide, also traces of any local impurities which may be present in the air from manufactories or towns, such as hydrochloric acid and sulphur dioxide.

The rain falling on the ground partly evaporates, partly runs off and partly sinks in, the relative amounts varying with the configuration and density of the ground.

In the magnesium limestone districts, about 20 per cent. penetrates; in the new red sandstone, 25 per cent.; in the chalk, 42 per cent.; and in the loose tertiary sand, 90 to 96 per cent. Sinking into the ground, the water comes in close contact with considerable quantities of carbon dioxide generated from the decaying vegetable matter in the subsoil, and it absorbs a considerable quantity of this gas, forming

with it carbonic acid, and then penetrates more or less deeply into the ground, dissolving anything it can take up, either by its own solvent properties or by the solvent power of the carbonic acid, formed by the solution of carbon dioxide in the passage of the rain through the air and top-soil. The carbonic acid so present in the water causes it to be fresh and sparkling, and where there is a deficiency of carbonic acid, as is the case in waters from some sandy soils, there the water is flat and unpalatable.

The water sinks through the soil until it comes to some strata which it cannot penetrate, and here it collects and forces its way to the surface in the form of springs, the water being laden with the various salts it has met with and dissolved in its passage through the earth. The springs form rills, and these are swelled by the rain which runs off from the surface of the soil, and this surface drainage brings with it more impurities, chiefly held suspended in it, such as dead leaves, dust, mud, etc. The rills increase in size, becoming streams, and join the rivers, which again flow back to the sea.

The Work of Water.—The sea may be looked upon as Nature's evaporating basin, as here, under the influence of the sun's rays, the pure water is once more converted into vapour, once more to go through its round of operations, whilst the salts it has dissolved from the earth, and the suspended matter it has swept down from the surface of the land, remain behind, and in the course of centuries build up fresh continents.

From the moment the rain reaches the soil it is the great agent of geological change, and is always at work dissolving out and washing away the existing land, only to build it up in fresh places; the amount of solid matter so removed by the rivers of the world amounting to millions of tons daily.

In falling from the clouds, the rain performs the important function of washing the air and collecting the ammonia and nitric acid necessary for plant life, and brings them down to the plants in the condition in which they can be

most readily assimilated; whilst in its passage from the springs to the ocean it washes away those waste products of animal life which, if they were allowed to remain, would breed pestilence and general decay; if the free flow of the rain and spring water be interrupted, stagnant pools and swamps, breeding disease and exhaling malaria, are the immediate result.

Water vapour rises most abundantly in the tropics, and in its evaporation renders latent an immense amount of heat, and this heat is again given out whenever the water vapour again undergoes condensation into rain. In this way water vapour tends to equalise the temperature of the earth, by carrying heat from the places where it is in excess to those places where it is wanted.

CHAPTER IX.

The Impurities in Water.

The natural impurities in rain, surface, spring, river and sea water —Hardness in water — Temporary hardness — Permanent hardness— The economic aspect of hard water—Natural impurities and their effect upon health—Sewage contamination—Sources of drinking water—Purification of water—Filtration on the large scale—Porter-Clark process—Anderson process—Anti-Calcaire—Domestic and ship filters—Filtering media — Animal charcoal — "Spongy iron"— "Carbalite" — Pasteur-Chamberland filters—Ready methods for the purification of water.

RAIN WATER.—There is no such thing in Nature as pure water. In passing through the atmosphere the rain becomes highly charged with gases, taking up from 3 to 30 cubic centimeters per litre; the oxygen is found in larger proportions than in air, reaching as much as 38 per cent. of the total amount of dissolved gas. It also contains about 3 per cent. of carbon dioxide and minute traces of carbonate and nitrate of ammonia, besides small particles of solid matter, such as dust (especially in very windy weather), salts, and organic matter. In the country, where the air is fairly clean, rain water, owing to its purity and great aëration, is both wholesome and pleasant to drink, but in or near towns the soot and dirt derived from the air and roofs make it unfit for drinking purposes.

Spring Water.—Spring water contains most of the gaseous impurities present in rain water, and beside these all the mineral impurities it has dissolved in its passage through the ground.

The most ordinary impurity of spring water is chalk or calcium carbonate, which gives the water those properties which we call "hardness," a hard water being a water containing calcium and magnesium salts in solution.

Hardness.—Pure water cannot dissolve calcium carbonate to any appreciable extent, but when it filters through decomposing vegetable matter, it dissolves carbon dioxide, which is produced by decaying leaves, etc., and water containing carbonic acid dissolves chalk, owing to the formation of soluble calcium bicarbonate: hence, when such water filters through or over chalk beds, some is dissolved, and the water becomes hard.

There are two kinds of hardness in spring water: "temporary hardness," due to calcium and magnesium carbonate dissolved by the carbonic acid in water, which can be got rid of by any method which will drive off or neutralise the carbonic acid; and "permanent hardness," due to the presence of any soluble salts of calcium or magnesium in solution by the solvent properties for the water itself.

Water Softening.—In chalk districts, where the water is very hard, it is rendered soft by removing the carbonic acid holding the chalk in solution, by adding to such water some lime water, which is a solution of calcium hydroxide. The calcium hydroxide combines with the carbon dioxide of the carbonic acid, forming calcium carbonate; and this is precipitated, together with the original calcium carbonate, which, no longer having any carbonic acid to hold it in solution, falls down as a white powder.

Calcium bicarbonate		Calcium hydroxide		Calcium carbonate		Water.
$CaCO_3.H_2CO_3$	+	$Ca(HO)_2$	=	$2CaCO_3$	+	$2H_2O$.

This is called Clarke's process for softening water, but on a large scale, the turbid solution obtained on stirring an excess of lime with water (*milk of lime*) is employed.

Waste from Hard Water. — Not only is hard water unpleasant for domestic use, but it causes an enormous amount of waste, and we become aware of the economic importance of the kind of water we use if we consider

merely one of its actions — the waste of soap which it causes.

Soap is a definite chemical compound, and consists of the oleates and stearates of sodium; these dissolve in soft water and form a lather when we wash with them, loosening the dirt on our skin.

If we examine the skin we find that it is full of minute pores, one set discharging waste secretions from the body, whilst a second set furnishes oily secretions which keep the skin smooth and soft; and it is these oily exudations which catch and fix the dirt on the skin, and inasmuch as oil is not soluble in water, no mere washing in cold water without soap will loosen the dirt; the soap, however, by acting on the oil, does this, and enables the dirt to be then removed by the water. If, however, the water contains lime or magnesium salts, these at once attack the soap and decompose it, forming insoluble oleates and stearates of lime and magnesium, a process known as "curding"; and until all the lime and magnesium salts present in the water have been in this way used up, no soap will be available for cleaning purposes.

We take advantage of this action to determine the relative hardness of waters, by seeing how much of a soap solution of known strength a given water can convert into these insoluble compounds.

The supply of water, for instance at Greenwich is derived from deep wells in the chalk, and on analysis is found to contain—

Temporary hardness.	Calcium carbonate	16·30	grains per gallon.
Permanent hardness.	Calcium sulphate	5·37	,,
	Magnesium sulphate	0·93	,,
	Magnesium nitrate	1·20	,,
	Sodium chloride	2·64	,,
	Sodium nitrate	1·21	,,
	Silica, alumina, etc.	0·97	,,
		28·62	

The hardness of a water is expressed in degrees, one degree of hardness representing the soap-destroying power imparted to one gallon of it by the presence in solution of one grain of chalk; so that when we say that a water has ten degrees of hardness, we mean that it contains ten grains of chalk per gallon of water, or its equivalent in other lime and magnesium salts. The Greenwich water supply is said to have twenty-four degrees of hardness, 16·5 of these being due to temporary and 7·5 to permanent hardness.

Now one degree of hardness will use up and waste ten grains of soap per gallon of water used, and with large quantities of a hard water this rapidly mounts up to a very high figure. For instance—

Degree of hardness of water used.	Pounds of soap wasted per 100 gallons of water
5°	3·66
10°	7·31
15°	11·12
20°	14·75
25°	18·41

Salts in Solution in Spring Water.—Besides calcium carbonate and sulphate, we find in spring water the sulphates, carbonates, chlorides and nitrates of magnesium, potassium, sodium, manganese, and iron, and also small quantities of organic matter and occasionally silicates.

In spring waters the constituents vary very much in quantity according to the soil through which they have filtered, and they may be classified according to the chief constituent they contain, into (1) Waters in which the saline contents are chiefly carbonates, such as the waters of Vichy, Ems and Spa. (2) Waters in which the salts are mostly sulphates, such as the waters of Carlsbad, Epsom and Bath. (3) Waters in which the salts are chiefly chlorides, like the waters of Wiesbaden, Leamington, Harrogate and Cheltenham. (4) Waters in which the chief salts are silicates, like the hot springs of Iceland.

When the water of a spring is so highly charged with saline or gaseous impurities as to be unfit for ordinary purposes, it is called a "mineral water."

The gases contained in spring waters vary very much in quantity; in some cases the amount is small, whilst in others the water having filtered through subterranean caverns containing carbonic acid or other gases under considerable pressure, the water has dissolved so much that when it escapes into air under the ordinary pressure it liberates some of the gas and effervesces.

In some springs sulphuretted hydrogen is found dissolved, which gives the water the odour of rotten eggs.

River Water.—River water, although it contains a large proportion of spring water, has generally a smaller quantity of dissolved solids in it, and this is partly due to its being largely diluted with surface water, which contains very little dissolved solid matter, and partly to the fact that water in flowing through the air gives up some of the carbon dioxide of the carbonic acid it contains and deposits calcium carbonate.

In river water we find, besides the dissolved mineral and gaseous impurities of spring water, dissolved and suspended organic substances derived from drainage discharging into the streams and also from decaying vegetable matter, and this organic matter gradually undergoes a process of purification, being oxidised by the oxygen dissolved in the water and gradually converted into carbon dioxide, water, nitrates, nitrites, and ammonia.

In addition to the dissolved solids and gases found in river water, there is also a quantity of waste matter in a state of suspension, generally known as suspended solids, consisting of small particles of insoluble matter carried into the rivers by the surface drainage.

The part played by the rivers of the world in changing the face of the globe may be imagined from the fact that in suspended matter alone the Amazon discharges into the

sea over 950 million tons of solids per annum, and it has been estimated that the suspended matter annually discharged into the sea by the Mississippi is equal to 4,000 million cubic feet of clay, and that the quantity thus conveyed into the Bay of Bengal by the Ganges and Brahmapootra amounts to ten times as much.

Sea Water.—Sea water is, to all intents and purposes, a mineral water of the third class, its principal constituent being sodium chloride, besides which it contains a large number of other salts, chiefly chlorides and sulphates of sodium, magnesium, potassium, and calcium.

The amount of solid matter varies but little in different parts of the ocean; in inland seas, where the evaporation is very great and the quantity of water supplied by rivers not very large, the proportion of dissolved solid matter present is generally above the average, as may be seen in such cases as the Dead Sea, and to a much smaller extent in the Mediterranean.

SALTS IN SPRING, RIVER, AND SEA WATER.

In grains per gallon.

	Spring.	River.	Sea.
Calcium carbonate	16·30	10·80	3·32
Calcium sulphate	5·37	3·00	93·21
Magnesium carbonate	1·34	1·25	trace
Magnesium chloride	0·68	0·42	220·55
Magnesium sulphate	0·93	0·00	144·62
Sodium chloride	2·64	1·80	1850·74
Silica, alumina, etc.	0·23	0·27	trace

The extraordinary differences in the composition of river and sea water at first sight do not appear compatible with the theory that sea water is usually concentrated river water. If we compare the analyses of a river water, and the sea near its mouth, it is seen that those substances brought down by the river in greatest abundance, such as the carbonates of lime and magnesia and silica, are present in the sea water in the smallest quantity, these substances

being abstracted from the water by marine animals and plants to form their shells and structures.

The Action of Impurities on Health.—The natural impurities in water nearly all exert a certain amount of influence upon our health, but the action is very slight, and it is only the constant drinking of the same water over very long periods that makes the result noticeable; for instance, there is no reasonable doubt that water containing calcium sulphate produces dyspepsia, and should be avoided, not only for that reason, but because it is suspected of being connected with goitre and calculous affections common in those districts where the water supply is derived from the limestone rocks; but at the same time, such water is usually very free from natural organic impurities, and it may take years to develop any ill effects. Besides these natural impurities, there are other sources of contamination to which water is exposed, of a much more dangerous description, the worst being sewage contamination; whilst in rare cases a water may become charged with dissolved metallic impurities, such as lead or copper.

A water may become contaminated with sewage either by leakage from a cesspool situated in the vicinity of a well, by leakage into water pipes in sewage laden ground, or by contamination of water in cisterns from sewer gas, due to the overflow from the cistern leading into the drains; such contamination nearly always produces diarrhœa, and often typhoid fever, whilst in hot climates it causes dysentery and cholera. In Nature, to a great extent, organic contaminations of this character in rivers and streams are destroyed and rendered innocuous by the oxidising action of the air dissolved in the water, the oxygen converting the organic impurities into carbon dioxide and nitric acid; but in confined spaces, such as cisterns and wells, this can only take place to a very small extent, and we must therefore consider the means by which such water can be rendered as little injurious as possible to health.

Sources of Supply.—The chief sources of water supply are: (1) Rain water collected from the roofs, etc., and this in the country is pure and soft. (2) Water from shallow wells; this is nearly always bad, and is more exposed to sewage contamination than any other kind of water. (3) Springs; these are fairly free from organic matter, although often very hard. (4) River water, which is made to pass through depositing and filtering tanks; this water has the disadvantage of having been contaminated with sewage and other impurities, so that there is a risk that if the purification process failed at any time, the impure water would be supplied for drinking. (5) From deep wells, the water from which is generally free from organic impurities but very hard.

The water obtained from any of these sources is supplied to the house by one of two methods—either by intermittent or constant service.

The advantages of the constant service, in which the pipes distributing the water are always kept charged, are very great, as the necessity for cisterns is done away with, and the pipes being always full of water, are not so liable to corrode as when they are alternately full of water and air, whilst the chance of sewage contamination from leaky pipes, etc., is very much diminished. In the intermittent water supply, the water is only turned on for a short time in the twenty-four hours, and it is necessary therefore to have cisterns which will hold a sufficient supply for the house, and which frequently become contaminated with dust, vegetable growths, and sewer gas, unless precautions are taken to prevent it.

Gaseous impurities in water can be got rid of by long boiling, which also tends to kill many of the organisms to be found in water.

Dissolved solids, such as common salt, calcium sulphate, and Epsom salts, can be got rid of by distillation—that is, by converting the water into steam, which escapes, and which can then be condensed into water by cooling it, leaving the salts behind.

Suspended solids, and under certain circumstances some of the other impurities as well, can be got rid of by filtration through various media.

Filtration.—In the purification of water by filtration for drinking purposes on a large scale, two distinct means are employed for the removal of foreign matter, viz., mechanical and chemical. The mechanical processes, as employed by most of the large water companies, consist of allowing the heavier impurities to subside in large reservoirs called settling tanks, and then passing the partially clarified water through filtering beds from six to eight feet in thickness built up in layers of gravel and sand of varying degrees of coarseness, through which the water filters at the rate of from 60,000 to 100,000 gallons per hour per acre of filter bed.

In filtration through filter beds of this kind the action which takes place is a good deal more than the mere separation of minute particles whilst the water is finding its way through the interstices between the fine grains of sand.

After a sand filter of this character has been in use for a short time a green growth forms on the surface of the sand, and biologists have shown that this is specially active in arresting bacteria and organic matter.

With a newly-made and perfectly clean sand filter bed the action at first is merely mechanical, and in Germany the filtered water is not sent out for distribution until the growth of algæ has begun to show itself in the filtering bed, and the bacteria have been reduced by its presence to a standard amount.

The drawback to this kind of filtration is that an increase in the rate of flow through the bed prevents purification being properly effected, whilst the area required is of necessity very large.

Of the processes which combine chemical with mechanical action, the "Porter-Clark" process may be taken as a type. In this system "milk of lime" (p. 121) is mixed, by means of agitators, with the water to be purified, and by combining

with the carbonic acid in the water, causes a deposition of the calcium carbonate as a very fine powder—the separation of the finely divided carbonate also mechanically removing a large portion of the organic matter—and the water is then clarified by forcing it through a filter press in which frames covered by stretched canvas or other filtering media retain the solid particles.

In "Maignen's" process a powder called "Anti-Calcaire" —containing chiefly lime, sodium carbonate and alum—is added; the alum causes a coagulation and precipitation of the organic matter, whilst the sodium carbonate attacks the salts of lime and magnesium.

In the "Anderson" process the action which iron has upon the organisms and organic matter in water is relied upon. When this process was first introduced, it was supposed to be essential that the iron should be in the finely divided spongy condition, which is obtained by reducing it at low temperatures from its ores, but it has since been found that scrap iron, when well agitated in contact with the water, answers the same purpose as well, if not better. The action here is probably mainly due to the formation of carbonates of iron by the carbonic acid in the water, and on exposure to air oxidation takes place, and causes a coagulation. Some other processes are in use to a small extent, and in nearly all, alkaline hydroxides or salts are first added to neutralise carbonic acid and precipitate salts of lime and magnesium, and the precipitated matter is then removed by rapid filtration.

The subject of filtration on a small scale has of late undergone a complete revolution owing to the large amount of biological work which has been done on the subject. Up to fifty years ago the media which used to be employed in domestic and ships' filters consisted almost entirely of substances which kept back the large suspended impurities and acted purely mechanically, such as sponge, sand, and indeed almost anything in which the pores were sufficiently small to retain visible particles.

Filters of this kind, however, gradually gave way to the use of materials which exercised a chemical as well as a mechanical action upon the foreign matters present in the water. Of these filters undoubtedly the most effective were carbon in its various forms, and spongy iron.

Carbon for Filters.—Carbon owes its position as a filtering agent to a combination of properties which occupy the borderland between chemical and physical action; a freshly burnt piece of charcoal has a wonderful power of absorbing gases, a cubic inch of the substance being able to compress into its pores 100 times its own volume of ammonia gas, whilst it absorbs other gases to a smaller extent. The gases so compressed are rendered excessively active in their chemical affinities, so that if a piece of freshly burnt charcoal be exposed to the action of sulphuretted hydrogen, until it has absorbed as much as it will of this gas, and be then plunged into oxygen, it is not unusual for the charcoal to burst into vivid combustion owing to the rapid conversion of the sulphuretted hydrogen in its pores into water and sulphur dioxide—hence the enormous value of charcoal for respirators, sewer traps, and deodorising animal matter which has commenced to putrefy. This power of absorption which charcoal possesses is not confined to gases, for many liquid and solid substances are removed from solution in water by its means, and the most active form of carbon for this purpose is that which is held in a very fine state of division on the surface of mineral matter. When bones are heated out of contact with air, the organic matter which they contain is broken up and the carbon is left deposited in this fine state of division upon the calcium phosphate and calcium carbonate which form the mineral structure of the bone, and the substance so formed goes by the name of bone-black or animal charcoal. If some of this substance be shaken up with port or claret, and the mixture be then filtered, it will be found to be rendered colourless, an effect due to the abstraction of the colouring matter by the carbon.

The colouring matter, however, seems only to have entered into very weak combination, if any, with the carbon, as it can be recovered by washing the bone-black with a weak alkaline solution.

Bone-black contains only 10 per cent. of pure carbon, and yet from the fineness of its state of division, it is far more active than wood charcoal containing 90 per cent. and upwards.

When a water containing organic impurities is filtered through a finely-divided carbon of this description, it was supposed that the organic matter was partly mechanically taken from it and partly destroyed, burnt up by the oxygen held by the carbon, and for this reason animal charcoal filters were long looked upon as perfect water purifiers; but as early as 1878, it was pointed out by the Royal Commission on River Pollution, that it had the serious drawback, that when water which had been filtered through it was allowed to stand, minute organisms, both animal and vegetable, made their appearance in the water and rendered it not only unfit to drink but actually offensive. Whilst if the animal charcoal has not been burnt at a sufficiently high temperature, which is rarely done, as it means a certain loss of carbon, some of the nitrogenised organic matter of the bone remains and becomes a breeding place for myriads of minute organisms which find their way into the water. Also fresh organic matter like the white of an egg (albumen), which had not yet entered into putrefactive change, passes through animal charcoal almost unacted upon.

Spongy Iron for Filters.—Spongy iron used in Bischof's filters is made by reducing hæmatite and other iron ores by carbon at a low temperature so as to avoid fusing the particles together, and to present as large a surface as possible to the water.

The power of metallic iron to purify water has been known for a long time, and it is a well recognised fact that if a ship takes in foul water, the impurities are greatly

diminished by keeping the water in iron tanks for a sufficient length of time, the rolling of the ship helping the action by agitating the water and bringing fresh portions in contact with the metal; and as early as 1857 it was proposed to purify water by suspending in it bundles of iron wire, and to leave them in contact for a couple of days—about 1 lb. of iron being used to 100 gallons of water—a process which gave good results, whilst the increase in surface given by using the iron in the spongy state rendered the filtering action much more rapid.

In the spongy iron filter the water dissolves a certain proportion of iron, and in order to remove this the water is made to pass through a layer of fine sand and black oxide of manganese, which precipitates and retains the iron as ferric hydroxide.

In Maignen's "Filtre Rapide," animal charcoal which has undergone a preliminary treatment with acetic acid and then neutralisation with lime water is employed, whilst great rapidity of filtration is effected by using a cone covered with asbestos cloth and thus greatly increasing the filtering surface.

Carbalite.—In the Service we are fortunate in having perhaps the best example of this form of filter. The filtering medium is neither animal charcoal nor spongy iron, but an artificial compound called "Carbalite," which possesses the best characteristics of both media.

During the last ten years biologists have shown that domestic filters of all these classes are worse than useless for the removal of germs and bacteria, and that while they act satisfactorily in arresting suspended particles, many filters, especially those dependent upon carbon blocks, serve as breeding grounds for the growth of various organisms, which are generally found in enormously greater numbers in the filtered than the unfiltered water, and although the majority of these bacteria may have no specific action, it is clear that such filtration would be also unavailing against those liable to set up disease.

It has moreover been shown that even though such filters be repeatedly cleaned and sterilised, they are absolutely useless as a safeguard against dangerous germs.

Pasteur-Chamberland Filters.—The filters which recent researches have shown to be the only effective ones are those consisting of a cylinder of unglazed porcelain clay of the Pasteur-Chamberland type, in which water under the pressure present in the supply pipes passes through the porcelain from without inwards. This form of filter, according to the researches of Plagge, seems to be absolutely impermeable to bacteria, and is so arranged that as the surface of the porcelain tube becomes choked with solid particles, it can be removed and scrubbed.

Other filters like the Berkefeld, which are also made on this principle but of infusorial earth instead of porcelain clay, have not the same effect in yielding a sterile filtrate for any length of time.

Fig. 24 shows a section of a single cell tap filter of the Pasteur-Chamberland type, in which (A) is the cylinder of unglazed porcelain, closed at the top, whilst the bottom is provided with an external flange and open nozzle. Surrounding the cylinder is a metal tube (B) sufficiently large in bore to leave a space between it and the sides and top of the porcelain tube. The upper end of this jacket is soldered to the water tap, whilst the lower end can be clamped tightly to the flange of the porcelain tube by the screw cap (C).

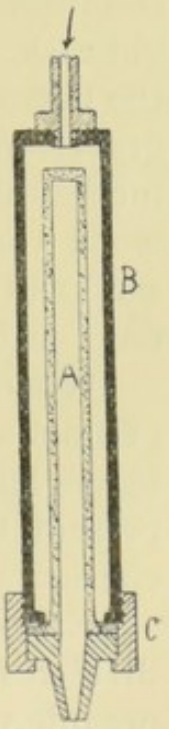


Fig. 24.

All that has to be done to clean the filter is to unscrew the cap (C), when the porcelain tube can be removed and scrubbed, and if necessary heated to redness in a bunsen flame. On replacing the porcelain and fixing on the screw cap the filter is once more ready for use. Such filters can of course

be fitted up in batteries to give a supply of any quantity needed.

Distillation.—On board ship distillation of sea water is commonly resorted to in order to render salt water fit for drinking, and although the water so obtained is pure, yet all gases having been driven from it by the boiling, it is insipid for drinking purposes until it is again aërated.

This is best accomplished by allowing it to trickle slowly down through a long column of wood charcoal or carbalite, up which air is passing.

Rough Purification.—In many cases, such as during expeditions up rivers, etc., when away from the ship, the use of regular filters is impossible, whilst the water derived from swampy ground, marshes, or streams full of vegetable matter, is quite unfit for drinking purposes, and tends to produce dysentery and other diseases of the same kind. Under these conditions a rough filter may be constructed by sinking an old cask, charred on the inside and with some holes bored in the bottom, in the bed of the stream, and putting into it fine gravel and the cleanest sand to be found, in a layer 6 to 8 inches thick, and if possible below the sand a layer of charred wood from the fire; a thin layer of gravel on the top of the sand will keep it from rising with the water and for several days such a filter will prove most effective.

Where even this is impossible a few grains (6 per gallon) of alum added to the water, or boiling the water with the leaves left after making tea, serve to cause the organic matter present to clot together and settle out, leaving the water considerably purified.

Exposing the water to the action of air, whilst in finely divided streams, is also very efficacious in removing offensive organic vapours and sulphuretted hydrogen from water, and also to a certain extent organic matter; this is best done by pouring the water several times through a fine sieve, held as high as possible above the vessel which is to catch the aërated water.

The determination in a rough way of the purity and fitness for drinking of a water is as a rule perfectly useless, as the presence of the more easily detected impurities may indicate the presence of organic contamination of the worst kind, or may be due to perfectly harmless circumstances. In selecting a water for drinking purposes, it is essential to know the source and history of the water as well as the nature of the impurities in it, before any conclusion can be come to as to its effect upon health. For instance, the presence of considerable quantities of chlorides in a shallow well water would at once condemn it as a drinking water, the chlorides being almost certainly derived from sewage, whereas the presence of the same amount of chlorides in a deep well water would not be any proof of its being unfit for drinking purposes, having most probably been derived from soluble chlorides in the beds through which the water has filtered.

CHAPTER X.

Boiler Incrustation.

Saline constituents of fresh and sea water — Incrustations from different kinds of water—Causes of boiler incrustation—Calcium carbonate —Calcium sulphate—Solubility—Effect of concentration on sea water—Effect of temperature and pressure on the saline constituents of sea water —Formation of magnesium hydroxide in marine boiler deposits—Action of distilled water on boilers—Waste of fuel entailed by boiler incrustation —Prevention of incrustation—Anti-incrustators—Chemical and mechanical action of anti-incrustators—Zinc in boilers—Feed water heaters.

Formation of Deposit.—When a natural water is boiled and the carbonic acid which it contains is expelled, the carbonates of calcium, magnesium and iron, which are only held in solution by water in the presence of free carbonic acid, are thrown down ; and as the remaining water in the boiler becomes more and more concentrated by the escape of steam, so the calcium sulphate which is but slightly soluble in water is also deposited, and with the separation of these mineral salts, organic matter which the water may contain is also to a certain extent mechanically carried down, and these various bodies forming in thin cohesive layers on the sides and bottom of the vessel give rise to the so-called fur in a kettle, or the more serious boiler deposit.

This deposit being a bad conductor of heat not only retards the transmission of heat from the furnace to the water, but also shortens the life of the boiler by corrosion and overheating.

As has been pointed out, fresh water is very variable in composition, but, as a rule, contains as its chief saline constituents the carbonates of lime and magnesia, held in solution by carbonic acid present in the water, and also small quantities of the sulphates of these metals, and traces of common salt.

Sea water contains a far higher proportion of saline matters in solution than fresh water, and also in totally different proportions, as although sea water is only river water concentrated by the evaporative power of the sun's rays during long ages, yet, owing to the deposition of calcium carbonate during the flow of the water down rivers, and also to its being used by certain forms of marine life, calcium carbonate (carbonate of lime), which is the chief saline constituent of fresh water, is reduced to a mere trace in salt water, whilst the salt has become the all-important constituent, and the sulphates of calcium and magnesia, together with chloride of magnesium, are also present.

The wide difference in composition of fresh and salt water may be seen from the following analyses :—

SALTS IN SOLUTION IN RIVER AND SEA WATER
GRAINS PER GALLON.

	River Water. THAMES.	Sea Water. LOWESTOFT.
Calcium carbonate (chalk) ...	10·80	... 3·9
Calcium sulphate (gypsum) ...	3·00	... 93·1
Magnesium sulphate	0·25	... 124·8
Magnesium chloride		... 220·5
Magnesium carbonate	1·25	... trace
Sodium chloride (salt)	1·80	... 1850·1
Silica (sandy matter)	0·56	... 8·4
Oxides of iron and alumina ...	0·27	... trace
Organic matter	2·36	... trace

In the older forms of marine boilers, working at comparatively low pressures, sea water was almost universally employed; but with the introduction of high-pressure tubular boilers the amount of deposit formed was so serious, and the difficulty of removing the incrustation from between the tubes so great, that it became almost imperative to discontinue the use of the sea water, and to rather accept the expense of supplying the boilers with distilled water than

risk the burning and destruction of the tubes and plates in inaccessible portions, where the deposit had to be allowed to collect until the time could be spared for a complete clean out and refit.

Distilled water is presumably free from all dissolved solids, but the condenser water always contains some of the lubricants from the cylinder; and when these find their way into the boiler they often cause trouble of a serious character.

Difference in Deposits.—The great difference existing between sea and fresh water would lead one to expect a wide difference also in the kind of deposit formed from them, and this is found to be the case, as the following analyses of incrustations formed in the boilers of steamers using fresh river water, the brackish water at the mouth of a river, and sea water respectively, show :—

	River.	Brackish.	Sea.
Calcium carbonate	75·85	43·65	0·97
Calcium sulphate	3·68	34·78	85·53
Magnesium hydroxide ...	2·56	4·34	3·39
Sodium chloride	0·45	0·56	2·79
Silica	7·66	7·52	1·10
Oxides of iron and alumina ...	2·96	3·44	0·32
Organic matter	3·64	1·55	trace
Moisture	3·20	4·16	5·90
	100·00	100·00	100·00

These may be taken as typical deposits, and show that with fresh water the incrustation may be looked upon as consisting of calcium carbonate, with small quantities of other compounds; that with a mixture of fresh and salt water the deposit consists of nearly equal parts of the calcium carbonate and sulphate; whilst the sea water gives practically pure calcium sulphate.

The presence of calcium sulphate exercises a very marked influence upon the condition and physical properties of the incrustation, as, under the conditions in which it is formed in

a boiler, it separates in a crystalline form, and binds the deposit into a hard mass, an action which is also aided by the presence of magnesium hydroxide.

A deposit consisting of calcium carbonate only, or of calcium carbonate and traces of the oxides of iron and alumina, sodium chloride, etc., is separated as a soft powder, which remains suspended in the water for some time, and which can fairly easily be removed from the boiler on cleaning; whilst, if calcium sulphate is present, the scale is extremely hard, and generally requires the use of hammer and chisel to detach it from the plates and tubes, an operation which is extremely injurious, and tends to shorten the life of the boiler.

The three principal constituents of boiler incrustations may therefore be looked upon as calcium carbonate, calcium sulphate, and magnesium hydroxide, and the causes which lead to their deposition must now be considered.

Calcium Carbonate is practically insoluble in pure water, that is to say, it requires more than 10,000 parts of pure water to dissolve one part of the carbonate; but carbonic acid, which is present in all natural waters, when in contact with calcium carbonate converts it into bicarbonate, which is soluble, and this forms the so-called "temporary hardness" in fresh water. On heating such a water the bicarbonate is decomposed, carbon dioxide gas escapes, and the calcium carbonate being insoluble, is deposited. Calcium carbonate is slightly more soluble in saline solutions, such as sea water, than in pure water, but the difference is so small that the above may equally be looked upon as applying to fresh and salt water.

Calcium Sulphate is to the marine engineer the most important constituent of boiler incrustation, and its separation as a deposit from water is dependent upon a totally different class of phenomena to those which bring about the precipitation of calcium carbonate. Calcium sulphate is dissolved in water by the solvent power of the water itself,

and not through the agency of carbon dioxide, and therefore merely boiling water at ordinary pressure does not suffice to cause its deposition, and for this reason it forms, together with soluble magnesium salts, the "permanent hardness" of fresh water.

The solubility of calcium sulphate in pure water varies very considerably with the temperature.

100 parts of water at a temperature of	Dissolve calcium sulphate.
0° C. or 32° F.	0·205
5° „ 41°	0·219
12° „ 53·6°	0·233
20° „ 68°	0·241
30° „ 86°	0·249
35° „ 95°	0·254
40° „ 104°	0·252
50° „ 122°	0·251
60° „ 140°	0·248
70° „ 158°	0·244
80° „ 176°	0·239
90° „ 194°	0·231
100° „ 212°	0·217

Calcium sulphate is most soluble in water at 35° C., one part of calcium sulphate being dissolved in approximately 400 parts of water; and, inasmuch as the solubility of the salt is considerably decreased at 100° C., if a solution be taken saturated at 35° C., and then heated to 100° C., precipitation of a portion of the calcium sulphate will take place.

Calcium sulphate is much more soluble in a saline solution, such as sea water, than in fresh water, but its solubility rapidly decreases, (1) on concentration of the saline solution, and (2) on increase of temperature and pressure.

If ordinary sea water be concentrated, three distinct stages of decomposition may be traced :—

(1) Deposition of basic magnesium carbonate.

(2) Deposition of calcium carbonate with remaining traces of the basic magnesium carbonate and hydroxide; and, finally,

(3) Deposition of the calcium sulphate.

Whilst the variation in the saline constituents of the remaining liquid may be seen from the following table:—

SALINE CONSTITUENTS PER CENT.

Density	1·029	1·05	1·09	1·225
Sodium chloride ...	2·6521	4·4201	7·9563	23·8689
Calcium sulphate ...	0·1305	0·2175	0·3915	none
Calcium carbonate ...	0·0103	0·0171	none	none
Magnesium carbonate...	0·0065	0·0032	none	none
Magnesium chloride ...	0·2320	0·3865	0·6960	2·0880
Magnesium sulphate ...	0·1890	0·3150	0·5670	17·010

If the sea water be heated and concentrated above a density of 1·225, the salt commences to crystallise out.

The deposition of the calcium sulphate during the concentration of the sea water is due to two causes: in the first place, although it is more soluble in a dilute solution of salt than in fresh water, yet it reaches its maximum solubility at a density of 1·033, and after this point concentration of the saline solution diminishes the amount which can be held in solution, and the calcium sulphate is perfectly insoluble in a saturated brine. The second cause for its deposition is the rise in boiling point which accompanies the increase in density, the higher the temperature the less the solubility of the calcium sulphate becomes, so that when 140° to 150° C. is reached it becomes perfectly insoluble, both in sea and fresh water.

If sea water be boiled merely under atmospheric conditions, it would be quite possible, by taking care that its density does not rise above a certain point (1·09), to prevent the deposition of the calcium sulphate; but any such regulation of the density is rendered abortive by the fact that pressure, and consequent raising of the boiling point, acts upon the calcium sulphate in solution in exactly the same

way as concentration and increased temperature, so that in the older forms of boiler, working even at a comparatively low pressure, most of the sulphate was deposited, whilst in the high pressure boilers now in use, if the water contains the smallest trace of calcium sulphate, it will be deposited ; and as any deposit formed amongst the tubes in such a boiler cannot easily be got at, it is practically impossible to use sea water in them, so that they are supplied with the water from the condenser augmented by distilled water made in special distilling plant. The question has been raised as to whether, if sea water were mixed with distilled water so as to greatly reduce its density, it would deposit the calcium sulphate ; but experiment shows that, even if sea water is mixed with many hundred times its bulk of distilled water, the minute trace present is deposited under pressure when the temperature approaches 140° C. So that when, through a breakdown in the distilling apparatus, sea water has to be used with the condenser water in even very small quantities, a slight scale is sure to be formed. When a saline solution containing calcium sulphate is heated under pressure or concentrated until calcium sulphate begins to separate, the sulphate will continue to precipitate even after the liquid has cooled down or the pressure has been removed ; and, finally, when calcium sulphate has separated at a high temperature or pressure from sea water, even though the water has only the ordinary density (1·027), the rate at which the sulphate will re-dissolve is so extremely slow, that its consideration may be neglected.

These two last properties are due to the form in which the calcium sulphate separates from sea water under pressure. Calcium sulphate occurs in Nature as gypsum, in which each molecule of calcium sulphate is combined with two molecules of water of crystallisation ; when calcium sulphate is deposited from sea water in a boiler it comes down in small crystals containing two molecules of calcium sulphate to one of water ; whilst, after deposition in the boiler and in contact with the heated plates and tubes, it undergoes a

further change of crystalline form, loses water, and becomes "anhydrite," which is pure calcium sulphate free from water of crystallisation, and it is this change in crystalline form which binds deposits containing it into such a hard mass.

Magnesium Hydroxide. — The presence of magnesium hydroxide in boiler deposits has given rise to many theories to account for its formation, the one most generally accepted being that it is due to the mutual decomposition of water and magnesium chloride, which give rise to magnesium hydroxide and hydrochloric acid, the action being accelerated by the presence of metallic iron.

Magnesium chloride Water Magnesium hydroxide Hydrochloric acid.

$$MgCl_2 + 2(H_2O) = Mg(HO)_2 + 2(HCl).$$

When sea water is evaporated in contact with a large surface of metallic iron, no chloride can be detected in the distillate until four-fifths of the solution has been distilled over, whilst if the sea water be evaporated alone, it can be taken nearly to dryness without any decomposition. At a high temperature under pressure in marine boilers this decomposition may take place, but only to a very small extent, a much larger proportion of the magnesium hydroxide being formed by the decomposition of the magnesium carbonate first deposited from the water in contact with the heated tubes, and also by the action of magnesium chloride in the sea water upon the deposited calcium carbonate which mutually react upon each other, soluble calcium chloride and magnesium oxide are formed, and the magnesium oxide united with water forms magnesium hydroxide, carbon dioxide at the same time escaping.

This explains many points which the former theory leaves untouched—for instance, the fact of calcium carbonate being absent from marine boiler deposit, or, if present, only in very small quantities; and also that chloride of iron is not found in the water of the boiler, which would be the case if any corrosion or pitting were due to the action of free hydrochloric acid.

In many analyses of boiler deposits no magnesium hydroxide is returned, but considerable proportions of magnesium carbonate, which naturally would be formed by the magnesium hydroxide absorbing carbon dioxide on exposure for any length of time to the air.

Sodium chloride, magnesium chloride, and sulphate are not found as usual constituents of boiler scale; but in cases of heavy incrustation, pockets are found in the deposit filled with microscopic crystals of these salts which have slowly filtered in solution into cavities in the incrustation, and have been deposited there on evaporation of the liquid.

Form of Scale.—An examination of the arrangement of the various portions of these deposits gives a fair idea of their formation. The crystalline crusts of calcium sulphate are always thickest and purest, and, for this reason, hardest in contact with the tubes or plates of the boilers where they have been most heated, but one also finds these layers throughout the deposit in many cases having a nodular form. This goes to prove that after the deposit has come down as a mud, the calcium sulphate being deposited already in small dense crystals, sinks through the lighter portions, and forms first a thin, and eventually a thick coating, which, by continuous heating under pressure, changes its crystalline form, giving up moisture, and becoming "anhydrite." The deposit above it gradually becomes thicker and thicker, and more crystallisation of the calcium sulphate takes place, pieces of mill scale and other foreign substances present in the mud forming nuclei round which the "anhydrite" crystallises; the lighter portions, consisting of magnesium hydroxide and traces of calcium carbonate, settling into any spaces that remain, and completing the deposit.

When distilled water only is used, a slight coating is formed, practically consisting only of organic matter, whilst if at any time through a breakdown in the distilling apparatus sea water is mixed with the distilled water, a thin and very

hard scale of calcium sulphate is formed. An incrustation of this character gave on analysis :—

Calcium sulphate	90·84
Magnesium hydroxide	·75
Sodium chloride	1·41
Silica	·85
Copper carbonate	1·11
Oxides of iron and alumina	·24
Organic matter	2·96
Moisture	1·84
	100·00

This scale is of great interest from the presence in it of the carbonate of copper. It is well known that distilled water has a far greater solvent effect upon metals than a water containing certain salts in solution, and it is quite conceivable that the distilled water from the surface condensers attacks the brass and copper tubes and fittings, and deposits the copper on the tubes of the boiler, although in only small quantities ; and it is interesting to note that the green spots due to the presence of the copper are all on the underside of the scale, that is, in contact with the metal of the boiler tubes, showing that in all probability it had been deposited, as suggested, from the water in the boiler, and in contact with the iron would set up local galvanic action and tend to produce pitting.

Waste of Fuel due to Scale.—The loss of heat and waste of fuel entailed by the presence of boiler scale is enormous, and has been estimated by various observers at very different values. The latest estimates, however, go to show that one-sixth of an inch of scale necessitates the use of 16 per cent. more fuel, one-fourth of an inch 50 per cent., and half an inch 150 per cent. additional coal ; the resulting waste of coal in the Service, however, being oftener laid to the credit of the state of the ship's bottom than to the condition of her boilers.

Waste of fuel, however, is not the only drawback brought about by incrustation ; the deposit being a bad conductor of heat, the tubes and plates of the boiler soon become overheated and burnt on the outside, whilst rapid corrosion is set up on the inner surface; iron at temperatures below visible red heat decomposing water and combining with the oxygen whilst hydrogen is liberated.

Even when calcium sulphate is not present, or is only present to a small extent, as in the deposits from fresh water, the tubes should be allowed to cool down before the boiler is blown off, as if this is not done, the loose soft deposit of calcium carbonate, when the water has all run off, bakes to a hard tough scale, which acts as a ground work for further deposits.

Prevention of Scale. — The importance of preventing boiler incrustation, and thereby avoiding the enormous waste of fuel and injury which it entails, has not been without its effect upon the minds of inventors, and almost every conceivable substance, from potato parings to complex chemical reagents, has from time to time been patented for this purpose, but they have all more or less failed for marine boilers, because either they have had an injurious effect upon the metal of the plates, or else have produced an enormous bulk of loose deposit, which although easily cleaned out if the various parts of the boiler were accessible, and if it were only being used intermittently, yet in a marine boiler continuously working, rapidly chokes the portions between the tubes, and brings about an even worse state of affairs than that originally existing.

For these reasons, no treatment of sea water in the boilers themselves is practically possible, and with high pressure tubular marine boilers, the water used must be condenser water made up to the required bulk with distilled water.

If the engines of a vessel are in good condition, she will approximately require 1 ton of water per 1000 horse-power

per twenty-four hours to make up the volume of the condenser water to the amount required for the boilers, so that even supposing the engines not to be in good order, and considerable waste to take place, twenty tons per diem would be an outside allowance for even very large vessels.

In fresh water boilers incrustation can to a certain extent be prevented, or at any rate diminished, by the addition of substances which will prevent the calcium sulphate binding the calcium carbonate into a hard mass, and these so-called "anti-incrustators" may be divided into two large classes: (1) Those which have some definite chemical action, and (2) those which are purely mechanical in their action.

Saline Anti-incrustators.—In this class sodium carbonate generally plays the principal part. Its action is to convert the calcium sulphate and magnesium chloride into carbonate, and at the same time to keep the water in an alkaline condition so as to prevent damage from acids.

Calcium sulphate Sodium carbonate Calcium carbonate Sodium sulphate.

$$CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4.$$

The hardening effect of the calcium sulphate being done away with, the calcium carbonate is precipitated in a soft condition, when it can be blown off.

Ammonium chloride is also used, and when boiled in presence of calcium carbonate decomposes it, forming soluble calcium chloride, whilst the ammonium carbonate volatilises.

Other alkalies and alkaline salts are also used, and even in some cases, acid mixtures, which latter, if they dissolve the scale, are fatal to the boiler plates.

Tribasic sodium phosphate, fluorides and also sulphites have been used in some cases with fair results.

Oils and Fats should never be used, as not only do the fatty acids and salts attack the metal and increase corrosion, but the insoluble soaps formed by the combination of the fatty acids with the lime and magnesium salts in the water cling to the side of the boiler, and being broken up by the heat, yield a very tough form of scale.

There are an enormous number of other organic compounds, proposed or in use, the action, if any, being mostly mechanical.

Zinc in metallic contact with the boiler plates in cases where sea water is used, acts beneficially in preventing corrosion of the plates, but is of no use with fresh water, whilst other electrical and mechanical applications seem to have met with little or no success.

For land boilers, where only hard water is to be obtained, it is better to soften the water by the Porter-Clark or other similar process, and to separate the precipitated lime salts by rapid filtration before supplying it to the boilers.

Feed water heaters act to a certain extent in softening the water supplied to a boiler and thus reducing incrustation; sometimes nearly 50 per cent. of the calcium carbonate contained by the water being deposited as mud in the heater.

Organic Deposits.—So far the deposits taken into consideration have been those formed from the impurities natural to the water itself; but with the introduction of high-pressure steam a new and highly dangerous form of deposit has added to the trouble of the marine engineer.

As early as 1878 the collapse of the furnaces of the boilers of the s.s. *Ban Righ* and a similar misadventure in the screw tug *Ich Dien*, with no apparent cause to bring about the damage, caused some attention to be paid in marine circles to the action which had taken place, and the only clue to be found was that a certain amount of oily deposit had formed on the tops of the furnaces. Experiments made by Mr Dunlop, of Port Glasgow, led to the conclusion that this oil, which had distilled into the boiler from the lubricants used in the cylinder, was so bad a conductor of heat that its formation on the plates allowed them to get superheated, with the result that they were unable to withstand the pressure of steam existing in the boiler, and in this way brought about the collapse.

Similar cases of collapse became frequent after that date, no less than thirty vessels being disabled from this cause during a few years.

Effect of Oily Steam.—The cause of this is that the steam brings over some of the lubricants from the cylinders, and the greasy steam being condensed and the water returned to the boiler, takes the oil with it in finely divided particles. Having thus entered the boiler, the minute globules of oil, if in great quantity, coalesce to form an oily scum on the surface of the water, or, if present in smaller quantities, remain as separate drops; but show no tendency to sink, as, their specific gravity being ·889, they are lighter than the water, and the difference in gravity is probably even greater at the temperature existing in the boiler.

Slowly, however, they come in contact with small particles of calcium sulphate and other solids separating from the water, and sticking to them, they gradually coat the particles with a covering of oil, which in time enables the particles to cling together or to the surfaces with which they come in contact. These solid particles of calcium carbonate, calcium sulphate, etc., are heavier than the water, and, as the oil becomes more and more loaded with them, a point is reached at which they have the same specific gravity as the water, and then the particles rise and fall with the convection currents which are going on in the water, and stick to any surface with which they come in contact, in this way depositing themselves, not as in common boiler incrustations chiefly on the upper surfaces, but quite as much on the under sides of the tubes as on the top, their position being regulated by whether they come in contact with the surface whilst descending or ascending.

The deposit so formed is a wonderful non-conductor of heat, and also from its oily surface tends to prevent intimate contact between itself and the water. On the crown of the furnaces this soon leads to overheating of the plates, and the deposit begins to decompose by the heat, the lower layer in

contact with the hot plates giving off various gases which blow the greasy layer, ordinarily only $\frac{1}{64}$th of an inch in thickness, up to a spongy, leathery mass often one-eighth of an inch thick, which, because of its porosity, is an even better non-conductor of heat than before, the plate becomes heated to redness, and, being unable to withstand the pressure of steam, collapses. During the last stages of this overheating, however, the temperature has risen to such a point that the organic matter, (oil, etc.), present in the deposit burns away, or, more properly speaking, is distilled off, leaving behind, as an apparently harmless deposit, the solid particles round which it had originally formed.

Such a deposit is much more likely to be produced with boilers containing fresh or distilled water, as the low density of the liquid enables the oily matter to settle more quickly, whilst with a strongly saline solution it is very doubtful if this sinking point would ever be reached; it is evident also that, when oil has found its way into the boiler and is causing a greasy scum on the surface, the most fatal thing that can be done is to blow off the boilers without first using the scum cocks, because as the water sinks so the scum clings to the tops of the furnaces and other surfaces with which it comes in contact, and, on again filling up with fresh water, it still remains there, causing rapid collapse.

The only prevention for this class of deposit is to use as little lubricant as possible in the cylinder, and to filter the condensed water through a coke scrubber or oil filter before returning it to the boiler, as even mineral lubricating oils of the best makers undergo a partial decomposition at the temperature of the cylinder with liberation of minute quantities of oil of lower boiling point, which then distil over, so that the boiling point of the original lubricant is no guarantee that none will come over with the steam, and the most satisfactory way of determining the suitability of an oil for cylinder lubrication is to ascertain the percentage of loss which it sustains on heating to the cylinder temperature in a current of steam.

Hydrogen Dioxide.

Hydrogen and oxygen form a second compound, in which thirty-two parts by weight of oxygen are combined with two of hydrogen, and the hydrogen dioxide or peroxide therefore has the formula H_2O_2. It is a colourless, syrupy liquid when concentrated, with strong bleaching properties, due to the ease with which the second atom of oxygen is liberated from the molecule of the dioxide; it whitens the skin and decolourises the hair, and for this reason the dilute solution is used as "Golden wash" or "Golden hair-dye," when it oxidises the colouring matter and so partially destroys it. It has a specific gravity of 1·43 and slowly decomposes at 21·1° C. into water and oxygen, the decomposition increasing in rapidity as the temperature rises.

It is neutral to test papers and bleaches litmus solution.

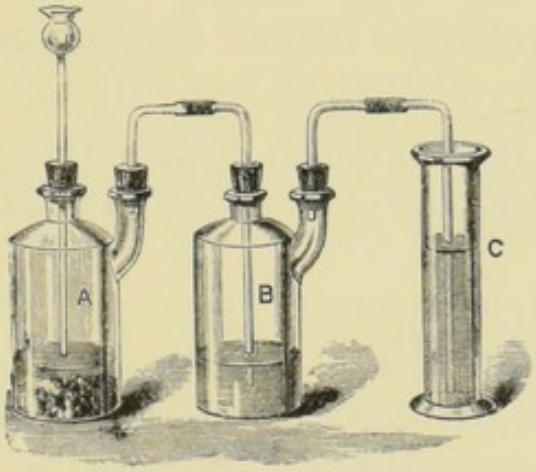


Fig. 25.

Preparation.—The most convenient method of preparing it is to pass a stream of well washed carbon dioxide through barium dioxide (BaO_2) suspended in water:

Barium dioxide		Carbon dioxide		Water		Barium carbonate		Hydrogen dioxide.
BaO_2	+	CO_2	+	H_2O	=	$BaCO_3$	+	H_2O_2.

The carbon dioxide is generated from marble and hydrochloric acid in the bottle (A, Fig. 25), and is washed by being made to bubble through water in the wash bottle (B), which frees it from any traces of acid which might be mechanically

brought over by the gas, and it is then passed through the barium dioxide suspended in water in the cylinder (C). The barium carbonate formed gradually settles down to the bottom of the cylinder, and the dilute solution of hydrogen dioxide can then be concentrated by evaporation over sulphuric acid in vacuo.

When hydrogen dioxide is brought in contact with finely divided metals, such as silver, gold, or platinum, it is decomposed and oxygen is liberated, the metals themselves undergoing no change.

Silver Hydrogen dioxide Silver Water Oxygen.

$$Ag + 2(H_2O_2) = Ag + 2(H_2O) + O_2.$$

It bleaches litmus and indigo by oxidising them, and will also oxidise arsenious and sulphurous acids into arsenic or sulphuric acid.

Sulphurous acid Hydrogen dioxide Sulphuric acid Water.

$$H_2SO_3 + H_2O_2 = H_2SO_4 + H_2O.$$

When the peroxides or oxides of certain metals are added to hydrogen dioxide, both oxides undergo decomposition at the same time:

Silver oxide Hydrogen dioxide Silver Water Oxygen

$$Ag_2O + H_2O_2 = Ag + H_2O + O_2.$$

Manganese dioxide Hydrogen dioxide Manganese oxide Water Oxygen.

$$MnO_2 + H_2O_2 = MnO + H_2O + O_2.$$

In all these cases the action is rendered more rapid by the presence of alkalies and retarded by acids.

Hydrogen dioxide may be detected by adding to the solution supposed to contain it a few drops of chromic acid which is oxidised, forming a blue solution containing an unstable perchromic oxide. If only small quantities of it are present, the solution is then shaken up with ether which dissolves the blue compound, and rising to the surface of the liquid renders it visible. Hydrogen dioxide will also turn a solution of potassium iodide and starch blue, by liberating the iodine which then forms the blue iodide of starch.

CHAPTER XI.

CARBON AND SOME OF ITS COMPOUNDS WITH HYDROGEN.

Allotropic modifications of carbon—Diamond—Graphite—Carbon from organic sources -- Absorbent properties of charcoal — General properties of carbon—Methane or marsh gas—Preparation and properties —Natural sources—Liberation of marsh gas in mines and coal bunkers —Fire-damp—Safety lamps—Ethylene or olefiant gas—Preparation— Coal gas and its manufacture—Structure of flame—Burners for gas— Illuminating power of gas.

CARBON, next to oxygen, is perhaps the most widely distributed of the elements; it occurs in the free state as the diamond and as graphite, substances which although they are physically dissimilar, yet can be proved to be chemically identical, the dissimilarity of physical properties being probably due to some difference in the atomic arrangement.

Where an element occurs in forms which are physically dissimilar but chemically identical, the substances are called "Allotropic modifications," and the diamond and graphite are said to be allotropic modifications of the element carbon.

That they are both pure carbon is proved by the fact that when equal weights of the diamond and graphite are burnt in oxygen gas, in each case the same weight of carbon dioxide, and nothing else, is produced, whilst if a diamond be heated in the electric arc it swells up and is converted into a black mass resembling graphite.

The diamond occurs in well defined crystals and has a specific gravity of 3·5. It is one of the hardest substances known, and is used for cutting glass and polishing other precious stones. Graphite on the other hand is so soft that

when drawn across a piece of paper some rubs off and leaves a mark, and on account of this property it is used as the core of pencils. It has a specific gravity of 2·2, and, unlike the diamond, is a good conductor of electricity.

Charcoal and Coke, obtained by heating organic substances out of contact with air, are often included as allotropic modifications of carbon, but they are not pure carbon, as they always contain oxygen, hydrogen, nitrogen and any mineral constituents which may have been present in the original substance.

Bone-black or animal charcoal, as we have seen, is a porous mass of calcium phosphate and carbonate containing carbon in a fine state of division, whilst lamp-black is finely divided carbon and generally contains some oily matter and hydrogen.

The wonderful absorptive power for gases possessed by the porous forms of carbon obtained by heating bones and other animal and vegetable matter out of contact with air, has already been described, as well as its power of oxidising easily decomposable organic matter and gases, and also its efficiency in decolourising solutions (p. 130).

Absorptive Power.—The absorbent power of charcoal for gases varies (1) with the nature of the charcoal, and (2) with the temperature; charcoal made from hard forms of woody fibre, such as the shell of the cocoanut, having the greatest absorptive power, whilst the lower the temperature the more gas will be absorbed.

This power of absorption varies with different gases; at ordinary temperatures a cubic inch of freshly prepared cocoa-nut charcoal will absorb 170 cubic inches of ammonia gas, but only 17 of oxygen. The oxygen absorbed from the air by fresh charcoal is in a highly active condition, and for a certain space of time can be utilised for the destruction of oxidisable gases, but after being kept for a long time, the oxygen by contact with the carbon gradually becomes converted into carbon dioxide. Finely powdered charcoal

sprinkled over decomposing animal matter absorbs the gases evolved, and oxidises them by virtue of the condensed oxygen in its pores, and for this reason it is largely used in the construction of sewer traps, and also in respirators.

ABSORPTION OF GASES BY CHARCOAL (HUNTER).

1 *Volume of Charcoal at* 0° C. *and* 760 *m.m. pressure, absorbs—*

Ammonia	171·7	volumes.
Cyanogen	107·5	,,
Nitrogen dioxide	86·3	,,
Ethylene	74·7	,,
Nitrogen monoxide	70·5	,,
Phosphuretted hydrogen	69·1	,,
Carbon dioxide	67·7	,,
Carbon monoxide	21·2	,,
Oxygen	17·9	,,
Nitrogen	15·2	,,
Hydrogen	4·4	,,

In Nature carbon is found combined with hydrogen in coal, bitumen, shale, naphtha, the paraffins and numerous other hydrocarbons; with oxygen it is found as carbon dioxide which is present in the earth in enormous quantities, and which forms the large class of metallic salts called carbonates. In the vegetable kingdom the dry solids contain nearly 50 per cent. of it, whilst all animal matter is largely made up of it, fat containing as much as 79 per cent.

Carbon is insoluble, non-volatile, and infusible at all ordinary temperatures, but signs of volatilisation are apparent in the electric arc. The diamond does not easily conduct heat or electricity, but the other forms of carbon are conductors.

Hydrocarbons.—Carbon forms an enormous number of compounds with hydrogen, these bodies being known by the generic name of *Hydrocarbons*.

Twelve parts by weight of carbon will unite with four parts by weight of hydrogen, and when these elements are

united in this proportion, the body formed is incapable of combining with chlorine or any other element of the same kind, the constituents having formed what is termed a *saturated compound;* but the compound may exchange the whole or part of its hydrogen for other elements.

Most elements in forming compounds only exist in the molecule in a very limited number of atoms, but carbon has the property of existing in different bodies to a very large number, so that although the simplest compound of carbon and hydrogen known is represented by the formula CH_4, it is only the first of a long series of compounds in which the carbon is saturated by hydrogen, each member of this series containing one atom of carbon and two atoms of hydrogen more than the members of the series preceding it.

This series is known as the saturated hydrocarbon or paraffin series, and all its members contain carbon and hydrogen in the ratio of C_nH_{2n+2}.

Besides this series there are many others in which the ratio of hydrogen to the carbon is not so high, and which can therefore unite directly with some other elements, and for this reason are called *unsaturated hydrocarbons.*

As examples of these series may be cited :—

The Ethylene series having the ratio C_nH_{2n+2}.
The Acetylene series having the ratio C_nH_{2n-2}.
The Benzene series having the ratio C_nH_{2n-6}.

In the paraffin series the lower members are gaseous, whilst as the molecule becomes more complex they assume the liquid state and become less volatile and more viscid as the series is ascended, the higher members being crystalline solids.

The first member of each of the above series may be taken as illustrating the general chemical behaviour of the whole of the members of the series.

Methane or Marsh Gas.—CH_4 is the first member of the C_nH_{2n+2} series, and is formed in Nature by the slow decay of vegetable matter out of direct contact with air; for

instance, the vegetable deposits under water in marshes and pools give off this gas in abundance, and it is also one of the products of the conversion of woody fibre into coal.

Preparation.—It is generally prepared for laboratory purposes by heating a mixture of sodium acetate and sodium hydroxide, when:

Sodium acetate Sodium hydroxide Sodium carbonate Methane.

$$NaC_2H_3O_2 + NaHO = Na_2CO_3 + CH_4.$$

The sodium hydroxide is, in order to facilitate the operation, mixed with quicklime, which, however, takes no part in the decomposition. The heat required to effect decomposition is considerable, and it is therefore found necessary to

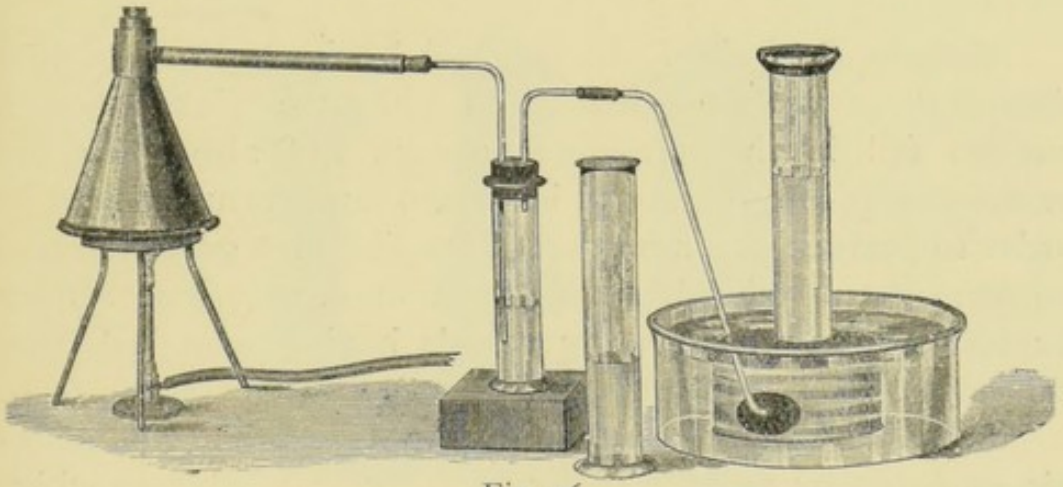


Fig. 26.

conduct the operation in a metal generator (Fig. 26); or, if a glass flask is to be used, to protect it by coating it with fire clay, otherwise it would soften at the temperature necessary to cause the evolution of the gas. Methane is a colourless, odourless, tasteless gas, with no distinctive poisonous action.

Properties.—It does not support combustion, but burns with a slightly luminous flame, forming carbon dioxide and water vapour. It is only slightly soluble in water, 100 volumes at 0° C. absorbing about 5·4 of the gas. Until lately it was supposed to be a permanent gas, *i.e.*, not reducible to the liquid state, but it has been liquefied by a com-

bination of great pressure and cold; the liquid boils at - 155° C.

Coal has the power of occluding methane and again evolving it if the pressure be reduced or the temperature increased. This may occur in coal mines and also in the coal bunkers of a ship. In some cases 100 grains (6·48 grams) of coal will give off as much as 200 cubic centimeters of gas, which on analysis proves approximate to:

Methane	89·61
Nitrogen	9·61
Carbon dioxide	0·23
Oxygen	0·56
	100·00

Methane Explosions.—In the coal bunkers of a ship this liberation of the occluded gases will take place when a sudden fall in the barometer occurs, and also when the vessel passes into regions of increased temperature. And in order to prevent accumulation of the liberated gases the coal bunkers should be adequately ventilated, otherwise serious explosions may ensue, many vessels having been lost from this cause.

Methane, when mixed with ten times its volume of air, or twice its volume of oxygen, forms a mixture which explodes with great violence on application of a light, forming carbon dioxide and water vapour:

Methane		Oxygen		Carbon dioxide		Water
CH_4	+	$2O_2$	=	CO_2	+	$2(H_2O)$,

and in coal mines not only is methane present occluded in the coal itself, and ready to issue into the workings when a fall of the barometer takes place, but also during the formation of coal under pressure great quantities of methane are generated; and this often is found accumulated under high pressure in the coal seams, discharging itself with considerable violence into the mines from the fissures made in hewing out the coal. The gas issuing from the fissure would burn

quietly if a light were applied to it, since methane is not explosive unless mixed with air; but when the gas escapes into the mine and mixes with air it forms an explosive mixture as soon as the proportion of gas amounts to one-eighteenth of the volume of the air, and the most explosive mixture consists of one volume of methane and ten volumes of air. The explosive mixture of methane and air is called *fire-damp;* and the gases resulting from the explosion—carbon dioxide, water vapour, and nitrogen—are called *choke-damp*, and this often is as fatal in its effect as the explosion itself.

Safety Lamps.—The mixture of oxygen and methane requires a fixed temperature to ignite it, and unless this

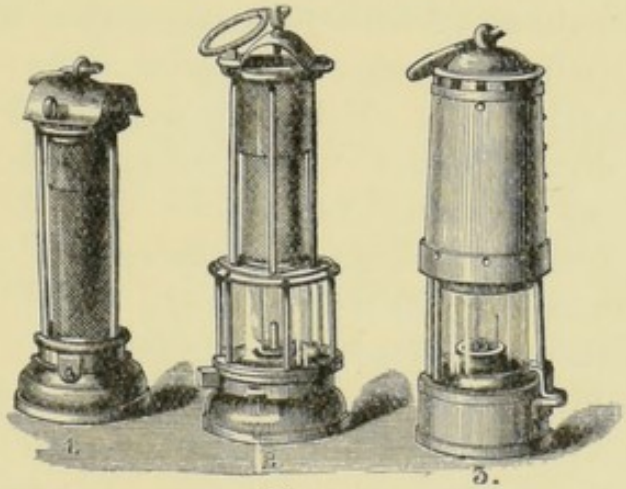


Fig. 27.

temperature be reached explosion cannot result. If a piece of wire gauze is held over a gas jet, the gas may be ignited above it without the flame passing through and igniting the gas on the under side; the metallic wires composing the wire gauze conducting the heat away so rapidly that the temperature of the gas on the lower side does not rise to the point of ignition.

This simple principle was utilised by Sir Humphrey Davy in the construction of the safety lamp for miners. It consists of an oil lamp entirely surrounded with fine wire gauze, through which the air can enter and through which the

products of combustion can pass out, but no flame can pass from the inside to the outside of the gauze, even if the explosive gases burn in the interior of the lamp.

In Fig. 27, three forms of safety lamps are shown; (1) is the old form first used and entirely surrounded with wire gauze, which, however, gave so feeble an illumination that the wire gauze immediately surrounding the flame was replaced by a glass cylinder (No. 2), and until 1887 this was the best form in use; it has been shown, however, that although the flame, when burning under ordinary conditions, cannot pass through the gauze, yet a sudden disturbance of the air, such as is caused by the blasting of coal in the mine, will sometimes jerk the flame by a sudden impulse through the gauze, and so communicate with the explosive mixture outside, and to do away with this risk, a new form of lamp has been introduced in which the wire gauze cylinder is entirely surrounded by a shield of iron plate (No. 3), which prevents the direct impact of the air upon the gauze, and greatly increases the value of the lamp.

It would greatly decrease the risk of explosion in coal bunkers and in coaling vessels if, when a light is required, only such lamps were used, and employment of a naked flame never allowed, as besides the gas present, it has been shown that the presence of fine dust of coal in the air of the bunkers very much increases the liability to explosion.

When methane or marsh gas is passed through a tube heated to bright redness it can eventually be decomposed entirely into carbon, which is deposited, and hydrogen which passes on, the same decomposition taking place when a series of electric sparks is passed through the gas, and the hydrogen liberated occupies double the volume of the methane decomposed:

$$\underset{\text{2 vols.}}{CH_4} = C + \underset{\text{4 vols.}}{2H_2}$$

As we have seen, methane is CH_4, and contains 1 carbon atom combined with 4 of hydrogen. Each member of the group gradually rises by an atom of carbon and 2

atoms of hydrogen at a time, so that its next member is ethane, C_2H_6, and so on to C_4H_{10}, these bodies being gaseous. The next number of the group is pentane, which is a liquid so excessively volatile that unless it be kept in well corked-up cans, very little of it will be left in the can after an hour's exposure on a warm day.

With pentane this series of hydrocarbons becomes liquid, and gradually, with increase in the number of carbon atoms, gets more and more viscid, with a higher and higher boiling point, until at about the fifteenth member of the group one arrives at substances which, although still liquid, are so viscid that the fifteenth member is that jelly-like substance known under the name of vaseline. For another five members they are still slightly viscid, and above the twentieth member of the group begin the real solids, a mixture of which constitutes paraffin wax.

Olefines (C_nH_{2n}).

The first member of this series is *ethylene* or olefiant gas (C_2H_4) which exists in small quantities in the gases evolved during the dry distillation of many organic bodies. It is prepared by acting upon alcohol with sulphuric acid, when the alcohol is dehydrated and olefiant gas liberated.

Alcohol		Sulphuric acid		Sulphuric acid and water		Ethylene.
C_2H_6O	+	H_2SO_4	=	H_2O,H_2SO_4	+	C_2H_4.

In preparing the gas one volume of alcohol and four volumes of strong sulphuric acid are mixed with sand, to prevent frothing, and are then heated, care being taken to avoid too high a temperature, which would cause the evolution of sulphur dioxide.

Ethylene or olefiant gas consists of two atoms of carbon combined with four of hydrogen; it is a colourless gas with a slightly sweetish taste; it can be condensed to a liquid by pressure at a temperature of - 100° and burns in air with a luminous smoky flame. When mixed with three times its own volume of oxygen it forms a highly explosive mixture,

which if ignited combines, forming carbon dioxide and water.

Ethylene		Oxygen		Carbon dioxide		Water.
C_2H_4	+	$3(O_2)$	=	$2(CO_2)$	+	$2(H_2O)$.

It used to be called olefiant gas because when mixed with its own volume of chlorine it forms an oily liquid. The members of this series can combine with other elements directly, hence these hydrocarbons are "*unsaturated.*"

Ethylene		Bromine		Ethylene dibromide.
C_2H_4	+	Br_2	=	$C_2H_4Br_2$.

Like methane, it can be decomposed by passing a series of electric sparks through it, and also by heat, which breaks it up in three stages, dependent upon the temperature employed.

Ethylene is one of the constituents of coal gas, which owes some of its illuminating power to its presence.

Acetylene (C_2H_2).—This gas is the first member of the C_nH_{2n-2} series. It is a colourless gas with a garlic-like odour as usually prepared, but with very little smell when quite pure. Water dissolves its own volume of the gas and under a pressure of 21.5 atmospheres at 0° C. the gas is liquefied. It is endothermic and can be detonated into carbon and hydrogen by firing a small charge of mercuric fulminate in it.

It has the formula C_2H_2 and can be most easily prepared by acting upon calcium carbide with water:

Calcium carbide		Water		Acetylene		Calcium Hydroxide.
CaC_2	+	$2H_2O$	=	C_2H_2	+	$Ca(OH)_2$

Mixed with air it forms an explosive mixture over a very wide range, any mixture containing from 3 to 82 per cent. of acetylene being explosive.

When burnt in a small flat flame it gives a very high illuminating value and is widely used where coal gas is not available.

Attempts have been made to use it in the liquid state as

a source of power and light, but this has proved too dangerous as the liquid alone is liable to detonation, but the gas is very soluble in acetone, and if porous material in a steel cylinder be saturated with acetone and acetylene be then compressed into it, a very large volume of the gas can be taken up, and under these conditions is free from any danger. In this form it is much used for lighting trains, omnibuses, motor cars and yachts.

It is formed by the action of heat on hydrocarbons as an intermediary product in their decomposition, and is itself decomposed by heat into its constituents with liberation of the heat taken up during its formation.

Benzene.—(C_6H_6) is the first member of the C_nH_{n-6} series of hydrocarbons. It is a colourless liquid having a specific gravity of ·899. Below 5° C. it forms a white solid, and cooling mixtures containing it to a low temperature is frequently used for its purification. It boils at 80·5° C. and yields a vapour having a distinctive but not unpleasant odour, and as several other hydrocarbons of this series have a similar smell, it was often called the *aromatic series.*

It can be obtained pure by heating benzoic acid with calcium hydroxide:

Benzoic acid		Calcium hydroxide		Calcium carbonate		Water		Benzene.
$C_7H_6O_2$	+	$Ca(HO)_2$	=	$CaCO_3$	+	H_2O	+	C_6H_6

It is present in coal tar which is the commercial source from which it is usually obtained, but perhaps the most interesting method of forming it is by heating acetylene when three molecules of the latter combine together to form benzene.

Acetylene		Benzene.
$3C_2H_2$	=	C_6H_6

Isomerism.—It will be seen that acetylene and benzene contain the same elements in the same proportions by weight, and substances which bear this relation to each

other, but are different in properties, are said to be "*Isomeric.*" When substances have the same percentage compositions but different molecular weights, as in the case of acetylene and benzene, they are said to be "*Polymeric,*" whilst compounds which agree both in percentage composition and molecular weight are said to be "*Metameric*"; the wide differences in physical and chemical characteristics which may exist between "metameric" compounds being due to the different relations which the atoms forming the compounds bear to each other and which can only be shown by the use of structural formula (p. 33).

Coal Gas.—The compounds of hydrogen and carbon we have taken as types all play an important part in products of the destructive distillation of coal for the production of coal gas.

Cannel, or other bituminous coal rich in hydrogen, is heated out of contact with air in elliptical retorts, and the products of distillation are then led off by an ascending tube from the mouth of the retort. This tube, after ascending above the level of the bench of retorts, bends over and descends into a cylindrical tube, which is about half full of tar; and into this the delivery tube from the retort just dips, the tar closing the mouth of it gas-tight. This main collecting tube runs horizontally over the whole of the front of the bench of retorts, and they all discharge into it by means of their delivery tubes, each of which is sealed off by the tar, kept at a constant level by means of an overflow siphon at the end of the collecting tube, which is called the hydraulic main.

Each retort is fitted at the end which projects from the furnace with a mouth-piece and lid, which can be removed to allow of the coke being withdrawn and the fresh charge of coal inserted, and the vertical pipes which lead up to the hydraulic main start from the top of the mouth-piece. The reason why these pipes are sealed by dipping under the surface of the liquid in the hydraulic main is that the gas from the other retorts cannot escape down the pipe,

as would be the case if they simply opened into the main, and this enables any of the retorts to be opened for recharging, whilst the others are still giving off gas, and also prevents leakage from the whole bench of retorts should one accidentally crack. A large quantity of volatile products escapes as vapour with the gas into the hydraulic main, where much condenses as tarry products and ammoniacal liquor (consisting of ammonia, carbonate and sulphide of ammonium, etc., in solution), and these run off through the overflow siphon to the tar well, where they are collected. The gas passes down from the hydraulic main to the atmospheric condensers, a series of tubes placed vertically, which are exposed to air, which cool down the gas as it passes through them and cause a further deposition of tar, ammoniacal liquor, and any easily condensable hydrocarbon which may be present. There is also generally an arrangement for artificially cooling the condensers in hot weather by means of water. After leaving the condensers the gas next passes through the scrubbers, which consist of towers built of iron plate and filled with coke, or brushwood, over which water or diluted ammoniacal liquor is sprayed and trickles down, meeting the gas which is made to pass up them. The alkaline liquor absorbs some of the sulphuretted hydrogen and carbon disulphide present in the gas, and also removes the last traces of tar and ammonia, and the gas still containing some sulphuretted hydrogen, carbon disulphide and carbon dioxide, passes on to the purifiers.

Purification.—It is important to get rid of these gases, as carbon dioxide when present even in small quantities affects the illuminating power of the gas to a serious extent, whilst carbon disulphide and sulphuretted hydrogen on combustion produce sulphur dioxide, which in contact with air and condensing moisture becomes oxidised to sulphuric acid, and this is credited with having a detrimental effect upon the furniture and drapery of rooms.

The gas first comes to the dry lime purifiers, where it

passes over trays or through grids, on which is placed slaked lime, and this absorbs the carbon dioxide, sulphuretted hydrogen, and a good deal of the carbon disulphide, forming calcium carbonate and sulphide, whilst cyanides are also found in the spent lime. To remove the last of the impurities the gas is now passed through other purifiers containing hydrated ferric oxide or else a mixture of sulphate of iron, sawdust, and slaked lime, which combining with the last trace of sulphuretted hydrogen keeps it back, whilst the gas passes on to the gasometer and thence to the mains.

The spent lime from the purifiers is difficult to get rid of, and as it gives off sulphuretted hydrogen in contact with air, its removal creates a nuisance in the neighbourhood of the works, and for this reason lime purification for sulphur compounds has been largely given up and iron purification used to remove the sulphuretted hydrogen.

Bituminous coal may be looked upon as containing carbon and also simple hydrocarbons, such as some of the higher members of the paraffin series, more complex alcohol acids, and likewise organic bodies containing carbon, hydrogen, nitrogen, oxygen, and sulphur. On submitting a complex substance of this character to destructive distillation, it will be found that the yield and quality of the products will vary very considerably with the temperature existing in the retorts, with the size of the charge of coal used, with its distribution in the retort, with the length of time the distillation has been going on, and with an infinity of other factors of a more or less complex nature. The products will, however, in their main characteristics remain the same. They may be divided into: (*a*) Solids, such as the coke and retort carbon; (*b*) liquids, consisting of the tar and ammoniacal liquor; and (*c*) gases, consisting of the unpurified coal gas.

Carbon Residue.—The chief solid residue is not absolutely pure carbon, as it contains the mineral non-volatile constituents which remain behind as ash when the original coal is burnt, and which, to a considerable extent, existed

in the sap that filled the cells of the plant from which the coal was formed. The retort carbon formed as a dense deposit on the crown of the retort by the action of the high temperature upon the hydrocarbons is, however, carbon in a very pure form; and, on account of its density, it is largely used for electrical purposes.

Tar.—The liquid products of the destructive distillation of coal are tar and ammoniacal liquor. Tar derived from ordinary bituminous coal is a black, somewhat viscid liquid, varying in specific gravity from 1·1 to 1·2. London tar, made from coal with an admixture of only about 2 per cent. of cannel, has usually a specific gravity of 1·2; while provincial tar, made from coal with a larger proportion of cannel, is reduced to near the lower limit, owing to the greater quantity of light oils yielded by cannel. The ultimate composition of a London tar is approximately as follows:—

Carbon	77·53
Hydrogen	6·33
Nitrogen	1·03
Sulphur	0·61
Oxygen	14·50
	100.00

These elements in tar are built up into about 140 different compounds, traces of which can be identified; but for all practical purposes we may take the following as being the chief constituents:—

	Neutral Hydrocarbons.	Boiling Point: Deg. Cent.	Formulæ.	Sp. Gr.
Liquid	Benzene	80	C_6H_6	0·88
	Toluene	110	C_7H_8	0·87
	Xylene	142	C_8H_{10}	0·87
	Isocumene	170	C_9H_{12}	0·85
Solid	Naphthalene	217	$C_{10}H_8$	—
	Anthracene	360	$C_{14}H_{10}$	—
	Chrysene	—	$C_{18}H_{12}$	—
	Pyrene	—	$C_{16}H_{10}$	—

Alkaline Products.	Boiling Point. Deg. Cent.	Formulæ.	Sp. Gr.
Ammonia ...	— ...	NH_3 ...	—
Aniline ...	182·5 ...	C_6H_7N ...	1·02
Picoline ...	130 ...	C_6H_7N ...	0·96
Quinoline ...	239 ...	C_9H_7N ...	1·08
Pyridine ...	117 ...	C_5H_5N ...	—
Acids.			
Carbolic acid ...	180 ...	C_6H_6O ...	1·07
Cresylic „ ...	— ...	C_7H_8O ...	—
Rosolic „ ...	— ...	$C_{19}H_{14}O_2$ ...	—
Brunolic „ ...	— ...	— ...	—
Acetic „ ...	118 ...	$C_2H_4O_2$ ...	1·06
Free Carbon.			

In roughly considering the proportions in which the main constituents occur in coal tar, we can still further simplify the composition, and look upon it as containing benzene, naphtha, naphthalene, anthracene, carbolic acid, and pitch; and if this tar be carefully re-distilled, we find it can be separated into the constituents which distil over at various temperatures.

First, light oils pass over, from which benzene and its homologues can be obtained; then heavy tar oil, from which carbolic acid is made; and pitch is left, from which a substance called anthracene can be separated. The benzene obtained is the source from which aniline is prepared; and it is from aniline that most of the coal-tar colours are derived.

When benzene is acted upon with strong nitric acid, *nitro-benzene* [$C_6H_5(NO_2)$] is formed. On treating this with dilute sulphuric acid and zinc dust, or acetic acid and iron filings, hydrogen is evolved, and in its nascent state attacks the nitro-benzene and removes its oxygen—leaving behind the compound of carbon, hydrogen, and nitrogen called *aniline* [$C_6H_5(NH_2)$]. It is from aniline that the brilliant colours mauve, magenta, and other purples and reds, are produced by acting upon it with oxidising agents;

and from it can also be obtained the beautiful series of aniline yellows, blues, and violet.

The naphthalene used in the albo-carbon system of enriching gas is prepared from coal tar, which is distilled; the first portion consisting of naphthas, etc., while the second portion is rich in phenols and cresols. The second distillate is again distilled; and the residue left becomes semi-solid, owing to the separation of naphthalene, which on standing collects and cakes on the top of the oil. This is then removed, and pressed by hydraulic power in a hot press, each plate of which contains a steam-pipe to heat it. The crude naphthalene so obtained is then distilled; but it still contains a number of impurities, which would cause it to turn yellow. To get rid of these, it is melted, and forced by steam pressure into a steam-jacketed cylinder, where it is washed in dilute alkali to get rid of the phenol, and four times with strong sulphuric acid to remove sulphonates, meta-naphthalene, etc. It is then water-washed free from acid. These washings take about seventy-two hours. The naphthalene now undergoes a final distillation, after which it is melted in steam-jacketed coppers, and is ladled out and cast into sticks in an apparatus of the same construction as the old-fashioned candle-machines; these sticks being afterwards cut into the smaller pieces used in the lamp reservoirs.

Gas Liquor.—The second liquid product of the destructive distillation of coal is the ammoniacal or gas liquor, which consists of water partly condensed from the hot gas, and partly added to wash the gas in the scrubbers. It contains, as its principal constituents, ammonia, partly combined with carbonic acid and sulphuretted hydrogen to form compounds which are decomposed on boiling, with evolution of ammonia gas, and partly combined with stronger acids to form compounds which require to be acted upon by a strong alkali before the ammonia contained in them can be liberated. The ammonia in the first class of com-

pounds is technically spoken of as "free"; that present in the latter as "fixed." The following analysis will give an idea of the relative quantities in which these compounds exist in the liquor :—

		Grammes per litre.
Free.	Ammonium sulphide	3·03
	Ammonium carbonate	39·16
Fixed.	Ammonium chloride	14·23
	Ammonium thiocyanate	1·80
	Ammonium sulphate	0·19
	Ammonium thiosulphate	2·80
	Ammonium ferrocyanide	0·41

From a scientific point of view, the term "free" is absolutely incorrect; and in using it, the fact must be clearly borne in mind that in this case it merely stands for ammonia which can be liberated on simply boiling the liquor.

Composition of Coal Gas.—The gas which is obtained by the destructive distillation of coal, and which we employ as our chief illuminant, is not a definite compound, but a mechanical mixture of several gases, some of which are reduced to the lowest limit, in order to develop as fully as possible the light-giving properties of the most important constituents of the gas.

The following analysis gives a fair idea of the composition of an average sample of gas made from coal and without enrichment :—

Hydrogen	52·22
Unsaturated hydrocarbons	3·47
Saturated hydrocarbons	34·76
Carbon monoxide	4·23
Carbon dioxide	0·60
Nitrogen	4·23
Oxygen	0·49
	100·00

These constituents may be divided into three classes :—

(*a*) light-yielding hydrocarbons; (*b*) combustible diluents; and (*c*) impurities.

The hydrocarbons, upon which the luminosity of the flame entirely depends, are divided in the analyses into two groups —saturated and unsaturated—according to their behaviour with a solution of bromine in potassium bromide, which has the power of absorbing those termed "unsaturated," but not affecting in diffused daylight the gaseous members of the saturated series of hydrocarbons; and they may be separated in the same way by concentrated sulphuric acid, which has an absorbent effect on the one class, and not on the other.

The chief unsaturated hydrocarbons present in coal gas are:

Ethylene	C_2H_4
Butylene	C_4H_8
Acetylene	C_2H_2
Benzene	C_6H_6
Naphthalene	$C_{10}H_8$

Whilst the saturated hydrocarbons consist chiefly of:

Methane	CH_4
Ethane	C_2H_6

The light-giving power of coal gas is undoubtedly entirely due to the hydrocarbons; and the idea held up to sixteen years ago was that the illuminating value depended upon the amount of ethylene present. This, however, is manifestly incorrect, as, if it were true, 4 per cent. of ethylene mixed with 96 per cent. of a combustible diluent such as hydrogen should give a 16 to 17 candle gas, whereas a mixture of 10 per cent. of ethylene and 90 per cent. of hydrogen is devoid of luminosity. In 1876, Berthelot came to the conclusion that the illuminating value of the Paris coal gas was almost entirely due to benzene vapour. But here, again, another mistaken idea arose, owing to a faulty method of estimating the benzene; and there is no doubt but that methane is certainly one of the most important of

the hydrocarbons present, when the gas is burnt in such a way as to evolve from it the proper illuminating power, while the benzene vapour, small as the quantity is, comes next in importance and the ethylene last. It is the combined action of the hydrocarbons which gives the effect; not any one of them acting alone.

Flame.—The use of coal gas for illuminating and heating purposes necessitates the consideration of the structure and properties of flame.

When a solid which is incapable of being volatilised burns under ordinary conditions, no flame is produced, but when a volatile solid, a vapour or a gas undergoes combustion in air, flame is formed.

Flame may therefore be looked upon as the combustion of gaseous matter, and as combustion is merely extremely vigorous chemical combination, it is manifest that if the gases only come in contact during combustion, the flame can only exist where the two gases meet.

If a jet of hydrogen be ignited in air, the conical flame which is produced consists of a hollow sheath of burning gas, surrounding an inner core of unburnt hydrogen, and flames formed by a simple gas which burns without decomposition and only forms one product from its combustion, all have this simple structure, the sheath of flame being produced where the combining gases meet.

The fact that such a flame is hollow can be at once proved by inserting a tube into the inner cone, when some of the unburnt gas will pass through it and can be burnt at the other end.

Compound gases, which undergo decomposition during combustion, or gaseous mixtures give flames with a rather more complex structure, and it is usual to describe the flame of coal gas or of a candle as consisting of three zones. The first of these is the inner non-luminous cone (A, Fig. 28), in which no combustion is taking place, but where some very important chemical changes are going on, the second (B),

is the zone of luminosity upon which the light-giving power of the flame depends, whilst the third is a thin non-luminous envelope which entirely surrounds the flame, and which is clearly seen if a small piece of card be held in front of the flame so as to shield the eye from the light emitted by it and only to leave the edge visible. This latter zone may be again divided into two parts, a small blue portion at the base of the flame and the envelope of the upper part of the flame.

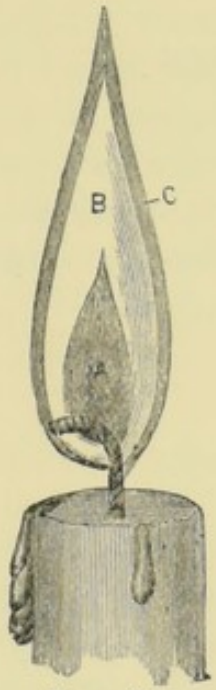


Fig. 28.

The Actions in a Candle Flame.—When a candle is lighted, the burning wick melts the wax or material of the candle in contact with it, and then by capillarity sucks up the liquid, and the heat of the burning wick in the first instance, and afterwards the heat of the flame, convert the hydrocarbons into a mixture of gases and vapours of much the same character as a rich coal gas.

In each case, therefore, the gases flowing from the wick or the jet contain unsaturated hydrocarbons, methane and hydrogen as their chief constituents.

These gases when ignited burn, but the lighter they are the more rapidly will they diffuse and so reach the outside of the flame; the result of this is that the hydrogen and the

methane are the first to burn, and the heavier hydrocarbons flowing upwards between the walls of flame become highly heated and converted into a mixture of acetylene and methane.

Taking ethylene as the type of the unsaturated hydrocarbons present in the gas, the change would be represented by:

Ethylene — Acetylene — Methane.

$$3(C_2H_4) = 2(C_2H_2) + 2(CH_4)$$

and at the top of the inner non-luminous zone 80 per cent. of the unsaturated hydrocarbons present are found to be acetylene. The temperature of the flame rapidly rises the higher the point, and at the spot where the luminosity of the flame commences the temperature is over 1,000° C., and this causes sudden and extremely rapid decomposition of the acetylene into its constituents:

Acetylene — Hydrogen — Carbon.

$$C_2H_2 = H_2 + C_2$$

Acetylene is one of those compounds termed endothermic, from the fact that heat is absorbed during their formation, and at the moment of decomposition this heat is again liberated, and having no time to dissipate itself amongst the other gases present, heats up the carbon particles to a temperature far higher than the average temperature of the flame, causing them to become incandescent and so rendering the flame luminous, the incandescence of these solid carbon particles being further aided by the temperature of the flame and by their own combustion, partly by the oxygen of the air and partly by the action of water vapour and carbon dioxide upon them:

Carbon — Oxygen — Carbon monoxide.

(*a*) $C + O = CO$

Carbon — Water vapour — Carbon monoxide — Hydrogen.

(*b*) $C + H_2O = CO + H_2$

Carbon — Carbon dioxide — Carbon monoxide.

(*c*) $C + CO_2 = 2CO$

and it is the combustion of the carbon monoxide and

hydrogen which gives the outer non-luminous envelope to the flame.

The small blue portion of the outer envelope at the base of the flame is caused by the rapid inrush of air, the nitrogen so diluting the hydrocarbon molecules at that point that they are burnt up without being first decomposed, and there being therefore no separation of carbon there is no luminosity, and the same blue colour may be observed when a gas flame is rendered non-luminous by dilution with nitrogen or carbon dioxide.

This explanation holds good for all luminous hydrocarbon flames, but the combustion of many other substances emits light, such as phosphorus, magnesium, zinc and arsenic, but in these cases the products of combustion are solid, and in the finely divided condition in which they are formed are rendered incandescent, and in the case of phosphorus and arsenic are again volatilised by the heat of their own formation.

Flames which can only contain gaseous matter can be rendered incandescent if a sufficiently high temperature can be obtained; for instance, if hydrogen be burnt in an atmosphere of oxygen under a pressure of several atmospheres, light is developed, but the temperature of such a flame is many times hotter than an ordinary hydrogen flame burning in oxygen, as pressure acts on flame in the same way as on a gas, and at a pressure of several atmospheres, several times the amount of hydrogen and oxygen would be consumed, as would be the case under ordinary conditions of temperature and pressure.

The luminosity of flame may therefore be stated to be due either to the presence of incandescent solid particles, or at a far higher temperature to incandescent gases.

Bunsen Flames.—If air be supplied to the interior of a flame it loses its luminosity, an effect partly due to the oxygen so supplied causing complete combustion of the

carbon, and partly also to the diluting influence of the other constituent of air, nitrogen.

It is upon this principle that the Bunsen burner is constructed.

Gas is brought through the tube (A, Fig. 29) under the ordinary pressure, and is discharged from a small orifice into a metal chamber, which has holes at the side open to the air, and into which is screwed a vertical tube (C) which is immediately over the orifice from which the gas is issuing.

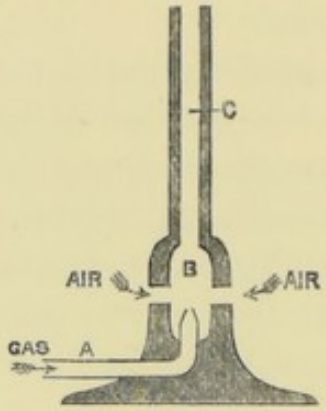


Fig. 29.

The gas rushes upwards and impinges on the side of the tube (C), diminishing the pressure at the sides of the chamber (B) by its uprush, and so the air is drawn in through the holes at the side, the mixture of air and gas passing together up the tube and being burnt at the top. That the non-luminosity of the flame is due to the air introduced can be proved by closing the air holes with the fingers, when the ordinary luminous gas flame is at once obtained. The Bunsen flame is smaller and more compact than the flame given by the same amount of gas burning without admixture of air.

Oxidising and Reducing Flames.—In the Bunsen flame, and also in a blowpipe flame obtained by blowing air through an ordinary flame, the different parts have different chemical functions.

If a piece of metallic copper be held just beyond the extreme tip of the flame (B, Fig. 30), it will quickly become coated with black copper oxide, because the flame will have

used up all the oxygen it requires for its own combustion, and the great heat generated will make any oxidisable metal combine with the oxygen of the air present, and for this reason the outer is called the *oxidising flame.* If, however, the copper oxide so formed is held in the inner zone of the flame at (A), there combustion is not complete, and the unburnt hydrocarbons or carbon monoxide will attack the metallic oxide and take from it its oxygen, forming carbon dioxide, at the same time reducing the copper oxide to metallic copper; hence the inner zone is called the *reducing flame.*

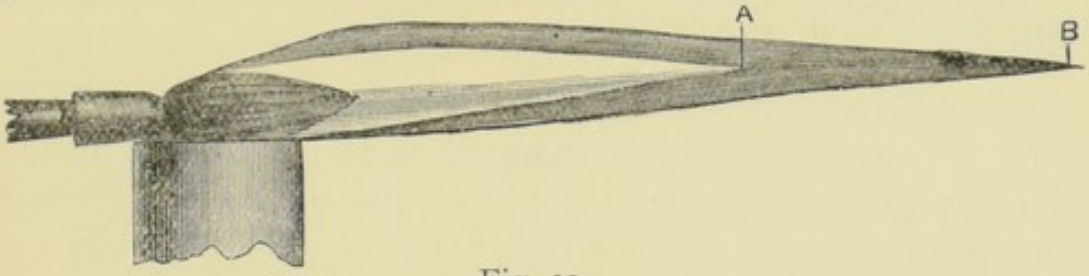


Fig. 30.

In the complete combustion of any of the hydrocarbons, carbon dioxide and water vapour are the products formed.

Gas Burners.—When coal gas is burned for the production of light, in order to obtain the maximum illuminating power, the first requisite is to have as high a temperature as possible, and to obtain this the top of the burner must be of a non-conducting substance such as steatite; next, the gas must be supplied to the burner in a steady flow and at the proper pressure, and the flame must be supplied with an even flow of air. Of ordinary gas burners there are two forms, those giving a flat flame such as the batswing and fishtail burners, and the Argand burners in which the burner is ring-shaped, forming a hollow cylinder of flame, acted upon by the air from both inside and outside; with this burner a chimney is needed to increase the draught and throw the air with sufficient force against the flame. The regulation of the air supply to a flame is a matter of great importance, as too great a supply of air decreases the illuminating power of the flame partly by dilution, and

partly by effecting a too rapid combustion of the carbon, and thus prevents it giving out the maximum amount of light; whilst too small a supply allows some of the carbon to escape unburnt, and gives rise to a smoky flame.

The importance of keeping the temperature of the flame as high as possible has been fully recognised, and the regenerative burners, in which the heat from the flame and the hot products of combustion are made to heat the gas and air before they enter into combustion, give the best results obtainable from the direct incandescence of carbon particles supplied by the decompositions taking place in the flame itself.

The Incandescent Mantle.—The discovery by Dr Auer von Welsbach in 1885 of the method of making the incandescent gas mantle, and the use of the oxides of thorium and cerium for its composition, discovered in 1892, gave a method of developing light from coal gas which has so far surpassed any other way of burning it, that the old forms of burner are now but little used. This system consists of consuming the gas in an atmospheric or bunsen burner, so as to obtain a non-luminous but very hot flame, and then utilising this to raise to incandescence a mantle made of:

Thorium oxide	99
Cerium oxide	1
	100

a mixture having a far higher power of light emissivity than carbon particles.

The mantles are made by saturating a cotton fabric with a solution of the nitrates of the two metals mixed in the right proportions. The fabrics are then shaped and dried and are burnt in a bunsen flame, the organic matter of the original fabric burning away and the nitrates being converted into oxides which retain the shape of the original structure. The oxide mantle is then shaped and hardened in a blowpipe flame and is rendered sufficiently

strong for handling and distribution by dipping it in a solution of collodion. When fixed on the burner the collodion is burnt off, and the mantle of oxides, which just fits the outer zone of the bunsen flame is heated to high incandescence and emits ten times the light that the same amount of gas burnt in a flat flame burner would have given.

The Standard of Light to which the illuminating power of gases is compared is that emitted by a sperm candle burning 120 grains per hour, but irregularities in burning have led to the adoption of a lamp burning pentane vapour (C_5H_{12}) as the standard for comparison, the results however being still expressed in terms of the standard candle.

Photometry.—When light diverges from a luminous source, its intensity diminishes as the square of the distance increases; so if we arrange two lights, one the standard candle, and the other the light to be tested, at such distances from a fixed object that the light thrown upon it from each source of light is equal, this being determined by the shadows thrown by the object on a screen fixed behind it being equal, the relative intensities of the two lights can be found by squaring the distance of each light from the object.

This method is, however, now rarely used for accurate measurements of illuminating value, various forms of photometers being employed. The best form of photometer for general use is the bunsen open bar photometer, in which the method of measuring luminosity first devised by Bunsen is utilised.

If a piece of paper be greased, the greased portion is more translucent to light than the part unacted upon, and therefore if a light be placed on one side of such a piece of paper, the grease spot shows out as a bright spot on a darker ground. If the second source of light be then placed on the opposite side of the piece of paper, the grease spot will appear bright on the side opposite to that on which the

strongest light is placed; and if the lights are so arranged that each side of the paper is equally illuminated, the grease spot will practically disappear.

The disc with its grease spot is arranged in the centre of a small box open on the side next the observer, and on each side of the disc a small mirror is arranged at such an angle that the observer standing in front of the photometer and with the edge of the disc towards him, can see the reflection of both sides of the grease spot.

The disc box travels on a graduated bar at one end of which is the standard to which the light is compared, and at the other end the light to be measured. The disc box is now moved along the bar until the grease spot ceases to show brighter on one side than the other, and the relative values of the lights can be ascertained by taking the square of the distance of the lights respectively from the disc.

CHAPTER XII.

The Oxides of Carbon.

Carbon dioxide—Preparation and properties—Solubility—Aërated waters—Liquefaction of carbon dioxide—Critical temperature—Composition of carbon dioxide—Carbon monoxide—Preparation and properties.

CARBON, when burnt in a free supply of air or in oxygen, forms carbon dioxide (CO_2), unless the combustion be checked or a large excess of red hot carbon be present, in which case a second oxide—carbon monoxide (CO) is formed.

Carbon dioxide (CO_2) occurs free in the air and is also present in many mineral waters, and is frequently found in wells and old mine shafts, and being irrespirable, often proves fatal to workmen who descend them without first taking the precaution of ascertaining its absence.

Carbon dioxide is found combined with various bases as carbonates, which are very plentiful in Nature, whole chains of hills being formed of calcium carbonate or chalk.

Preparation.—The most convenient way of preparing it is to act upon calcium carbonate with a strong acid, which expels the carbon dioxide and unites with the calcium, at the same time forming water.

Calcium carbonate		Hydrochloric acid		Calcium chloride		Water		Carbon dioxide.
$CaCO_3$	+	$2(HCl)$	=	$CaCl_2$	+	H_2O	+	CO_2.

This is most conveniently done by taking a dense form of calcium carbonate, either limestone or marble (which, as well as chalk, are all the same composition but formed under different circumstances) in order to avoid frothing which would follow if the less dense substance (chalk) had been

used, and after breaking into small pieces, placing it in the two-necked bottle (A, Fig. 31), the calcium carbonate is now covered with water and hydrochloric acid is poured down the thistle funnel (B); carbon dioxide escapes in abundance and is conducted by the leading tube (C) under water in the pneumatic trough (D), where it can be collected by displacement of water. Carbon dioxide is a colourless, odourless gas which will not burn or support ordinary combustion; it has a slight acid taste and reaction.

Solution. — Nearly all spring waters contain the gas carbon dioxide dissolved in them in greater or less quantity;

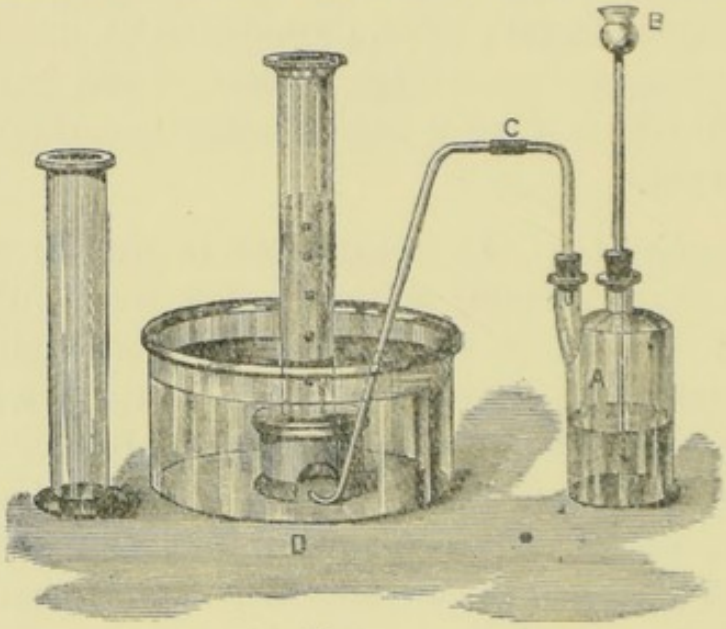


Fig 31.

and many of the properties of spring water, such as temporary hardness, are due to its presence, the carbon dioxide in solution forming an unstable acid called carbonic acid, which is able to dissolve many substances, such as chalk (calcium carbonate), magnesium carbonate, and ferrous carbonate, which the water alone is unable to do, or at any rate only to a small extent. The carbon dioxide so present is obtained by the water partly from the subsoil through which it has filtered, and to a much larger extent from subterranean sources. It is well known that caverns, deep wells, mines, etc., nearly always contain large quantities of this gas, and

also that it issues in enormous quantities from fissures in the ground in various parts of the globe; and as it is always present in underground strata, it is evident that water permeating these strata will become charged with as much of this gas as it can take up.

Water, under ordinary conditions of temperature and pressure, dissolves its own volume of the gas—that is to say, at 15° C., and with the barometer standing at 30 inches (760 m.m.) a pint of water will dissolve a pint of the gas; but a change either in the temperature of the water or in the pressure of the atmosphere, will be accompanied by a change in the quantity of gas dissolved, so that if the water were cooled down to 0° C., the pint of water, instead of dissolving one pint of the gas, would dissolve nearly one and three-quarter pints. Any increase of the atmospheric pressure, shown by a rise in the barometer, would also cause an increased absorption of the gas, and if the water be then brought to its initial temperature of 15° C., or if the extra pressure were removed from its surface, the amount of carbonic acid over and above the pint it can dissolve under those conditions once more escapes and causes the water to effervesce.

In the case of many springs which rise from considerable depths, the water has come in contact with carbon dioxide under considerable pressure, the gas being confined in subterranean caverns through which the water passes; and such springs, on reaching the outer air, give off once more the excess of gas which they have taken up, the pressure being reduced to ordinary atmospheric pressure. Such waters sparkle and effervesce, and being very pleasant to the palate were much sought after as table waters; but, from the rarity of the springs and the paucity of the supply, waters of this kind, such as the natural seltzer water, commanded a high price, and attempts were made to manufacture them artificially.

Aërated Waters.—The machines in use for saturating

water with carbon dioxide are numerous, but the principle in nearly all is the same. (Fig. 32.)

Carbon dioxide is generated by acting upon some carbonate, generally carbonate of lime in the form of whiting, with dilute sulphuric acid, and the gas so generated is led into a gasometer, after having been washed by passing through water; the gasometer is connected with a gun-metal pump, which also is connected with a reservoir containing pure water, in which about one ounce of bicarbonate of soda has been dissolved to every gallon of water; this solution and the carbon dioxide are forced together by means of a pump into a very strong condenser lined with tin, and in which the

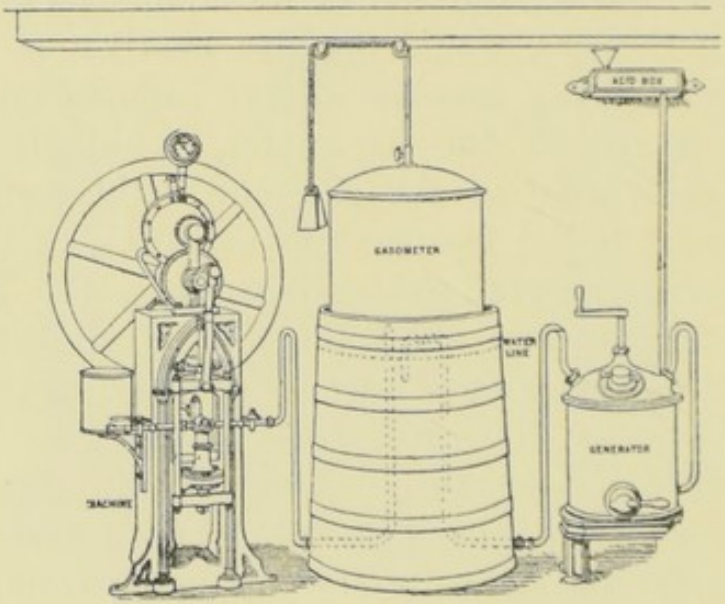


Fig. 32.

gas and liquid are agitated together by means of revolving arms fixed on a spindle and driven at high speed, and it is in this condenser that the water becomes highly impregnated with the gas under pressure. Liquid carbon dioxide is now largely employed by mineral water manufacturers. It is obtained from the vats in which malt liquors are fermented, whence it is drawn off, compressed and sent into the market in steel cylinders.

The liquid is then drawn off, corked and wired down whilst still under pressure, and so long as the cork fits air-tight into the bottle the pressure will be maintained, but the

moment the cork is taken out the liquid is brought back to ordinary atmospheric pressure, and the excess of gas escapes.

The main points to be attended to in making a highly aërated water are to drive all air out of the apparatus before the manufacture commences, and to maintain a regular, but not too high pressure in the condenser chamber.

The earliest forms of aërated waters were made by mixing together in the bottle two solutions which would act upon each other and generate carbon dioxide in the liquid itself; the great drawback to this being that the salts so introduced have an effect upon the system, which, except in special cases, it is well to avoid.

In sparkling wines and the old-fashioned ginger beer, carbon dioxide is generated in the bottle by fermentation of the liquid present, and this gas as it escapes into the space above the liquid creates a greater and greater pressure, and assists its own solution.

In the various forms of gasogenes used for making effervescing drinks in the house, a mixture (usually consisting of tartaric acid and bicarbonate of soda) is introduced into the lower portion of a glass apparatus, and generates carbon dioxide, which passing up through a tube develops pressure, and saturates water in the upper part of the arrangement.

Liquid Carbon Dioxide.—Carbon dioxide can be condensed to a liquid by cold or by a pressure of 36 atmospheres, and if the liquid carbon dioxide is allowed to assume the gaseous state, by letting some of the liquid escape into the air, the cold produced by the sudden transition from the liquid to the gas is so intense that some of the liquid is frozen into the solid form, and produces a snow-like substance which blisters the hands when pressed upon the skin and has a temperature below $-78°$ C.

To produce the solid carbon dioxide, the gas is first liquefied by pressure in an iron cylinder (Fig. 33), and then by opening a valve the liquid carbon dioxide by its own pressure is driven up a tube which goes to the bottom of the

cylinder and escapes into a brass box; here under ordinary atmospheric pressure the liquid rapidly assumes the gaseous state, and abstracts heat from the surrounding objects, and so reduces the temperature that it freezes to a solid, the gas escaping through the wooden handles of the box which are hollow; on opening the box the solid carbon dioxide is found as a white substance like snow, and if some of this be placed on mercury and a little ether added, so intense a degree of cold will be produced that the mercury is frozen to a solid. By mixing this solid carbon dioxide with ether a tempera-

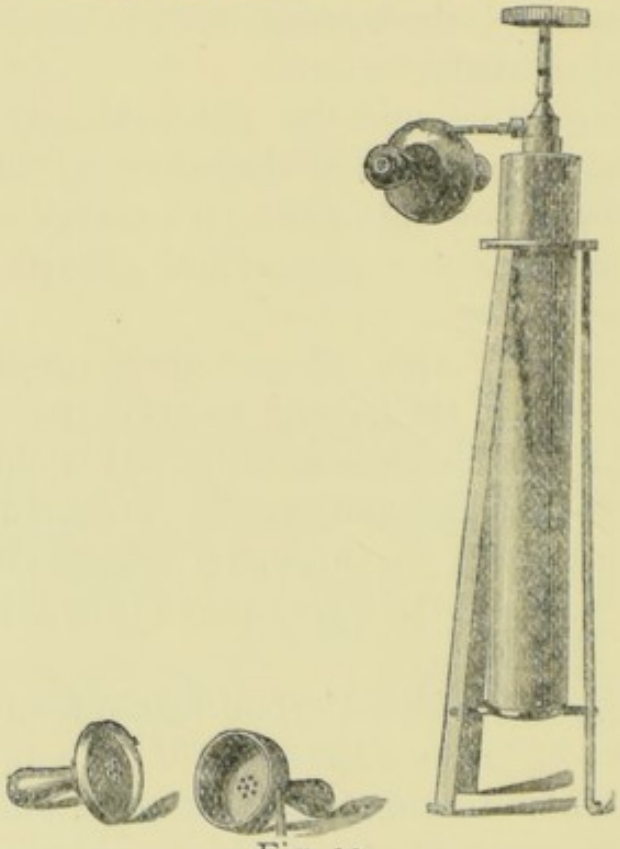


Fig. 33.

ture of -101 degrees can be obtained. If carbon dioxide be compressed at a temperature of 32° C. it refuses to liquefy even under a pressure of 109 atmospheres (109 × 15 lb. on the square inch), but on cooling the compressed gas it is suddenly converted into a liquid (see p. 13).

Carbon dioxide is twenty-two times as heavy as hydrogen, and may be poured from one vessel to another like water. It does not burn or support combustion in the ordinary sense of the word, but the metal potassium when heated

will burn in it, decomposing it, and forming potassium oxide, at the same time depositing carbon. This may be shown by passing the well dried gas over a piece of the metal potassium heated to the melting point in a thin glass tube. (Fig. 34.)

The carbon dioxide is generated from marble and hydrochloric acid, and is then passed through a wash bottle and a calcium chloride tube in order to dry it. The potassium is placed in a drawn out test tube, and heated by a bunsen flame, when it burns with a red glow, at the expense of the oxygen contained in the carbon dioxide, and deposits carbon as a black mass.

Carbon dioxide — Potassium — Potassium oxide — Carbon.

$$CO_2 + 4K = 2(K_2O) + C$$

and the potassium oxide so formed at once combines with the excess of carbon dioxide present, forming potassium carbonate.

Potassium oxide — Carbon dioxide — Potassium carbonate.

$$K_2O + CO_2 = K_2CO_3.$$

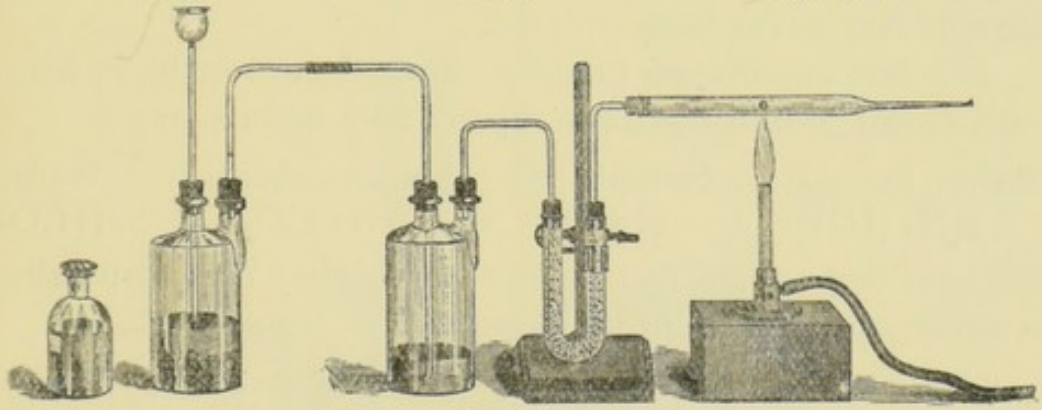


Fig. 34.

In most of its properties it resembles nitrogen, but can be distinguished from it by giving a white precipitate with lime water, with which it combines, forming calcium carbonate, and as this is practically insoluble, it is thrown down as a precipitate.

Lime water or calcium hydroxide — Carbon dioxide — White precipitate of calcium carbonate — Water.

$$CaH_2O_2 + CO_2 = CaCO_3 + H_2O.$$

Carbon dioxide is completely absorbed by sodium or potassium hydroxide, whether in solution or when the solid

is moistened. The carbon dioxide unites with the alkaline hydroxide forming a carbonate and liberating water.

Potassium hydroxide Carbon dioxide Potassium carbonate Water.

$$2(KHO) + CO_2 = K_2CO_3 + HO_2$$

a reaction frequently used to separate carbon dioxide from other gases not absorbed by the alkaline hydroxide.

Carbon dioxide in presence of water or moisture has faint acid properties, but does not completely neutralise the alkalies, and when added to a solution of blue litmus turns it claret red; but the original blue colour can be restored by boiling which drives off the carbon dioxide; other acids, like sulphuric or nitric, give with blue litmus a bright red, which is permanent on boiling.

Carbonic Acid.—The solution of carbon dioxide in water is supposed to contain the hydrogen salt H_2CO_3, carbonic acid, from which the class of salts called carbonates is produced by replacement of the hydrogen by metals, but the acid has never been isolated.

It forms two classes of salts—normal carbonate, in which both atoms of hydrogen are replaced by metals, as:

Sodium hydroxide Carbonic acid Sodium carbonate Water.

$$2(NaHO) + H_2CO_3 = Na_2CO_3 + 2(H_2O);$$

and acid carbonates, or bicarbonates as they are often called, in which only half the hydrogen present is replaced:

Sodium hydroxide Carbonic acid Sodium bicarbonate Water.

$$NaHO + H_2CO_3 = NaHCO_3 + H_2O.$$

When carbon is burnt in oxygen gas, the oxygen is converted into carbon dioxide, which occupies the same volume as the oxygen used in its formation.

Carbon Oxygen, 2 vols. Carbon dioxide, 2 vols.

$$C + O_2 = CO_2$$

This may be shown by burning carbon in oxygen confined over mercury in the apparatus. (Fig. 35.)

A bulb tube is closed by a glass stopper (B) through which pass a small deflagrating spoon (D) and a thick copper

wire (E); these are joined by a piece of thin platinum wire, which is coiled round a small lump of charcoal in the spoon (D).

The bulb having been filled with oxygen, the stopper is closed, and the height of the mercury at (F) having been noted, a current from a battery is passed through the connections (C C), and heats the thin platinum wire to redness, igniting the charcoal, which burns in the oxygen forming carbon dioxide. The heat generated by the combustion expands the gas and depresses the mercury, but on allowing the gas and apparatus to cool down to its original temperature, the mercury again rises to the point (F), showing that no change in volume has taken place.

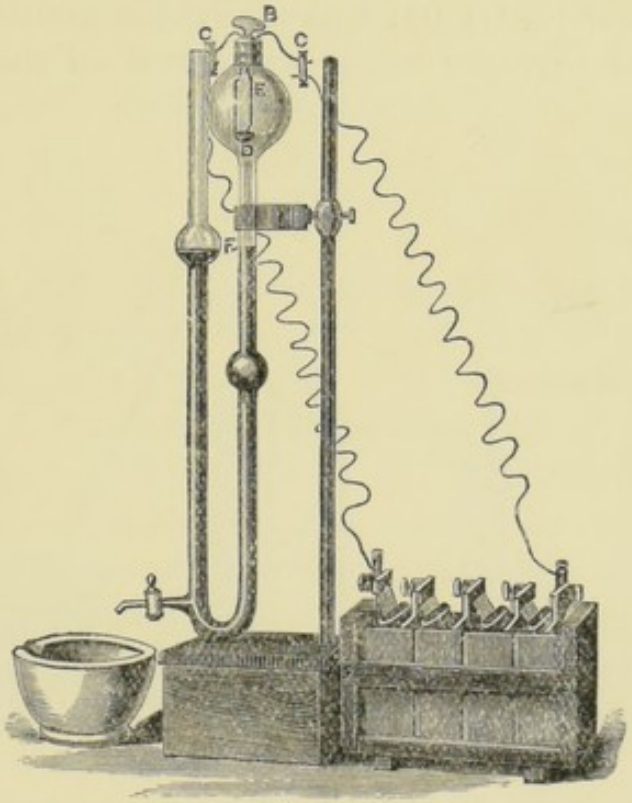


Fig. 35.

Carbon Monoxide (CO) is a colourless, tasteless gas, highly poisonous and very little soluble in water; it does not support combustion but burns with a pale blue flame, taking up another atom of oxygen and becoming carbon dioxide. It may be prepared by acting upon oxalic acid with sulphuric acid, oxalic acid consisting of hydrogen, carbon and oxygen in the proportions necessary to form water, carbon dioxide,

and carbon monoxide. When this is heated with sulphuric acid, the elements of water are taken up by the sulphate, and carbon dioxide and monoxide are set free; these mixed gases are now led through sodium hydroxide, which absorbs the carbon dioxide, forming sodium carbonate and water, and the carbon monoxide passes on free.

The operation is carried on in an apparatus such as is shown at Fig. 36.

The mixture of oxalic and sulphuric acids is heated in the flask (A), fitted with a safety funnel (B), and the mixed carbon monoxide and dioxide pass by means of the leading tube (C) through a solution of sodium hydroxide in the wash bottles (D D); this absorbs some of the carbon dioxide, the remainder being got rid of in the absorption

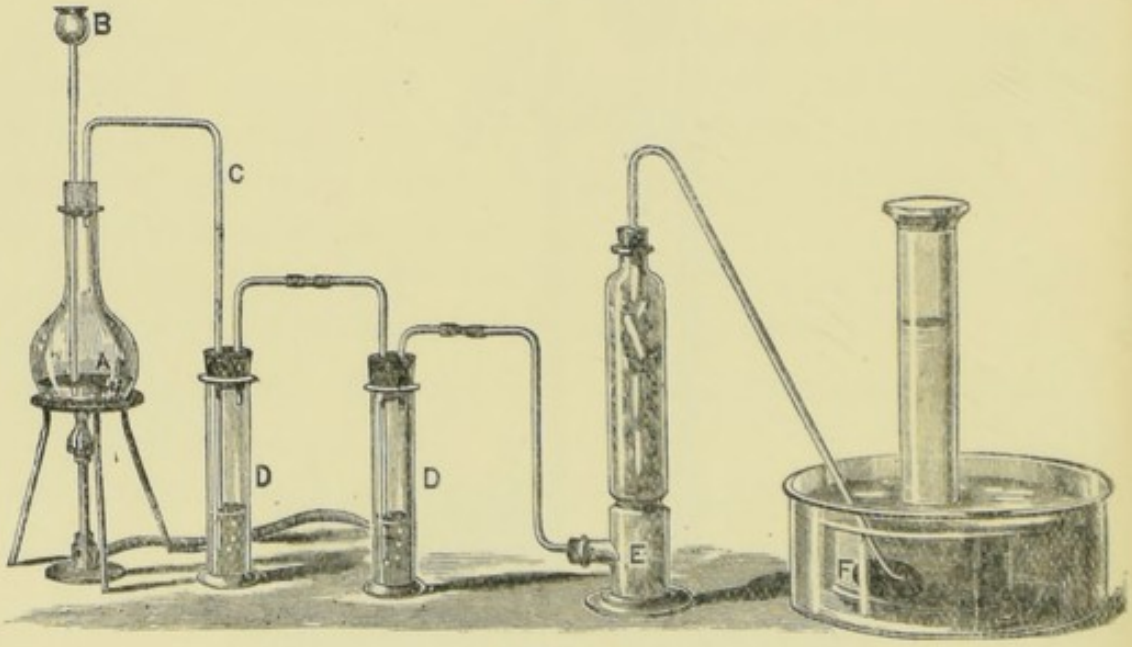


Fig. 36.

tower (E), which is filled with glass marbles, on the top of which are sticks of moistened sodium hydroxide; the purified carbon monoxide then passes on and is collected over water in the pneumatic trough (F). The action may be represented by the equations:—

Oxalic acid		Water		Carbon dioxide		Carbon monoxide.
$\begin{cases}COOH \\ COOH\end{cases}$	=	H_2O	+	CO_2	+	CO.

The mixed gases then pass through the sodium hydroxide solution when :—

Carbon monoxide	Carbon dioxide	Sodium hydroxide	Sodium carbonate	Water	Carbon monoxide.
CO	$+ CO_2 +$	$2(NaHO)$	$= Na_2CO_3 +$	H_2O	$+ CO.$

The pure gas may be made by heating formic acid with sulphuric acid, the decomposition being of the same character as with oxalic acid, but carbon monoxide only being evolved :—

Formic Acid		Water		Carbon Monoxide.
$\begin{cases} H \\ COOH \end{cases}$	$=$	H_2O	$+$	$CO.$

When carbon dioxide is passed over red hot charcoal, the dioxide gives up one half its oxygen to the carbon, and forms twice its own volume of carbon monoxide.

Carbon dioxide, 2 vols.		Carbon		Carbon monoxide, 4 vols.
CO_2	$+$	C	$=$	$2(CO).$

The blue flame of carbon monoxide may often be seen at the top of a clear coke fire, and its formation may be explained in the following way : At the bottom of the fire the fuel is in contact with excess of air drawn through it by the up-draught of the chimney, and here the fuel burns to water and carbon dioxide ; carbon dioxide passing up through the red hot coke, becomes reduced to carbon monoxide, and this in time coming in contact with more air at the top of the fire, burns with its characteristic pale blue flame, again forming carbon dioxide, which, with the water vapour and nitrogen of the air, pass up the chimney.

Carbon monoxide has a powerful reducing action, and will take oxygen from several of the metallic oxides, under the influence of heat, forming carbon dioxide, and leaving the metal free, an action which is utilised in metallurgical processes.

Poisonous Properties.—The gas has such powerful poisonous properties, that less than one per cent. of it in air renders the air fatal to breathe, and many fatal accidents have arisen

from its being formed during checked combustion, as when metallic surfaces cooled on one side by water are exposed to a gas flame, as is found in some forms of "water heaters;" also by the imperfect combustion taking place in kilns, in slow combustion stoves, and in charcoal pans.

The gas acts as a poison by forming a compound with the hæmoglobin of the blood and preventing it from carrying out its natural function of taking up oxygen during respiration and carrying it to the capillaries of the body.

A man who has been affected by carbon monoxide should be treated in the same way as for drowning, artificial respiration and the application of oxygen as a rule soon restoring consciousness.

It may be distinguished from carbon dioxide by burning with a blue flame, and not affecting lime water until combustion has converted it into carbon dioxide.

Carbon monoxide forms metallic compounds, as for example, iron carbonyl, $Fe(CO)_5$, and nickel carbonyl, $Ni(CO)_4$. These substances are liquid at ordinary temperatures, but can be easily volatilised, and are broken up at a higher temperature depositing the metal, a process utilised by Mond in the production of nickel.

CHAPTER XIII.

FUEL.

Woody fibre—Wood as a fuel—Circumstances affecting its value—Moisture in wood—Wood charcoal—Peat—Coal—Formation of coal—Effect of hydrogen on combustibility—Composition of coal—Stowage—Heating of coal—Ash—Coke—Liquid fuels—Russian and American petroleum—Heavy tar oil—Dead oil—Injectors for liquid fuel—Gaseous fuel—Coal gas—Water gas—Generator gas—Calculation of calorific value of fuels—Evaporative power of fuel—Determination of the thermal value of fuels—Calorific intensity.

IN order that any substance should take rank as a fuel it must be of such universal occurrence as to be easily obtainable in all inhabited countries, and this restriction has practically reduced our common fuels to wood and the substances which have been derived from it by either natural or artificial processes. Woody fibre or cellulose forms the basis of all vegetable solids, and on analysis it has the percentage composition :

Carbon	44·44
Hydrogen	6·17
Oxygen	49·39
	100·00

which gives us the empirical formula $C_6H_{10}O_5$.

Wood.—In wood, the main constituent cellulose, is common to all species, the chief differences being in the density and constituents of the sap.

As a fuel, the value of wood varies with the amount of moisture it contains and the ash, which is made up chiefly of the mineral constituents of the sap.

The moisture in wood varies with many circumstances, such as the season of the year at which it was cut down, the species of tree, and the way in which it has been kept

between the time of cutting and burning. When wood is cut in the spring, say during April, it will often contain nearly 10 per cent. more water than the same species of timber cut in the winter. For instance:—

Wood	Cut in January Water	Cut in April Water
Ash	28·8	38·6
Sycamore	33·7	40·3
Horse chestnut ...	40·2	47·1
White fir	52·7	61·0

It also varies in quantity according to the species of tree, the average quantity of moisture present being shown in the following table:—

Water contained in 100 parts of fresh cut wood:—

Hornbeam	18·6
Willow	26·0
Sycamore	27·0
Ash	28·7
Birch	30·8
Oak	34·7
Horse chestnut	38·2
Pine	39·7
Elm	44·5
Larch	48·6
Poplar	51·8

A certain amount of this moisture can be got rid of by exposing the wood to air and at the same time protecting it from rain, but under favourable circumstances, and after a year's exposure, air-dried wood will still contain about 20 per cent. of moisture, whilst after several years keeping in a warm room it will often retain 17 per cent. of moisture.

For all practical purposes, therefore, wood will, under favourable circumstances, only contain 80 per cent. of solid matter, whilst the large amount of heat absorbed in heating and evaporating the water present is a serious drawback to its employment as a fuel. The ash left on burning wood

varies from ½ to 5 per cent., and an excess of ash, as it is incombustible, must be looked upon as diminishing the value of fuels for heating purposes.

The amount of combined oxygen present in any fuel seriously detracts from its value, as its presence means that some of the combustible constituents of the fuel are already combined with oxygen, and are no longer available for generating heat.

Wood when heated out of contact with air yields a variety of volatile products and leaves a residue of charcoal. This charcoal is not pure carbon; it always contains oxygen, hydrogen, and a small quantity of nitrogen, in addition to the mineral constituents or ash of the wood, but the moisture and a large percentage of the combined oxygen having been got rid of, the charcoal is bulk for bulk a much more valuable fuel than wood, so that in cases where great local heat is required, it is preferable to convert the wood into charcoal before using.

Charcoal which is to be used as fuel is nearly always prepared in this country in charcoal heaps, in which the combustion of some of the wood subjects the remainder to destructive distillation, air being as far as possible excluded by coating the heap with clay or loam. During the partial burning of the heap, some moisture is distilled off as water, whilst the combined oxygen and most of the hydrogen escape, partly combined together and partly combined with carbon as tar, naphtha and other hydrocarbons, which distil out of the heap and are lost. In foreign countries, however, wood is frequently subjected to destructive distillation almost entirely for the sake of the tar (Stockholm tar) and pyroligneous acid which are evolved, and in order to collect these substances, the carbonisation is carried on in closed vessels. When the charcoal is to be used for the manufacture of gunpowder, it must be prepared with great care, and at a low temperature; superheated steam being often employed as the heating power. The rate at which the

carbonisation takes place has a great effect upon the yield of charcoal obtained; with rapid heating there is a considerable loss, not more than from 17 to 20 per cent. by weight of charcoal being obtained, whilst with careful heating, as much as 25 per cent. of the weight of wood taken remains as charcoal.

As a fuel charcoal has about double the calorific value of air-dried wood.

Peat.—Another kind of fuel much employed for domestic purposes in certain parts of the world is peat, which is composed of vegetable matter, generally mosses and aquatic plants, which, under the combined agency of time and pressure, has been converted into the spongy brownish-black substance found in the peat bogs. This peat is cut out in long square blocks, and is piled up exposed to air until dry. The relative heating power of dense, well dried peat, is about the same as wood and half that of coal. In composition peat occupies a position intermediate between wood and coal, and there is no doubt that the formation of peat is a stage in the great natural process by which woody fibre is converted into the most valuable of our fuels—coal.

Coal is now ascertained to be of entirely vegetable origin, and is the remains of a vegetation which covered the land long before it was inhabited by man. This vegetation has undergone partial decomposition and has been covered by accumulations of clay and sand; the pressure of these deep overlaying strata has prevented the evolution of gas, and has destroyed most traces of vegetable structure and given to the pit-coal its close and compact form; but ample proof of its origin is to be found in the strata immediately above the coal seams, which abound in the fossil remains of upwards of five hundred different kinds of mosses and ferns, whilst in the layer immediately below the seam, fossil roots are found in abundance.

The three principal varieties of coal are lignite, bituminous coal, and anthracite, the lignite or brown coal being the least

carbonised, showing indications of organised structure, and containing considerable proportions of hydrogen and oxygen; whilst anthracite is the most carbonised, and often contains little else than carbon and the mineral matter or ash.

When moist vegetable matter undergoes fermentation and decay, carbon dioxide and methane are the gaseous compounds which escape, and it is easily conceivable that the final action taking place during long ages, aided by pressure and the internal heat of the earth, is the conversion of woody fibre into carbon in the dense form known to us as graphite; whilst intermediate steps in the decomposition give us peat, lignite, bituminous coal, and anthracite. The complete reaction could be represented by the equation:—

Woody fibre		Carbon dioxide		Methane		Carbon.
$2(C_6H_{10}O_5)$	=	$5(CO_2)$	+	$5(CH_4)$	+	$2C$

which is supported by the fact that these two gases are always found in the coal seams. The theory that bituminous coal is a "younger coal" than anthracite is not, however, borne out by the fact that in the eastern part of Wales the coal is of a bituminous nature, gradually shading away into the anthracite found in the western portion of the Principality, as it is extremely unlikely that there is any very great difference in the age of the different parts of the Welsh coal field.

The gradual conversion of woody fibre into peat, coal and graphite, is illustrated by the following table, in which to show the gradual elimination of hydrogen and oxygen, the carbon is kept as a constant number:—

	Carbon	Hydrogen	Oxygen.
Wood	100 ...	12·18 ...	88·07
Peat	100 ...	9·85 ...	55·67
Lignite	100 ...	8·37 ...	42·42
Bituminous coal ...	100 ...	6·12 ...	21·23
Anthracite (Wales) ...	100 ...	4·75 ...	5·28
„ (Pennsylvania)	100 ...	2·84 ...	1·74
Graphite	100 ...	0·00 ...	0·00

The amount of hydrogen present in a fuel exercises an important influence upon the way in which it burns, as hydrogen is expelled at a fairly low temperature in combination with some of the carbon as gases which are inflammable at a moderate temperature; the burning gas surrounds the fuel and continues to heat it, whilst the escape of the gas leaves the remaining and less inflammable carbon in a porous condition, which is favourable to carrying on the combustion. Flame is burning gas, and therefore the nearer to pure carbon that our fuel approaches, the less the amount of flame produced by its combustion, because the smaller will be the quantity of inflammable gas evolved.

Lignite contains more hydrogen than any other variety of coal, and is for this reason more easily ignited and burns with more flame than any of the others; the next in this respect being the bituminous coals such as the Silkstone and Wallsend, while the harder forms of anthracite are difficult to ignite, and when lit, can only be kept burning by a strong draught, thus rendering them unfit for use in ordinary grates.

The tarry products which distil out of bituminous coals when heated, cause them to cake together, and this property enables the dust to be used for firing if certain precautions be taken.

It was decided by a Commission appointed in 1851 to consider the characteristics of a good coal for Service purposes, that it should possess:

1. High evaporative power.

2. The property of burning readily with a moderate draught.

3. It must not produce much smoke, which in time of war would reveal the whereabouts of the ships; and it must not cake enough to choke the fire bars.

4. It must be cohesive; or if it break up on heating, should cake moderately.

5. It should be dense, so that in storing it does not take up too much room.

6. It should be free from any large proportion of sulphur or sulphur compounds, and on burning should leave but little ash.

In order to ascertain the relative merits of the various coals in the market, an exhaustive series of trials was made under the conditions then in vogue.

For the evaporating power and rate of evaporation a Cornish boiler was used, and the average of a large number of trials taken with the following results:—

	A	B	C	D	E	F
Welsh Coal	9·05	448·2	53·1	42·71	60·9	1·42
Newcastle „	8·37	411·1	49·8	45·3	67·5	0·94
Lancashire „	7·94	447·6	49·7	45·15	73·5	1·42
Scotch „	7·70	431·4	50·0	49·99	73·4	1·45
Derbyshire „	7·58	432·7	47·2	47·45	80·9	1·01

A. Evaporating power.
B. Number of pounds evaporated per hour.
C. Weight of a cubic foot of the coal as used.
D. Number of cubic feet occupied by one ton.
E. Cohesive power (*i.e.*, percentage of large coal).
F. Percentage of sulphur.

From these results it is evident that the Welsh and North Country coal most nearly approach the standard required, and in order to combine as far as possible the merits of each class of coal, a mixture of two-thirds Welsh and one-third North Country coal was generally adopted for use in the Navy.

The introduction of new forms of engines and boilers and the use of forced draught rendered the necessity for the coal burning well with a moderate draught less important, whilst the cohesive power of coal is not a factor of the same importance; and at the same time the evaporative power and freedom from smoke, ash, and caking became of increased importance, with the result that little else than Welsh coal was used in the Service.

Experiments made in 1905 on smoke abatement during combustion point to the possibility of using North Country

coal with the formation of no more smoke than with steam, coal which would be an enormous advantage as it would widen the sources from which Service fuel could be obtained.

The stowage values as recognised in the Navy are not quite the same as those given in the table, a ton of Welsh coal being estimated to fill forty cubic feet of space, and the Newcastle coal forty-three cubic feet. It is most important that in a coal for Service use there should be as little sulphur present as possible, as the general form in which it occurs is iron pyrites—a sulphide of iron which may be represented by the formula FeS_2—and in the presence of moisture and air, this compound undergoes oxidation and was at one time thought to help the actions which lead to spontaneous ignition.

A more insuperable objection to the presence of sulphur in coal is, that when it is heated in the presence of iron it renders the metal fusible at a much lower temperature, and also by entering into combination with it renders the iron brittle when cold, both these actions being highly detrimental to the fire bars.

When coal containing iron pyrites burns at the high temperature of the furnace, the sulphur escapes either in combination with oxygen as sulphur dioxide, or else distils out and combines with the furnace bars or boiler plates, leaving the iron with which it was originally combined as ferric oxide.

Iron pyrites		Oxygen from air		Ferric oxide		Sulphur dioxide.
$4(FeS_2)$	+	$11(O_2)$	=	$2(Fe_2O_3)$	+	$8(SO_2)$.

This residual ferric oxide colours the ash left by the coals reddish-brown, a colour which is generally supposed to indicate sulphur, when it is seen in the ash.

The ash of coal consists of silica, alumina, oxide of iron and sulphates and phosphates of calcium and magnesium, varying with the description of coal from 0·5 to 30 per cent. Much ash is objectionable, as not only does it detract from the quantity of the fuel present, but also as the coal burns

the ash forms on its surface and retards the combustion of the coal by keeping air from it.

Coke.—In the same way that charcoal is obtained from wood by destructive distillation, so coke may be obtained from coal, the hydrogen and traces of other substances which it contains being driven off on heating it out of contact with air.

When this is done in the manufacture of coal gas, the resulting coke is called gas coke, but for many metallurgical processes coke is specially prepared in ovens, temperatures being reached at which the escaping gases are of no use for illuminating purposes, and can only be used to heat boilers, etc., but at which temperatures a superior quality of coke is produced. This kind of coke is called oven or metallurgical coke.

The advantages of coking coal are that it yields a more intense local heat than coal, it does not cake, and the heat at which it is produced drives off a large proportion of the sulphur contained in the original coal, a most important factor in many metallurgical operations, in which sulphur, in even small traces, is most objectionable; whilst another advantage in the use of coke is that it gives off little or no smoke during combustion: it, however, requires a high temperature to ignite it, and a brisk draught in the chimney to carry on combustion, properties which render it more fitted for use in manufacturing processes than for domestic consumption.

The heating effects produced by coke are, by calculation, a little better than those obtained from coal; but in practice the amount of heat obtainable from coal and coke is practically the same.

Liquid Fuel.—It was not until the middle of last century that the oil industry and oil as a fuel may be said to have originated.

Introduction of Mineral Oil.—The first step in the introduction of mineral oil dates back to 1849, when James Young

had his attention drawn to the small driblets of oil that ran down from the shale measures in the Riddings Colliery near Alfreton. Taking this oil and distilling it, he made from it an excellent lubricant, but no sooner had he got a good market for his lubricant than he found that the supply was totally insufficient, and showed signs of being exhausted; but on distilling some of the Scotch shales he obtained an abundant supply of the oil, and so started the Scotch Oil Industry. Later on, in 1859, the oil fever broke out in America. In Pennsylvania the oil, which had been collected for centuries in small quantities, was suddenly obtained in enormous volumes by Drake, who started the idea of boring wells, which gave him an abundant and enormous supply. Financial booms took place in America, which led to the sinking of innumerable wells over that district, and the flooding of the markets of America and the civilised world with oil. By 1870 also the Russian oil fields were opened up, yielding an amount of oil which very soon made them an important competitor of the American trade.

Oil as a Fuel.—In 1865 the idea of using oil as a fuel was started by Captain Selwyn, and although not adopted in this country, by 1870 it was used on a number of small vessels on the Caspian, while later on the use of liquid fuel spread to the Black Sea.

At that time the supplies of petroleum were practically confined to the American and Russian coal-fields, but now, owing to the discoveries of petroleum in almost all the countries of the world, a much wider distribution brings it nearer and nearer to a universal fuel, and moreover prices, owing to the large quantities of it available, are also likely to be kept down by competition; so that the time is now ripe for petroleum as a liquid fuel to take its proper place.

All forms of mineral oil as they leave the oil wells are mixtures of hydrocarbons which, however, vary a good deal in composition according to the part of the world from which they are obtained.

In the American oil fields, natural gas occurs, and methane, the simplest member of the $C_nH_{2n}+_2$ or paraffin group, is the chief constituent, and in the oil from these fields liquid members of the group are practically all of them represented.

With oil from the Russian fields, on the other hand, you find hydrocarbons of a different character, belonging to a curious class of bodies called naphthenes. These bodies are isomeric with ethylene, and really may be looked upon as belonging to that series, and in their simplest form may be represented as allied to the C_nH_{2n} type. They are not, however, unsaturated hydrocarbons, and this difference in the behaviour of these bodies, although it has but little effect on their action during combustion when used as a fuel, makes a very great difference in their chemical properties, and the alterations which can be brought about in them by heat and other processes.

Theories of Origin.—There are several theories to account for the formation of petroleum. One class of theorists insists upon its vegetable origin, declaring that it is the result of distillations from such fossilised vegetation as coal. Another and perhaps a larger class argues that it has been formed from animal remains, whilst a third party is perfectly clear in its views as to these hydrocarbons having been formed by the action of water or steam under considerable pressure upon metallic carbides. Carbides are substances formed by the combination of metals and carbon. There is one carbide perfectly well-known—calcium carbide—and by the action of water it yields acetylene. In the same way as water and calcium carbide give acetylene, so water and some of the carbides of the rarer earths will give hydrocarbons of exactly the same composition as many of the hydrocarbons found in the mineral oils.

Advantages of Liquid Fuel.—With land boilers, the use of oil has great advantages, but for use on board ships, the advantages are greater still. One of the worst jobs on board ship is coaling. All the coal has to be got into the bunkers,

meaning an enormous amount of extremely hard labour, everything on the ship is made filthy by the coal dust, necessitating cleaning and polishing up afterwards. As regards the advantages of oil in this direction, there can be no reasonable doubt. Taking the oil in from big storage tanks alongside the wharf, it can either be run by gravity into the portions of the ship which are reserved for storage, or it can be pumped in, and instead of having the coal bunkers, as one is obliged to for coal, above the level of the stoke-hold, the storage tanks for the paraffin, or whatever liquid fuel it may be, may be in practically the ballast tanks, and as the oil is used it can be replaced by water. That gives an enormous increase in capacity to the vessel. If it be a ship of the Mercantile Marine, it gives a large amount of cargo room, which means, of course, greater earning power for the ship; if it is a man-of-war, it does more; it gives the power of storing a much larger amount of energy in the same space as coal would have occupied.

Liquid fuel is far in advance of coal as a steam raising agent, as we shall see later. In point of fact, it is found that one ton of oil is about equal to 1·5 of coal, and the result is that for the same weight an amount of fuel can be carried which will give a very much greater radius of action, and that at the present time in the Navy is of the very greatest possible importance. Again in the feeding of the oil to the furnaces, instead of needing a very large number of stokers for trimming the coal in the bunkers and keeping up the fires, the use of oil will reduce that number to about one-fourth, whilst there being no ash, cinder and clinker to clear out of the furnaces and throw overboard, another economy in labour is effected.

These factors have led to the introduction of liquid fuel in nearly all the Navies of the world, but as the total supply would at present be a mere fraction of that needed if it were burnt alone, it is mostly used as an adjunct to coal when full power is required.

It is manifest that crude petroleum, being a mixture of

many hydrocarbons, will have so low a flash point that its use as a fuel would be attended with danger on land, and would certainly never be permissible afloat, and it is to such residues as are left after the distillation of the more volatile portions and the lamp oil that we must look for the chief source of our liquid fuel.

Flash Point.—The flash point of an oil is the temperature at which it begins to give off inflammable vapours in an enclosed space, and for liquid fuel the Admiralty have decided that it shall not be below 200° F.; in the Mercantile Marine and German Navy the flash point is fixed at 150° F.

Heat Value of Fuel Oils.—The fuel oils differ but little in the ratio of carbon and hydrogen present, and the following table gives the ultimate composition of the chief available fuel oils, showing the Texas oil to be a little the best:—

FUEL OILS.
(Orde.)

	Carbon.	Hydrogen.	Oxygen, etc.	B.T.U.'s.
Borneo ...	87·8	10·78	1·24	18,831
Texas ...	85·6	11·03	3·31	19,242
Caucasus ...	84·9	13·96	1·25	18,611
Burmah ...	86·4	12·10	1·50	18,864

Taking a good sample of liquid fuel, its theoretical evaporative efficiency would work out at about 20 lbs. of water, whilst the best steam coal will work out at about 15, a gain of only 33 per cent. In practice the evaporative power to be obtained from oil averages 15 as against 10 obtained with steam coal in the same boiler, a gain of 50 per cent., and there is no doubt that when the methods of burning oil have been as fully studied and worked at as the combustion of coal, liquid fuel will show an even greater advantage. It is quite likely that the double value which the advocates of liquid fuel have been so fond of talking about, may be attained, this being due, not to the difference in calorific power, but to the greater ease of manipulation and to the power of being able to suit the combustion to the work which the fuel has to do. It is quite clear, however,

that the methods by which the oil is to be consumed must be a most important factor in the results which are to be obtained.

The Combustion of Oil.—The first successful attempt to use liquid fuel was to burn the oil from a series of open troughs, so arranged that the unburnt oil flowed downwards from trough to trough. This system was generally known as "Nobel's troughs," and gave good results in practice, an evaporate efficiency of as high as 14½ lbs. of water being obtained in stationary boilers. The troughs are generally fitted at the mouth of the boiler, and a strong draught draws the flame, together with the requisite quantity of air, into a mixing chamber, from whence it passes with more air through the furnace, combustion chamber and flues. This method of burning the oil has also been applied frequently to metallurgical and other furnaces with considerable success, but it must be remembered that such an arrangement would be impossible to use with oils of the high density it is necessary now to employ as fuel, and that complete combustion would be very difficult to attain.

Soon after this the methods which are now most extensively used began to be introduced, and consisted of bringing the oil into the combustion chamber either as a gas or in such a finely divided condition of spray as to ensure its rapid and complete combustion.

It is well known that if oil be subjected to the action of heat it can be converted into a gas rich in hydrocarbons, with simultaneous formation of tar and deposition of more or less solid carbon, and the idea of first gasifying the oil before burning seems to have originated with Colonel Foote of the United States.

The United States gunboat *Palos*, was in 1867 fitted for burning liquid fuel by Colonel Foote, and on her trial trip ran over 14 knots per hour, whereas 8 knots had been her best previous record with coal. It was also found that instead of twenty firemen required with solid fuel, the stokehold staff could be cut down to three.

The liquid fuel consisted of petroleum, which was carried in two large iron tanks placed on deck, and from the description given these were fitted with a vent pipe on top to allow the escape of vapours, so that it is evident that crude petroleum and not residuum was being used. The oil was allowed to flow by gravity through half-inch pipes to a retort placed some little distance inside the furnace, where it was gasified, and the oil gas was led back towards the furnace mouth by pipes having suitable apertures and giving a large flame, which swept back over the retort, keeping it heated to the necessary temperature to continue the decomposition of the oil. The oil gas so formed was diluted with hydrogen, made by passing steam through tubes filled with heated scrap iron, and the flame was fed with air forced in by an air pump.

The combustion is recorded as being very intense and perfectly smokeless, but nothing more was heard of the system, this being probably due to the costly method of diluting the gas, and the trouble from choking of the retort and tubes with carbon, which must inevitably have taken place.

Soon after, a system of a similar character was patented by Simms & Barff, the oil being injected and vapourised in a retort placed in the furnace, and although satisfactory results were obtained, it was found that considerable trouble was experienced with the retorts, which being exposed to a very high temperature had a very short life.

Several systems of this kind have been proposed, and also others,in which the vapourisation of the oil should take place in retorts external to the furnace. The best known of these are those processes patented by C. Eames, in 1875, and by Dürr. In the Eames' system, the oil was fed into an externally-heated cylindrical retort with round ends, in which it flowed downwards over a series of horizontal iron plates, whilst superheated steam was passed upwards, and being decomposed by the hydrocarbons at the high temperature formed a mixture of what was practically oil gas and water gas, which was burned as it issued from the vapouriser at suitable burners

In the Dürr apparatus, the oil is supplied by air pressure through a heated retort in which it is vapourised, and the vapour is then gasified in a chamber in the mouth of a furnace heated to a high degree. The gas is led straight for combustion into the furnace.

It is, however, quite evident that for the successful use of liquid fuel, auxiliary apparatus and sources of heat must be done away with and the furnaces made practically self-contained, if anything approaching success is to be attained, as it is upon simplicity, ease of working, and freedom from

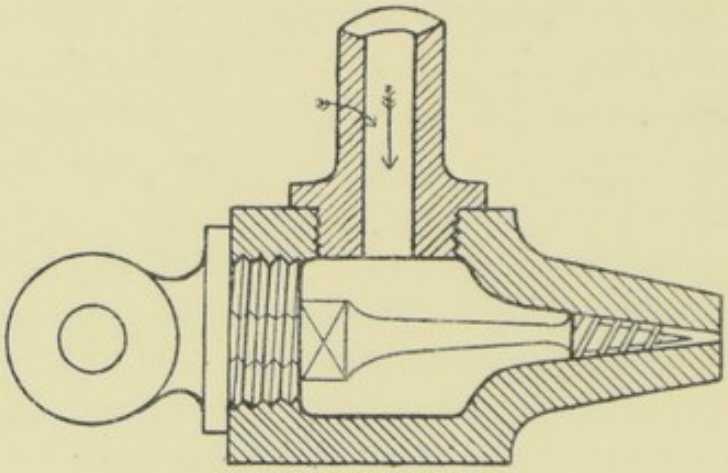


Fig. 37.

complicated parts that the claim of liquid fuel for supremacy over solid is largely based.

The pulverisation of the oil so as to drive it direct into the furnace chamber in a spray sufficiently divided to act almost as a gas, is the method now practically universally adopted, and this pulverising or atomising action may be brought about either by forcing the oil out from a jet at considerable pressure, by injecting with steam, or by compressed air, or by a combination of the two.

The Körting Injector.—The system of direct pulverisation, *i.e.*, by pressure, is perhaps the latest and most promising method of consuming the oil. Körting's injector or burner (Fig. 37) is the best known arrangement for this purpose, and has been employed with great success on ships of the Hamburg-American Line, and in many German vessels. The oil is

heated to a temperature of 130° C., and is then forced into the injector under an air pressure of 50 lbs. on the square inch. In the injector the oil flows into a chamber feeding the jet, and into this jet is fitted a spindle carrying a spiral screw. The oil at a pressure of 50 lbs. is forced down this spiral, and acquires a centrifugal action which sprays it out of the jet in a very finely divided condition.

Another form of burner, the action of which also is merely dependent upon the pressure, is the Swensson, in which the oil under pressure is heated in a steam jacketed tube, and is then forced out from a fine jet on to the point of a V-shaped metal cutter, which has the effect of pulverising it into a very fine spray.

By far the best known and most used of the burners are those in which the oil is pulverised by steam, a method that was first used by Messrs Aydon, Wise & Field in 1865-7, the general principle being that the oil is led down to the injector by gravity, and there meets a steam jet which drives it out from the nozzle of the injector with high velocity and in a fine state of division, whilst the outrush of the steam and oil is usually made to suck in air around the jet to aid the combustion in the furnace. Of these burners, perhaps at the present time the best known are those of the Holden type, and it is a form of these that is employed in the highly successful installations of liquid fuel that Mr Holden has fitted up, and which have shown themselves to be of a most satisfactory character. One form of the injector or burner is that used on locomotives, which is made to serve the double purpose of injecting the fuel and also maintaining the vacuum necessary for the brakes. In a second pattern, however, arranged for marine work, valves are designed to supply the oil in two portions to the steam injector, in order that if a change from half speed to full speed, or *vice versa*, be desired, the supply of fuel can be arranged without any alteration in the steam consumption. At the mouth of the burner an ingenious arrangement of a steam ring performs the important function of allowing jets

of steam at various angles to catch the oil spray as it leaves the burner and to more evenly distribute it through the furnace, the steam ring also serving to draw in air for the primary combustion.

Another form of steam pulverising burner largely used in practice is that designed by Messrs Rusden & Eeles (Fig. 38), which is the burner employed on the vessels of the Shell Transport Company. This excellent burner has shown itself very successful in working, and in it oil, after having been heated by a steam jacket, is sprayed out by the steam, and as the burner is so made as to allow of separate adjustments of the

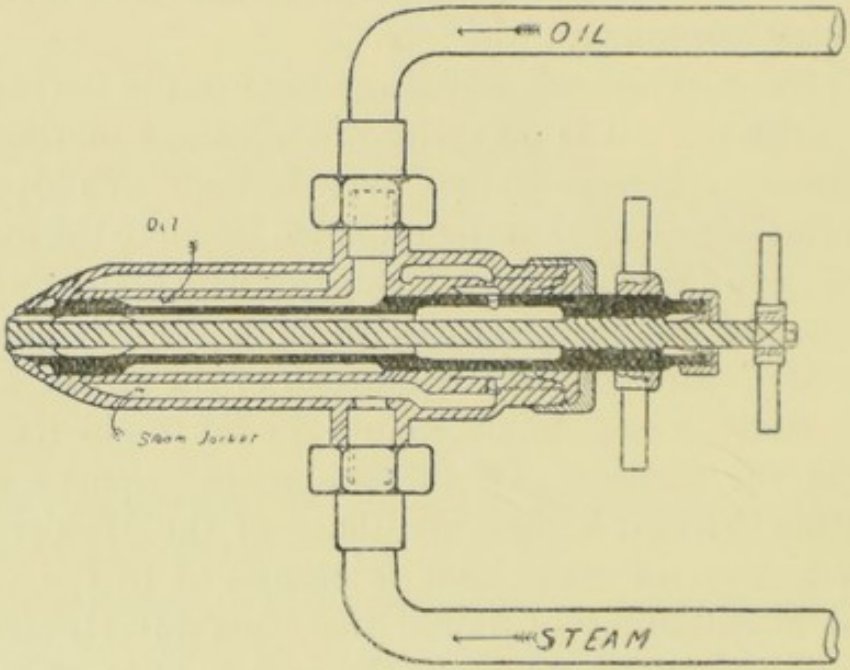


Fig. 38.

steam and oil jets, the consumption of the fuel can be nicely adjusted to the work which it has to do.

The burner used by Messrs Armstrong, Whitworth & Co. is that designed by Mr E. L. Orde. In this burner highly superheated steam is employed, 600° F. being the temperature at which it probably works best, and the steam is so arranged as to sweep out and spray the oil with a very high velocity, thus inducing a current of heated air together with the jet of steam and oil, this being found to help the combustion.

Although there have been many other forms of burner employed, these types may be taken as fairly covering the most successful methods of bringing the oil into a sufficiently finely divided condition to allow of rapid and complete combustion.

The method now employed in the Service consists of direct pulverisation by pressure, as, if steam is used for injection, 0·2 lb. of steam per I.H.P. per hour is required, which could not be obtained at full power without extra boilers.

When the liquid fuel has been disintegrated by the injectors or vapourised, in most cases it is brought in contact either with a layer of fuel or brickwork near the mouth of the furnace, and in some cases, as in the Körting system adopted by the Hamburg-American Line, the furnaces are bricked right round. Under these conditions the brickwork can be made to fulfil two requirements: in the first place it gets heated to a very high temperature, and serves to ignite the oil vapour and air coming into the furnace, and in the next place if the oil jet is made to dash straight against it, it serves to disintegrate and gasify it, prevents the burning oil and flame being driven too rapidly through the furnace, and saves the plates from the direct impact of the flame. For these latter purposes also various forms of brick baffle are frequently employed.

In burning oils there is always a risk that there may be present small particles of solid matter which may choke the injector, and also water, the latter being present when the oil has been stored in the double bottoms and ballast tanks of the vessel, and also in crude oil. It has been found that the presence of drops of water in the oil is apt to extinguish the flame at the injector nozzle, and if that were to take place, and the finely-divided oil spray or oil gas were to get into the furnace mixed with air in any large quantity, it would give rise to an explosion.

Use of Settling Tanks.—In order to get rid of solid particles and water, the oil is pumped into settling tanks, fitted with a steam coil, which can be used to raise its temperature, the necessity for this being found in the fact

that the specific gravity of the oil generally used as a fuel is only a little below that of water, and that therefore the separation would be very slow, but when slightly warmed the oil expands at a much greater rate than the water, and the separation, therefore, takes place with much greater rapidity.

In some systems two settling tanks are employed, each capable of containing twelve hours' supply, and the one which is out of use, after standing twelve hours, has the water drawn off from the bottom, whilst the oil is pumped out through a wire gauze filter. In other forms of settling tanks, a filtering cage of wire gauze is employed, which is kept by a float near the surface of the oil, whilst a steam coil is used as before to aid the separation.

When experiments with liquid fuel were first made in the English Navy great difficulty was experienced from the smoke produced and the comparatively low evaporative results obtained; this resulted from the small combustion space available as compared with the space in vessels of the Mercantile Marine, and also to the largely increased quantity of oil that had to be burnt to give full power.

These troubles have now been entirely overcome and from the liquid fuel an evaporation of 15 lbs. of water per 1 lb. of oil can be obtained with almost complete freedom from smoke.

Gaseous Fuel.—The ease of application and the many advantages presented under certain conditions by the use of gaseous fuel in various manufacturing processes have led to considerable attention being paid to the subject, and ever since the discovery of water gas by Fontana in 1780, engineers have busily attempted to perfect methods for its economical production.

Under the head of gaseous fuel may be comprised:—

(1) Generator or producer gas, made by the passage of air through incandescent carbon.

(2) Water gas, made by the action of steam on incandescent carbon.

(3) Mixed producer and water gases, made by the passage of both air and steam over the highly heated fuel, and

(4) Coal gas.

Generator or Producer Gas is a mixture of carbon monoxide and nitrogen, having the theoretical composition:

Carbon monoxide	34·3
Nitrogen	65·7
	100·0

and is the least efficient of the gaseous fuels. It is formed by passing air through a column of heated coke, when the carbon at the lower surface of the column burns to carbon dioxide, combining with the oxygen of the air; and the carbon dioxide, by contact with the heated carbon over which it has to pass, is then reduced to carbon monoxide:

Carbon + Air = Carbon dioxide + Nitrogen.

$$C + 2(N_4 + O) = CO_2 + 4(N_2)$$

and—

Carbon dioxide + Carbon = Carbon monoxide.

$$CO_2 + C = 2(CO),$$

the carbon monoxide and residual nitrogen from the air forming the "generator gas."

The heating power of such a gas is very low, but its production is inexpensive, and when burnt hot is a very effective form of fuel for glass melting, the heating of gas retorts, brick burning, pottery kilns, and many processes of this character, in which, used in connection with a Siemens regenerative furnace, it has given splendid results.

Siemens Gas.—This only differs from generator gas in that small coal or slack is used as the fuel instead of coke, with the result that the gas contains a small proportion of gaseous hydrocarbons which increase its thermal value.

Water Gas.—Water gas depends for its formation upon the fact that at high temperatures carbon has a greater affinity for oxygen than hydrogen has, and that when steam

and carbon (in any of its amorphous forms) are heated to such temperatures, the steam is decomposed with liberation of hydrogen and either carbon monoxide or dioxide, the oxide formed being to a great extent dependent on temperature, and the quantities of steam and carbon interacting.

The action may be represented as follows:—

Carbon		Steam		Carbon monoxide		Hydrogen.
C	+	H_2O	=	CO	+	H_2

or—

Carbon		Steam		Carbon dioxide		Hydrogen.
C	+	$2(H_2O)$	=	CO_2	+	$2(H_2)$,

and the value of the gas produced, as a fuel, largely depends upon the closeness of approximation to the first reaction, but the ideal composition is rarely, if ever, reached, water gas practically consisting of a mixture of carbon monoxide and dioxide, hydrogen and small quantities of methane formed by the direct combination of the liberated hydrogen and carbon.

The following analysis will give a fair idea of the composition of ordinary water gas:—

	Per cent.
Hydrogen	48·31
Carbon monoxide	35·93
Carbon dioxide	4·25
Nitrogen	8·75
Methane	1·05
Sulphuretted hydrogen	1·20
Oxygen	0·51
	100·00

The ratio of carbon monoxide and carbon dioxide present depends entirely upon the temperature of the generator and the kind of carbonaceous material employed. Using a hard anthracite coal, a temperature can be reached at which practically no carbon dioxide is formed; but with an ordinary generator and a loose fuel like coke, a large percentage of that gas is generally produced. The sulphur present in gas coke gives rise to the sulphuretted hydrogen; but by using a material like anthracite, practi-

cally none is formed. The nitrogen is the result of heating the fuel by air blast, which leaves the pipes full of producer gas—nitrogen and carbon monoxide—which is carried over into the holder by the first portions of water gas. Water gas so produced is non-luminous; and many attempts have been made to use it as an illuminant by heating with it mantles or combs of some refractory material until they become incandescent and emit light.

Water gas forms an effective fuel in many metallurgical operations, and is largely used for welding and other engineering work.

It is largely used as the basis of an illuminating gas, by mixing with it the gases formed by the decomposition of various grades of oil; these gases being rich in hydrocarbons endow it with illuminating power, and the mixture is generally known as carburetted water gas.

The various forms of generator employed for the manufacture of carburetted water gas are very numerous. The most successful can be divided into two classes: (1) Continuous processes, in which the heat necessary to bring about the interaction of the carbon and steam is obtained by performing the operation in retorts externally heated in a furnace. (2) Intermittent processes, in which the carbon is first raised to incandescence by an air blast. When the air blast is cut off, steam is admitted until the temperature falls too low for the action, when the air is again admitted. The process, therefore, consists of alternate "blows" and "runs."

The first class of processes has not as yet been commercially successful. The best of the intermittent processes, and the only one used in this country is that originally devised by Lowe. In this apparatus, the coke is heated to incandescence by an air blast in a generator lined with fire-brick; and the producer gas thus formed passes on to the superheaters—more air being admitted to ensure its combustion. By this means the superheater is raised to a high temperature. When the fuel and superheater are sufficiently hot, the air blast is cut off, and steam blown through the generator,

forming water gas, which meets the enriching oil at the top of the first superheater, called the carburetter, and then passes on to the fixing chambers, where the hydrocarbons are rendered permanent gases. The chief advantage of this apparatus is that a low temperature can be used for fixing, owing to the large amount of surface for superheating, which o a great extent does away with deposition of carbon.

Mixed Fuel Gas.—In the formation of generator or producer gas heat is evolved by the processes taking place in the generator, whilst in the making of water gas a very large amount of heat is absorbed, so that the temperature of decomposition has to be attained and kept up either by exterior heating, as used in the retort processes of making water gas, or by blowing up the fuel to incandescence by an air blast, as practised in all the successful water gas processes. A large number of gas generators are now made in which air and steam are simultaneously passed through the incandescent fuel in such proportions that the formation of producer gas by the partial combustion of the carbon by oxygen of the air shall raise the temperature in the same ratio that the decomposition of the steam by the red hot carbon into water gas lowers it, the result being a uniform temperature in the generator, and the production of a gas which is practically a mixture of generator or producer gas with water gas, and which has a higher thermal efficiency than the producer gas alone, and answers well in gas engine practice.

Producers for making these mixed gases are known by the names of their inventors, and the Wilson, Dowson, Dawson and Duff processes are all of this character. Mond gas however differs from these in as much as by using an excess of steam in the generator the temperature of the fuel is kept low, and a large proportion of the carbon monoxide is converted into dioxide, this however being accompanied by an increase in the volume of hydrogen produced, and the low temperature favouring the formation of ammonia from the nitrogen in the slack used as fuel yields a valuable by-product.

Blast furnace gas consists of the gases which until lately were blown to waste from the mouth of the blast furnace during the reduction of iron from its ores, and which has a composition not very different from that of producer gas.

Coal Gas as a Fuel.—Coal gas is year by year rapidly increasing in favour for power purposes and as a fuel for domestic purposes, such as heating and cooking, the only drawback being the cost of gas as compared with coal as a fuel. When used for such purposes the gas is burnt mixed with air in atmospheric burners, and during complete combustion a very high temperature is attained; but per unit of heat evolved the cost is nearly three times that of coal, against which, however, must be set the economy of being able to turn on the gas just when required, and to turn it off when the desired effect has been produced, and this, when taken in conjunction with the saving of labour and absence of dirt and smoke, considerably decreases the margin in favour of coal.

The composition, thermal values, etc., of the various gaseous fuels are given in the following table:—

Constituents	Blast furnace gas	Producer gas	Siemen gas	Wilson gas	Dowson gas	Mond gas	Water gas	Coal gas.
Carbon monoxide ...	27·11	29·0	22·6	26·9	25·07	11·0	40·08	3·6
Carbon dioxide ...	8·62	4·0	4·4	4·0	6·57	16·0	4·80	0·3
Hydrogen	1·34	2·5	7·8	11·5	18·73	29·0	51·89	52·1
Methane	0·00	0·0	1·5	1·5	0·64	2·0	0·10	38·6*
Nitrogen	61·23	64·5	63·7	56·1	48·98	42·0	3·13	1·0
Combustible ...	28·45	31·5	31·9	39·9	44·44	42·0	92·0	98·7
Non-combustible ...	71·55	68·5	68·1	60·1	55·56	58·0	8·0	1·3
Thermal value in B.T.U.'s ...	70	72	125	135	148	154	290	640
Volume of gas needed to give I.B.H.P. in gas engine ...	—	—	120	100	80	80	31	17
Fuel used	coke	coke	slack	slack	anthracite	slack	coke	coal
Cubic feet per ton of fuel ...	—	200,000	190,000	180,000	170,000	160,000	70,000	10,000

* Contains also 4·4 per cent. of unsaturated hydrocarbons.

The great value of gaseous fuel however is now the creation of power by means of the gas engine, which has practically revolutionised the generation of power. When the gas engine was first introduced it was entirely with a view to using it with coal gas, and the only drawback was the price of the gas, but in large cities where space was cramped the gas engine made rapid headway, owing to its convenience, cleanliness, and the advantage of being able to dispense with furnaces and boilers for the generation of steam. The expense however greatly militated against the use of engines of 20 H.P. and upwards. It was then found that even gases so poor in calorific value as the mixed producer and water gas gave excellent results, and since then the gas engine has grown with such rapidity that it is now made up to 2000 H.P., whilst its use is so extended that in Germany steam as a motive power for stationary work is looked upon as practically dead.

Suction Plant.—A type of gas generator known as a suction gas plant is now being made which does away with all the paraphernalia of blowers, oilers, and gasometers needed for the earlier forms of fuel gas generators.

In this form of apparatus the stroke of the gas engine draws air and steam through a bed of incandescent fuel and so converts it into gas, which is then purified by passage through a washer, condenser, and scrubber before entering the engine cylinder. The fact that in such a plant the whole of the apparatus is never above the ordinary atmospheric pressure renders it far safer and far more convenient to use than the old forms of apparatus in which the pressures were obtained by means of fans or blowers for driving the air into the generator, which of course always leads to a tendency to leakage.

Marine Gas Engines.—The latest developments in the gas engine have been in the direction of trying to adapt it for marine purposes, and Capitaine, who played a leading part in developing the oil motor, has been working at the

marine gas engine for the past twenty-five years. Although at first there seems little or no chance of success, marine suction gas plants and engines are now *un fait accompli* for small powers, and the possibility of manufacturing marine engines on this principle from 25 to 1000 H.P. has been entirely demonstrated.

The floor space occupied by the suction generator and engine for the larger powers may be taken as half a square foot per H.P., which compares favourably with the space taken up in vessels of the Mercantile Marine using steam power, although of course considerably above that possible in the Service or fast liners. The superficial area of engine and boiler space in various vessels is shown in the following table :—

Ship	s.s. Deutschland	s.s. König Wilhelm der Grosse	H.M.S. King Alfred	s.s. Celtic	s.s. Duke of Cornwall	H.M.S. Juno	s.s. Indian.
Total I.H.P.	38,900	30,000	30,000	13,000	5520	9830	2120
Highest mean speed in knots	23·51	22·79	23	16	19·75	20	10·75
Superficial area of engine and boiler space per I. H. P. square feet	0·425	0·42	0·346	0·96	0·405	0·44	0·949
Total weight machinery in tons	5670	4460	2575	2975	612	904	455
I.H.P. per ton of machinery	6·35	6·71	11·65	4·37	9·02	10·88	4·66

Gas engines for small powers show a very great economy over the steam engine, as small 10 to 20 B.H.P. steam engines will consume between 3·3 and 5·5 lbs. of fuel per B.H.P. hour, but with the enormous powers used in the Service vessels with all the refinements and improvements introduced into them, the consumption of coal is often under two lbs.

Using the suction gas plant, the consumption of fuel per B.H.P. hour for a 10 H.P. engine is equal to 1·1 lb., but the economy rapidly increases with the size, so that for a 50 H.P. it is only about 0·88 lbs.

The Determination of Calorific Value.

The heating value of a fuel, solid, liquid or gaseous, may be arrived at by one of two methods :—

1. By analysis of the fuel and calculation of its calorific value from that of its individual constituents.
2. By direct determination in a calorimeter.

Calculation of Calorific Values. — The heat generated during the combustion in oxygen of different elements and compounds was first determined by Andrews, and later by Favre and Silberman, Thomson and others. Some small discrepancies exist between the values obtained by these observers, which must have an influence on the calculated results, but figures derived from determinations in some form of bomb calorimeter must be accepted in preference to those obtained by older methods. The results are generally expressed in *calories*, that is the number of grams of water raised in temperature 1° C. at the point of maximum density by the combustion of 1 gram of the substance. Amongst engineers the Fahrenheit scale is employed and the *British Thermal Unit* (B.T.U.) is the number of pounds of water raised 1° F by the combustion of 1 lb. of the substance. If results are expressed in calories then the B.T.U.'s corresponding will be $\frac{212-32}{100}=\frac{9}{5}$

When water is one of the products of combustion, it is clear that the available heat will depend upon whether this water escapes as steam (as under a boiler) or is condensed to the liquid form, as in most calorimeter determinations. In practice it is usual to assume that the water formed is always condensed, but allowance can readily be made for its escape as steam by taking the latent heat of steam into account.

Heats of Combustion.

Combustible.	Products of combustion.	Calories per gram.
Hydrogen	Water (condensed)	34,500
Carbon	Carbon dioxide	8,140
Carbon monoxide	Do.	2,490
Methane (CH_4)	Carbon dioxide and water	13,240
Ethylene (C_2H_4)	Do. do.	11,900

When a fuel consists of carbon and hydrogen only, it is considered sufficiently accurate in practical working to determine its composition, and then to multiply the carbon present by 8,140, and the hydrogen by 34,500, the sum of the numbers so obtained being taken as representing the calorific value of it as a fuel; for instance, on analysing methane we find that it has a percentage composition of:—

Carbon	75
Hydrogen	25
	100

and—

$$\frac{(75 \times 8{,}140) + (25 \times 34{,}500)}{100} = 14{,}730.$$

14,730 would therefore be taken as the calculated calorific value of methane.

This value however is far higher than the figure obtained by direct determination, and this is due to the heat of formation of the compound being neglected in the calculation.

We have seen that when a chemical compound is formed, heat is either absorbed or given out, and when the compound is again decomposed during combustion, as much heat reappears or is absorbed as was the case during its formation, and to make the calculation of calorific value correct, this must be allowed for.

The heat of formation of the molecule of methane (CH_4) is + 20,414 thermal units, and our value for methane so corrected would be $14{,}730 - \frac{20{,}414}{16}$, or 13,450 ther-

mal units, a number much more nearly approaching that obtained by actual experiment, namely 13,240.

The calculation becomes rather more complicated when the fuel already contains a certain amount of oxygen already in combination, for those elements being already partially oxidized can only yield a portion of their total heating value; further, if moisture be present, a certain amount of the heat will be used up in vapourising this.

Since in an ordinary analysis the oxygen and nitrogen are usually determined by difference and the amount of nitrogen in coal approximates closely to 1 per cent., the oxygen present will be $[(O+N)-1]$ and this oxygen is always assumed to be wholly combined with the hydrogen, which requires eight times its weight. A formula suitable for coal therefore is :—

$$\frac{1}{100}\left[\,8{,}140C + 34{,}500\left(H - \frac{(O+N)-1}{8}\right) - \left(600H_2O\right)\right]$$

the latter term making a sufficiently close approximation to the loss of heat in vapourising the water present in the coal from ordinary temperatures.

An example of the use of such a formula may be cited. A sample of coal gave an analysis :—C = 76·71 : H = 4·67 : H_2O = 1·94 : O + N = 7·46 per cent., then—

$$\frac{1}{100}\left[\left(8{,}140\times 76{\cdot}71\right) + \left\{34{,}500\times\left(4{\cdot}67 - \frac{7{\cdot}46-1}{8}\right)\right\} - \left(600\times 1{\cdot}94\right)\right]$$

$$= 7564 \text{ calories per gram.}$$

whilst the actual determination in a bomb calorimeter gave 7527 calories.

The results expressed in calories or B.T.U.'s serves for a comparison between different fuels, but to the engineer the evaporative duty of the coal is the important factor, and this is usually stated as "lbs. of water at 100° C (or 212° F) converted into steam at 100° C (or 212° F)," therefore by dividing the calories (or B.T.U.'s) by the latent heat of steam on either the centigrade or Fahrenheit scale, the

number of units of water evaporated per unit of fuel is obtained, whether these units be grams or pounds.

Thus, in the example given :—

$$\frac{7564}{536{\cdot}5} \text{ cals.} = 14{\cdot}1 \text{ grams from and at } 100^\circ \text{ C.}$$

or in B.T.U.'s—

$$\frac{13{,}615}{965{\cdot}7} = 14{\cdot}1 \text{ lbs. from and at } 100^\circ \text{ C.}^1$$

Calculated heating and evaporative values are open to certain objections. In the first place there is the difference in heating value given by different observers for the same combustible. Again the process of analysis requires expert skill in order to obtain accurate results, and any errors become largely multiplied in the calculation. As already pointed out, heat is required to break down most forms of chemical combination and as to the amount of heat used up in this way we have no actual knowledge in reference to most fuels, but recent researches show that coal is slightly exothermic and that any heat required to break it down may be practically disregarded. Close agreement is obtained between calculated and determined values with a large number of coals, but occasionally one meets with large differences, which are quite inexplicable and therefore cast a doubt upon calculated values generally.

Calorimeters.—The most satisfactory method of determining the calorific value of a fuel is undoubtedly by direct measurement of the heat evolved during combustion in a calorimeter.

[1] In the Service and Mercantile Marine the Fahrenheit scale is still retained and the evaporative value is mostly calculated from the percentage composition by the formula,

$$0{\cdot}15 \left\{ C + 4{\cdot}28\left(H - \frac{O}{8} \right) \right\} = \text{lbs. from and at } 212^\circ.$$

Hydrogen has approximately 4·28 times the heating value of carbon, which in the above formula is taken at Favre and Silberman's number—14,540 B.T.U.'s, then $\frac{14{,}540}{966} = 0{\cdot}15$

In all forms of calorimeter the principle relied on is to burn the fuel to be tested in a vessel entirely surrounded by water and to calculate its heating power from the increase in temperature of the water.

Many forms of calorimeter have been devised, but they may be classified into the following types:—

1. Where combustion of the fuel is effected by admixture with a solid oxidising agent, as is done in the Lewis Thompson calorimeter.
2. Combustion with oxygen at constant pressure.
   (*a*) Where the temperature of the escaping gases is undetermined, as in the William Thomson calorimeter.
   (*b*) Where the temperature of the escaping gases is under control, as in the Fischer calorimeter.
3. Combustion with oxygen at constant volume, as in the Mahler bomb.

Of these various types of calorimeter undoubtedly the best and most accurate is the Mahler bomb, the chief drawback to it being the expense of the apparatus, whilst the least accurate and most used is the Lewis Thompson, which has gained popularity amongst engineers owing to its ease of manipulation.

In *Mahler's Calorimeter* the combustion of the material takes place in a closed bomb or cylinder of steel in oxygen under a pressure of 25 atmospheres. The bomb is of the shape shown at B, Fig. 39, and is coated internally with a thin lining of porcelain in order to resist the corrosive action of the trace of nitric acid formed during combustion. The cover of the bomb screws down on to a leaden washer placed in a groove on the rim, thus ensuring a tight joint. A tube on the cover serves for the admission of the oxygen, and is fitted with a screw-down conical valve. Through the cover also passes an insulated rod to the lower end of which a platinum rod is attached by means of a clamp, E. Attached to the cover and in electrical contact with it is a second

platinum rod, to which is clamped yet a third platinum rod carrying the platinum capsule C, in which is placed the substance to be burnt. The two ends of the platinum rods can be connected by a fine iron or platinum wire, which is caused to rest on the combustible material.

The bomb is placed in the calorimeter vessel D, which contains about 2·25 litres of water, the volume of water being capable of thorough agitation by means of the vanes on the

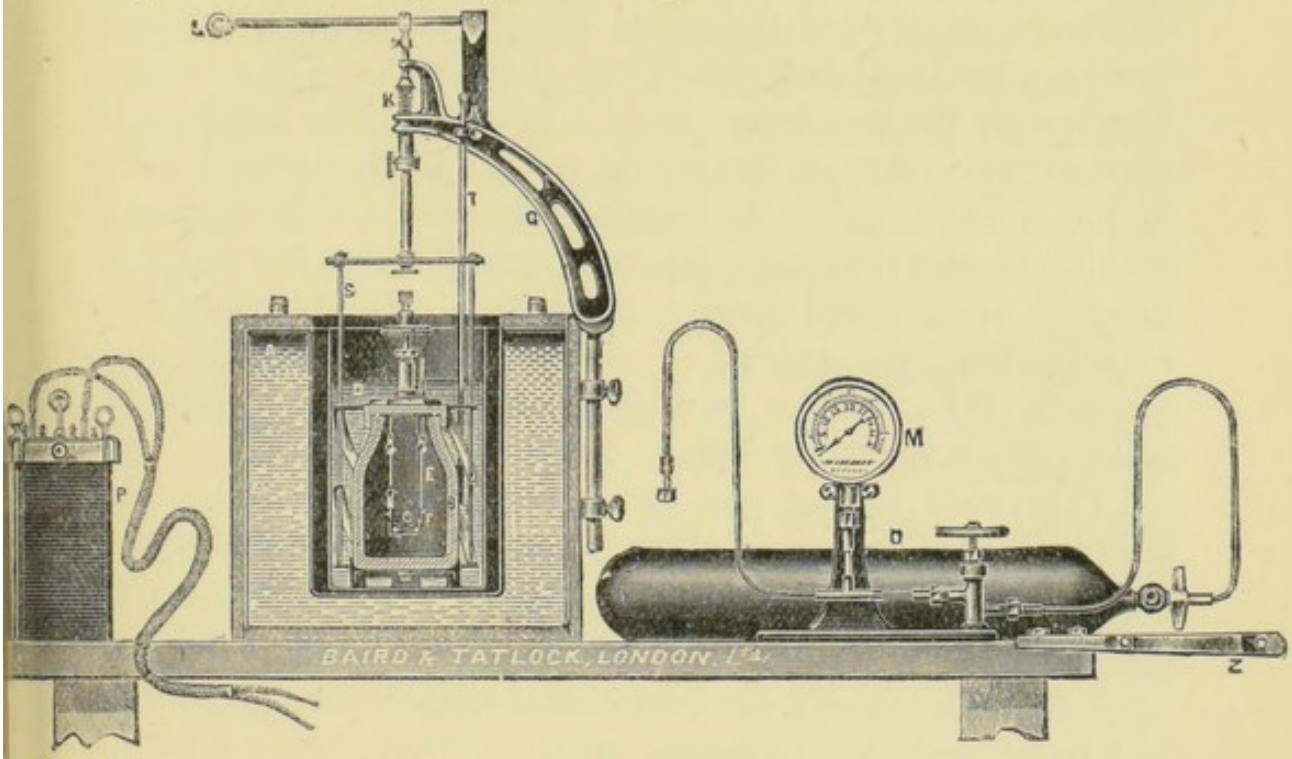


Fig. 39.

frame S, worked by the lever L through the rod K, on which a spiral thread is cut, thus causing the vanes to have a circular motion. The standard carrying the agitator is also fitted with a small clamp for the thermometer T, graduated to read to the hundredths of a degree.

In actual working the charge of combustible is weighed into the platinum capsule, which is then clamped on to its rod, and a fine iron wire is attached to the platinum rods so that it rests on the charge. The cover is then screwed down firmly on to the bomb, a wrench being applied to the cover whilst the bomb is held in its special clamp Z. The connecting tube from the oxygen cylinder is attached to the tube in

the cover of the bomb, and oxygen is slowly admitted from the cylinder until the pressure gauge shows 25 atmospheres. The valve is then screwed down, and the oxygen tube removed. The bomb is placed in the calorimeter, which has previously been filled with the required amount of water, and the water is thoroughly stirred to obtain a uniform temperature. Observations of the thermometer are taken at frequent intervals for a few minutes to determine the rate of change of the temperature of the water, and the charge is ignited by touching the insulated rod in the cover and any part of the bomb with the two wires from a battery. The agitator is kept at work during the whole time, and the temperature of the water is taken at regular intervals until it reaches a maximum and then falls regularly, and then for another five minutes to ascertain the rate of cooling. The bomb is now removed from the water, the valve opened and the cover unscrewed. The interior is rinsed out with distilled water to collect any acid that is formed during combustion.

The result is then calculated from the observed rise in temperature of the water, which is corrected for radiation ; the weight of the water-equivalent of the bomb, appendages, and gas being added to the weight of the water originally taken.

Lewis Thompson's Calorimeter.—In this instrument the fuel to be tested is burnt by combined oxygen in a small metal diving bell, under the surface of a known weight of water, and the calorific value is then determined by the increase in temperature of the water.

These instruments are graduated for use with the Fahrenheit thermometer, and on this scale the latent heat of steam is 967, that is to say, the amount of heat rendered latent in converting a pound of water at 212° F. into steam at the same temperature, would raise 967 lbs. of water 1° F. It is clear then that if a unit weight of fuel is burnt under the surface of 967 unit weights of water, and if all the heat is imparted to the water and raises it one degree, the same amount of heat would have converted a unit weight of water at 212° F. into steam at the same tempera-

ture. In practice, two grams of the fuel in a finely divided condition are taken, and having been mixed with eleven times the weight (22 grams) of a finely powdered mixture of chlorate of potash and nitrate of potash (three of the former to one of the latter)—which is to supply the oxygen for its combustion—the mixture is then pressed a little at a time into a small brass crucible. When the mixture is all introduced, a small fuse, made of cotton soaked in nitrate of potash, is placed in a cavity in the top of the mixture, and the crucible is then fixed by means of a brass plate with clutch springs in the mouth of the diving bell or chamber; having first ignited the fuse, the whole arrangement is plunged under the surface of $967 \times 2 =$ 1,934 c.c. of water of known temperature. The fuse ignites the mixture, and the fuel burns at the expense of the combined oxygen present in the chlorate and nitrate of potash, whilst the products of combustion escaping through small holes in the bottom of the chamber pass up through the water, and are supposed in this way to be cooled. When the combustion is complete the water is admitted to the chamber by opening a tap in the tube connected with it, when the water rushes in and cools the crucible. After having well agitated the water by raising and lowering the whole apparatus several times so as to obtain a uniform temperature, the apparatus is withdrawn and the thermometer again inserted, and the rise of temperature observed. Ten per cent. is now added to the number so obtained to make up for loss of heat absorbed by the apparatus, radiation, etc., and the total is looked upon as giving the number of unit weights of water which a unit weight of the fuel would evaporate. For instance:—

Temperature of water before combustion	= 62° F.
,, ,, after ,,	= 75° F.
Rise in temperature	13
10 per cent.	1·3
Evaporating power	= 14·3

As a gram of the fuel will evaporate 14·3 grams or c.c. of water, therefore one pound will evaporate 14·3 lbs. The objections to this form of calorimeter are that the fuel is never completely consumed, particles of unburnt carbon being ejected from the crucible during combustion; that the products escape too rapidly through the water to be properly cooled and that the apparatus is very liable to loss of heat by radiation.

The calorific value of a fuel is very different from its calorific intensity, which is entirely dependent upon the rate of burning. It must be remembered that a pound of wood, when completely converted into carbon dioxide and water vapour, will, during the process of conversion, give out a certain quantity of heat; and that the same amount of heat will be given out, whether the wood rots away by slow combustion, is burnt in an open grate, or in a furnace urged on by a blast of air. In each case the total amount of heat given out is the same, but the intensity in each case is very different. The shorter the space of time in which the complete combustion of the wood takes place, the greater will be the intensity of the heat.

It must also be remembered that besides having to vaporise moisture, the combustion of the fuel has also to raise the carbon dioxide (formed by the burning carbon) and the residual nitrogen of the air used, to a high temperature; and this must be allowed for in any calculation which is to at all fairly express the heat available for other purposes.

CHAPTER XIV.

NITROGEN AND ITS COMPOUNDS.

Nitrogen, occurrence in Nature—Preparation—Properties of nitrogen—Ammonia—Formation in Nature—Preparation and properties of the gas—Liquid ammonia—Decomposition of ammonia—Ammonium salts—Ammonium amalgam—The oxides of nitrogen—Preparation and properties of nitrogen monoxide, dioxide, trioxide, tetroxide, pentoxide—Nitric acid—Oxidising action of nitric acid—Nitrates—Nitre for gunpowder—Tests for nitrogen.

NITROGEN.—This gas was first discovered by Rutherford in 1772, and its properties were afterwards fully examined by Scheele and Lavoisier, the latter giving it the name "azote," from its inability to support life; the name "nitrogen" being given to it at a much later date, to denote that it was one of the principal ingredients of potassium nitrate or nitre.

Nitrogen constitutes 79·1 per cent. by volume, and 76·9 per cent. by weight of the atmosphere; and is also found widely distributed as nitric acid and metallic nitrates, as well as in ammonia and in animal and vegetable organisms.

Preparation.—It can be prepared from air by taking away the oxygen, and this can be conveniently effected by burning some phosphorus in a jar of air standing over water. The phosphorus combines with the oxygen of the air, forming white fumes of phosphorus pentoxide, which dissolve in the water, leaving fairly pure nitrogen gas behind.

Phosphorus		Air		Phosphorus pentoxide		Nitrogen.
P_2	+	$5(N_4+O)$	=	P_2O_5	+	$10N_2$.

Air may also be passed over copper turnings heated to redness, when the copper takes up the oxygen, forming

copper oxide, and nitrogen passes on free, but the gas is not pure nitrogen, containing notable quantities of argon.

If it is required perfectly pure it is made from a compound called ammonium nitrite, which, when heated, breaks up into water and nitrogen.

Ammonium nitrite		Water		Nitrogen.
NH_4NO_2	=	$2(H_2O)$	+	N_2.

Instead of using ammonium nitrite direct, it is more convenient to heat together saturated solutions of potassium nitrite and ammonium chloride, which interact with the formation of ammonium nitrite (which decomposes further) and potassium chloride.

Potassium nitrite		Ammonium chloride		Potassium chloride	Water	Nitrogen.
KNO_2	+	NH_4Cl	=	KCl	+ $2(H_2O)$	+ N_2.

If a stream of chlorine gas, generated by the action of hydrochloric acid on black oxide of manganese, be led through a saturated solution of ammonia, nitrogen is liberated, and the hydrochloric acid produced unites with some of the ammonia to form ammonium chloride.

Ammonia		Chlorine		Ammonium chloride		Nitrogen.
$8(NH_3)$	+	$3Cl_2$	=	$6(NH_4Cl)$	+	N_2.

When nitrogen is prepared in this way, it is important to keep the ammonia in excess, for if chlorine were to predominate, it would react upon the ammonium chloride, and form a highly explosive combination of chlorine and nitrogen called nitrogen trichloride.

The gas can be collected over water as it is very sparingly soluble, 100 volumes of water only dissolving 1·5 volumes of the gas at ordinary temperatures.

Properties.—Nitrogen in the free state is the most inert of gases, and is characterised by its inability to burn or to

support combustion, and generally by its disinclination to combine directly with other elements.

If we measure off 11·16 litres of the gas at normal temperature and pressure we find that it weighs fourteen grams, and is therefore, atom for atom, fourteen times as heavy as hydrogen.

It is a colourless, tasteless and odourless gas, which will not support life.

It is evident that it has no poisonous properties, as our atmosphere contains so large a proportion of the gas.

Although so inert in its relations towards most substances, it combines with the elements tungsten and titanium with great energy, converting them into nitrides and causing them to become incandescent when they are thrown in a finely-divided state into a jar of the gas, and it also forms compounds with boron, silicon and magnesium termed "nitrides."

Ammonia.—Nitrogen cannot be readily made to unite directly with hydrogen, but by indirect means an important compound of 14 parts by weight of nitrogen and 3 of hydrogen can be obtained, viz., ammonia gas.

In Nature ammonia is chiefly produced during the spontaneous decomposition of nitrogenised organic matter, such as animal excreta, and the name ammonia was given it because the Arabs first prepared it from camel's dung, near the temple of Jupiter Ammon in the Libyan desert. Ammonia is found during the manufacture of coal gas as one of the by-products, and is obtained in combination with hydrochloric acid as sal ammoniac or ammonium chloride, and it is from this salt that we can most conveniently obtain the gas. If we mix together powdered ammonium chloride and quicklime and gently heat the mixture, ammonia gas is given off, and calcium chloride and water are formed.

Ammonium chloride Quicklime Calcium chloride Water Ammonia.

$$2(NH_4Cl) + CaO = CaCl_2 + H_2O + 2(NH_3).$$

Properties.—Ammonia gas so prepared cannot be collected over water on account of its great solubility, water dissolving 1,149 times its own volume of the gas at normal temperature and pressure. It is best collected over mercury, but being much lighter than air can also be collected by upward displacement in the same way as hydrogen.

Ammonia gas is readily recognised by its pungent odour and strong alkaline reaction, turning yellow turmeric paper brown, and red litmus paper blue. The test papers which have been acted upon, however, soon regain their original colour when exposed to air, as the ammonia rapidly volatilises, hence it is sometimes called a "volatile alkali." The gas does not support combustion, nor does it burn in the ordinary sense of the word; but if it be ignited in oxygen, it readily burns with a non-luminous flame forming water and liberating nitrogen; and a mixture of ammonia and oxygen will explode when a light is applied to it, the products of the explosion also being nitrogen and water.

Ammonia		Oxygen		Nitrogen		Water.
$4(NH_3)$	+	$3O_2$	=	$2N_2$	+	$6(H_2O)$.

When ammonia gas comes in contact with hydrochloric acid gas, dense white fumes of ammonium chloride are formed.

Ammonia gas can be liquefied by a pressure of about 7 atmospheres, and this liquid if cooled below $-75°$ freezes to a transparent solid.

Ammonia Freezing Machines.—The ease with which ammonia can be liquefied, the great cold produced when it again assumes the gaseous state, and the amount of the gas dissolved by water, renders it eminently adapted for use in freezing machines, one of the best known of which is "Carré's ice making apparatus," in which ammonia, evolved by boiling a strong solution of the gas, is condensed by pressure in a strong iron reservoir, in the centre of which is a chamber to receive the substances to be frozen. The

pressure is then taken off the iron reservoir and the liquid ammonia once more rapidly assumes the gaseous state, producing so intense a cold that water, etc., placed in the chamber is frozen. The escaping gas is once more absorbed in cooled water, and can be utilised again and again.

Composition.—If ammonia gas be passed through a red hot tube, or if electric sparks be passed through it for some time, its volume is doubled, and on analysis is found to consist of a mixture of one volume of nitrogen and three of hydrogen, hence the formula NH_3 is given to the gas. 22·32 litres of the gas at normal temperature and pressure are found to weigh 17 grams, hence its density as compared with hydrogen is $\frac{17}{2}$ or 8·5.

Ammonia acts as a strong base, being able to neutralise the strongest acids, forming with them salts analogous in composition to the salts formed by potassium or sodium.

Ammonia		Hydrochloric acid		Ammonium chloride.
NH_3	+	HCl	=	NH_4Cl.
Ammonia		Nitric acid		Ammonium nitrate.
NH_3	+	HNO_3	=	NH_4NO_3.
Ammonia		Sulphuric acid		Ammonium sulphate.
$2(NH_3)$	+	H_2SO_4	=	$(NH_4)_2SO_4$.

If these ammonium salts are contrasted with the corresponding potassium or sodium salts, it will be seen that in them the metal potassium (K) or sodium (Na) is replaced by the group (NH_4).

Chlorides	Sulphates	Nitrates.
$NaCl$	Na_2SO_4	$NaNO_3$.
KCl	K_2SO_4	KNO_3.
NH_4Cl	$(NH_4)_2SO_4$	NH_4NO_3.

So strong is the analogy between them that this group

(NH_4) is often looked upon as a metal, and is called ammonium, its salts being called ammonium salts.

Ammonium Amalgam.—If a strong solution of ammonia is electrolysed, the negative pole being in contact with some mercury in the bottom of the cell, and the positive above it in the liquid, the mercury swells up into a bulky buttery mass, which still retains its metallic appearance, and on allowing this to stand it evolves ammonia gas and hydrogen, and once more contracts to its original volume. This experiment was considered by Berzelius to show that ammonium (NH_4) was liberated at the negative pole and formed an amalgam with the mercury, but all attempts to isolate the ammonium have so far failed.

Another way of forming this "ammonium amalgam" is to put some freshly prepared sodium amalgam into a saturated solution of ammonium chloride, when sodium is replaced by ammonium, and the amalgam at once swells up to many times its former bulk, forming a spongy substance lighter than water, whilst sodium chloride passes into solution.

Ammonium compounds may be recognised by their giving off ammonia gas when heated with a strong alkali such as sodium hydroxide, the gas evolved being identified by its pungent odour, and by its forming white fumes with hydrochloric acid gas.

Strong solutions of these salts also give a yellow crystalline precipitate with a solution of platinum chloride, and a white crystalline precipitate with a saturated solution of sodium hydrogen tartrate.

Oxides of Nitrogen.—When through a mixture of oxygen and nitrogen a series of electric sparks is passed for some time, a gradual combination of the two gases takes place, and reddish-brown fumes form in the vessel. The tendency, however, to combine is very slight; but by indirect methods,

oxygen and nitrogen can be obtained in combination in five distinct proportions, as :—

Nitrogen monoxide	N_2O
Nitrogen dioxide	NO
Nitrogen trioxide	N_2O_3
Nitrogen tetroxide	NO_2 or N_2O_4
Nitrogen pentoxide	N_2O_5

Nitrogen Monoxide.—Nitrogen monoxide, nitrous oxide, or laughing gas, is prepared by heating ammonium nitrate, the salt formed when nitric acid is neutralised with ammonia, and this breaks up into nitrogen monoxide and water.

Ammonium nitrate		Nitrogen monoxide		Water.
NH_4NO_3	=	N_2O	+	$2(H_2O)$.

Properties.—The gas is best collected over hot water or water saturated with salt, as cold water dissolves more than two-thirds its own volume of the gas. It is colourless and odourless, but has a sweetish taste; when inhaled it produces a kind of intoxication, hence its name; it is also used as an anæsthetic in slight operations. It can be condensed to a liquid at a pressure of 30 atmospheres, or if cooled down to —88° C.

The gas will not burn; but if a combustible be burning with vigour, nitrogen monoxide will support its combustion nearly as freely as oxygen, the heat of the burning body tending to decompose the gas and liberate oxygen, which then supports the combustion. If feebly burning sulphur be plunged into the gas, it is extinguished because the heat is not sufficient to effect decomposition; but if the sulphur be burning strongly, then it continues to burn in the gas with increased brilliancy.

When carbon is burnt in nitrogen monoxide, more heat is evolved than when it is burnt in oxygen, showing that the decomposition of the monoxide is attended with liberation of heat, and it is therefore called an "endothermic" compound.

Nitrogen monoxide can easily be distinguished from oxygen by shaking it up with water, which absorbs the former, but would not appreciably diminish the bulk of oxygen, and also by bringing it in contact with nitrogen dioxide, which forms red fumes with oxygen but none with the monoxide.

Composition.—Potassium or sodium heated in the gas burn with formation of potassium or sodium oxide, and the residual nitrogen is found to occupy the same volume as the nitrogen monoxide used; and as its molecular weight is forty-four, it is evident that the molecule contains two atoms of nitrogen to one of oxygen, and its formula therefore is N_2O.

Nitrogen Dioxide (NO) or nitric oxide is a colourless gas obtained by acting upon metallic copper with nitric acid. The reaction which takes place may be represented by the equation:

Copper		Nitric acid		Copper nitrate		Water		Nitrogen dioxide.
$3Cu$	+	$8(HNO_3)$	=	$3[Cu(NO_3)_2]$	+	$4(H_2O)$	+	$2(NO)$.

Properties.—In contact with oxygen, nitrogen dioxide instantly forms red fumes of the higher oxides; it is insoluble in water, does not burn, and only supports the combustion of bodies which are burning very fiercely.

It will extinguish a burning splint of wood or burning sulphur, but phosphorus when strongly burning is able to decompose it, and burns with increased brilliancy.

It is the most stable of the oxides of nitrogen, a low red heat not sufficing to break it up; it may be slowly decomposed into its constituents by a series of electric sparks. Nitrogen dioxide is readily absorbed by solutions of ferrous salts, forming a dark brown compound, which is decomposed by heat. When potassium or sodium is burnt in the gas, the oxygen is absorbed, and the residual nitrogen is found to occupy one-half the volume of the original gas. The mole-

cular weight of the gas is thirty, and it is therefore built up of one atom of nitrogen = 14, and one atom of oxygen = 16, and its formula is NO.

Nitrogen Trioxide (N_2O_3.)—When nitric acid of a specific gravity of 1·34 acts upon starch or arsenic trioxide, a reddish brown gas is evolved, which led to it being regarded as nitrogen trioxide. On passing the gas through tubes surrounded by a freezing mixture, it condenses at about —21° to a bluish liquid.

There has been much controversy as to the existence of N_2O_3 as a definite chemical substance, the vapour density of the gas as prepared by the above method agreeing with that of a mixture of equal volumes of NO and NO_2. There seems little doubt but that at low temperatures it can exist as a definite compound in the liquid condition, but with slight rise of temperature it dissociates into a mixture of nitrogen dioxide and tetroxide.

Nitrogen trioxide may be looked upon as the anhydride of *nitrous acid.*

Nitrogen trioxide		Water		Nitrous acid.
N_2O_3	+	H_2O	=	$2HNO_2$.

Nitrogen Tetroxide.—When nitrogen dioxide comes in contact with free oxygen it combines with it to form another reddish-brown gas, nitrogen tetroxide, which contains an atom more oxygen than the dioxide, and at low temperatures has the composition N_2O_4; but this undergoes complete dissociation at 140° C. into $2(NO_2)$, and NO_2 is therefore generally adopted as its molecular formula. At ordinary temperatures the gas will consist of a mixture of N_2O_4 molecules with NO_2 molecules.

The gas can be obtained pure by heating lead nitrate, which breaks up into lead oxide, oxygen and nitrogen tetroxide.

Lead nitrate		Lead oxide		Nitrogen tetroxide		Oxygen.
$2[Pb(NO_3)_2]$	=	$2(PbO)$	+	$4(NO)_2$	+	O_2.

Properties.—Nitrogen tetroxide forms colourless crystals at—10° C., and these fuse to a colourless liquid which soon assumes a yellow colour, the tint increasing with the temperature up to 22° C., when the liquid is converted into a reddish-brown vapour which continues to deepen in colour, until at 40° C. it is nearly black, and this leads to the conclusion that N_2O_4 is nearly colourless whilst NO_2 is very dark brown.

In ice cold water nitrogen tetroxide dissolves with formation of nitrous and nitric acids:

Nitrogen tetroxide		Water		Nitrous acid		Nitric acid.
$2(NO_2)$	+	H_2O	=	HNO_2	+	HNO_3.

In water at ordinary temperatures it dissolves forming liquids which are blue, green or orange, according to the amount of the gas dissolved.

The gas (NO_2) may be heated to low redness without undergoing any actual decomposition.

Vigorously burning phosphorus and charcoal decompose it and burn with great energy, whilst potassium inflames spontaneously in the vapour and burns with a red flame.

Nitrogen Pentoxide.—The highest oxide of nitrogen—nitrogen pentoxide (N_2O_5)—was discovered in 1849 by Deville, who prepared it by acting upon fused silver nitrate with dry chlorine.

Silver Nitrate		Chlorine		Nitrogen pentoxide		Silver chloride		Oxygen.
$4(AgNO_3)$	+	$2Cl_2$	=	$2(N_2O_5)$	+	$4(AgCl)$	+	O_2.

It is a colourless solid, and forms prismatic crystals which melt at 30° C.; when brought in contact with water it combines with it, with great evolution of heat, forming nitric acid:

Nitrogen pentoxide		Water		Nitric acid.
N_2O_5	+	H_2O	=	$2(HNO_3)$.

Nitric Acid.—On an experimental scale nitric acid can be easily made from one of the more commonly occurring

nitrates, such as potassium nitrate (saltpetre) or sodium nitrate (Chili saltpetre) by heating with concentrated sulphuric acid. Equal weights of dry potassium nitrate and concentrated sulphuric acid are mixed in the retort (Fig. 40)

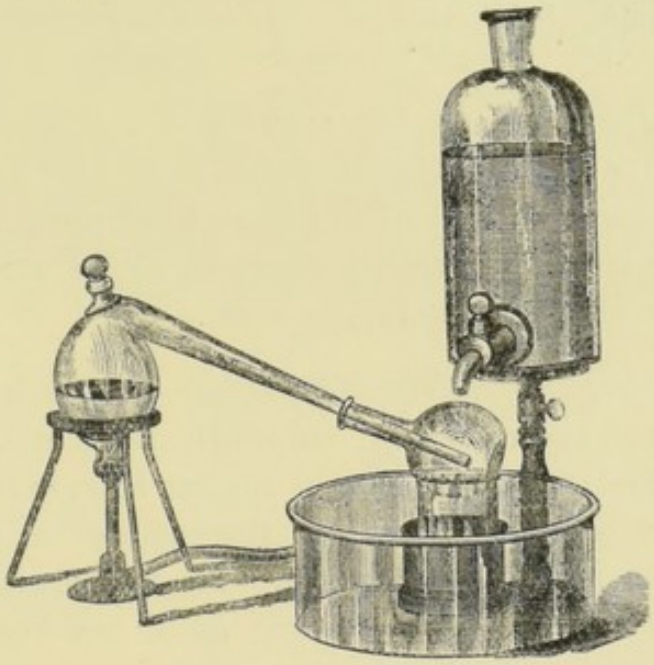


Fig. 40.

and gently heated, when nitric acid escapes as a vapour, and is condensed to a yellowish liquid in the receiver, which is kept cool by water dripping upon it.

Under these conditions, and at a temperature to which a glass retort can be safely subjected, the reaction is represented by the equation:

Potassium nitrate		Sulphuric acid		Acid potassium sulphate		Nitric acid.
KNO_3	+	H_2SO_4	=	$KHSO_4$	+	HNO_3.

That is to say, one-half of the hydrogen present in the sulphuric acid is replaced by the metal potassium, whilst the hydrogen combines with the nitric acid radicle to form nitric acid. Nitric acid, when pure, is colourless; but some is decomposed by heat into nitrogen tetroxide, the ruddy fumes of which may be noticed in the retort, and which, dissolving in the condensed acid, colour it yellow.

When a higher temperature than that obtainable in a

glass vessel is employed, the whole of the hydrogen of the sulphuric acid is replaced, hence half the amount of sulphuric acid is required for the preparation of the same quantity of nitric acid.

Potassium nitrate Sulphuric acid Potassium sulphate Nitric acid.

$$2KNO_3 + H_2SO_4 = K_2SO_4 + 2HNO_3.$$

This is of importance in the commercial production of the acid, and since sodium nitrate gives a greater yield of nitric acid for the same weight of salt than does potassium nitrate, and is moreover considerably cheaper, the former is always employed on the manufacturing scale.

Manufacture of Nitric Acid.—On the large scale the action between the nitre and sulphuric acid is carried on in cast iron vessels, in order that a higher temperature may be attained. It is possible to get the whole of the sodium nitrate converted into sodium sulphate by employing a little over half its weight in sulphuric acid, but there are two objections to this. In the first place the residue is solid and not easily removed from the retort, and in the second the higher temperature leads to the decomposition of the acid produced, increasing the amount of nitrogen dioxide present. Usually therefore about equal weights of nitre and acid are employed, so that a liquid mixture of sodium sulphate and bisulphate results, which may easily be run off.

The purity of the acid produced largely depends on the freedom from impurity of the Chili saltpetre employed, sodium chloride being the chief one, leading to contamination of the acid by chlorine. The strength of the product mainly depends on that of the sulphuric acid used, and on the moisture present in the nitre. For nitric acid to be used in the production of explosives the nitre is usually dried, the sulphuric acid employed being quite concentrated.

For the weaker acids the retort is generally cylindrical, its length being from 5 to 6 feet with a diameter of $2\frac{1}{2}$ to 3 feet. It is provided with either flag or cast iron ends which can be luted in, each end having a hole at the upper portion,

one of which serves for charging and the other as an exit for the vapours.

For the manufacture of strong acid to be used in the production of explosives, retorts of the type shown in Fig. 41 are employed. The retort (A) is provided with a collar into which the lid portion can be luted, this latter having a charging hole (C) through which the nitre is introduced, and the cover of this has another small hole (c) through which the acid can be charged. An outlet for the vapours is shown at (D) and the discharge pipe for the residual products at E. The most convenient condensing arrangement is that de-

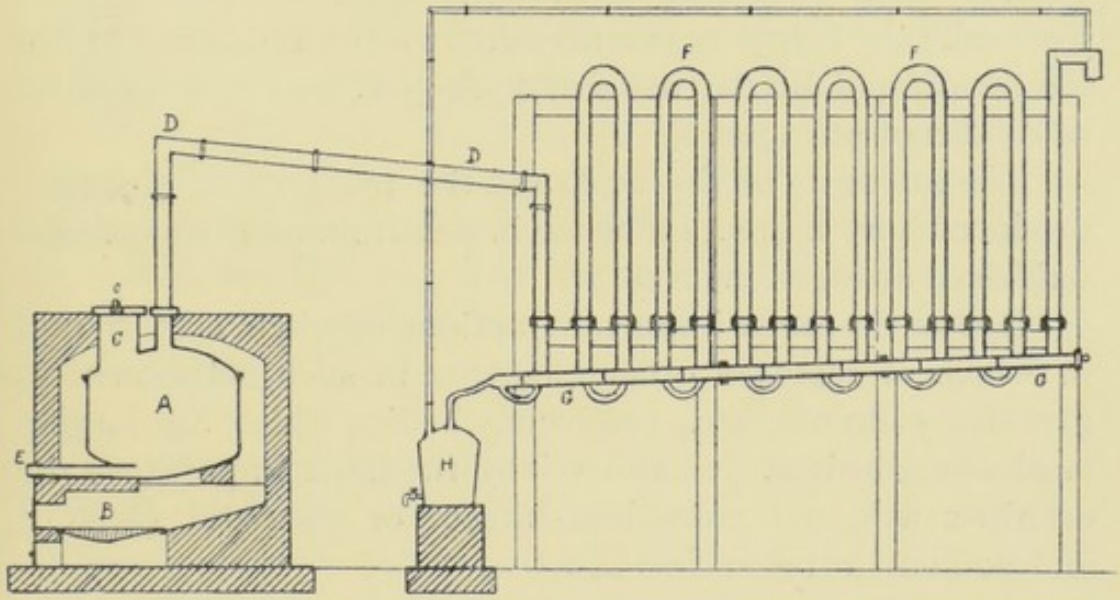


Fig. 41.

vised by Guttmann, which consists of a slightly inclined main, 4 inches internal diameter (G G) made up of sections divided by a partition, each section carrying two sockets, into which the vertical condensing tubes (F F) are fitted, these being slightly over 4 feet in length. Each section of the main connects with the adjacent sections by means of a syphon tube. The acid as it condenses flows through these tubes, which being full of liquid, seal it so far as the passage of vapours is concerned, and then passes into the receiver (H). Any uncondensed vapours are absorbed in a suitable

tower. The whole of the condensing apparatus is of glazed earthenware.

Properties.—Pure nitric acid is colourless, but as ordinarily obtained has a yellow colour due to the presence of nitrogen dioxide, nitrous acid, etc. It has a specific gravity of 1·53. It is a most powerful oxidising agent, oxidising such elements as sulphur, phosphorus and iodine into the corresponding sulphuric, phosphoric and iodic acids. The strongest acid attacks many organic substances, such as turpentine, with such vigour that they are inflamed.

Its action on metals is of importance, in most cases it results in the formation of the nitrate, but hydrogen is not evolved, this being apparently due to the reduction of the excess of acid by the nascent hydrogen, with the evolution of oxides of nitrogen.

The strength of the acid and the presence of the salts produced have a great influence in determining the particular oxides of nitrogen evolved.

One of the most important actions of nitric acid is that in which it replaces other elements in such substances as glycerin, cellulose, etc., producing bodies which are largely used as explosives. Commercially the most important salts of nitric acid are potassium nitrate or saltpetre (KNO_3) and sodium nitrate ($NaNO_3$).

Nitrates.—Saltpetre occurs in Nature as a deposit in certain parts of India, and large quantities are obtained from Bengal and Oude, where it is extracted from the earth by treating it with water, and, after filtering, allowing the solution to evaporate in shallow pans, the crystals so obtained being exported under the name of "grough" saltpetre, which, however, is far from pure, the usual composition being about:—

Potassium nitrate	93·95
Sodium sulphate	3·21
Sodium chloride	·85
Sand	·25
Water	1·74

If this saltpetre be heated to 335° C. it melts, and can be cast into cakes, which on breaking exhibit a crystalline fracture, which varies in appearance with the amount of impurity present, a property which at one time was used to roughly indicate the value of any sample of the salt, and was called the "refraction" of the nitre. The term is to a certain extent still retained to indicate the amount of impurity present, and the sample of nitre, of which an analysis is given above, would be quoted as having "6 per cent. refraction."

This "grough" saltpetre, has to be very carefully purified for use in the manufacture of gunpowder, which is done by recrystallising it. 100 grams of water will at 100° C. dissolve 200 grams of saltpetre, whilst at 21° C. it will only dissolve 30 grams; if therefore a saturated solution of saltpetre is made in boiling water and is then allowed to cool down, $\frac{17}{20}$ths of the dissolved salt will crystallise out, and the impurities present being not much more soluble in hot water than in cold, will remain in solution.

Saltpetre for Gunpowder.—In the Government Powder Mills at Waltham Abbey, nothing is used but Indian saltpetre, purified as described, but most of the small grain powder is now manufactured by private firms, and a considerable portion of the saltpetre is obtained from sodium nitrate, found in Chili and Peru in large deposits and called "Chili saltpetre." Sodium nitrate itself could not be used instead of saltpetre as an ingredient of gunpowder in climates containing much water vapour in the air, as it is hygroscopic—that is, it has the power of attracting and absorbing moisture, which would cause the disintegration of the powder; but in hot, dry climates it is often used for making rough and blasting powders. Sodium nitrate can, however, be easily converted into potassium nitrate by double decomposition with boiling concentrated solution of potassium chloride, which forms potassium nitrate and

sodium chloride, these two salts being separated by crystallisation.

Sodium nitrate Potassium chloride Potassium nitrate Sodium chloride.

$$NaNO_3 + KCl = KNO_3 + NaCl.$$

This reaction being due to the fact that sodium chloride is far less soluble in hot water than potassium nitrate.

	100 parts of	
	Boiling water dissolve	Cold water dissolve
Sodium nitrate	218 ...	50
Potassium nitrate ...	200 ...	30
Sodium chloride	37 ...	36
Potassium chloride ...	53 ...	33

So that when a hot concentrated solution of sodium nitrate is taken and potassium chloride added to it little by little, sodium chloride forms and crystallises out, being removed from the solution by perforated ladles, whilst the mixture of salts remaining behind is roughly separated by crystallising, and then purifying in the same way as the "grough saltpetre." The potassium chloride used in this process is obtained from the great mines at Stassfurth, in Saxony, and also from the vegetable refuse left after the manufacture of sugar from beetroot.

The deposits of saltpetre in India and elsewhere are due to the decomposition of animal refuse containing carbon, hydrogen, nitrogen and oxygen, which, during processes of decay, become chiefly converted into ammonia and carbon dioxide, and the ammonia by a process of oxidation in the porous soil, aided by a certain form of " mycoderm," becomes converted into nitric acid, which combines with the potassium which is to be found in all fertile soils and forms saltpetre.

Tests for Nitrates.—When nitric acid is added to metallic copper a colourless gas is given off which instantly becomes ruddy brown on coming in contact with the air, and this reaction constitutes a test for the acid. If, however, the

nitrate is present as a salt, it is necessary to liberate the acid by warming with excess of sulphuric acid.

When the nitrate is only present in very small traces a still more delicate test is necessary.

An equal bulk of strong sulphuric acid is added to the solution supposed to contain the nitrate. The mixture is then cooled and a solution of ferrous sulphate is carefully poured on to the surface of the mixture, and if a nitrate is present a brown ring forms at the junction of the two liquids.

CHAPTER XV.

The Atmosphere and Ventilation.

The extent of the atmosphere—Weight of the atmosphere—The barometer—Composition of the atmosphere—Air a mechanical mixture and not a chemical compound—Gases other than oxygen and nitrogen present in the atmosphere—Argon, ammonia, water vapour, carbon dioxide—The natural actions which keep the composition of the atmosphere constant—Solid, liquid, and gaseous impurities present in the atmosphere—Amount of air required for respiration—Air space—Air currents—Effect of various methods of heating upon ventilation—Open fires—Closed grates, hot air, steam—Vitiation of the atmosphere by illuminants—Candles, oil lamps, gas burners—Relative effects of various types of burners—Heat evolved by illuminants—Ventilation of ships.

THE air in which we live and breathe is essentially a mixture of the two elementary gases, nitrogen and oxygen, containing also small quantities of carbon dioxide, water vapour, argon, and ammonia, which are always present—and have special functions to perform with regard to the economy of Nature—and is also charged with all the gaseous impurities formed both naturally and artificially on the earth's surface.

Extent of the Atmosphere.—The atmosphere forms a gaseous layer surrounding the earth, and, according to calculations made by Wollaston, based upon the duration of twilight, it extends about forty-five miles above the surface of the earth; whilst other observers, basing their calculations upon purely mathematical data, urge that there is no such limit, and that the atmosphere extends through space. It is well-known, however, that the density of the atmosphere rapidly diminishes as we ascend from the earth's surface, and that at an elevation of three-and-a-half miles its density is reduced to one-half that at the sea level.

Weight of Air.—The fact that the air has weight, and is therefore exerting a pressure upon all objects, was not proved until the middle of the seventeenth century, when Torricelli, in trying to find an explanation of the fact that a pump would only raise water a little over thirty-three feet, discovered that if water were enclosed in a tube which dipped into a reservoir of water open to the air, and if there were a perfect vacuum in the upper portions of the tube, the water would stand at a height of thirty-three feet; whereas, under the same conditions, mercury only stood at a height of thirty inches. On determining the relative weights of mercury and water, he at once found that if he employed tubes of equal diameter, the column of mercury

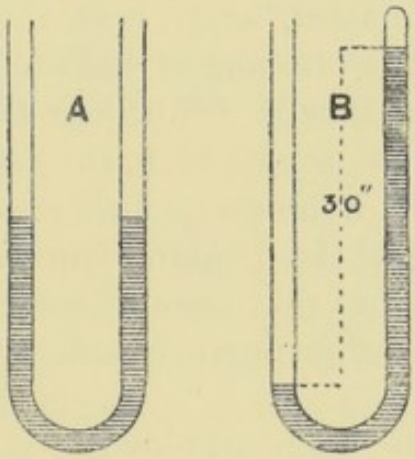


Fig. 42.

thirty inches in height weighed the same as the column of water thirty-three feet in height; and from this he concluded that there must be some natural sustaining force of which this weight of mercury or water was a measure, and after searching for a cause, he finally came to the conclusion that it must be the pressure of the atmosphere which was balancing the columns of liquids; a conclusion which was verified by Blaise Pascal, in 1648, taking Torricelli's tubes up a high mountain, when he found that as he ascended and the amount of atmosphere above his instruments decreased, so the height of the liquid columns was diminished.

If a large glass U tube is taken, each arm of which is thirty-three inches long and open at each end, and if into this

mercury be poured, the mercury will stand level in each arm of the tube (A, Fig. 42), but if now one end is closed and is then completely filled with mercury, on replacing the tube in position, the mercury will only fall in the tube until the difference between the levels of the mercury is thirty inches (B, Fig. 42), that is to say, the pressure of the atmosphere on the surface of the mercury in the open tube is able to balance a column of thirty inches of mercury in the closed arm of the tube with no air above it. The vacuum left in the closed arm of the tube is called after its discoverer the "Torricellian vacuum."

The Barometer.—Torricelli's tube was afterwards named by Boyle the "Barometer," and it is the instrument in general use for measuring the pressure of the atmosphere; if in the experiment with the U tube, a tube had been chosen having a sectional area of one square inch, the atmospheric pressure on the square inch of mercury exposed would have been equal to the weight of the column of mercury supported, *i.e.*, thirty cubic inches, and this amount weighs 15 lbs., so that the pressure of the atmosphere is said to be 15 lbs. on the square inch.

The effect upon the height of the mercurial barometer exerted by the pressure of the air can easily be shown by placing a barometer tube under the receiver of an air pump, when each stroke of the pump will cause a corresponding fall in the column of mercury.

29·96 inches is equivalent to 760 millimetres, which is taken as the normal height of the barometric column in all scientific work, whilst the pressure exerted by the atmosphere would be expressed in the metrical system as 1·03296 kilograms on a square centimetre.

The pressure of 15 lbs. on the square inch is taken as the pressure of one atmosphere, and pressures are often expressed in this way; if, for instance, the pressure of steam in a boiler was equal to 60 lbs., it would be said to exert a pressure of four atmospheres.

If, taking 15 lbs. on the square inch, we calculate the pressure exerted on any extended surface, it is found to be very considerable, an ordinary sized man sustaining a pressure of nearly sixteen tons on the surface of his body. This pressure, however, is so counterbalanced that he is perfectly unaware of its existence.

If water be boiled for some time in a circular tin bottle, the escaping steam drives all air out of the vessel, and being itself at the same pressure as the atmosphere balances it; if, however, the tin be corked air-tight whilst still full of steam, and cold water is thrown over the vessel, the steam is condensed, and the vessel being unable to withstand the external pressure of the atmosphere is at once crushed.

Air a Mechanical Mixture.—Air is not a chemical compound, but a mechanical mixture of the two elements, oxygen and nitrogen.

Percentage composition of air:—

	By weight	By volume.
Nitrogen	76·9	79·1
Oxygen	23·1	20·9

or roughly, four volumes of nitrogen to each volume of oxygen.

During the years 1774-75 oxygen gas was discovered independently by Priestley in England and Scheele in Sweden, and three years later the great French chemist Lavoisier discovered and pointed out the functions of oxygen and the part played by it in all cases of combustion in air—a discovery which is by many considered to be the birth of modern Chemistry.

It has been shown (page 7) that a mechanical mixture retains the properties of the substances forming it, and we have in it the component parts merely lying side by side in a state of physical mixture; in a chemical compound, on the other hand, we have all the properties of its components merged, and new properties developed which are characteristic of the compound formed.

The reasons for considering air to be a mixture and not a compound are as follows :—

1. If we bring oxygen and nitrogen together in the proportions in which they occur in air, there is no elevation of temperature or alteration in volume, and yet the mixture has all the properties of air.
2. The relative quantities of the two gases present are not those of their combining weights, nor of any simple multiples of these weights.
3. When air is shaken up with a small quantity of water some of it is dissolved, and if this dissolved air be expelled from the water by boiling, it is found to consist of oxygen and nitrogen, in the proportions of 1 to 1·87 and not 1 to 4. Now had air been a chemical compound it would have dissolved as a whole, and on being expelled from solution the oxygen and nitrogen would still be in the original proportion of 1 to 4.
4. The proportions in which the two gases occur occasionally vary slightly.
5. Nitric oxide forms ruddy fumes in contact with air, showing that the oxygen present is uncombined.

Analysis of Air.—The volumetric composition of air is best determined by means of the eudiometer, the same method being employed as in the volumetric synthesis of water, the only difference being, that instead of experimenting with pure oxygen we use air, and having passed up excess of hydrogen, we explode the mixture and notice the diminution of volume. Now we know that two volumes of hydrogen combine with exactly one volume of oxygen to form water; hence, one-third of the observed diminution in volume must represent the oxygen which has disappeared and therefore the volume of oxygen in the air taken. The amount of oxygen by weight in air is determined by passing a known volume of purified air slowly over red hot copper turnings in a hard glass tube; the copper takes all the oxygen from

the air, forming copper oxide, and by carefully weighing the tube of copper before and after the experiment, the increase in weight—due to the oxygen in the volume of air taken—is determined.

Argon.—Cavendish, who was the first to carefully analyse air, found that atmospheric nitrogen contained a minute trace of something which appeared more inert than nitrogen itself; and Lord Rayleigh, whilst determining the density of nitrogen, found that when that gas was obtained from air it had a slightly higher density than when prepared by chemical means.

This was found to be due to the trace of inert gas noticed by Cavendish, and this having been isolated by Lord Rayleigh and Sir William Ramsay, was found to be a new element to which the name "Argon" has been given.

Preparation.—Argon is found in the atmosphere to the extent of 0·9 per cent. by volume or 0·2 per cent. by weight. It is obtained by passing air over red hot copper, in order to remove the oxygen, and then through a long series of tubes containing red hot magnesium, which absorbs the nitrogen. After repeating the latter portion of the process several times the argon is obtained by itself.

Other methods are to add some oxygen to the air and to pass induction sparks through the mixture for a very long period over potassium hydroxide, which absorbs the oxides of nitrogen produced, the process being continued till all the nitrogen has disappeared. The excess of oxygen can then be absorbed by phosphorus, heated copper, or pyrogallate of potassium, when the argon is left.

The newest method for obtaining it is to heat air with a mixture of magnesium, sodium, and freshly ignited lime; calcium is formed in a finely divided condition, and both the oxygen and nitrogen are absorbed, the argon remaining behind.

The gas occurs in small quantities in solution in some mineral waters and rare minerals.

Properties.—Argon is a colourless gas, having a specific gravity of 19·9 and a molecular weight of 40. The molecule consists of only one atom, the atomic weight therefore is also 40. By cooling it with boiling oxygen under a pressure of 50 atmospheres it has been condensed to a liquid. It is so inert in all its characteristics that no compounds of argon have been prepared, and there is no doubt now that it is an element.

Traces of four other rare gases have also been discovered in air by Sir William Ramsay—helium, neon, crypton, and xenon. These bodies all display characteristic lines in their spectra and like argon their molecule consists of only one atom.

Functions of the Constituents.—Air being a mechanical mixture and having the properties of its constituents, it is at once evident that oxygen is the great supporter of life and combustion, whilst the function of the nitrogen is to dilute it and keep its action within the proper limits. This fact having been established by Priestley and Lavoisier, it was imagined that the great secret of health had been discovered, and that air was wholesome in proportion to the amount of oxygen it contained; but of late years this theory has been exploded by the fact that the variation in the percentage of oxygen in good and bad air is very slight. In a long series of analyses made by Angus Smith of samples of air, the extreme variations are 20·99 per cent. in a sample of air from the Scotch Moors, and 20·63 per cent. in air collected in the gallery of a London theatre towards the close of the performance.

Volume for volume air is 14·47 times as heavy as hydrogen.

Minor Constituents of Air.—Besides oxygen and nitrogen, there are three other important gaseous bodies present in air—water vapour, carbon dioxide, and ammonia—which have distinct parts to play in natural processes, and must

not therefore be looked upon as impurities until the amount exceeds a certain limit.

AVERAGE COMPOSITION OF THE ATMOSPHERE.

Oxygen	20·61
Nitrogen	77·95
Carbon dioxide	0·04
Aqueous vapour	1·40
Nitric acid, Ammonia	traces
	100·00

Functions of the Minor Constituents.—Ammonia is present in very small traces, but is of great importance to vegetable life, as it is from this gas that plants obtain a large proportion of the nitrogen which they require to form their seeds and fruit. It is evident that ammonia could not be present in large quantities in the air unnoticed, on account of its pungent odour; but small as are the traces present its great solubility enables every shower that falls to collect it from the air, and bring it down to the vegetation which needs it.

Water vapour is present in varying quantities dependent chiefly upon the temperature. The warmer the air the more water it can hold in suspension as vapour; when warm air is cooled by coming in contact with colder layers of air, it cannot any longer hold so much moisture, and deposits the surplus as rain. In the night time, while the surface of the ground is receiving no heat from the sun, it is constantly losing heat by radiation, and on a clear night soon becomes colder than the air above it, the lower strata of air being cooled by contact with it, so causing a condensation of moisture in the form of dew.

Water vapour in the air has an enormous influence upon our comfort and health. The human body is largely composed of water, and if the air becomes too dry, evaporation from the skin and lungs is increased, causing great discomfort.

The aqueous vapour in the atmosphere also plays an important part in warming the air, as the vapour contains a large amount of latent heat which is given up to the air during condensation, besides which its presence retards the passage of heat rays through the air and so raises the atmospheric temperature.

Withdrawal of Oxygen.—When animals or human beings breathe, the life supporting principle of the air is exchanged for carbon dioxide, which by this process is continually being poured into the atmosphere, and this gas is also formed during all processes of combustion, whether they be rapid, as when wood is burnt in a fire, or slow, as when vegetable matter rots away. It is also produced by processes of fermentation, and escapes in enormous quantities into the atmosphere from the earth, from natural sources.

It must be remembered that during most processes which give rise to carbon dioxide, oxygen is being absorbed, and it has been computed that this takes place at the rate of over three-and-a-half million tons per diem—a rate which would rapidly diminish the percentage of oxygen and increase that of carbon dioxide, the air being rendered unfit to support animal life.

It has, however, been shown by the researches of Fruchot, Schultze, and others, that in the open air the percentage of carbon dioxide varies but little, the average amount being four volumes in 10,000 of air—this quantity decreasing after rain and increasing during frost and fog and at night time, but again diminishing after sunrise; it is therefore evident that there is some natural agency at work which tends to neutralise the effects of animal life and decay, and it is found that vegetable life plays an important part in this process of purification.

Action of Vegetable Life.—If the leaves of any form of vegetation be examined, they will be found to be covered with minute funnel-shaped pores which are in connection

with small cells containing a green matter called "chlorophyll," which gives the colour to vegetation.

Under the influence of the sun's rays the growing plant absorbs carbon dioxide from the air through the pores in the leaves, and it is then decomposed by the chlorophyll, the carbon being mostly assimilated together with water by the plant to form its woody fibre and so carry on its growth, whilst the oxygen is once more returned to the air, tending to keep it in a condition fit for respiration.

Diffusion.—This wonderful process would, however, be of little use by itself, as in large towns and manufacturing districts where enormous amounts of carbon dioxide are formed, there is, as a rule, but little vegetation and still less sunshine, so that the gas would accumulate and seriously impair the purity of the air were it not that the diffusion of gases, aided by the winds and air currents, tends to mix all the constituents of the atmosphere evenly together, and where sunshine and vegetation exist, there the carbon dioxide is decomposed, and the oxygen once more spread throughout the air by diffusion, a practically constant proportion being thus maintained.

Were it not for the action of gaseous diffusion the constituents of the atmosphere would arrange themselves in layers according to their densities, and life would be an impossibility.

Organic Matter.—When we breathe, the exhalations from our lungs contain not only carbon dioxide but also water vapour. If we breathe into a glass jar for twenty-four hours, keeping it cold so as to condense the water vapour, it is found that nearly a pint of water is condensed in the jar, and if this be allowed to stand for a few days, or even hours, it will putrefy and become offensive, showing that besides water there is present organic matter. It is this organic matter which is accompanied by the germs of disease, and is one of another class of impurities which are to be found in the atmosphere, and which are purely local and have local

causes, and which perhaps affect health more than anything else.

True Impurities.—These are—First, suspended solids, which we find floating in the air as dust; partly mineral substances which induce certain diseases from the merely mechanical effect of local irritation; and partly organic bodies, such as the germs of infusoria, fungi, etc., which have come into great prominence during the last few years from the investigations of Schrœder, Davaine, and Pasteur, and which at the present moment are the favourite explanation of the spread of many kinds of disease.

Secondly, suspended liquids, such as the fog formed by partly condensed water vapour, which, by keeping down the smoke and solid impurities, irritate and affect respiratory organs and eyes; and thirdly, gases, such as sulphur dioxide and sulphuretted hydrogen in volcanic districts, hydrochloric acid and chlorine in manufacturing districts, and marsh gas or methane on bog lands, these gases having a greater effect on vegetation than on human beings.

Action of the Impurities.—These impurities all have prejudicial effects upon health and life, but it is the effect of several impurities acting together which most ordinarily affects us; for instance, four volumes of carbon dioxide in 10,000 of air is the normal quantity, whilst fifty in 1,000 prove fatal to life, and fifteen to twenty cause severe headache, yet in the act of respiration headache and giddiness are produced when the amount of carbon dioxide is not more than 1·5 volumes in 1,000; but then organic matter is present as well, and exerts a very considerable influence upon the functions of the body.

Air which has been once breathed contains nearly 5 per cent. of carbon dioxide, and is totally unfit to be again drawn into the lungs as the rate of interchange between carbon dioxide and oxygen is disturbed; dark venous blood is distributed through the system instead of being converted into red arterial blood, and death is ultimately caused by suffocation.

Natural Purification.—Rain assists in purifying air, by dissolving soluble gases such as ammonia and carbon dioxide, and washing the atmosphere from germs and dust. The oxygen in the atmosphere, in the presence of moisture, has the power of slowly oxidising or burning away organic matter; a heap of dead leaves or wood slowly is converted into carbon dioxide and water, a dead animal slowly disappears with certain changes in its composition. A still more active agent in thus keeping the face of the earth free from impurities is the modification of oxygen known as ozone.

When we are in the open air these provisions of Nature are ample to maintain the air in a fit condition for breathing; but when we are in an enclosed space, such as a room, then it is necessary to provide means to help Nature carry out her processes, or else we rapidly contaminate the air to a point at which it becomes unfit for respiration.

Sanitary Limit of Impurity.—The average amount of carbon dioxide in the outer air is four parts in 10,000, and experiment has shown that whenever the amount of carbon dioxide in the air of a room exceeded the amount in the open air by more than two parts per 10,000, then the air of the room was not fresh and had a stuffy smell owing to the organic matter and moisture present; hence, six parts per 10,000 are fixed as the limit of impurity.

An adult breathes out about six cubic feet of carbon dioxide gas in ten hours, and, therefore, in order that the air of the room he is in may be kept fresh, it is evident he must be supplied with 30,000 cubic feet of air in ten hours, or 3,000 in one hour.

Ventilation.—A person inhabiting a bedroom for seven hours would require 21,000 cubic feet of air, and if no means were provided for changing the air of the room, it would have to be 70 feet long by 30 feet wide by 10 feet high. It is clear that we cannot have rooms of this size, and, therefore, in the rooms we use there must be a change of air, and this is

obtained by the process called ventilation. We cannot change all the air in a room more than three or four times in an hour without creating a draught, and so for each person there should be allowed from 1,000 to 750 cubic feet of space, the air of which should be changed three or four times in the hour, thus providing the requisite amount of fresh air.

In ventilation, attention should be paid to the following points: (1) The air which enters should be pure; (2) Its movement should be imperceptible, otherwise it causes what we call a draught and sensation of chill; (3) The incoming air must be evenly distributed through the room, so that every part shall be undergoing change; (4) The air should be removed so quickly that there is no risk of the same air being breathed more than once.

The means by which air is set in motion for purposes of ventilation may be natural or artificial; in nature, the causes at work are, diffusion, wind, and the differences in weight between unequally heated masses of air. Air diffuses with great rapidity through chinks and openings due to bad carpentry, and also through bricks and walls built of porous materials. The amount of purification effected by diffusion is, however, insufficient.

Wind acts as a powerful ventilating agent. If it can pass freely through a room with open doors and windows at a rate of two miles an hour, which is almost imperceptible if the room is 20 feet wide, it will change the air of the room 528 times in one hour. Air is called "still" when in reality it is moving a mile or a mile-and-a-half per hour. The average movement of air in England is six to eight miles per hour.

Effect of Temperature.—Wind is caused by the air in certain places becoming heated, when it expands, becomes lighter than the surrounding atmosphere, and ascends, cool air rushing in to take its place.

When any gas, measured at a temperature of 0° C., is heated, it expands $\frac{1}{273}$ of its bulk for each degree centigrade,

so that supposing we had a cubic foot of air measured at 0° C., at 273° C. it would have doubled its volume, and each cubic foot of the expanded air would weigh half as much as the original air. From this it is evident that in an enclosed space, such as a room, the impure air after respiration or combustion has been carried on, being at a higher temperature, will rise, and that therefore the worst air in a room is to be found near the ceiling.

Expansion from heat is not the only cause of air rising and thus forming currents; water vapour is lighter than air, hence, when air contains much water vapour in suspension it is lighter than dry air, and ascends.

From these facts it will be seen that the methods employed in heating and lighting a house not only play an important part in deteriorating the quality of air by removing oxygen and giving back to the air carbonic acid, but they also may be made important factors in the ventilation, owing to the tendency to upward movement produced in the foul air by rise of temperature and moisture formed during combustion; and one of the most ordinary forms of ventilation consists in making openings near the top of the room, leading either into the flue or into the open air, whilst corresponding openings are arranged near the floor for the admission of fresh air.

Methods of Heating a House.—The method generally adopted for warming rooms is, in England, the open fireplace—perhaps the most comfortable and most wasteful that could be adopted. If a pound of coal could be burnt, and all its heat of combustion utilised in heating a room 20 feet square and 12 feet high, it would be more than sufficient to raise the temperature of the room ten degrees above the temperature of the outside air, and if there were no ventilation, and the walls were non-conductors of heat, the amount of fuel required to keep up this temperature would be very small. As it is, in an ordinary grate the consumption averages eight pounds per hour, but this consumption of fuel enables

the open fire to perform other functions besides those of heating, and it may be said to be the great engine of ventilation.

One pound of coal requires for its complete combustion about 160 cubic feet of air, and the eight pounds would require 1,280 cubic feet; but at a very low computation of the velocity of the gases in an ordinary chimney flue, the air would pass up at a rate of from four to six feet per second, or 14,000 to 20,000 cubic feet per hour, while with a velocity of 10 to 15 feet per second, which is often attained, the flow of air would be 35,000 to 40,000 cubic feet per hour. All this volume of air which passes out of the room is warm and carries heat away with it, whilst the fresh air which takes its place is cold, and lowers the temperature of the room. Another drawback is that this great volume of air drawn out by the chimney has to be replaced, and the fresh air rushing in through crevices and other small openings gives rise to draughts.

Heating by Radiation.—When an open fire burns, the radiant heat from it does not directly warm the air of the room, but the fire heats the back, bars and sides of the grate, and these in turn radiate heat to the walls and ceiling of the room, which in turn warm the air in contact with them. A good fireplace should, for this reason, have its sides and back made of a bad conductor of heat, but a good radiator, thus bricks or tiles are better for this purpose than iron.

The normal temperature of the human body is 98° F. or 36·8° C., and this temperature is maintained by a continuous process of combustion going on in our bodies, which are continually giving off a certain amount of heat. According to the laws of radiation, any heated substance parts with its heat more or less rapidly according to the temperature of the surrounding bodies, so that if a person is sitting in a room full of warm air, but near a wall that is colder than the air, his body rapidly loses heat by radiation to the wall, and

a sensation of chill is experienced. With an open fire this is never the case, as the radiation from the fire heats the walls of the room to a higher temperature than the air; but when a room is heated by means of hot water pipes or by means of warmed air, the walls are not heated in the same proportion, and although the air may feel warm the walls may remain cold, so that the heat of the body may pass by radiation to the walls and give rise to a sensation of chill.

It is much more healthful to breathe cool than hot air, as bulk for bulk it contains a greater weight of oxygen.

Other Methods of Heating.—If the open fire is done away with, it has to be replaced, either by closed slow combustion stoves, by heating by warmed air, by hot water, by steam, or by gas. In slow combustion stoves, a much larger amount of heat is obtained per pound of fuel consumed, but they have several drawbacks, such as allowing carbon monoxide and other injurious products of combustion to escape into the air, and should only be used in lobbies or galleries where there is ample ventilation.

In heating by hot air, cold air may be raised to a certain temperature by passing over heated surfaces, and can then be discharged into the building to be warmed, the drawbacks to this system being that the air is generally warmer than the walls, and also that it does not allow of any one room being made hotter or cooler than the rest. In warming by hot water pipes, the water is heated to a given temperature in a central boiler, and is then made to circulate through iron tubes in the chambers to be heated; this system is, of course, open to the same objections as the last.

In the United States, heating by steam is the most generally adopted plan. The steam is conveyed from the basement by means of pipes to the room or passage in which it is to be used, and there it is passed into a coil of pipes, called a radiator, which gives an increased heating surface; here the steam gives up some of its heat and becomes condensed to water, forming a partial vacuum in the tubes and

sucking up fresh steam to take its place, the condensed water flowing back once more to the boiler and being converted into steam. The difficulty in steam heating is to regulate the temperature of the pipes, as the temperature rises very rapidly when the steam is turned on, and falls as rapidly when turned off.

Gas Stoves.—The popularity of coal gas as a fuel is not to be wondered at considering the convenience of being able to light the gas fire when needed, and to put it out when no longer required. Used in the right form of stove, gas is undoubtedly the ideal fuel, and an extension of its use would do much towards the purification of the town atmosphere, but it must be clearly borne in mind that except for use in a hall or large open space no flueless stove should be admitted in the house.

Vitiating Effect of Illuminants.—The subject of lighting is so intimately connected with that of heating and ventilation that it is impossible to pass away from these subjects without taking into consideration the amount of vitiation of the atmosphere due to the various forms of illuminant we employ.

If good sperm candles are used for illuminating purposes the consumption of sperm will be 120 grains per hour for each candle of light emitted, whilst in mineral oil lamps of the best construction the consumption will be 50 grains of oil per candle per hour. With coal gas the amount of light developed entirely depends upon the burner in which it is consumed; with a 16 candle coal gas the following average results are obtained:—

Burner	Candles per cubic feet of gas consumed.
Incandescent mantle	17·00
Regenerative	8·00
Standard Argand	3·20
Ordinary Argand	2·90
Flat flame No. 7	2·44
„ „ No. 6	2·15
„ „ No. 5	1·87
„ „ No. 4	1·74

Calculating the amount of carbon dioxide and water vapour respectively in order to obtain 1 candle of light, we get the following result:—

Illuminant	Cubic feet per candle. Carbon dioxide	Water vapour.
Candle	0·41	0·41
Oil lamp	0·24	1·18
Gas—Flat flame	0·26	0·67
Argand	0·17	0·45
Regenerative ...	0·07	0·19
Incandescent mantle	0·03	0·08

From these data it appears that if the sanitary condition of the air of a dwelling room be measured by the amount of carbon dioxide present, as is usually done, candles are the most prejudicial to health and comfort, oil lamps less so, and gas least—an assumption which practical experience with the old forms of gas burner did not bear out, the discomfort and oppression felt being distinctly less in a room lighted by candles or oil than in one lighted by any of the older forms of gas burner. The explanation of this is to be found in the facts: First, that where we illuminate a room with candles or oil we are contented with a less intense and more local light than when we are using gas, and in a room of ordinary size would be more likely to use a lamp or two candles placed near our book or plate than the far higher illumination we should demand if gas were employed. Secondly, because the amount of water vapour given off during the combustion of gas in the old form of burner is greater than in the case of candles, and water vapour absorbing radiant heat from the burning gas becomes heated, and diffusing itself about the room causes great oppression. Also the air being highly charged with moisture is unable to take up so rapidly the water vapour which is always evaporating from the surface of our skin, and in this way the functions of the body receive a slight check, resulting in a feeling of malaise. Further, in burning coal gas, if the gas be pure and combustion

perfect, the products may be looked upon as carbon dioxide and water vapour only, but in all gas we find small quantities of sulphur compounds which add slightly to the vitiation of the atmosphere. The introduction of the incandescent gas mantle has however entirely changed this, owing to the high degree of illumination obtained with a small consumption of gas.

Heating Effect of Illuminants.—The amount of heat emitted is also a point of importance, and the following table shows the amount developed by the oil lamp and various forms of gas burner per candle of illumination per hour—

BRITISH THERMAL UNITS DEVELOPED FOR EACH CANDLE OF ILLUMINATION PER HOUR

Oil lamp	336 B.T.U.'s
Gas—Flat flame	310 ,,
Argand	207 ,,
Regenerative	88 ,,
Incandescent mantle	36·4 ,,

It is clear from these data that the introduction of the incandescent mantle has not only provided us with the cheapest but also with the most healthful form of illumination.

Ventilation of Ships.—In the ventilation of ships it must be remembered that the important factor of diffusion through the wall space is entirely eliminated, and that it is therefore necessary to pay all the more attention to artificial ventilation, a subject which has received but scant attention in the Navy, owing to the structural difficulties which have to be contended with, and which do not exist in the fast ocean steamers and Mercantile Marine.

In the older boiler and furnace arrangements, burning with natural draught, the stokeholds and engine rooms were practically open, whilst the other portions of the ship were in connection by means of air tubes with canvas cowls, which, whilst the vessel was in motion, kept up a constant air supply. With the introduction of the forced draught,

however, a change had to be made, as it was not considered desirable to feed the draught directly to the fire-boxes, as is done in most of the fast liners, but to make the stokehold as air-tight as possible, and to feed warm air into it by means of fans, so as to make it an air reservoir, with practically the only outlet through the furnace; this arrangement being considered necessary, in order that when the vessel was not required to go full speed, natural draughts could be used by opening up traps over the stokehold, whilst, when great speed was required, the stokehold was battened down, and the pressure of air obtained by the use of the fans.

The great objection to this is that the outlet for the air is at the bottom of the stokehold, whilst the hot foul air accumulates above, and being under pressure leaks out into other portions of the vessel, heating and vitiating the air.

The objection which exists to making any openings in the steel deck, which can possibly be avoided, renders any definite statement on ventilation of war ships very difficult, but it is desirable that some more efficient system than that at present adopted should be employed in the newer types of war ship.

The bellmouth canvas cowls when properly set and when the ship is going at full speed act in driving air into the ventilation trunks between deck, but when the ship is at rest, unless a high wind is blowing, they are perfectly inactive, and in bad weather have to be closed in order to prevent water finding its way down, besides which, even when they are acting, no provision is made for removing the vitiated air.

In some of the big liners cowls are replaced by water-tight down draughts, which supply an abundant quantity of air to all parts of the vessel, whilst self-acting air pump ventilators extract the vitiated and heated air from every part of the ship.

CHAPTER XVI.

EXPLOSIVES—GUNPOWDER.

Nature and causes of explosion—Exothermic and endothermic compounds—Classification of explosives—Gunpowder—Ingredients and composition—Saltpetre—Purification—Chemical decompositions of saltpetre—Charcoal for gunpowder—Sulphur—Manufacture of gunpowder—Mixing, milling, breaking down, pressing, granulating, dusting, glazing, stoving, finishing, and blending—Pebble and prism powder—S.B.C. and E.X.E. powder—Built up charges—Requirements of a good cannon powder—Effect of the prismatic form on the rate of burning of powder—Measurement of the pressure during firing powder—Crusher gauge—Muzzle velocity—Boulengé chronograph—Chemical changes taking place during the combustion of gunpowder—Gaseous and solid products formed—Method of calculating volume of gases produced and pressure exerted—Gases from S.B.C. and E.X.E. powders.

EFFECT of Time on Intensity in Combustion.—It can readily be proved that when organic substances containing hydrogen undergo decay, some of the hydrogen present unites with the oxygen of the air to form water, and the heat generated by the combination is spread over so long a period that at no one moment of time is it perceptible to the senses. If, however, hydrogen gas is confined under pressure in a gas holder, and allowed to escape through a jet into the air, on being ignited it burns with an intensely hot flame. In this case, as much hydrogen is converted into water in the course of a minute as would have been formed in some years by the process of slow combustion, and the increase in calorific intensity obtained is solely due to the increased rate of combustion, the total thermal value of the hydrogen being the same, whether it is burnt by a slow process taking years, or rapidly in a minute. If now the same volume of hydrogen be mixed with sufficient air to supply it with the oxygen required to convert it into

water, and if a light be applied to the mixture, the molecules of hydrogen being side by side with the oxygen necessary for their conversion into water, combustion takes place with enormous rapidity, and the intense heat generated expands the vapour formed to such an extent that an explosion results.

It is, therefore, evident that explosion may be looked upon as intensely rapid chemical action giving rise to gases or vapours which, being largely expanded at the moment of their formation by the heat developed during the action, occupy an enormously larger volume than the original substance.

Effect of Temperature.—Rapidity of combustion, by increasing the calorific intensity, expands the products of combustion, if they be gaseous, to an enormous extent at the moment of their formation, and as the effect of explosion is dependent upon the sudden generation of a large volume of gas from as small a volume as possible of original matter, the amount of heat generated during explosion is an important factor in the value of an explosive.

Requirements for an Explosive.—In an effective explosive these two essentials must be combined, and a solid or liquid occupying a small bulk must contain within itself the constituents necessary for building up a large volume of gas, whilst the change in condition must take place infinitely rapidly and generate so much heat that the volume of the gaseous products is again largely increased by expansion.

Effect of Initial Space.—The smaller the space into which the original explosive can be packed the greater will be the effect produced; a mixture of air and hydrogen explodes, but the explosion is much more violent if the same quantity of hydrogen is mixed with pure oxygen instead of air, as the retarding influence of the nitrogen is removed, and the mixture occupies less than one-half of the space occupied by the air and hydrogen.

The explosion of a mixture of hydrogen and oxygen produces a pressure of 240 pounds on the square inch, which is very small as compared with gunpowder, which gives on explosion a pressure of forty-two tons on the square inch, this being due to the fact that the ingredients of the powder are solid, and therefore occupy the minimum amount of space; if the mixture of hydrogen and oxygen were compressed to the same density as gunpowder, it would develop on firing a pressure of over 300 tons on the square inch.

Oxidising Agents.—Oxygen in the gaseous form could not be used in explosives, as it would occupy too large a space, but there are certain compounds rich in oxygen, which hold it in such feeble combination and are so ready to give it up to bodies capable of being oxidised, that they can be used as a form of compressed oxygen, and by their decomposition they supply to the combustibles present in the explosive the oxygen necessary to convert them into large volumes of gases.

In nearly all cases of chemical decomposition heat is absorbed, and the compounds which behave so are called "exothermic," because in their formation heat was given out, but the oxidising compounds used in some of the explosives are exceptions to this law, and during decomposition evolve heat which helps the action, these compounds being called "endothermic."

Importance of Fine Division.—It is of great importance that the combustible and the supporter of combustion in an explosive mixture should be in as fine a state of division as possible and well mixed, so that at the moment of explosion, each molecule of combustible shall find itself side by side with the molecules with which it is to combine, and that as little inactive material as possible should be present. The important effect of these conditions may be shown by taking four small pieces of phosphorus of equal size, and placing one on a saucer, when it will enter into slow combustion with the oxygen of the air, and if the day be warm the

temperature may rise to the point necessary for rapid combustion; but if not, many hours will have elapsed before the action is complete and the last of the phosphorus oxidised. The second piece can now be ignited in a deflagrating spoon and immersed in a bell jar of air, when it will burn away in a few minutes with evolution of heat and light; whilst if the third piece be now in the same way ignited and plunged into a jar of pure oxygen, it will burn away still more rapidly, and the increase in calorific intensity is shown by the bright light produced.

If now the fourth piece of phosphorus be dissolved in a few drops of carbon disulphide, and this solution be poured upon a small heap of powdered potassium chlorate, placed on a piece of blotting paper supported on the ring of a retort stand, the disulphide will evaporate and will leave the phosphorus in a very finely divided condition on the surface of the chlorate, a violent explosion at once ensuing, caused by the spontaneous ignition of some of the finely divided phosphorus, which causes the chlorate to decompose and give up its oxygen. This is an "endothermic" decomposition, and the heat so generated, together with the heat produced by the combination of the phosphorus and oxygen, gives, on account of the rapidity of the action, great calorific intensity, and causes enormous expansion and consequent violence of explosion.

The intense rapidity of combustion was in this case due to the fineness of division of the phosphorus, and to the small bulk into which the oxygen was compressed, the chlorate necessary to burn the phosphorus only occupying roughly $\frac{1}{600}$th the volume of oxygen necessary, or $\frac{1}{3000}$th the volume of air.

Classification of Explosives.—The explosives in use may be classified into mixtures and compounds, the former class containing the combustible and the oxygen-supplying substance in the condition of intimate mechanical mixture, whilst the latter class consists of organic compounds, con-

taining oxygen loosely held in combination by nitrogen, the oxygen on any disturbance of the molecular structure of the compound entering into new combinations with the carbon and hydrogen already present in the molecule. In some of the new explosives these two classes are combined, and the gas-generating power of the second class is augmented by the admixture of highly oxidising substances, which tend to render the combustion more complete, and so increase the amount of heat generated.

Gunpowder, which is the most important and most commonly used of the explosives, is an example of the first class, being an intimate mixture of potassium nitrate or saltpetre (which supplies the oxygen), sulphur and charcoal. English black service powder has the average composition :

Potassium nitrate	75
Charcoal	15
Sulphur	10
	100

Although in some of the new slow-burning prismatic powders the percentages of potassium nitrate and charcoal have been increased, and less sulphur used, the black Service powders of various foreign Governments approximate closely to this composition.

Country.	Potassium nitrate.	Charcoal.	Sulphur.
England—			
Black powders ...	75	15	10
Brown „ ...	79	18	3
Sweden	75	15	10
Russia	75	15	10
Germany	74	16	10
United States ...	75	15	10
Austria	75	15	10
France	75	15	10
Belgium	75·5	12·5	12

The value of a powder is to a great extent dependent upon the purity of its constituents and the processes by which it is mixed, as well as on the form in which it is finally made up; and in the manufacture of service powder all these points must receive the greatest attention.

Historical.—Discovered and used long before the Christian era, gunpowder has undergone but few changes in composition, and it is remarkable that these changes have been restricted to comparatively short periods; the first of which may be taken as comprising the fifteenth century, whilst the second and most important has occurred during the past thirty years.

Discovery of Gunpowder.—Invented according to tradition by the Chinese, and rediscovered, probably independently, by Roger Bacon in 1267, and by Berthold Schwartz in 1320, we have ample proof of its being used for warlike purposes at the battle of Crecy in 1346, but it was not until the last years of the fourteenth century that any improvement was made in the proportions in which the ingredients were present. Up to that time, the carbon, sulphur, and saltpetre had been blended in practically equal proportions, but at the end of the fourteenth century a gradual increase in the quantity of saltpetre used began to be observable, and the writings of the Italian Sartaglia show us that before 1537 the proportions of the ingredients had been improved until they closely approximated to the composition of the ordinary powders of to-day.

Potassium nitrate, nitre or saltpetre (KNO_3) is the ingredient in powder which supplies the oxygen necessary for the combustion of the carbon.

Saltpetre for Powder.—In making Service powders all the saltpetre used is obtained from native or grough saltpetre, found as a deposit in certain parts of India and carefully purified by recrystallisation before use.

It is especially important that no trace of chloride should

be left in the saltpetre, as both sodium and potassium chlorides tend to reduce the power and rapidity of explosion of the powder, and would also cause the grains to crumble.

Saltpetre crystallises in long grooved six-sided prisms; when heated it fuses at 335° C., and on continuing the application of heat it commences to decompose. At a red heat this decomposition consists of the evolution of one-third the oxygen contained in the salt and the formation of potassium nitrite.

Potassium nitrate		Potassium nitrite		Oxygen.
$2(KNO_3)$	=	$2(KNO_2)$	+	O_2.

When dried and finely powdered saltpetre is thrown upon red hot charcoal, the carbon undergoes rapid combustion at the expense of the oxygen of the nitrate, and in the same way, when powdered carbon is thrown upon fused potassium nitrate, violent combustion takes place, the reaction probably being:

Potassium nitrate		Carbon		Potassium carbonate		Carbon dioxide		Nitrogen.
$4(KNO_3)$	+	C_5	=	$2(K_2CO_3)$	+	$3(CO_2)$	+	$2N_2$.

One part (by volume) of solid potassium nitrate contains as much oxygen as 3,000 times its own bulk of air, and it is this fact which renders it so valuable in gunpowder, in which it may be looked upon as being a store of condensed oxygen to be used for the combustion of the carbon.

Charcoal for Powder.—The carbon used in gunpowder consists of charcoal prepared with great care from various vegetable tissues, the nature of which depends upon the character of the powder in which it is to be used. Great care has to be taken in regulating the temperature at which the substances are carbonised, as, if a high temperature is employed a very dense charcoal is obtained, which, as it is not easily combustible, is not so good for use in powder as a charcoal made at a lower temperature. The reason of this is that woody fibre consists mainly of cellulose ($C_6H_{10}O_5$), and the higher the temperature employed the greater the

percentage of oxygen and hydrogen eliminated, and with the elimination of the hydrogen the inflammability is decreased.

Effect of Temperature on Composition.—The difference in composition of the charcoal formed at various temperatures is strikingly shown by the following table:—

PERCENTAGE COMPOSITION OF CHARCOAL.

Temperature	Carbon	Hydrogen	Oxygen	Ash.
270° C. ...	71·0 ...	4·60 ...	23·00 ...	1·40
363° ...	80·1 ...	3·71 ...	14·55 ...	1·64
476° ...	85·8 ...	3·13 ...	9·47 ...	1·60
519° ...	86·2 ...	3·11 ...	9·11 ...	1·58

Woods Used.—In the Government Powder Factory the following woods are used:—

Powder	Wood	Time of burning (hours)
$M.G_1$., R.F.G. ...	Dogwood	... 4
$R.F.G._2$		... 8
$R.L.G._2$	Alder and willow	... $3\frac{1}{2}$
$R.L.G._4$, P. ...		... 4
P_2		... 6
Prism (black) ...		... 4
S.B.C. (slow-burning cocoa prism)	Straw	

The temperature of carbonisation varies between 360° C. and 520° C., whilst the rapidity with which the maximum temperature is reached also has an important influence on the quality of the charcoal formed, the quicker the heating the higher being the percentage of carbon formed.

Low-burnt Charcoal.—Charcoal which has been carbonised at temperatures below 260° C. has a brown colour and is highly inflammable, and although the large percentage of oxygen left in it reduces its calorific value (*see* Fuel), yet where it is important to retain a certain portion of moisture

in the powder, as is the case with the E.X.E. and S.B.C. prism powders, in which a given quantity of moisture is almost as important an ingredient as the sulphur, then the hygroscopic properties of the lightly burnt charcoal are of great value in the closely pressed prisms. Some of the brown charcoals are carbonised in retorts heated by superheated steam instead of directly by fire.

Sulphur.—The sulphur used in powder manufacture is native sulphur purified by re-distillation, and on testing should not leave more than 0·25 per cent. of residue when burnt, and when boiled with water should not render it perceptibly acid, although a very faint reddening of litmus is not considered sufficient ground for rejecting a sample.

Sulphur in gunpowder has several important functions to perform; in the first place it lowers the point of ignition by itself inflaming at a temperature of 250° C., and by its combustion quickly raising the temperature to the fusing point of the saltpetre, 335° C., which, but for the presence of the sulphur, would determine the point of ignition of the powder. The action of sulphur in lowering the ignition point of powder is very much the same as the part it plays on a match; being itself easily ignited it burns, and by its combustion raises the other ingredients of the powder to the requisite temperature.

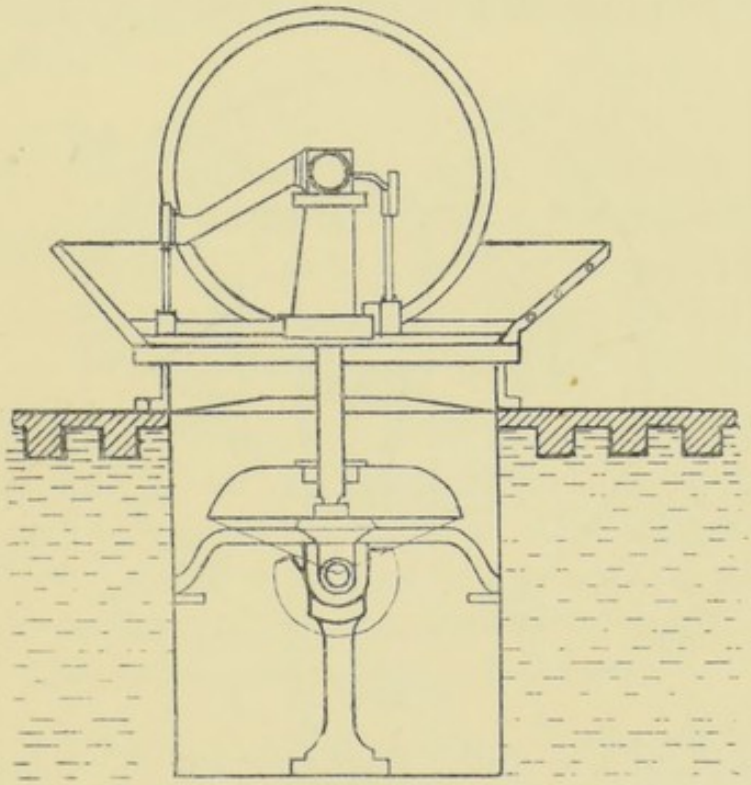
The effect which sulphur has in increasing the rate of combustion may be shown by making two trains of equal length, one of ordinary small grain powder, and the other of the same powder from which sulphur has been abstracted by treating it with carbon disulphide, and if these be simultaneously fired it will be found that the one containing sulphur will have burnt through its entire length, whilst that without sulphur will not have burnt through more than half its length in the same time.

Manufacture of Gunpowder.—The saltpetre is not ground before use, but the charcoal is ground in an enclosed mill until it will pass through a 32-mesh sieve, and the in-

gredients are then ready for the manufacture of the powder: the first three processes entailed are the same for all kinds of powder; they are:—

1. Mixing the ingredients.
2. Incorporating or milling them.
3. Breaking up the mill cake.

The ingredients of the powder are first accurately weighed out, allowance being made for the moisture present in the refined saltpetre, and are then mixed in charges of from fifty to sixty pounds in a revolving gun-metal drum,



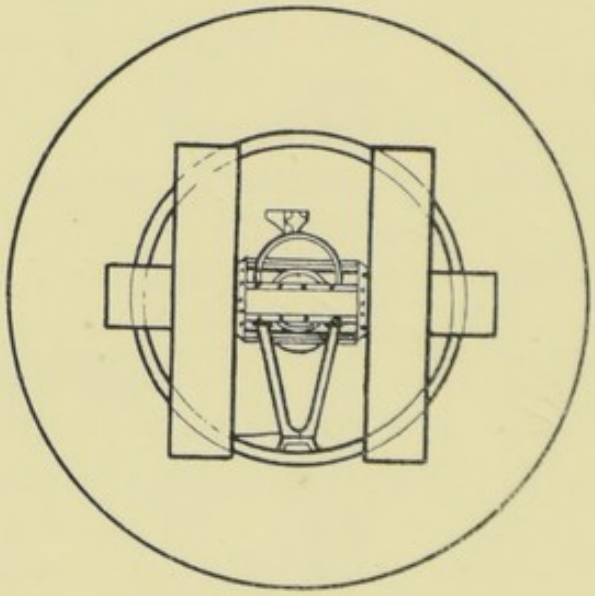
(A)—Fig. 43.

which contains arms moving in an opposite direction to the drum itself; the mixture is then passed through a coarse copper sieve to make sure that no foreign solid material is present, and is then called *green charge*. This is now taken to the incorporating mill, which consists of two iron or stone edge runners, weighing from three to four tons, which revolve on a bed made of the same material as the runners themselves

and having a sloping rim (Fig. 43). The runners are worked by machinery from below, and make seven to eight revolutions per minute.

Milling.—The green charge is placed on the bed of the mill, and is moistened with a very small quantity of distilled water to prevent any of the charge flying about as dust and also to aid the incorporation, and is milled for from three to eight hours, according to the nature of the powder.

The incorporating mills are in a long building containing six mills, each of which is shut off from the next by a partition, whilst over each mill is an iron cistern, connected by a lever arm to a large wooden shutter which is exactly



(B)—Fig. 43.

over the bed of the mill. Explosion of the charge would raise the shutter and deluge the mill by upsetting the tank; all the tanks work on one shaft, so that the upsetting of one would drown the charges in all the mills.

Mill Cake.—The "*mill cake*," as the charge is now called is perfectly uniform in appearance and should contain from 1 to 3 per cent. of moisture if it is to be used for small grain powders, and 3 to 6 for the larger kinds. It is next conveyed to the breaking down machine, where the mill cake is placed

in a hopper, and is carried by an endless band to the top of the machine, and then falls between a pair of grooved rollers, and afterwards between plain rollers which break it into what is termed "*meal.*"

Press Cake.—In making all the small arm and R.L.G. powders, this meal is now packed in layers in the press box, and subjected to a pressure of about seventy tons on the square foot for about a quarter of an hour, which renders it excessively hard and compact, and as far as its composition goes, it is now gunpowder; but in order to regulate its rate of combustion it must be granulated to the required size, which is done in a machine much resembling the breaking down machine.

Granulating.—Here the "*press cake*" has to pass through successive pairs of grooved gun-metal rollers, which break it up into grains, and from which it falls into sieves which are continually vibrating, and are fixed at an angle below the rollers. The grains are thus sorted into the various sizes required, and are shot out into boxes placed to receive them.

Dusting.—Powders made with "dogwood" charcoal are very dusty, and when they leave the granulating machine are passed through an inclined wooden framed cylinder covered with 20-mesh copper gauze and making about forty revolutions per minute, the dust passing through the gauze, and the grains passing out at the lower end.

Glazing.—The powder now goes to the glazing drums in which it is placed in charges of about 900 lbs. at a time, and the drums are driven at about twelve revolutions per minute, for from one-and-a-half to ten hours, according to the kind of powder; this imparts by mere friction a fine glaze to the surface of the smaller grained powders, but with the larger powders it is necessary to add a small quantity of graphite.

Drying, Finishing and Blending.—The glazed powder is now put in a drying room heated by steam pipes, and

through which a constant stream of air is passing to remove excess of moisture, and then is "finished" by a second glazing in a horizontal "reel," which rotates at high speed. The finished powders are finally blended, *i.e.*, several batches are mixed together so as to give as uniform a quality of powder as possible, and are ready for use.

Pebble Powder.—In making pebble powders the press cake is made of particular thicknesses, $\frac{5}{8}$ and $1\frac{1}{2}$ inch. respectively, and the press cake is then cut into cubes of the required size, which are glazed, stoved, finished, and blended as before.

Changes in Form of Powder.—Simultaneously with improvements in the composition of the powder attempts were made to improve its mechanical condition, and undoubtedly the most important of these consisted in converting the finely powdered and mixed constituents, which were known by the name of meal powder, into grains which would be more convenient for handling, and which at the same time, by opposing less resistance to the passage of the flame between the particles, increased to a great extent the rapidity of its combustion.

The earliest attempt in this direction was to sprinkle the meal powder with a spray of water, which caused the fine meal to collect into small spherical masses. These were afterwards gathered together and dried, but the ease with which such grains crumbled into fine powder again prevented any important increase in the rate of combustion being attained, and it was not until the idea was adopted of compressing the meal powder into dense hard cakes, and then again breaking these up into grains of the required size, that any great advance in this direction was made.

These improvements having been effected, the importance of mixing the ingredients in such a way that the maximum intimacy of the mixture should be attained, began to attract attention, and the perfection in this direction which has been reached in the manufacture of English powder shows in

marked contrast to the powders used in some Eastern countries. The most important era in the history of powder is undoubtedly to be found in the improvements and alterations made during the last forty years.

The Growth of Guns.—The causes which led to these alterations were to be found in the new forms of guns which were introduced soon after the close of the Crimean War. With the changes from the short smooth-bore cannon to the long-rifled ordnance of to-day, a corresponding alteration became necessary in the rapidity with which the powder developed its propulsive force, as the sudden impulse which the grain powders employed at that time gave to the projectile in the guns then in use, would have developed strains of a dangerous character in the breech of some of the modern forms of artillery, and at the same time would have given an extremely low muzzle velocity to the projectile.

With the introduction of rifled ordnance, a change came over the science of gunnery, and an enormous increase in the size of the guns and in the charge of powder used followed. During the Crimean War, the largest guns used were the 68 pounder smooth-bore guns, weighing 112 cwt. and using a charge of 18 lbs. of powder, whilst at the bombardment of Alexandria, the smallest gun used was a 6½ ton one, using a charge of 30 lbs. of powder, and at the present time 110 ton guns are being employed with a charge of 960 lbs. of powder, and it is evident that the form of the powder must be modified to keep pace with such radical alteration in the conditions under which it is to be used.

Desired Action of Charge.—It is required of a perfect powder that when the charge is fired in the breech of the gun, the combustion shall commence comparatively slowly so as to gradually overcome the *vis inertiæ* of the projectile without throwing too great a strain on the gun, and that, as the projectile passes up the bore of the gun, the combustion shall increase in rapidity so as to supply gas more and more rapidly to increase the momentum of the shot

which should leave the muzzle of the gun with the maximum velocity. In the old-fashioned grain powders this was never secured, and such powders could not have been used in the modern long-bore guns, as the rapidity with which they burnt threw an enormous strain upon the breech, and would have given the maximum velocity to the projectile before it was half way up the bore of the gun, leaving friction to reduce the velocity to a considerable extent before the muzzle was reached.

Methods of Retarding Burning.—The rate at which the combustion of gunpowder takes place, and at which therefore the pressure is developed, can be modified in various ways by mechanical means. As has already been seen, the rate can be diminished by burning the powder in the form of meal, but such a method would be inadmissible in practice, as the density of the mixture is very low, and the charge would occupy too large a space.

The combustion might also be retarded by reducing the intimacy with which the ingredients are mixed, but this again would be a bad and unscientific method to adopt.

The elimination of these two methods practically reduces the mechanical means for modifying the rapidity of the burning of the powder to three.

1. Varying the size and form of the grains of powder.
2. Varying the density of the powder.
3. Varying the surface-coating of each individual grain or mass, so as to retard or accelerate the ignition.

The English Committee of 1857 was strongly of opinion that it was not right to modify the proportions in which the ingredients existed in gunpowder until they had exhausted all other devices for reducing the rate of burning, as an alteration in the proportions would sacrifice a certain amount of the total explosive force developed by a given weight of powder, and as the result of their labours, the first methods employed were of a purely mechanical nature.

Increase in Size of Grains.—The first step was to increase

the size of the grains used for cannon powder at that time, and the larger grain powder gave fairly good results with the first modified forms of guns then introduced, but as the guns and charges increased in size, this powder in burning became too violent, and the next step was to produce a powder in which the grains should be uniform in shape and size.

This was done by compressing the meal powder into small moulds, so as to obtain small cylindrical pellets of about three-quarters of an inch in diameter, and three-eights of an inch in height, with indentations at each end in order to increase the surface.

The manufacture of this powder was, however, somewhat costly, and in order to facilitate the manufacture, a powder less regular in size than the pellet powder was produced by compressing the meal powder into cakes, and then cutting these cakes into small cubes of about five-eighths of an inch, and from these small cubes the charges of powder in the guns were built up, and later on experiments were made by increasing the size of these cubes until a large pebble powder, consisting of cubes of one-and-a-half inches, was arrived at.

With all these forms of powder, however, maximum rapidity of burning and evolution of gas takes place at first, owing to the ignition spreading over the whole surface of the cubes, and instead of the gas coming off with more and more rapidity as the space in the gun became larger, the evolution rapidly diminished with the decrease of surface caused by the burning away of the powder.

Built up Charges.—In order to avoid this defect as far as possible, built up charges were resorted to, and it was General Rodman, of the American Service, who first tried to overcome this difficulty by building up the charge of solid slabs perforated with holes, so as to expose the minimum surface of powder at the commencement of combustion, whilst the enlarging holes produced a greater and greater surface of powder as the space behind the projectile increased.

This idea has been revived, but large perforated cakes are always liable to break, and it was found far better to build up the charge of hexagonal prisms with a central core moulded in them.

Prism Powder.—It was in accordance with this idea that the black prism powder was first made, and the increase in rapidity in combustion is due to the enlargement of the core and subsequent exposure of a larger surface, and to the fact that as the walls of the prism grow thin they break up across the lines of least resistance (A A^1, Fig. 44), converting the powder during the last moments of its existence into what is practically a R.L.G. powder, thus giving enormously rapid combustion, due to the exposure of a large number of fresh faces.

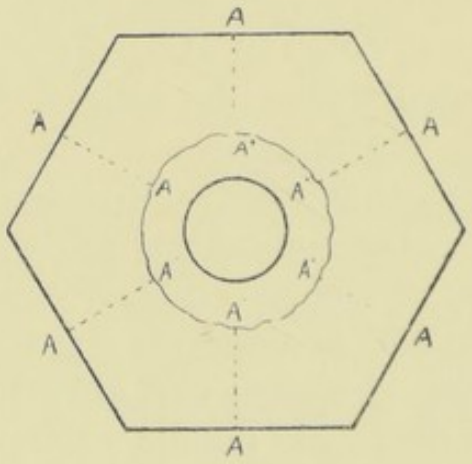


Fig. 44.

That this is really the case is shown by a prism being occasionally blown out with the projectile and extinguished by the sudden rush through the air, when it is seen to have been partly consumed and broken up in this way.

Side by side with these advances in the mechanical tempering of the combustion, other advances equally great in the manufacture were being made. It was realised that in order to obtain uniformity of results, absolute uniformity of ingredients, mixing, incorporation, pressure, density and degree of dryness, as well as uniformity in size, must be

attained, and new methods were introduced into the process of manufacture with this object in view, great attention being also paid to the "finishing" of the powder prisms and the blending together of various batches of powder which presented any variation in their ballistic properties.

With the continued growth, however, in the size of the guns employed, other changes became necessary, as even when using the black prism powder for built up charges the pressure given began to throw too severe a strain upon the breech of the gun, even when the cartridges were made up in such a way as to leave air spaces at the seat of the charge, in order to relieve as far as possible the initial pressure.

Changes in Composition.—In order to secure further modifications in the pressure developed, it soon became manifest that chemical alterations in the composition of the powder would be necessary. Sir Frederick Abel and Sir Andrew Noble had already made researches which conclusively showed that advantages might be secured in powder to be used in heavy guns by increasing the proportion of carbon and reducing the quantity of sulphur present, when Mr Heidmann and Mr Duttenhofer almost simultaneously produced a prismatic powder, in which the saltpetre was increased in quantity, the sulphur reduced, and low burnt charcoal in larger proportion was employed. This powder, which received the name of "Cocoa powder," from the brown colour imparted to it by the semi-charred woody fibre, gave a considerably lower initial strain and a much longer sustained action when used in large guns.

In the powders not only did the change in the proportions of the ingredients effect a considerable alteration in their point of ignition and rate of combustion, but the introduction of charcoal produced at a comparatively low temperature also brought into play other important considerations.

Where it is important to retain a certain proportion of moisture in powder, low burnt charcoal is of the greatest value, and the straw carbonised by superheated steam,

which was used in the cocoa powder, played a most important part in imparting to the densely pressed prisms sufficient hygroscopic power to enable it to hold the necessary percentage of moisture.

The introduction of the cocoa powder was a great advance, but with the heaviest guns it became necessary to obtain even slower combustion, and by slight modifications in composition, the present Service powders known as S.B.C. and E.X.E. prism were introduced.

The E.X.E. prism is distinguished by its slate colour and by a groove moulded round the core, whilst the S.B.C. prism is recognisable by its brown colour and by a circular indentation round the core.

Manufacture of Prism Powder.—The processes employed in making the prism powder are the same as were used for the black grain powder, with the exception that the granulated press cake, instead of being glazed, is compressed in a hydraulic press into regular six-sided prisms.

Great attention is paid to the stoving of the later forms of prism powder—E.X.E. and S.B.C.—as the amount of moisture in them has an important bearing upon their rate of explosion, and they are dried first for twenty-four hours at 32° C., and then for twelve hours at 60° C., which leaves them with from 1·7 to 2·2 per cent. of moisture, this being the normal amount which these powders retain under ordinary atmospheric conditions.

Proofing and Blending.—A day's production at the Royal Government Factory represents about 100 barrels, or 10,000 lbs. of powder, and it is essential that this large quantity should be as nearly as possible uniform in itself, so that when fired in charges the results, both as to muzzle velocity and pressure, should only vary within extremely narrow limits.

The 10,000 lbs. of powder, however, are made in many machines, and it is manifest that not only atmospheric conditions, but also slight differences in the methods of work

employed by the different men tending the machines, will make considerable differences in the batches turned out by each machine, and, if unadjusted, the batches of powder would of necessity give irregular results when used in guns.

In order to overcome this the batches of powder are blended, that is to say, the results obtained by firing a charge or charges from each batch are carefully noted, and the prisms from each batch are then mixed in such proportions as to give uniformity in the results obtained from the whole output.

Crusher Gauge.—The pressure exerted in the breech of a gun during the explosion is measured by a contrivance called a "crusher gauge" (Fig. 45), which consists of a steel cylinder into which a collar screws gas-tight, and carries a steel piston also rendered air-tight by a gas check.

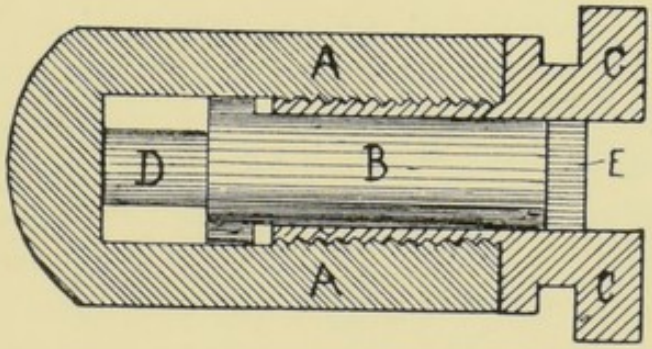


Fig. 45.

A small cylindrical piece of copper (D), which has been compressed to a known density by exposing it to a hydraulic pressure of twelve tons, and which is 0·5 of an inch in length, is placed in the bottom of the steel cylinder; the piston is then put in its place and the collar screwed up, the gas check fitted and the crusher gauge placed in the base of the cartridge, the solid end of the cylinder being against the breech of the gun and the gas check towards the projectile. On firing the gun the gauge is subjected to the full pressure developed by the explosion of the powder, which forces the steel piston down upon the copper cylinder and compresses

it. The crusher gauge, having no powder behind it, is left after the explosion in the breech of the gun, and is opened, the length of the copper being accurately measured on a micrometer scale, the amount of compression indicating the pressure in the breech of the gun. Used in this way, the crusher gauge gives very reliable results, but it has been shown that when inserted in the wall of the gun, certain waves of pressure and difficulties of adjustment occasionally interfere with the results obtained.

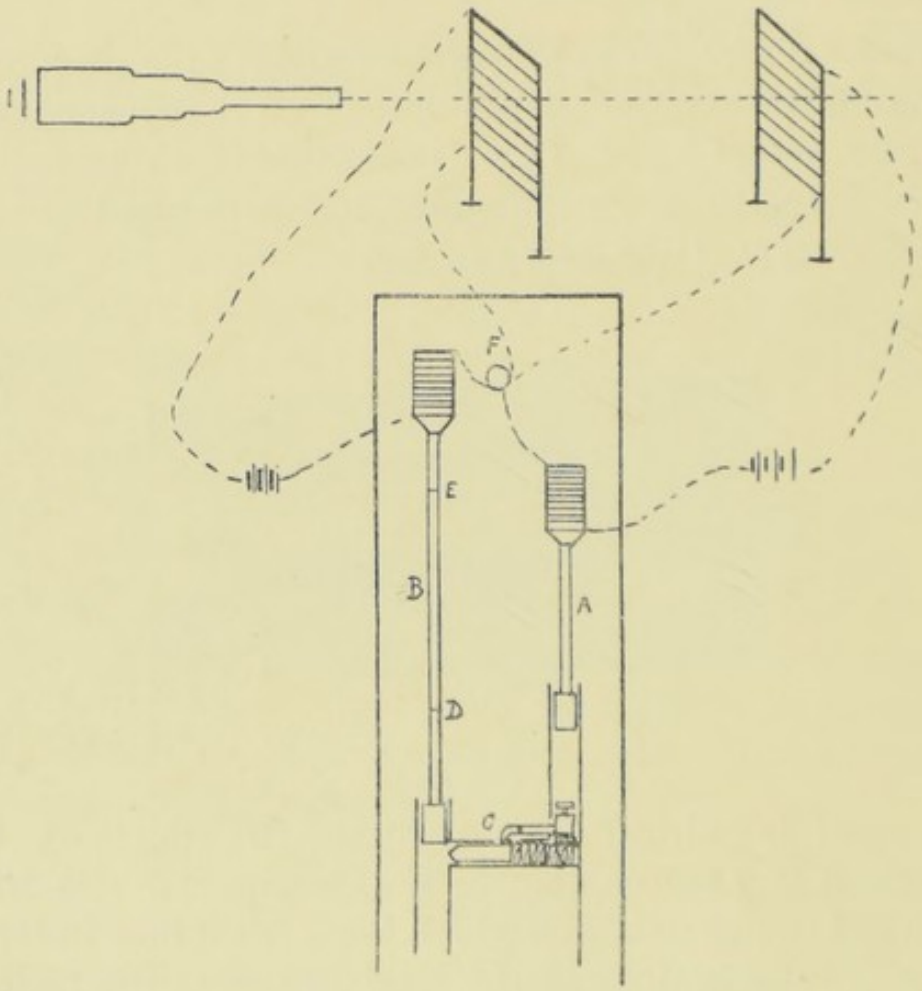


Fig. 46.

The Chronograph.—The muzzle velocity of the shot is determined by means of the chronograph (Fig. 46). Two screens are arranged, one about 120 feet from the muzzle of the gun, and the second 120 feet beyond the first. These screens consist of wooden frames strung with fine copper wire,

the disruption of a single strand of which is sufficient to break the flow of the galvanic current. In the Boulengé chronograph, a current from a battery of eight Bunsen cells flows through these wires and back to the instrument house, where the wire from each frame is coiled round a separate soft iron core, and converts it into an electro-magnet, each of which attracts and holds a rod of iron. The electro-magnet in connection with the second frame is fixed at a lower level than the electro-magnet connected with the first, and carries a short rod (A) with a weight at the bottom, whilst the first magnet is at a much higher level, and carries a longer rod. The current being allowed to pass through both electro-magnets, the rods are suspended in position. By pressing a key, (F) both circuits can be simultaneously broken, with the result that both the rods are liberated, and drop down guide tubes; the short rod strikes a catch (C) and causes a knife edge to be brought against the longer falling iron (B) and to make a nick in it. When both rods are liberated simultaneously, this nick is at the point (D). The current is again allowed to pass, and the rods hung on the electro-magnets, and the gun containing the charge, the power of which is to be tested, is fired, the projectile passing through the screens 1 and 2 and breaking the current by cutting the wires. Under these conditions the long rod (B) is liberated a fraction of a second sooner than the rod (A), the result being that the nick from the knife blade is now at the point (E) instead of at (D), as in the previous case. By now measuring the distance between (E) and (D), and knowing the length of time to which this is equivalent, allowance being made for time taken in liberating knife, catch, etc., the interval of time which elapses whilst the projectile passes between screens 1 and 2 can be calculated, and being corrected for distance of screen 1 from muzzle, gives the muzzle velocity of the projectile.

Each batch of powder made is tested in this way, and the batches are then blended according to the results they have given, so as to obtain a powder best suited to the work required of it.

The best proof that can be adduced to show that the pressure gauge, when used in this way in the breech of the gun, gives reliable results is that an expert operator can, from the pressure recorded, predict within a few feet per second what the muzzle velocity as recorded by the chronograph will be.

Influences affecting Burning.—The way in which powder burns is influenced to a great extent by the conditions under which it is ignited; if some powder is placed in a cylinder and touched with a hot wire it catches fire and burns with a "puff," but if the powder is heated in a test tube at a certain temperature it explodes. In the one case the combustion spreading from grain to grain, whilst in the second case the whole mass is heated to a high temperature, and the increase of rapidity in burning is manifested by explosion.

Variation in pressure has a considerable influence upon the rate at which powder will burn, as under low pressures the flame from the powder escapes so rapidly that its power of passing on the combustion from grain to grain becomes seriously impaired. If some powder is placed on a watch glass under the exhausted receiver of an air pump, and is then heated by a thin platinum wire in connection with a voltaic battery, the grains of powder in contact with the wire will fuse and burn, but the remainder of the powder will not be ignited; on now allowing air to enter and again heating the wire the powder at once inflames.

The retarding effect of a low barometric pressure on powder fuses is well known; a fuse arranged to burn for thirty seconds will be retarded in its combustion one second for each inch the mercury of a barometer falls.

The Chemical Reactions when Powder Burns.—The chemical reactions taking place during the combustion of gunpowder are, in the first place, fairly simple, the oxygen of the potassium nitrate converting the carbon into carbon monoxide (CO) and carbon dioxide (CO_2), whilst the nitrogen is liberated; the potassium unites partly with carbon dioxide

and oxygen to form potassium carbonate (K_2CO_3), and partly with sulphur and oxygen to form potassium sulphate (K_2SO_4), and the following might be taken as the simplest equation representing this principal reaction :

Potassium nitrate		Charcoal		Sulphur	
$4KNO_3$	+	$4C$	+	S	=

Potassium carbonate		Potassium sulphate		Carbon dioxide		Carbon monoxide		Nitrogen.
K_2CO_3	+	K_2SO_4	+	$2CO_2$	+	CO	+	$2N_2$

but this equation does not even approximately represent the proportions in which the ingredients are present in powder, the ordinary service powders having the molecular proportion $16KNO_3 + 21C + 6S$, whilst the products of combustion vary with every change in the methods of burning, also with the pressure under which the combustion takes place. Probably also the size of the charge used exercises an influence on the products.

Moreover, the powder contains moisture and the carbon contains hydrogen and oxygen condensed in its pores, and the hydrogen from both these sources plays an important part in the reactions taking place in the breech of a gun, so that to represent the chemical changes taking place by an equation with any degree of accuracy is an absolute impossibility.

The Researches of Debus.—Dr Debus has shown that it is probable from the work of Bunsen and Schischkoff, Linck, Karolyi, Noble and Abel, that during the combustion of gunpowder in the breech of a gun two distinct stages may be traced.

The first reaction is a process of oxidation occupying a very short space of time and constituting the explosion, during which, as in the previous equation, potassium sulphate, potassium carbonate, carbon dioxide, and traces of carbon monoxide, together with nitrogen, are formed. The proportions in which the original ingredients are present,

and the proportions of the resulting products showing that the equation must be taken as:

$$16KNO_3 + 13C + 5S =$$
$$3K_2CO_3 + 5K_2SO_4 + 9CO_2 + CO + 8N_2.$$

Some of the carbon and sulphur are left unacted upon, and these in the second stage of the action, which goes on whilst the products of the first stage are under great pressure and at a very high temperature, partly reduce the potassium carbonate and potassium sulphate, with formation of more carbon dioxide and potassium disulphide according to the equation:

$$4K_2CO_3 + 7S = K_2SO_4 + 3K_2S_2 + 4CO_2.$$
$$4K_2SO_4 + 7C = 2K_2CO_3 + 2K_2S_2 + 5CO_2.$$

During the combustion of the powder also a small quantity of the sulphur present unites with the metal of the gun, and some also with both the hydrogen occluded by the charcoal and that liberated by the decomposition of the moisture present in the powder, giving small traces of sulphuretted hydrogen gas. Deducting an atom of sulphur from the equation in order to allow for this secondary action, it is found that the final combustion of the ordinary Service powder can be approximately represented by the equation :—

Potassium nitrate		Charcoal		Sulphur		Potassium carbonate	
$16KNO_3$	+	$21C$	+	$5S$	=	$5K_2CO_3$	+
Potassium sulphate		**Potassium disulphide**		**Carbon dioxide**		**Carbon monoxide**	**Nitrogen.**
K_2SO_4	+	$2K_2S_2$	+	$13CO_2$	+	$3CO$	+ $8N_2$.

Using this equation, the volume of gas generated by one gramme of the powder can be readily calculated.

				Grammes
Saltpetre	$16KNO_3$	= 16 × 101	=	1,616
Carbon	$21C$	= 21 × 12	=	252
Sulphur	$5S$	= 5 × 32	=	160
				2,028

The gaseous products of the combustion are:—

		Litres.		Cubic Centimetres.
Carbon dioxide	...	$13CO_2 = 13(22{\cdot}36)$	=	290680
Carbon monoxide	...	$3CO = 3(22{\cdot}36)$	=	67080
Nitrogen ...	...	$8N_2 = 8(22{\cdot}36)$	=	178880
				536640

2,028 grammes of powder therefore yield, according to this equation, 536,640 cubic centimetres of gas, measured at 0° C., and 760 m.m pressure, or one gramme of the powder yields 264·6 c.c. of gas. The mean of the results experimentally obtained by Captain Noble and Sir Frederick Abel for Pebble R.L.G. and F.G. powders is, under these conditions, 263·74 c.c. of gas, a quantity which, considering the risk of experimental error and slight unavoidable inaccuracies, agrees wonderfully closely with the calculated result.

The volume of the gas being measured at 0° C. and 760 m.m. pressure, it is evident that at the moment of explosion the high temperature attained will expand it to an enormously larger volume.

Heat of Combustion.—Noble and Abel found, as the mean of a number of experiments, that one gramme of powder during combustion gave off enough heat to raise 714·5 grammes of water from 0°C. to 1° C., that is, gave out 714·5 thermal units, whilst Dr Debus calculated that the heat generated by the reactions between the saltpetre, sulphur, and charcoal in one gramme of English Service powder is 660 thermal units, but the difference would be much smaller if the amount of heat produced by the action of the sulphur upon the iron of the apparatus were known and could be subtracted from the experimental number.

Combustion of Cocoa Powder.—Noble gives the composi-

tion of the residue and gases formed during the combustion of cocoa powder under pressure as:—

SOLID RESIDUE

Potassium carbonate	64·12
Potassium bicarbonate	13·55
Potassium sulphide	none
Potassium sulphate	22·33
	100·00

GASES

	Volume
Carbon dioxide	51·30
Carbon monoxide	3·42
Hydrogen	3·26
Methane	0·31
Nitrogen	41·71
	100·00

giving at standard temperature and pressure 195 litres of permanent gases and 837 units of heat for each kilogramme of powder fired.

The larger quantity of water vapour, however, formed during the combustion of the cocoa powder, makes the volume of gas at the moment of explosion practically the same as in the case of black pebble powder.

One kilogramme of powder gives at standard temperature and pressure:

	Black		Cocoa
Permanent gas, litres	263·7	...	195·4
Water vapour	40·9	...	122·5
	304·6	...	317·9

When fired under ordinary atmospheric pressure, the products of combustion are very different, large quantities of potassium nitrate being left undecomposed.

CHAPTER XVII.

EXPLOSIVES—GUN-COTTON AND NITRO-GLYCERIN.

History—Action of nitric acid upon organic compounds—Cellulose—Collodion cotton—Gun-cotton—Gun-cotton an explosive compound and not an explosive mixture—Manufacture of Service gun-cotton—Precautions to be taken during manufacture—Testing finished gun-cotton—Properties—Explosion of gun-cotton by detonation—Theories of detonation—Wet gun-cotton—Storage—Products of combustion of gun-cotton—Force of fired gun-cotton—Nitro-glycerin—Manufacture of nitro-glycerin—Properties and decomposition—The downward action of high explosives.

GUN-COTTON and nitro-glycerin differ from gunpowder in being chemical compounds, which contain within their own molecules atoms of carbon and hydrogen which can be oxidised, and oxygen which can be rendered available for this purpose, the action being prevented in the compound by the presence of the element nitrogen, which, loosely holding the oxygen, prevents any re-arrangement of the atomic constituents of the molecule until such time as heat or a sudden jar causes a redistribution of the atoms with evolution of gaseous products.

It is manifest that in an explosive chemical compound, there being only one action to convert the solid into gas, the combustion must of necessity be more rapid than in a mechanical mixture, in which there has first to take place a breaking up of saltpetre in order to render available the oxygen and then, a combination of that with the combustibles present to evolve the gaseous products.

History.—It was in 1832 that Braconnot, in France, observed that by acting with nitric acid upon starch he could convert it into an easily combustible body, to which he gave

the name of xyloidin, whilst some six years later Pelouze noticed that when some fabrics, or unsized paper, were soaked in this highly corrosive acid they underwent but little change in appearance, but had increased in weight by nearly 80 per cent., and that after all the acid had been washed out from the substance, they manifested a most extraordinary increase in the rapidity with which they were able to burn, and there is no doubt that Pelouze in this observation laid the foundation of the discovery of what is now one of our most important explosives.

It was, however, not until seven years later that the rediscovery of this interesting substance by Schönbein, in 1845, attracted much attention, and it was his proposal to use cotton wool which had been soaked in a mixture of the strongest nitric acid with sulphuric acid, and then washed and dried, as a substitute for gunpowder that drew general attention to the use of nitrated compounds as explosives. The process which Schönbein employed he kept secret, and in August 1846, Böttger found how to prepare this substance, and they together submitted their discovery to the German Federation, but did not make it generally public. In 1847, however, several others discovered the method of preparation, and the manufacture of gun-cotton became general.

At this time the European Powers were nearly as anxious as they are now to obtain a powder which would evolve little or no smoke in its combustion, and when the discovery was made that cotton wool treated by nitric acid had the power of burning with enormous rapidity and without the formation of solid residue, Schönbein conceived that it could with great advantage be utilised as a smokeless explosive, but neither he nor any of the chemists of that period were able to make it answer their expectations in this direction, and although nearly every European Power commenced experimentalising with it, it took thirty-five years to bring it within the range of practical utility in guns.

Experiments were at once instituted on a large scale and

its manufacture carried on in England and also on the Continent, but in 1847 a very serious explosion occurred at the works in which it was manufactured by Messrs Hall, at Faversham, whilst a year later an even more serious explosion took place in the gun-cotton factory at Bouchet, near Paris. As no reason could be assigned for these and other similar explosions, gun-cotton was looked upon as too dangerous an explosive for ordinary use and its manufacture was discontinued ; a result which was further borne out by the decisions of committees, which reported against gun-cotton as an explosive for use in guns. In Austria, however, General Von Lenk continued to experiment upon the causes which had led to the previous disasters and failures, and he succeeded in showing that if the gun-cotton were entirely freed from every trace of the acids used in its manufacture, it could be stored and kept with perfect safety, and it is also to the same officer that we owe many experimental facts connected with this substance.

The apparent success of the experiments in Austria attracted attention once more to the subject, and in 1862, the British Association appointed a committee to ascertain all that was known, and to inquire into the possibility of applying gun-cotton to warlike purposes. Much valuable information was obtained by this committee, with which Sir Frederick Abel was associated, and it was he who first introduced the improved processes of manufacture at present employed in the Government factory.

Action of Nitric Acid on Organic Compounds.—When an organic body is nitrated, *i.e.*, acted upon by strong nitric acid to form a compound containing the nitrogen and oxygen radicle (NO_2), the compound so formed may be either—

(1) A nitric derivative, or

(2) A nitro-substitution compound.

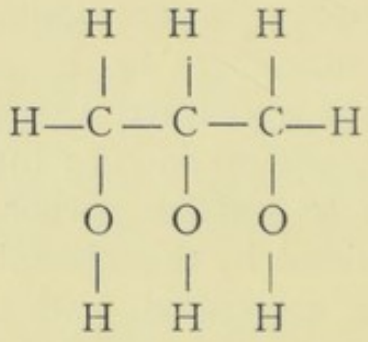
The difference between these two classes of bodies is that when a nitric derivative is acted upon by a reducing agent, the original compound is wholly or in part reformed, whilst

with a nitro-substitution product no reproduction of the original compound is possible.

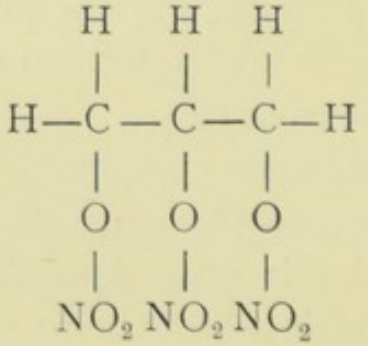
Nitro-cellulose and nitro-glycerin are nitric derivatives, and by the action of reducing agents upon them cellulose and glycerin can be again reproduced, whilst picric acid is a nitro-substitution product, and cannot be decomposed so as to reproduce the carbolic acid from which it was formed by nitration.

The chemical difference between these two classes of compounds is due to their structural formation; in a nitro-substitution product the nitrogen and oxygen introduced are linked directly to the carbon atoms, whilst in a nitric derivative the nitrogen and oxygen derived from the nitric acid are linked to the oxygen of hydroxyl (HO) contained in the organic body nitrated.

For instance, if we consider glycerin as an example, its molecular arrangement may be structurally shown as follows:—

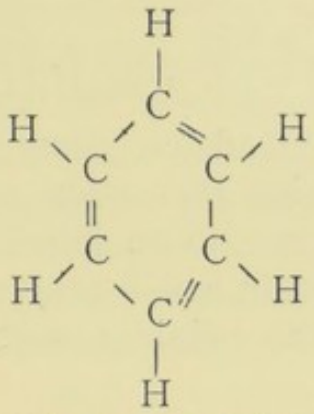


Upon acting on this with the strongest nitric acid the hydrogen atoms attached to the oxygen of the original compound are replaced by the nitrogen and oxygen radicle, nitryl, (NO_2), and we obtain nitro-glycerin.

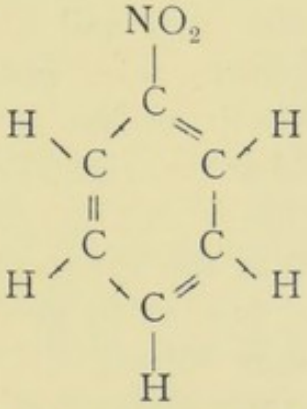


By acting upon this with reducing agents glycerin can again be obtained and this is typical of a nitric derivative.

On the other hand if we take benzene, C_6H_6, it has a structural formula



Upon acting on this with nitric acid the hydrogen attached to one of the carbon atoms is replaced by nitryl, and nitrobenzene is produced,



By acting on this with reducing agents the benzene is not reproduced, and we call it a nitro-substitution product.

We may look upon nitric acid as having been formed from water by the replacement of one atom of hydrogen by the radicle (NO_2), so that its structural formula would be $HONO_2$.

Cellulose.—In the same way cotton is one of the purest forms of cellulose or woody fibre ($C_6H_{10}O_5$), which is one of a class of organic compounds called "alcohols," in which one of the atoms of hydrogen in water has been replaced by some group consisting of hydrogen and carbon, or carbon, hydrogen and oxygen, so that its formula might be expressed as

$C_6H_7O_2(HO)_3$, and when a small portion of cotton is acted upon by the strongest nitric acid, the hydrogen of the group HO in the cellulose is replaced by the NO_2 group from the nitric acid with the simultaneous formation of water.

Cellulose Nitric acid Gun-cotton Water.

$$C_6H_7O_2(HO)_3 + 3(HNO_3) = (C_6H_7O_2)O_3(NO_2)_3 + 3(H_2O).$$

If gun-cotton were made on a large scale in this manner, the water formed during the action would dilute the nitric acid and would give rise to an inferior kind of gun-cotton called collodion cotton, in which only two-thirds of the HO groups contained in the cellulose would have the hydrogen replaced by NO_2.

Cellulose Nitric acid Collodion cotton Water.

$$C_6H_7O_2(HO)_3 + 2(HNO_3) = (C_6H_7O_2)(HO)O_2(NO_2)_2 + 2(H_2O).$$

In order to prevent this dilution taking place, the strongest nitric acid is mixed with two and a half times its own volume of strong sulphuric acid, which, having a strong affinity for water, absorbs it as fast as it is formed, and so maintains the nitric acid at its original strength.

Accepting the formula $(C_6H_7O_2)O_3(NO_2)_3$ as representing gun-cotton, it is seen that the group (NO_2) is the oxidising portion of the molecule, just as in gunpowder the NO_2 contained in the potassium nitrate (KNO_2O) supplied the oxygen necessary for the combustion of the charcoal and sulphur.

Taking the formula of the molecule of cellulose as $C_6H_7O_2(HO)_3$, it is clear that three forms of nitro-cellulose would be possible:

Mono-nitro-cellulose	...	$(C_6H_7O_2)(HO)_2O(NO_2)$
Di-nitro-cellulose	...	$(C_6H_7O_2)(HO)O_2(NO_2)_2$
Tri-nitro-cellulose	...	$(C_6H_7O_2)O_3(NO_2)_3$

and the proportions of nitrogen in these would be 7·34, 11·13 and 14·14 per cent. respectively. The researches of Eder and Vieille, however, show several forms of nitro-cellulose in which the percentages of nitrogen lie between those necessary for the di- and tri-nitro compounds, and it is probable, there-

fore, that although $C_6H_{10}O_5$ is the simplest formula that will represent the proportions of the elements in cellulose, yet that the true molecular composition is some multiple of it.

Manufacture.—In the manufacture of gun-cotton the best white cotton waste only is used, and is supplied free from all grease and dirt, which has been previously extracted by boiling it with dilute alkaline solutions: this is important, as, if any greasy or resinous substances remained in the cotton, they would form compounds with the acids employed, which would be liable to cause decomposition.

The cotton is first picked over by hand, all foreign substances being removed, and it is then passed through the "teasing machine," in which rollers bearing iron teeth rotate and tear up any knots or lumps which exist in the waste; after this it is passed through the "cutting machine," which chops it into pieces not exceeding two inches in length. If any moisture were present in the waste, it would cause evolution of heat on dipping it in the acids; the cotton is therefore dried by passing it through a chamber heated to about 83° C., in which the cotton placed on endless bands travels backwards and forwards for about twenty minutes; it is then weighed up into lots of 1 lb. 5½ oz., called a charge, and is placed in an air-tight box, to keep it dry until it has cooled down and is ready for dipping.

Acids Used.—The mixture of acids consists of one part by weight of nitric acid of specific gravity 1·52 to three parts by weight or 2·45 by volume of sulphuric acid of specific gravity 1·84. These are forced by compressed air in the right proportions into a mixing tank fitted with a lid, through an opening in which they can be thoroughly mixed by means of jets of air under pressure. Mixing the acids is attended by evolution of a considerable amount of heat, and the mixture is allowed to stand until thoroughly cool, when it is run into a dipping-pan, a small cast-iron tank, holding about 220 lbs. of the mixed acids, and surrounded on the outside by running water, in order to guard against

rise of temperature during the formation of the gun-cotton, which would tend to increase the percentage of collodion cotton present in the finished product.

Nitration.—The charge of dry cotton is now taken from its tin, and is stirred as quickly as possible into the mixed acids, in which it is allowed to remain five or six minutes; it is then lifted on to a perforated shelf at one end of the dipping-pan, and the large excess of acids squeezed out by a plate worked by a lever. The 1 lb. $5\frac{1}{2}$ oz. of cotton, which has absorbed 14 lbs. of acids, is now transferred to an earthenware pot fitted with a cover, the pot being placed in running water to prevent any rise in temperature, and the charge remains under these conditions for upwards of twenty-four hours, when the excess of acids present completes the conversion of the cotton. In some works the charge of cotton is put into an aluminium pan which is dipped in the acid mixture, and the pan with its contents is then put in the stream of water to soak for two hours, the large excess of acid completing the action in the shorter time.

Washing.—The next step is to get rid of the free acids which are still present in quantity. To do this the contents of six pots are transferred to a centrifugal machine consisting of a perforated iron cylinder made to rotate at a rate of 1,200 revolutions per minute, about 10 lbs. of acids being in this way separated from each charge of cotton.

The converted cotton is now placed in a cistern of water, where it is kept continually stirred in running water until it no longer tastes acid to the tongue. The gun-cotton is now again wrung out in a centrifugal machine, and is then boiled in wooden tanks heated by steam coils, the water is wrung out as before, and finally the gun-cotton should be so far free from acid that it does not redden blue litmus.

The gun-cotton is now reduced to pulp in a machine of the same construction as a paper-maker's "hollander," in which the fibre suspended in water is made to continually pass between a bed-plate and a roller, both being armed

with knives, and after being pulped for five hours, is reduced to a very fine state of division and then passed through a pipe into the "poaching machine." This is another large oval tank in which paddle wheels keep the pulp constantly agitated with a large volume of fresh water, which owing to the fine state of division of the pulp, thoroughly washes every portion of it. After six hours in the poacher, samples of the pulp are tested, and if the requirements of the test are satisfied, enough lime water, whiting, and caustic soda—sodium hydroxide—are mixed with it to leave between one and two per cent. of free alkali in the finished gun-cotton. The pulp is now drawn up by means of a vacuum pump into an iron reservoir called the "stuff chest," in which revolving arms keep the pulp from settling, and from which measured quantities can be run off into moulds, the bottoms being made of a very fine wire gauze, that allows the water to pass through but keeps back the fine pulp, the filtration being aided by the action of a partial vacuum maintained below the moulds.

Casting.—When most of the water has been in this way separated, hydraulic pressure of about 34 lbs. on the square inch is brought to bear upon the semi-solid pulp, which expels a large proportion of the remaining water, and renders the blocks sufficiently hard to bear careful handling. The moulded gun-cotton is now taken to the "press-house," where it is subjected to hydraulic pressure of about six tons on the square inch, which reduces it to one-third of its original bulk, making it so hard that it does not perceptibly yield to the pressure of the finger, and when dry will just sink in water.

"Displacement" Process.—Important alterations in the manufacture have recently been introduced at Waltham Abbey. Nitration is now performed in shallow earthenware pans, having a pipe at the bottom which serves for either an inlet or outlet, this being covered by two perforated plates. Four pans form a "set" for charging purposes. 700 lbs. of

the acid mixture are introduced into each pan from below, and 20 lbs. of dried cotton are immersed in this. An aluminium hood, connected to a draught, conveys away any fumes, perforated plates are laid on the charge, and a thin layer of water run over the acids to absorb fumes whilst nitration is proceeding, the hoods being then removed. Nitration proceeds for two-and-a-half hours, when the acid is allowed to slowly run off, being replaced by water fed in from above. Washing proceeds in this way until the nitrated cotton is ready for the subsequent boilings, no centrifugal wringings being necessary.

Great economy in acid, labour and time results, and the product obtained is more uniform and stable.

Precautions.—During the process of manufacturing gun-cotton, every precaution is taken to prevent any great rise of temperature during the period when the cotton is in contact with free acid, which would lead to decomposition of the gun-cotton with evolution of large quantities of red fumes—oxides of nitrogen—and the formation of oxalic acid and other products, whilst even a small rise in temperature increases the proportion of collodion cotton present, and so detracts from the value of the finished product.

In the second stage of the manufacture—from the removal of the superfluous acid in the centrifugal wringing machine to the moulding of the blocks—the object of all the operations is to thoroughly free the converted fibre from every trace of free acid, as it has been conclusively proved that it was to a great extent owing to the retention of free acid that the explosions which attended the early manufacture of gun-cotton were due.

Cotton when examined under the microscope is seen to consist of minute tubes, which during immersion in the mixed acids become filled with them, and the last traces cannot be removed by any ordinary rinsing process such as was at first considered sufficient. When such impure gun-cotton is packed in cases chemical action is maintained

by the traces of acid present, the heat generated being confined to the centre of the mass by the non-conducting properties of the cotton surrounding it; the action increases very rapidly with the rise of temperature, and a point is soon reached at which the gun-cotton becomes ignited.

The liability to spontaneous decomposition is much increased when cotton which has not been thoroughly cleaned, or which contains any fatty or resinous matter, is used, and also by the presence of a large proportion of collodion cotton, which is not so stable as the completely nitrated product.

This latter cause undoubtedly was a source of danger in the gun-cotton first manufactured. This was not left long enough in contact with the acids, so that the complete conversion of the whole of the cotton had not taken place, and some less stable products were present.

Testing the Finished Gun-cotton.—It is first tested for alkalinity; the amount of free alkali present should not be more than 2 per cent or less than 0·5 per cent.

Stability.—The stability test is now in a transition stage, but the method most used for gun-cotton has been to dry it, and then to see for how long it can be kept at a temperature of 65·5° C. (150° F.) before oxides of nitrogen are evolved in sufficient quantity to liberate iodine from potassium iodide. This was done by taking a small portion of the finely divided substance and placing it in a test-tube with a piece of test paper, moistened with a mixture of potassium iodide and starch, and then gently heating the tube in a water bath at a temperature of 66° C. No discolouration of the paper must take place for at least ten minutes. If there is any free acid present nitrous fumes will be evolved which will attack the potassium iodide, liberating iodine, which at once gives an indication by forming the blue iodide of starch.

The more modern tests for stability, however, are based

on the method first devised by Professor Will, which consists of determining the rate of evolution of oxides of nitrogen when the gun-cotton is heated to 135° C.

Nitrogen.—The determination of nitrogen in the gun-cotton depends upon the fact that when nitro-cellulose is treated with sulphuric acid in the presence of mercury it is decomposed with the formation of nitrogen dioxide which can be measured and the percentage of nitrogen calculated, the operation being carried out in a Bunté nitrometer.

Lower Nitro Compounds.—The percentage of collodion cotton present is next determined by treating a carefully weighed sample of the gun-cotton for some hours with a mixture of alcohol and ether, which dissolves the collodion cotton but not the fully nitrated product. When fifty grains of the gun-cotton are treated in this way for three hours, with frequent shaking, with four ounces of a mixture of two parts by volume of ether and one volume of alcohol, the loss of weight, due to collodion cotton dissolved out from it, should be very small.

Unconverted cotton can be detected by treating the gun-cotton with acetic ether, which dissolves the converted but not the unconverted cotton fibre.

Properties.—Gun-cotton differs very widely from gunpowder in its properties, requiring a much lower temperature for its ignition, as gunpowder has to be heated to a temperature of at least 250° C., whilst gun-cotton will often take fire at 136° C., and invariably does so below 204° C. Gun-cotton can be fired by striking it with a steel hammer on an anvil. The explosion, however, is confined to the portion struck, but it is very difficult to ignite powder in this way.

The rate at which gun-cotton burns is dependent upon the mode of its ignition, and the conditions under which it is placed. A piece of loose gun-cotton, placed on the hand, and touched with a hot glass rod, burns away so rapidly that

the skin is not scorched or burned. For the same reason, a piece of gun-cotton can be fired upon a small pile of gun-powder without igniting the powder, and grains of powder can indeed be wrapped up in gun-cotton and the gun-cotton ignited without the powder being burnt.

Rapid as this combustion is, however, it occupies an appreciable time, as may be seen by igniting a train of loose gun-cotton, which takes several seconds to burn a few feet, giving at the same time a large flame. If gun-cotton be confined at the moment of ignition this flame is forced back into the mass, and by rapidly heating it brings it to the point at which combustion passes into explosion. Prior to 1868, when gun-cotton was required for destructive purposes, it was always confined in strong cases, but in that year Mr E. O. Brown, of Woolwich, discovered that when a detonating fuse was exploded in contact with compressed gun-cotton, the unconfined mass at once exploded with enormous violence, and this discovery of the possibility of detonating gun-cotton marks the second great stage in the history of the substance.

Detonation.—The fact that certain unstable compounds could be caused to undergo instantaneous decomposition by the sympathetic vibration set up in them by a sharp explosion, either in contact with or close to them, had been previously known, and Nobel had exploded nitro-glycerin by detonation some years previously, but another new and most important fact was discovered nearly at the same time, namely, that gun-cotton, when wet, and containing 15 to 29 per cent of water, could be detonated, and gave even better results than when dry, provided that a small portion of dry gun-cotton was placed in contact with the detonating fuse, the explosion of this portion ensuring the detonation of the wet mass.

The great importance of this discovery is seen when one considers that the sudden conversion of the solid mass into gaseous constituents endows gun-cotton, when exploded in this way, with an enormous destructive power, which is as

great when the explosive is free as when it is confined, and that although it can be detonated when wet, in this condition it is not inflammable, and that a hole may be bored through a block of wet gun-cotton with a red-hot iron without inflaming it, a fact which renders it the safest explosive we possess, as it can be stored wet in closed vessels and dried as it is required for use, or even used wet with a small primer of dried gun-cotton.

Wet Gun-cotton.—The non-explosive properties of wet gun-cotton, under all ordinary conditions, were demonstrated by the Government Committee of 1871, who constructed two small magazines, and in one placed a securely-fastened tank, containing 2,240 lbs. of gun-cotton in discs, whilst in the second magazine the same amount was packed in eighty closed boxes, 28 lbs. in each; in both cases the gun-cotton contained about thirty parts of water to 100 of dry material. The remaining space in the magazines was now filled with shavings and other inflammable material, which was fired. In two hours the entire contents had burnt away, but without the slightest sign of explosion, although the heat generated was very great, as was shown by the distortion of iron bars upon which the cases had rested.

If dry compressed gun-cotton is ignited by touching it with a hot rod, it burns away with a fierce flame, but without explosion, but if larger quantities were ignited in this way, the portions first burning would quickly heat up other parts of the mass to the temperature at which combustion becomes explosively rapid, and as soon as this point was reached detonation of the whole mass would take place.

Action of Detonation.—The great increase in effect gained by detonating such explosives as gun-cotton arises from the enormous increase in rapidity of explosion. A train of ordinary gun-cotton fired by a hot rod takes several seconds to burn a distance of a few feet, but if a train of compressed gun-cotton be fired by detonation, the explosion would travel at the rate of 200 miles a minute. When gun-cotton

is fired by touching it with a red hot rod, its combustion occupies an appreciable time, and the gaseous products evolved have time to find space for themselves in the surrounding air. If, however, detonation be employed, the conversion of the solid into an enormously increased volume of gas takes place instantaneously, and the atmospheric pressure forms just as good a "tamping" for the gun-cotton as the strong metal cases which were employed before the principle of detonation was recognised.

In order to detonate gun-cotton, fuses charged with mercuric fulminate are now generally employed.

Theory of Detonation.—Several theories have been brought forward to explain the phenomenon of detonation, the first being that the vibrations caused by the detonator are able to set up similar variations in the body detonated, and that these vibrations start a sympathetic decomposition, and determine its instantaneous resolution into the products of explosion.

Abel.—When a particular note is sounded on a violin, the string of a second similar instrument will spontaneously vibrate and emit the same note, and the same synchronism of vibrations in the detonator and explosive are—according to Sir Frederick Abel's theory of detonation—the cause of the explosion.

The facts which most strongly support this view are that the detonators which will cause explosion of one compound must be varied to fit them for producing a similar result with a different explosive, and also that the detonation of a small disc of gun-cotton at one end of a tube three feet long will produce detonation of a similar disc at the other end of the tube, although if the discs are in the open air, they must be placed within half-an-inch of each other for detonation to take place.

Berthelot.—This theory assumes that the vibrations are transmitted through and by the explosive, but Berthelot

contends that the explosive substance does not detonate because it transmits the movement, but because it stops it, and transforms its mechanical force into calorific energy capable of suddenly raising the temperature of the substance to a degree at which its decomposition is effected, this in turn giving rise to the reproduction of a similar shock.

This vibratory movement Berthelot regards as a complex movement of a chemical and physical order when it is going on in the explosive, whereas it is purely physical when being transmitted through a substance like air whose nature is not changed by the wave, but on impact with the explosive body the wave is propagated by reason of a series of similar shocks incessantly reproduced in the explosive material, and which, as they continue, regenerate the energy throughout the wave and propagate the action with increasing velocity.

When, however, the shock has to be transmitted through air, the propagation is effected solely by reason of the last shock communicated to the air by the explosive, and which being no longer regenerated rapidly weakens by distance.

If Berthelot's theory be correct, the increase in velocity during detonation ought to admit of measurement by means of Noble's chronoscope, and experiments made by Sir Frederick Abel showed that when 170 cylinders of compressed gun-cotton were placed end to end and detonated from one end of the series, the rate of detonation for the first six feet was 17,466 feet per second, and for the last six feet 17,738 feet per second, an observed increase which might well come within the limit of experimental error. It is probable, however, that no matter how closely the cylinders are placed together, the break in the continuity of the compressed cotton must tend to check the rapidity of propagation, and would therefore invalidate the results.

If a heavy ball be allowed to fall through the air from a height under the influence of gravity, the fall becomes more and more rapid as the distance from starting point increases,

but if the ball be allowed to roll down a long flight of steps, the total vertical fall being equal to that of the previous case, each step breaking the fall, the increase in rapidity observed on the last step is but small.

Threlfall's Theory.—Threlfall has also investigated the phenomenon of detonation, and concludes that the shock of explosion is transmitted in one of three ways:—

1. By the rush of the products of explosion;
2. By undulations of the medium;
3. By vortex ring motion;

the action being transmitted in slow explosives by 1 + 2, whilst 3 comes into play with fulminates and nitro-glycerin.

Products of Combustion.—When gun-cotton is fired under ordinary atmospheric pressure, the products of combustion are found to be carbon dioxide, carbon monoxide, methane, nitric acid, nitrogen, water vapour, and sometimes traces of cyanogen and hydro-cyanic acid; but as the rapidity of explosion and the pressure increase, so the products become less complex. When detonated the gaseous products of the decomposition are:—

	Dry gun-cotton	Wet gun-cotton.
Carbon dioxide	24·24	32·14
Carbon monoxide ...	40·50	27·12
Hydrogen	20·20	26·74
Nitrogen	14·86	14·00
Methane	0·20	None.
	100.00	100.00

An equation suggested to represent the combustion of gun-cotton is:—

$$2(C_6H_7O_2)O_3(NO_2)_3 = 9CO + 3CO_2 + 7H_2O + 3N_2.$$

At the temperature of explosion, which varies from 3700° C.

to 4400° C., the steam would be dissociated and would oxidise some of the carbon monoxide. Various observers give the volume of gas evolved on the explosion of 1 gram of gun-cotton at from 483 c.c. to 829 c.c.

Detailed information on the products, etc. will be found in the Appendix.

Pressure.—Estimations of the pressure developed by the detonation of gun-cutton differ greatly in value, Berthelot placing it as high as 24,000 atmospheres, or 160 tons on the square inch, whilst other authorities estimate it as not much more than half this pressure.

The experiments of Sir Frederick Abel show that the detonation of moist gun-cotton is rather quicker than of dry, whilst the work done by the same weight of cotton appears to be equal in either case. The presence, however, of water in the moist gun-cotton must use up a certain amount of the heat, but this will be accompanied by an increase in the volume of the gases owing to the extra hydrogen liberated. It has been proposed to soak the gun-cotton in paraffin instead of water in order to get over the trouble of evaporation, and this has been tried with fairly satisfactory results, but the addition of a hydrocarbon to a substance already containing too little oxygen for its complete combustion seems hardly advisable.

Nitro-glycerin.—This compound is a nitric derivative, and was discovered in 1847, when Sobrero, whilst experimenting with glycerin, found that by treating this substance with strong nitric acid he obtained a compound which, on account of its exploding on a sudden rise of temperature, he called "pyro-glycerin"; but its value as an explosive was not realised until 1863, when Alfred Nobel showed that by firing it by detonation an excessively powerful effect could be obtained.

Glycerin or glycerol—$C_3H_8O_3$—is a sweet, syrupy liquid having a specific gravity of 1·269 and a boiling point of 290° C., at which temperature, however, it undergoes partial

decomposition. It is soluble in water and in alcohol, but it is insoluble in ether. It is contained in the liquor left after the separation of soap in the manufacture of that article, being one of the products formed when oils or fats are acted upon by alkalies, and is obtained in still larger quantities during the manufacture of palmitic acid for candle making.

The vegetable fat, palm oil, which chiefly consists of palmitin, when acted upon by superheated steam, is broken up into palmitic acid and glycerin which can afterwards be separated.

Palmitin + Steam. = Palmitic acid + Glycerin.

$$C_3H_5(C_{16}H_{31}O_2)_3 + 3H_2O = 3H(C_{16}H_{31}O_2) + C_3H_5(HO)_3.$$

When acted upon by strong nitric acid, glycerin, like cellulose, is converted into a nitrate with simultaneous formation of water:

$$C_3H_5(HO)_3 + 3(HNO_3) = (C_3H_5)O_3(NO_2)_3 + 3(H_2O).$$

Manufacture.—In the manufacture of nitro-glycerin, a mixture of 992 lbs. of nitric acid, specific gravity 1·48 and 1,680 lbs. of sulphuric acid, specific gravity 1·84, is thoroughly cooled and run into the mixing vat made of chemically pure lead, all the joints of which are autogenously melted together. The glycerin is then slowly and carefully added by means of an injector which regulates the rate of supply, whilst the whole charge is kept well agitated by blowing air through it, which not only thoroughly mixes the glycerin and the acids but also prevents local heating. In this way 330 lbs. of glycerin are mixed in with the acids, the process taking about an hour, and every precaution is taken to prevent the temperature rising above a limit of 22° C. (71·6° F.), the mixture being cooled by cold water, which is run through a coil of lead pipes inside the vat. If by any chance the temperature should rise to a higher limit, a valve in the bottom of the vessel can be opened, and the whole charge run into a tank of water placed below it.

Purification.—As soon as the nitrating is completed, the charge is run into a second lead tank or vat and allowed to stand for an hour, when the nitro-glycerin separates and rises to the top of the mixed acids. When the separation is completed the acids are drawn off, and the nitro-glycerin is run off into lead vessels, where it is first washed with water, and then with a solution of soda. The washing process is repeated three times with hot water and soda, and after separating from the wash water is filtered through table salt, and run into the store tanks.

In the modified process at present employed at Waltham Abbey, the nitration and separation are carried out in one vessel. As the nitro-glycerin separates, waste acids are fed in at the bottom, causing the lighter nitro-glycerin to overflow through a suitable channel at the top.

By introducing some 2 per cent. of water to the waste acids, any further separation of traces of nitro-glycerin (which formerly took many hours) is obviated, and the acids may be run straight to the recovery plant.

Properties.—Nitro-glycerin so prepared is an oily, colourless liquid, which has no odour and is insoluble in water, although it rapidly dissolves in ether, benzol, wood spirit, and hot alcohol, and from the solution so formed can again be precipitated on dilution with water.

It has a violent effect upon the system, acting in large doses like strychnine, whilst even traces produce vertigo, and, as it is absorbed through the skin, people working with it are frequently at first seriously affected, but after a time experience no ill effects and, it is said, present a more than usually healthy appearance.

When cautiously heated to 100° C. it slowly evaporates, at 200° C. it burns, and detonates at 257° C. When a lighted match is applied to it, it burns quietly away, and when the light is removed, the flame generally goes out; indeed, a lighted match may be extinguished by plunging it into nitro-glycerin. It is, however, detonated by a sudden

blow or by heating it to 257° C. Nitro-glycerin becomes solid at 4° C., and in this condition it is comparatively inert, hence it is necessary to thaw it before use, an operation attended with considerable risk.

It is stated that exposure to the direct rays of the sun will convert it into a very unstable and explosive substance, and also that the presence of ozone will sometimes cause its spontaneous decomposition.

Products.—When nitro-glycerin is exploded it is instantaneously decomposed into gaseous products, the probable decomposition being:

Nitro-glycerin		Carbon dioxide		Water		Nitric oxide		Nitrogen.
$2(C_3H_5)O_3(NO_2)_3$	=	$6(CO_2)$	+	$5(H_2O)$	+	NO	+	N_5

showing that the amount of oxygen present is more than sufficient for complete combustion, which is not the case in any other explosive compound.

Nobel has found that about 12,000 times its own volume of gas, calculated at normal temperature and pressure, is generated by the explosion of nitro-glycerin; whilst the heat evolved expands it to nearly eight times this volume. Its explosive force, volume for volume, is nearly thirteen times as great as gunpowder.

Downward Effect of High Explosives.—The rapidity of detonation of nitro-glycerin is very great, and it is this which gives rise to the downward effects noticeable in all nitro-glycerin or dynamite explosions.

Six cubic inches of nitro-glycerin when exploded would yield about a cubic yard of gas, and would require approximately $\frac{1}{40000}$th of a second for conversion into the gaseous form. A square yard of surface carries an atmospheric pressure of, roughly, nine tons, so that the gaseous products would have to lift nine tons to a height of one yard in $\frac{1}{40000}$th of a second, and the earth, being rigid, is broken up by the recoil from this enormous strain.

CHAPTER XVIII.

Smokeless Powders.

Necessity for smokeless powders for Service purposes—Amide powders—Attempts to use gun-cotton—Schultze and E.C. powders—The modern smokeless Service powders—Cordite Mark I—The erosion of guns—M. D. Cordite—Tubular Cordite—Pyro-cellulose—The foreign smokeless powders—Rottweil powder—American pyro-collodion—French B. N. powder—Picric acid and the picrates—Lyddite.

ALTHOUGH the idea of smokeless powders for warfare has always been a dream with strategists, it is only within recent years that they have become an absolute necessity, as with the introduction of quick-firing and machine guns into the Navy, it became necessary to have a powder giving little or no smoke if the guns are to be of any use for the objects for which they were intended. For instance, in repelling the attack of torpedo boats, the use of black or brown powder would entirely defeat the purpose of the guns, as after the first few shots the cloud of smoke would entirely obscure the whereabouts of the attacking force, and render, for some time at any rate, the further use of the guns abortive.

Cause of Smoke.—The formation of smoke during the combustion of powder is entirely due to the presence amongst the products of combustion of solid compounds, which, although liquid at the time of explosion, rapidly solidify as the temperature falls, and with the black powders, potassium carbonate, potassium sulphate, and potassium disulphide are the products which cause the fouling of the gun, and, together with condensing water vapour, form the dense cloud of smoke which follows the firing of a shot. When using brown powder, although the smoke cloud ap-

pears at first to be as dense as with the black powder, it is noticed that it clears away far more rapidly. This is due to the fact that whereas the products of combustion of the black powder only contain 12·8 per cent. of water vapour, the products of combustion from the cocoa powder contain 38·5 per cent. of water vapour, which in condensing carries down with it, by absorption and solution, the finely-divided potassium salts.

Ammonium Nitrate Powder.—The fact that the solid residue from powders consists entirely of potassium compounds from the base of the salt potassium nitrate employed in powder, naturally suggested the idea of using some nitrate which would give up its oxygen for the combustion of the carbon and sulphur in the same way that saltpetre does, but should have as its base some body which would yield volatile or gaseous compounds. The only inorganic nitrate which would in any way answer this requirement is ammonium nitrate, and many attempts have been made to utilise this in forming a smokeless powder.

Unfortunately, however, ammonium nitrate is a highly deliquescent body, which has the property of so readily absorbing moisture from the atmosphere that the powder made with it would rapidly be converted into mud if exposed to atmospheric influences.

Amide Powder.—In order to obviate, as far as possible, this difficulty, F. Gans conceived the idea of replacing only a certain proportion of the potassium nitrate in the gunpowder by ammonium nitrate, imagining, by so doing, the hygroscopic character of the ammonium salt would be got over, whilst the formation of a volatile compound, called potassium amide, caused by the union of the potassium with the nitrogen and hydrogen of the ammonium, would occur, and being volatile, would render the products practically smokeless, and in view of this theoretic action he christened his compound "amide powder." His views, however, were founded upon considerations which have not stood the test of

practice, as the powder so produced was hygroscopic, and by no means smokeless.

The most successful attempt to produce a smokeless powder by the use of ammonium nitrate was made by Mr Heidemann, one of the original patentees of cocoa powder, whose large knowledge of powder-making and the requirements to be observed, enabled him to so modify Gans' idea as to obtain a powder which not only gave most excellent ballistics, but which was decidedly less hygroscopic than the ordinary ammonium nitrate powder, and gave but little smoke. This powder, like the cocoa powder, contains a certain definite amount of water as one of its constituents, and, with a comparatively dry atmosphere, shows no tendency to absorb more, but with a saturated atmosphere it rapidly shares the fate of the ammonium nitrate powders generally, and becomes pasty. In order to overcome this defect, the cartridges were enclosed in hermetically-sealed metal cases, so as to prevent any absorption taking place, but it was found the storage of these in ships' magazines caused the moisture already present in the powder to become unequally distributed in the cartridges, with the result that there was occasionally a want of uniformity in the action of the powder in firing, and a tendency to the occasional development of high pressure, and this was considered a drawback to its adoption in the Naval Service.

Early Attempts to Use Gun-cotton.—When Schönbein discovered gun-cotton, it seemed at first as if the question of a smokeless powder had been solved, but as soon as experiments came to be made, it was found that on account of its low density it occupied far too large a volume, whilst when it was rammed into cases, the explosion was often of so violent a character as to produce disastrous results. Many attempts were made by Von Lenk to obviate this trouble by converting cotton threads into gun-cotton, and winding these threads with different degrees of tightness, generally upon a core of wood, but this system of taming the explosive

power of the gun-cotton proved unreliable, and although Von Lenk's system was introduced on a somewhat extensive scale, the unsatisfactory results obtained soon led to its abandonment.

Von Lenk's results having been investigated by Sir Frederick Abel, the experiments were repeated in England with wound cartridges of gun-cotton threads, but with no better results than had been obtained in Austria, and Abel having in the meantime completed the improvements in the manufacture of compressed gun-cotton discs, attempts were made to use these built up into cartridges with varied air spaces, with the object of regulating the rapidity of explosion. No certainty in results could, however, be obtained, and the attempts to utilise it were for the time abandoned.

Smokeless Sporting Powders.—About this period Messrs Prentice, of Stowmarket and Colonel Schultze, in Prussia, had succeeded in making practically smokeless powders for sporting purposes. The Stowmarket preparation consisted of felt-like paper made of a mixture of gun-cotton and ordinary cotton, containing 30 per cent. of gun-cotton and 10 per cent of ordinary cellulose, together with oxidising bodies, made in sheets which were afterwards rolled up into the cartridges. This cartridge depended to a great extent on the presence in it of moisture for the ballistics which it gave, the unchanged cellulose being itself hygroscopic, and aiding hygroscopic action in the gun-cotton. It was impossible, however, to regulate the amount of moisture present, and when the cartridges had been kept in a warm place the moisture would become too low and the danger of detonation of the gun-cotton would increase, whilst if the cartridges had been kept in a damp place they were apt to burn more like squibs than explosives.

When this trouble was realised, the rolled cartridge was replaced by a cylindrical pellet of slightly compressed gun-cotton pulp, attempts being made to tame down the rapidity of the explosion, and also to waterproof it by impregnating

it with a certain proportion of india-rubber, but neither of these cartridges gave sufficiently uniform results to fulfil Service requirements.

Schultze Powder.—The Schultze powder on the other hand consisted of granulated wood which, after purification by boiling with dilute sodium carbonate, was washed and treated with a solution of bleaching powder; the mass was then washed, dried, and soaked in the mixture of strong nitric and sulphuric acids for two or three hours, the temperature at the same time being kept as low as possible, and after getting rid of the free acid in a centrifugal machine, the nitrated wood was washed with water until free from acid, boiled with dilute sodium carbonate, and dried, after which it was steeped in a solution of the mixed nitrates of barium and potassium, and again dried at a low temperature.

E.C. Powder.—Another powder which became very popular for sporting purposes was the well-known E.C. powder, which was first made by Mr Reid in 1882, and consisted of gun-cotton incorporated with 35 to 40 per cent. of the mixed nitrates of barium and potassium, the mass being granulated and gelatinised by means of mixtures of ether, alcohol, and benzoline, which gave a hard coating to the grain. In this powder the presence of gun-cotton constituted a source of trouble, as the action was occasionally unduly violent, and the hard coating resisted ignition by the flash, and necessitated the use of a powerful cap.

In 1888, the E.C. powder No. 2 was introduced by Mr W. D. Borland, and in this powder the use of true gun-cotton was entirely done away with, the nitro-cellulose being completely soluble, and the hardness of the grain was obtained by treatment with a solvent containing camphor, which acted uniformly throughout the mass, whilst it left the surface in a slightly roughened condition, which enabled the flash to rapidly ignite the powder.

These powders gave very satisfactory results for sporting purposes, and also gave good ballistics with smooth-bore

guns, but both the E.C. and Schultze powder left an ash which was considerably harder than that afforded by the old black powder, and which instead of forming a partial lubrication for the succeeding shot, tended to choke rifled guns, so interfering with accuracy in shooting. Moreover, these powders could not be made on a large scale with a sufficient degree of uniformity to fulfil the requirements of Service powders.

Influence of the Metallic Base on Smoke. —None of these powders were absolutely smokeless, as the inorganic nitrate used to supply the oxygen necessary for making up the deficiency in the nitro-cellulose always gave a certain amount of solid residue, but the amount of smoke given varied a great deal with the kind of nitrate used, the presence of potassium nitrate in the original powder undoubtedly making the smoke much denser than when other metallic nitrates were substituted for it, this being one of the reasons why barium nitrate is employed to replace some of the potassium nitrate in these compounds, and also, of course, because the barium nitrate slows down the combustion.

The Causes of Failure with Gun-cotton.—It has been shown that the compression of gun-cotton causes it to burn much more slowly when ignited under ordinary atmospheric conditions, and it was in this direction that all the early experiments tended, but it was soon found that in the chamber of a gun the pressure forced the flame first formed into the interior of the mass and produced detonation, which, giving no time for overcoming the *vis inertia* of the projectile, threw an enormous strain on the gun, and gave very unsatisfactory muzzle velocities. Many attempts were then made to so dilute and tame the gun-cotton by admixture with inert or less explosive substances so as to render it sufficiently slow for this purpose, but with little success, as inequality in ballistics and the risk of detonation always remained insuperable objections.

Destruction of Structure.—The first important step toward

doing away with these troubles was the recognition that the cause of them was in the hollow fibre of the nitrated cotton, and that no matter how thoroughly the gun-cotton was disintegrated in the hollander during manufacture, or how closely the pulp was compressed in pressing the cartridges, discs, or slabs, you had merely shortened the tubes, and had not done away with them, and that it was only by absolute destruction of the structure of the cotton that the too rapid combustion could be checked and the risk of detonation avoided.

Tri-nitro-cellulose is soluble in ethyl acetate and nitrobenzene, whilst some other substances will convert it into a gelatinous mass, and by utilising such bodies to absolutely destroy the structure of the cotton, and by converting it into a solid substance, which can only burn regularly from the surface, the rate of combustion can be controlled, and the risk of detonation overcome. This method of taming the explosive has made the modern smokeless powder a practical possibility.

Qualities to be sought in a Smokeless Powder.—Bernadou has arranged the positive and negative qualities of smokeless powders in the following convenient form—

Positive.	Negative.
(1) Non-liability to detonation ...	... Detonation.
(2) Development of minimum heat	... Erosion.
(3) Formation of minimum residue	... Smoke and bore deposit.
(4) Good keeping qualities ...	... Decomposition.
(5) Maximum propulsive effect ...	... Low value of v/p.

It has already been pointed out that the difficulty experienced with gun-cotton, owing to its liability to detonation, has been overcome by destroying its fibrous character. The pure nitro-cellulose powders first prepared belonged to one of two main classes—(*a*) those obtained from highly nitrated insoluble nitro-celluloses gelatinised by acetone; (*b*) those from soluble collodion cottons of medium nitration, gelatinised

by ether-alcohol. The former class gave as a rule uncertain pressures, owing to brittleness, whilst the latter, owing to a deficiency of oxygen, gave smoke and bore deposits.

Naturally the difficulty of brittleness with the first would be overcome by toughening the material, and the second by the addition of some oxidising agent. Barium or potassium nitrate was therefore frequently incorporated, or, since nitro-glycerin is an explosive which has an excess of oxygen over that required for the oxidation of the carbon and hydrogen, this was also employed, as in ballistite and cordite.

With all such nitro-cellulose—nitro-glycerin powders, however, serious erosion was found to take place, and Sir Andrew Noble made a large number of experiments, and came to the conclusion that the principal factors determining its amount are—(1) the actual temperature of the products of combustion; (2) the motion of these products. But little erosive effect is produced, even by the most erosive powders, in closed vessels, or in those portions of chambers of guns where the motion of the gas is feeble or nil, but the case is widely different where there is rapid motion of the gases at high densities. It is not difficult to retain absolutely without leakage the products of explosions at very high pressures, but if there be any appreciable escape before the gases are cooled they instantly cut a way for themselves with astonishing rapidity, totally destroying the surfaces over or through which they pass.

The most erosive powders which have been used for charges in heavy guns were the brown prismatic powders, and there is one essential difference with the erosion produced by them and that with cordite. When the erosion is due to gunpowder the metal is pitted and grooves are formed, which are liable to develop into cracks, whilst with cordite this form of erosion is absent, and the action appears to consist of a simple washing away of the surface of the steel barrel by the enormously heated gases.

Experiments soon showed that it was the high percentage

of nitro-glycerin present in the cordite which was doing the mischief, as it developed a temperature on burning well above the melting point of steel. Sir Andrew Noble then made a series of experiments which showed that in mixtures of nitro-cellulose and nitro-glycerin the temperature on explosion increased with increase of nitro-glycerin, whilst the volume of gas increased with increase in nitro-cellulose, and further experiment showed that by varying the size of the cords of explosive the same ballistics as with the cordite could be obtained with a mixture much poorer in nitro-glycerin.

The following table, corrected by Noble in 1905, shows the heat developed by, Cordite Mark I, Cordite M.D., and a nitro-cellulose powder, with three different densities of charge.

Density of Charge.	Cordite Mark I.		Cordite M.D.		Nitro-cellulose.	
	a	*b*	*a*	*b*	*a*	*b*
0·45	5090	5090	4713	4624	4305	3954
0·40	4902	4970	4494	4411	4007	3890
0·35	4710	4860	4200	4215	4630	3795

The figures show the temperature of explosion in centigrade degrees, those under *a* being calculated from the pressures, whilst those under *b* from specific heats.

The Potential Energy of any explosive will depend on two factors, namely, the actual volume of the gas generated (calculated for comparison under standard conditions) and on the temperature developed on explosion, whereby the gases become enormously expanded. It has been shown that high temperatures are undesirable, hence to obtain the same potential energy the gas yield must be increased, either by actual chemical decomposition or increase of charge.

The production of carbon dioxide leads to high temperatures and low gas volumes (under standard conditions of measurement) whilst the production of carbon monoxide yields much lower temperatures but greater gas volume, thus a much greater gas volume (at 0° and 760 m.m) is obtained with low percentages of nitro-glycerin with nitro-cellulose, but since carbon dioxide is only produced in smaller quantities the actual temperature is low, the effect of increasing the nitro-glycerin being to produce larger and larger amounts of carbon dioxide with great increase of temperature, for the heat developed when carbon burns to one or other of its oxides is—

$$C + O = CO + 2472 \text{ calories.}$$
$$C + O_2 = CO_2 + 8140 \text{ ,,}$$

The researches of Mendeléeff, Lunge and others have shown that by careful attention to the ingredients and process of manufacture it is possible to obtain perfectly uniform nitro-cellulose, which shall be soluble in ether-alcohol, but insoluble in alcohol alone, which contains approximately 12·4 per cent. of nitrogen, and which theoretically yields carbon monoxide only, according to the following equation:—

$$C_{30}H_{38}O_5(NO_2)_{12} = 30\,CO + 19H_2O + 6N.$$

To this body Mendeléeff gives the name of *pyro-collodion.*

By proper adjustment of the charge, size of cord, etc., it is clear that a powder to give efficient propulsive effect within the limits of pressure permissible in a gun, may be prepared from either a suitable nitro-cellulose-nitro-glycerin mixture, or from a nitro-cellulose alone, with or without the addition of some metallic nitrate.

Keeping Qualities.—The pure nitro-cellulose powder has the advantage of greater homogeneity, but the important question of stability has yet to be considered. It is generally understood that the nitro-cellulose powders require very careful treatment in magazines; many cases of serious decomposition have occurred, and for this reason foreign ships on which such powders are employed have to be provided

with special means for keeping down the temperature of the magazine. The nitro-cellulose-nitro-glycerin powders appear to have a distinct advantage in this respect.

Weight of Charge.—Experiment shows that the potential energy increases far more rapidly with rise of temperature than it increases with rise of gas volume (calculated at 0° and 760 m.m.), that is to say, that a given weight of nitro-cellulose-nitro-glycerin powder will develop a greater potential energy than the same weight of a pure nitro-cellulose powder. To again quote Noble's results (1905), for a density of charge 0·25 :—

	Cordite, Mark I.	Cordite, M.D.	Nitro-cellulose.
Volume of total gases per gram	871·3 c.c.	888·6 c.c.	922·3 c.c.
Temperature °C.	5086	4220	3667
Comparative potential energy	0·97	0·82	0·74

Clearly, then, to develop the same propulsive effect, larger charges must be used for M.D. cordite than for Mark I. cordite, and still larger charges for a nitro-cellulose powder. The effect of this is far-reaching, for not only will the cost of material be greater, but a type of gun suitable for a cordite powder would be quite unsuitable for the much greater charge of a nitro-cellulose powder, and further the influence of increased bulk on magazine space must not be overlooked.

The Smokeless Powders of To-day.—The successful smokeless powders at present in use may be all divided into two classes :—

1. Powders consisting of nitro-cellulose and nitro-glycerin either alone or mixed with some material to regulate the combustion.
2. Powders consisting of nitro-cellulose with regulating and sometimes oxidising materials, but no nitro-glycerin.

History.—The history of the present smokeless powders may be said to have its commencement when Mr Alfred Nobel, who has done so much in the history of explosives of all kinds, showed in 1875 that when the two most powerful of the compound explosives were blended together their properties became beautifully tempered, so that, although the power of doing their full meed of work was still retained, the violence of the action was so far reduced that they became applicable for purposes for which neither of them alone could have been employed.

Blasting Gelatine.—He found that when nitro-cotton is thoroughly saturated and digested with nitro-glycerin the cotton loses all trace of its fibrous quality, and absorbing the nitro-glycerin, becomes converted into a gelatinous body having almost the character of a compound. The nitro-cotton, macerated with 90 per cent. of nitro-glycerin, and the mixture being kept warm, causes the formation of a plastic material from which neither of the components can be easily separated, and this substance, which has become of world-wide repute as a mining explosive under the name of blasting gelatine, will always be regarded with even greater interest as being the parent of the modern smokeless Service powders.

In January, 1888, Mr Nobel took out a patent for using nitro-cellulose mixed with nitro-glycerin, with or without the addition of a retarding agent, to form a powder which could be relied upon for use in guns.

It had been found by experiments made in Austria for adapting blasting gelatine to military purposes, that this substance might be exploded by the penetration of a bullet or fragments of a shell into the transport waggon, and Colonel Hess, whilst endeavouring to make it less susceptible to accidental explosion, found that by incorporating with the components a small proportion of camphor, and also by increasing the proportion of nitro-cotton used, the rapidity of the explosion of the material could be reduced, and the

product made of a horn-like character, which had remarkable ballistic properties, and which was uniform and practically smokeless.

Some of the camphor, however, used in the substance remains in it, and this being volatile, its evaporation causes modifications in the ballistic properties of the powder, and attempts have been made to improve upon this by replacing the camphor by other substances which would play the same part as the camphor, but which would not have the same drawbacks.

Ballistite.—The powder so made by Nobel, and known by the name of Ballistite, was extensively used in Italy and Germany. As manufactured in Italy, it contained equal parts of nitro-cellulose and nitro-glycerin, with the addition of a half per cent. of aniline, and when used in the form of threads or cords was called "Filite." The German ballistite contained a rather larger percentage of nitro-cellulose, and the finished material was coated with graphite.

Mark I. Cordite.—In the above powders the collodion cotton (di-nitro-cellulose) is employed, as it was well known that nitro-glycerin alone does not dissolve the tri-nitro-cellulose; but whilst endeavouring to avoid slight imperfections which had been noticed in the behaviour of the ballistite, Sir Frederick Abel and Professor Dewar found that if tri-nitro-cellulose and nitro-glycerin were mutually taken up by a liquid capable of dissolving them both, on evaporating off the solvent, the tri-nitro-cellulose and the nitro-glycerin remained behind in the most perfectly incorporated and gelatinised condition. It was on this principle that our English smokeless Service powder, Cordite, which contained 58 per cent. of nitro-glycerin, 37 per cent. of tri-nitro-cellulose, and 5 per cent. of vaseline, was introduced.

Cordite could be perfectly well made by incorporating tri-nitro-cellulose with nitro-glycerin by aid of such a solvent as acetone, but the perfect freedom from any solid or liquid products of combustion during the explosion of such a

mixture leaves the bore of the gun so clean that great friction is set up between the metal of the lining and the bullet, with the result that metallic fouling of the bore, due to abrasion of the bullet, and wear of the lining due to the same cause takes place. It is chiefly to overcome this trouble that the vaseline or petroleum jelly is incorporated with the other ingredients, as it gives a thin film of solid matter in the bore and greatly reduces this trouble, besides giving the cordite the power of resisting water, and facilitating the squeezing of the material into threads.

Acetone, which is used in making the cordite and also as a solvent in some other smokeless powders, is a compound having the formula C_3H_6O. It is a colourless, fragrant liquid, having a specific gravity of 0·79 and boiling at 56·3° C. or 133·3° Fahr. It is inflammable, burning with a luminous flame, and will mix with water, alcohol, and ether. It is essential, for purposes such as the making of smokeless powders, that it should be as pure as possible, as any traces of impurity would probably be left behind on its evaporation and remain in the powder. That used at Waltham Abbey has a specific gravity of 0·7965, and 98 per cent. of it distils off between 56·2 and 56·4° C. When such acetone is treated with a 0·1 per cent. solution of potassium permanganate, it should retain its rose colour for more than two minutes, and the Waltham samples will generally do so for nine. In addition to this point, it should not have more than 0·005 per cent. of acidity nor contain more than 0·1 per cent. of aldehyde.

Vaseline.—Vaseline or mineral jelly used is obtained during the distillation of petroleum, and consists mainly of portions distilling at temperatures above 200° C.; it has a boiling point of about 278° C., and has been given the formula $C_{16}H_{34}$, but is probably a mixture of this with higher and lower members of the C_nH_{2n+2} group of hydrocarbons.

Products of Explosion.—We have seen that the composition of finished cordite is:—

Nitro-glycerin	58
Tri-nitro-cellulose	37
Vaseline	5
	100

The proportions of the atoms of carbon, hydrogen, nitrogen, and oxygen in the compounds forming it would approximately be $C_5H_8N_3O_{10}$.

Such a mixture of compounds might be expected to give on explosion:—

$$2(C_5H_8N_3O_{10}) = 4CO_2 + 6CO + 6H_2O + 2H_2 + 3N_2$$

and this is fully borne out by an analysis of the permanent gases yielded by cordite on explosion:—

	I.	II.	Calculated from Equation
Carbon dioxide ...	25·40	... 24·9 ...	26·66
Carbon monoxide	37·62	... 40·3 ...	40·00
Hydrogen	17·43	... 14·8 ...	13·33
Nitrogen	19·55	... 20·0 ...	20·00
	100·00	100·0	99·99

Drawback to Cordite.—Cordite at first appeared to be a perfect smokeless powder; it gave excellent ballistics, its stability under trying conditions of temperature was better than with any other smokeless powder, and it showed no tendency to detonate or give unduly high pressures in the guns.

Erosion.—Soon however it became noticed that the enormously high temperature developed on firing large charges began to seriously erode the guns, and that this took place to a much more serious extent with large than with small guns, a rapid washing away of the surface of the bore taking place. It was at first hoped that by modifying the

form of the driving band of the projectile this trouble might be got over, but directly an increase in muzzle velocity was required the trouble became accentuated, and the experience of the South African war showed that even the 4·7 guns had their shooting rendered inaccurate at long ranges by the erosion caused after a comparatively small number of rounds.

M.D. Cordite.—This led to the adoption of what is known as M.D. cordite, which has the composition—

Tri-nitro-cellulose	65
Nitro-glycerin	30
Vaseline	5
	100

Experience shows that this modification of cordite is, if anything, more stable, and that for charges of the same size the life of the gun is nearly doubled, the heat developed on explosion being reduced from 1253 calories per gram with cordite to about 1000 with the M.D. cordite.

In the Manufacture of M.D. Cordite as at present carried out the tri-nitro-cellulose and nitro-glycerin are manufactured by the processes described in the last chapter, the only variation being that in the last stage of manufacturing the gun-cotton free alkali is not added, and instead of the gun-cotton being highly compressed under a pressure of six tons, it is lightly compressed into small cylinders, in which condition it contains roughly 45 per cent. of moisture. When required for use the cylinders of gun-cotton are placed upon trays of copper wire gauze, arranged in the stoving or drying room in racks, and subjected to the action of warm air for 80 to 100 hours, in which period the moisture is reduced to 1 per cent.

It is then weighed out in lots of 24 lbs. 6 oz., which are put into brass lined wooden boxes, and 11¼ lbs. of nitro-glycerin, which has been weighed out from store into gutta-percha jugs, are poured over the gun-cotton. The boxes containing these ingredients are removed to the

mixing house, in which their contents are kneaded together by hand and then rubbed through half-inch mesh copper wire gauze, the nitro-glycerin being absorbed under these conditions by the gun-cotton, and the mixture being known as "*cordite paste.*"

The next stage is to thoroughly incorporate the cordite paste with the acetone, that is, to destroy the structure of the tri-nitro-cellulose and blend it with the nitro-glycerin. The incorporating machine consists of an iron box formed of two semicircular troughs open at the top. In each trough is a spindle carrying a propeller-shaped blade, the spindles being made to revolve in opposite directions, one twice as fast as the other. The lower portion of the incorporating box is water-jacketed in order to keep down the temperature, which is never allowed to exceed 104° F.

Half the acetone to be used having been put into the incorporating vessel, the cordite paste with the remainder of the acetone is added, a wooden cover is put on top of the machine to prevent evaporation of the acetone, and the spindles are then run for three hours. At this point 9½ lbs. of vaseline are added, and the incorporating is continued for another three hours, during the last fifteen minutes of which the blades are reversed in order to break up the mass, which is now called "*cordite dough.*" This dough is removed in barrels to the press-house where it is compressed into cylinders which are placed under a hydraulic ram, the mass being forced out through dies into threads or sticks.

Below the die is an endless band carrying knife edges, the band travelling at the same rate as that at which the cordite issues from the dies. The band with the cordite on it passes under a roller so adjusted as to force the cordite on to the knife edges, which cut it into sticks of the required length. These lengths of cordite are arranged on trays and are stoved at 110° F. for periods varying from 272 hours up to 880 hours, according to their diameter, this removing the acetone. After this the cordite only needs to be blended so as to obtain uniform ballistics.

Tubular Cordite.—In order to as far as possible reduce the initial pressure when using cordite and to gain as great an increase as possible whilst the projectile travels along the bore of the gun, attempts are now being made to produce the cordite in tubes instead of in cords, as if the combustion can be started in the interior of the tubes a moderate initial velocity of gas is obtained which increases with increase of the burning surface. Experiment soon showed that tubular cordite gave better results than the modified cordite, as larger charges could be more completely consumed in a given length of gun, thus enabling higher muzzle velocities to be obtained without waste of powder, the great disadvantage being the increase in bulk as compared with the cords for the same weight of charge.

In the manufacture of tubular cordite there are two practical difficulties, one of which is that in the flexible condition in which it comes from the die, it is difficult to cut it into lengths without pressing together to a certain extent the walls of the tube, which impedes regular ignition, and does away with much of the benefit derived from the form of the cordite, whilst the second is that it is difficult to obtain perfect smoothness and uniformity of the interior surface of the tube.

Smoke Haze from Cordite.—Although nitro-glycerin and gun-cotton are both of them absolutely smokeless, yet the rapid firing of a number of guns using this powder gives rise to a fog or haze, and with the increase in charges necessitated by the introduction of modified cordite, this has shown itself to be rather troublesome and hampers the use of the guns to a certain extent. This haze, which in some cases becomes a thick yellow cloud, is due to several factors, consisting of condensing water vapour, smoke from the powder primer, vaseline, and the cartridge bag, and oxide of copper from the driving bands ; and as the moisture, vaseline, and cartridge bagging increase directly with the charge, this trouble necessarily increases with the use of the modified cordite.

Foreign Service Smokeless Powders.—All foreign Governments have now practically abandoned smokeless powders containing nitro-glycerin on account of the erosion to guns caused by them, and smokeless powders of the second class, in which nitro-cellulose gelatinised by suitable solvents, and with or without regulating and oxidising materials, have been adopted. This is due to the fact that modern gunnery demands higher and higher muzzle velocities, and that in order to obtain the 2,500 to 3,000 foot-seconds now considered necessary, larger charges are required, which with nitro-glycerin powders generate too high a temperature. The necessity for an increased charge over cordite powders and its influence on gun construction has already been referred to (p. 324).

Rottweil Powder.—Probably the most important of these is the German Service Powder manufactured by the Chilworth Company of Rottweil, and named from the fact Rottweil Powder. By insisting on great purity in the ingredients used and carrying out the nitration in such a way that the product is of uniform character, a pyro-collodion is produced which contains 12·4 of nitrogen, and is at the same time so soluble as to be readily gelatinised into a uniform plastic mass, which is pressed into the form of tubes of varying diameter, strongly resembling cordite in their appearance except that they are of a drab colour instead of the amber brown of cordite. It contains no volatile ingredients, so that the drying offers no drawbacks, and great stability is claimed for it.

American Pyro-collodion Powder is nitro-cellulose made like the German from a nitro-cotton of uniform composition, needing careful adjustment of the strength of the acids and of the temperature of nitration.

In making this powder damp nitro-cellulose is dried by adding to it a large excess of alcohol, which mixes with the water present, and by then subjecting the mass to pressure, the excess of alcohol and water is squeezed out, this process

of drying being far superior to drying in a current of warm air, which was found to give rise to a large quantity of dry nitrated dust, which rendered the atmosphere excessively explosive and gave rise to so much danger that it had to be abandoned. The method also has the advantage that the percentage of moisture left in the nitro-cellulose can be readily adjusted by altering the amount of alcohol added and the pressure in the dehydrating press.

The nitro-cellulose when removed from the dehydrating press is moist with alcohol, and is then transferred to the mixing machine where alcohol and ether are added. The mass is kneaded to a paste by revolving blades, the machine, however, having to be closed by an air-tight lid to prevent the evaporation of the solvents. After mixing for about an hour the pasty mass is pressed into cylindrical blocks of uniform density, which are then placed in the hydraulic press from which the paste is forced out in the form of strips, tubes, or multi-perforated rods, and whilst still soft is cut to the required size. After this it is dried at a temperature not exceeding 100° F. to expel the excess of solvent.

The French Smokeless Powder (B.N.) is also of the nitro-cellulose type, and gives practically the same results as the Rottweil and American pyro-collodion. It contains about 90 per cent. of mixed soluble and insoluble nitro-cellulose, the remainder consisting of a yellow nitrogenous body, which is probably nitro-naphthalene.

In the early attempts to make a smokeless powder many substances have been tried, and one of the early French smokeless powders, called the Vieille or Poudre B., contained as its chief ingredient picric acid, which has also been largely used as a bursting charge for shells under the name of Melinite in France, and Lyddite in the English Service.

Picric Acid, which was originally made by the action of nitric acid upon indigo, is now prepared far more cheaply by the action of nitric acid at a low temperature on carbolic acid and some other derivatives of coal tar.

Phenol, or carbolic acid—C_6H_5OH—is one of the compounds obtained from heavy tar oil, and is much used as a constituent of disinfecting powders and liquids. It is obtained in needle-shaped crystals, possessing a strong, tarry smell, and has a fusing point of 42° C., the liquid boiling at 182° C.; and when a small quantity of the fused acid is poured into nitric acid a violent action takes place, with evolution of red fumes. When this action has moderated, some of the strongest nitric acid is added, and the liquid boiled until red fumes nearly cease to be evolved; on cooling, a yellow substance called picric acid crystallises out, and can be purified by re-crystallising from water.

The change which takes place during the action of the nitric acid upon the carbolic acid may be represented as follows:—

Phenol		Nitric acid		Picric acid		Water.
C_6H_5OH	+	$3(HNO_3)$	=	$C_6H_2(NO_2)_3OH$	+	$3(H_2O)$.

Picric acid may be regarded as a nitro-substitution product, in which three atoms of the hydrogen in the original phenol are replaced by the radicle NO_2, and by the action of picric acid on metals or metallic bases, is obtained the class of salts known as picrates.

Picric acid		Potassium hydroxide		Potassium picrate		Water.
$C_6H_2(NO_2)_3OH$	+	KHO	=	$C_6H_2(NO_2)_3OK$	+	H_2O

Many of these salts have the property of exploding when heated or struck.

Picric acid is a pale yellow crystalline solid, having the form of plates or prisms, and is but little soluble in cold water, although readily soluble in alcohol. It derives its name from its intensely bitter taste, and for this reason has been used in some hop substitutes for bitter ales. It is extensively used as a dye for silk and wool, which it colours a fast yellow.

On heating the crystals of picric acid, they fuse at 119° C. with partial sublimation. It can only be exploded with difficulty by simply heating.

When exploded the decomposition is somewhat complicated. Nitrogen, carbon dioxide, carbon monoxide, nitric acid, water vapour, and hydrocyanic acid are produced, and a residue of unburnt carbon left behind. An inspection of the formula for picric acid makes it at once evident that there is clearly not nearly enough oxygen for the complete combustion of the carbon and hydrogen present, and for this reason nearly all the picric powders and explosives consist of mixtures of picric acid and its salts, with oxidising substances of a character suitable for supplying this deficiency.

It is now more than thirty years ago since Désignolle first introduced potassium picrate and saltpetre for use as bursting charges for torpedoes and shells, and this was improved upon by Sir Frederick Abel, who substituted ammonium picrate for the potassium salt, the same composition also being adopted in Brugère's picric powder. Soon after this Dr Sprengel showed that the picric acid by itself was capable of being detonated by mercuric fulminate, and in 1885 E. Turpin patented the use of picric acid for shells and torpedoes, and proposed to make it less sensitive to percussion by melting it and pouring it whilst hot into the shells, or by making the grains into a solid mass by means of collodion ; in this way a very great weight of the explosive can be got into a small space on account of the high specific gravity of the fused mass.

Lyddite.—Melinite contains picric acid as its chief constituent, mixed with some oxidising substance, or as stated by some authorities, merely made into a compact mass with collodion, and the explosive "lyddite" is practically the same substance.

The lyddite shells used in the South African campaign showed great diversity of behaviour, at one time exploding with tremendous effect, and at others giving a very low order of explosion and dense yellowish green fumes. This was due to the fact that for its proper explosion picric acid needs a powerful detonator, and fear of premature explosion of the

shell in the gun prevented fulminate detonators being used, with the result that many shell charges burnt instead of exploding. In the war between Japan and Russia it is believed that detonators of mercuric fulminate were used, and that several guns were burst by premature explosion.

With all smokeless powders a smaller charge is required than with the old black powder or the more modern forms of prismatic powder, the reason being that the charge has less work to do.

It must be clearly borne in mind that not only the projectile but also the products of combustion have to be expelled from the gun, these latter having ultimately even a higher velocity than the shot, and in using black powder the weight of the charge is far greater than with a smokeless powder. In powder also 57 per cent. of the charge is inert, whereas in the case of smokeless powder the whole is operative, and gives the charge a great gain in efficiency over the gun powder.

A table showing the heat values, products of combustion, etc., for the best known smokeless powders will be found in the Appendix.

CHAPTER XIX.

BLASTING EXPLOSIVES.

Requirements in blasting explosives—History—Blasting gunpowder—Sprengel explosives—Ammonite—Roburite—Bellite—Securite—Nitro-glycerin explosives—Dynamite—Carbo-dynamite—Dynamite No. 2—Lithofracteur—Carbonite—Blasting gelatine—Factors of safety required in blasting explosives—Safety from accidental explosion—Safety during explosion—Noxious fumes from blasting explosives—The fulminates—Mercuric fulminate—Detonators, etc.

IN explosives for blasting purposes, the study of ballistic effects has to be abandoned for considerations of a totally different character. When the explosive is required by the engineer for such mechanical work as tunnelling and the removal of rocks and other obstacles in a water-way, or when such bodies are required for the purpose of bringing down masses of slate and stone in quarries, the primary points which claim attention, are, first, safety in handling; secondly, the fitness of the explosive to do the work required of it, *i.e.*, shall it have a shattering and disintegrating effect which shall allow of the ready removal of the *débris*, or shall its action partake more of an upheaval and steady push, which will separate the mass in blocks fitted for cutting into slabs or other forms? thirdly, during its combustion such an explosive must not give off gases which, in the confined and ill-ventilated spaces in which they have often to be used, are likely to be actively dangerous to the life and health of those exposed to the air contaminated by such fumes.

For use in coal mines, however, these points, although of great importance, are overshadowed by the question of safety, and the ideal in explosives for such work must also

be free from the risk of giving rise to the ignition of explosive mixtures existing in the mine, whether the mixture be firedamp, traces of firedamp and dust, or mixtures of dust and air alone. Inasmuch as all explosives of this class claim perfection in both directions, it will be best to consider the composition and effect of those mining explosives most largely used in this country, and afterwards to discuss how nearly they approach to these requirements.

History.—In the earlier days of mining, gunpowder was the only blasting agent employed, but the discovery by Alfred Nobel, in 1864, that nitro-glycerin could be used with tremendous effect for blasting purposes, and his patenting it under the name of "Nobel's blasting oil," gave rise to an entirely new era, and when, in 1866, the dangerous character of this substance led to legislative restrictions, it was Nobel who complied with the requirements of the time by converting his blasting oil into the powerful and effective explosive which will be treated later under the name of dynamite.

During the succeeding years many attempts were made to modify and improve upon this idea, but the next great era in blasting explosives may be taken as commencing in 1873, when Dr Sprengel read a paper before the Chemical Society on a new class of explosives. In this paper he pointed out that in the then existing explosives there were considerable variations between the amount of available oxygen present and the amount of combustible matter to be burnt by it, and that the proportions, as a rule, were not such as to give the highest explosive value, some of these bodies, as in the case of gun-cotton, containing too small an amount of oxygen for complete combustion, whilst nitro-glycerin contains more than sufficient. He suggested that higher explosive values could be obtained by employing mixtures which might either be solid, liquid, or the two combined, one of which should be a hydrocarbon, containing the elements carbon and hydrogen in a condition

favourable to their rapid combination with oxygen, whilst the second should be an easily decomposable compound, which could be made available for supplying the necessary oxygen for the combustion of the hydrocarbon, and which could be mixed with it in the proportions necessary to give the highest explosive value.

Amongst the advantages claimed for such explosives is the important one of safety in transit, as the mixing of the ingredients need only take place when the body is required for use, and the two constituents when separate being non-explosive, there would be no danger until such admixture was made. Dr Sprengel showed also that mixtures of potassium chlorate and such bodies as benzene, petroleum, and phenol could be detonated and exploded with great violence. This class of explosives, named after the inventor, "Sprengel explosives," has been largely adopted for blasting purposes. The principal are:—

Rack-a-rock, a mixture of potassium chlorate and petroleum, or, in some cases, nitro-benzene, which obtained notoriety from being the material used in the Hell-gate explosions, when the rocks at the mouth of New York Harbour were destroyed.

Hellhoffite, a mixture of nitrated tar oils with the strongest nitric acid.

Oxonite, containing picric acid and nitric acid, which are mixed just before use.

The foregoing explosives are all prohibited for use in England, on account of their sensitiveness to friction and their general instability.

Safety Explosives.—On this account, in 1886 a group of safety explosives was introduced, consisting of di-nitro-benzol or nitro-naphthalene, mixed with either nitrate of ammonium or nitrate of potassium. The principal of these are known as ammonite, bellite, roburite, and securite, and have been specially introduced as safety explosives for mining work.

The next era in blasting explosives may be taken as dating from 1875, when Nobel in December of that year took out his first patent for blasting gelatine, a substance which figures so prominently in the foregoing pages as the parent of our successful Service explosive.

In discussing the composition and properties of these mining explosives it will be convenient to divide them into three classes:—

(1) Blasting powders of the same character as gunpowder; (2) Sprengel explosives; (3) nitro-glycerin explosives; which will cover all the explosives most used for blasting purposes, with the exception of tonite, which is a mixture of nitro-cotton with mineral nitrates.

Blasting Powder.—Under the first heading we find ordinary gunpowder, and also the commoner forms of blasting powder, in which the sulphur is considerably increased at the expense of the potassium nitrate.

The following table gives an idea of the composition of such powders:—

	England	France	Italy
Potassium nitrate ...	65	62	70
Sulphur	20	20	18
Charcoal	15	18	12

The result of this alteration of composition is to increase the volume of permanent gases given off by the powder, and at the same time to reduce the heat energy of the explosion; but in obtaining a slight lowering of temperature, the poisonous constituent of the products of combustion, carbon monoxide, is increased to a very serious extent. This alone should render the use of such powder inadmissible, whilst it has several other very serious disadvantages, which will be discussed later on.

The following table gives a clear idea of the alteration brought about in the composition of the products of com-

bustion by the increase in the amount of sulphur present, and reduction in the potassium nitrate:—

	Gunpowder, fine grain.	Mining powder.
Carbon dioxide	50·62	32·15
Carbon monoxide	10·47	33·75
Nitrogen	33·20	19·03
Sulphuretted hydrogen ...	2·48	7·10
Methane	0·19	2·73
Hydrogen	2·96	5·24
Oxygen	0·08	0·00
	100·00	100·00

The Sprengel explosives have been largely used for blasting purposes, both abroad and in this country; those used in England consist of mixtures of nitrated hydrocarbons and ammonium or potassium nitrate.

Roburite, introduced by Dr Carl Roth, is a simple mixture of ammonium nitrate with chlorinated meta-di-nitro-benzene. The ammonium nitrate is first dried and ground, then heated in a closed steam-jacketed vessel to a temperature of 80° C.; the melted organic compound is added, and the whole stirred until an intimate mixture is obtained. On cooling, the yellow powder is ready for use, and is stored in air-tight canisters or is made up into cartridges. Owing to the deliquescent nature of the ammonium nitrate, the finished explosive must be kept out of contact with the atmosphere, and for this reason the cartridges are waterproofed by dipping them in melted wax.

This mixture is not exploded by ordinary percussion, firing, or electric sparks. If a layer of the explosive is struck a heavy blow with a hammer, the portion directly receiving the blow is decomposed owing to the heat developed, but no detonation whatever takes place, nor are those portions of the substance around the spot struck in any way affected; whilst, if roburite be mixed with gunpowder and the gun-

powder be then ignited, the latter explodes and scatters the roburite without firing it.

The roburite can only be exploded by a specially powerful detonator, and on decomposition the gases evolved contain no combustible constituents, but consist only of carbon dioxide, water, and nitrogen, with a small trace of hydrochloric acid gas, which is at once condensed by the large volume of water vapour evolved, and gives rise to no inconvenience.

Ammonite is another explosive of this class, which is manufactured from ammonium nitrate and di-nitro-naphthalene, these substances being blended in the proportions to give, as the products of combustion, carbon dioxide, water vapour, and nitrogen, but during the decomposition taking place, probably some more complex action occurs, as small traces of ammonia can generally be detected.

Naphthalene, $C_{10}H_8$, which is obtained from coal-tar, and which is, perhaps, better known as the "albo-carbon" employed in certain forms of gas-lamps, is acted upon with strong nitric acid, with the replacement of two equivalents of the hydrogen by the NO_2 radicle. The resulting compound is carefully freed from acid, and is ready for use. Ammonium nitrate, carefully dried, is then incorporated with it by heavy edge-runners in mills, which are heated by steam, and which are also fitted with arrangements by which the temperature of the charge can be controlled.

One hundred and fifty pounds of this mixture are ground in this way until the required degree of fineness and incorporation is arrived at, and the mixture, whilst warm, is passed through a sifting machine, which separates any particles not sufficiently ground, these being returned to the mill. The finished explosive is then ready for making up into cartridges, and the temperature is kept constant until the whole of the operations are finished.

The cartridge-cases consist of solid-drawn tubes of a lead and tin alloy, in which the compound can be kept from the

action of the atmosphere upon the deliquescent ammonium nitrate. When the cartridge is required to be prepared for firing, a part of the metal tube at the end of the cartridge is cut off by a special tool, and the detonator with fuse attached inserted, the soft metal of the tube being pressed tight round the fuse. This substance, like roburite, only explodes when detonated by a strong charge of fulminate of mercury.

Bellite, which was patented in 1885, consists of a mixture of di-nitro-benzene with ammonium nitrate, the latter being kept rather in excess.

Securite consists of ammonium nitrate and di-nitro-benzene, but from the proportion of nitrate used it is probable that carbon monoxide is produced. These cartridges are coated with nitrated resin, in order to protect them from the action of the atmosphere.

The third class of mining explosives consists of nitro-glycerin absorbed by various substances, which will render it less liable to accidental detonation.

For blasting purposes nitro-glycerin was at one time very extensively used ; the fact of its being unaffected by moisture gave it a great advantage, whilst the rapidity of its explosion made it only necessary to prepare a bole-hole, partly fill it with nitro-glycerine, and then fill up the hole with water ; the water forming just as good a tamping for the nitro-glycerin, when fired by detonation, as if the hole had been plugged with wood or metal. The use of nitro-glycerin for blasting purposes is, however, attended with several inconveniences, as being fluid it can only be used in downward bore-holes, whilst its transport in the liquid form has given rise to many accidents ; and, finally, the liquid state is not very suitable for detonation, as the fluid yields to the sudden blow, and is often scattered instead of being completely exploded, so reducing its power, and becoming a source of danger in subsequent operations. In order to avoid these drawbacks, Nobel made the nitro-glycerin into certain plastic prepara-

tions by mixing it with various absorbent substances, and these mixtures, in many cases, have a higher explosive power than the nitro-glycerin itself.

Dynamite.—These nitro-glycerin preparations to which Nobel gave the name of dynamite may be divided into two classes; first, those containing non-explosive absorbents; and, secondly, those with explosive absorbents. The majority of these will be considered under the heading of blasting explosives.

When first working in this direction, in 1866, Nobel used charcoal as an absorbent for nitro-glycerin, and, encouraged by the success of his experiments, tried various other bodies which were capable of taking up and holding the nitro-glycerin, and he came to the conclusion that the infusorial earth first found at Oberlohe, in Hanover, gave the most satisfactory results. This earth consisted of the remains of diatoms, and contained ninety-five per cent. of silica, which is so finely divided as to be free from any grit, and which, after having been heated to a moderate temperature to remove moisture and organic matter, can be ground and sifted.

This substance is called kieselguhr, and is mixed with three times its weight of nitro-glycerin, the mixture being made by hand kneading. It is sometimes squeezed by hand through the meshes of a coarse sieve, and sometimes is forced out of a metal tube by means of a peculiarly constructed Archimedean screw, the resulting mass being cut into lengths to form cartridges of the required size.

During the mixing of the substance 8 per cent. of sodium carbonate, barium sulphate, mica, talc, ochre, and ammonium carbonate, are allowed to be added to it. This substance is generally known by the name of dynamite No. 1. In the large factory at Ardeer, the kieselguhr employed comes from Aberdeenshire, and is of considerable purity, containing 98 per cent. of silica, whilst in France a similar earth, called "Rhandanite" is employed.

The finished dynamite is a semi-plastic substance of a reddish-brown colour, containing 75 per cent. of nitro-glycerin and has a specific gravity, as made at Ardeer, of about 1·6. Under normal conditions dynamite can be set fire to by the application of a flame, and even when in considerable quantity can be burnt in this way without explosion, but, like nitro-glycerin, if the temperature rises above a certain limit, the combustion increases in rapidity until the temperature of detonation is reached.

This phenomenon of the gradually increasing of combustion and consequent increase in temperature is found in all substances capable of undergoing detonation. If a mixture of nitrogen dioxide and carbon disulphide be inflamed in an open-mouthed jar, not more than eight or ten inches in height, it burns quietly, emitting a most brilliant light, but if a long cylinder be employed, the flash of light is seen in the upper part of the cylinder whilst the mixture in the lower portion violently explodes. The same phenomenon may be observed when burning mixtures of acetylene and air, as with a long tube or cylinder, containing a mixture, the combustion will often commence quietly with deposition of large volumes of carbon, but the flame rapidly becomes quicker and quicker until the last portion of the mixture detonates and generally breaks the vessel to pieces. In the case of gun-cotton also, it is well known that small quantities burn away perfectly quietly, but large masses will first burn in the ordinary way, then the temperature generated will often rise until the remainder explodes.

Dynamite, like nitro-glycerin, freezes at a temperature of about 4° C. The frozen cartridges are less sensitive to shock and detonation, and therefore have to be thawed before use for blasting purposes, and it has been found that frozen dynamite burns very slowly, the first portion of the heat being used to thaw the substance before combustion takes place, but the burning frozen dynamite cartridges are much more likely to explode than when the dynamite is in its ordinary state.

Dynamite is not so easily detonated by shock as nitro-glycerin, and Berthelot states that this is due to the inert mass present having a cushioning effect upon the mechanical force of the blow, the energy imparted being divided between the absorbent and the nitro-glycerin, and for the same reason the dynamite is less crushing in its action than nitro-glycerin, because the heat evolved in its detonation is shared between the products of explosion and the inert body present.

Experiments made by Sir Frederick Abel gave a velocity of propagation of detonation in dynamite as 20,000 feet per second, but the experiments having been made with half-inch cartridges placed end to end in a continuous train, forty-two feet in length, the break in the homogeneous nature of the train may have introduced error into the result.

It is interesting to note that experiments made by General Abbott in submarine mining, show that the intensity of the action of such dynamite containing 75 per cent. of nitro-glycerin is greater than that of nitro-glycerin itself, and a confirmation of this was obtained in the fact that Sir Frederick Abel found the rate of detonation of dynamite was much quicker than that of nitro-glycerin; this, however, being to a certain extent due to the liquid particles of the latter having a tendency to escape from the blow of the detonator.

One of the great troubles with kieselguhr dynamite is that under certain conditions some of the nitro-glycerin will exude from it, this being specially the case when wet or placed in water. In 1886 Mr Walter Reid utilised the idea of making dynamite in which low burnt charcoal, made from cork rich in hydrogen, is used as the absorbing material instead of kieselguhr, and the absorbent power of this charcoal is so great that a dynamite can be made containing only 10 per cent. of the cork charcoal and 90 per cent. of the nitro-glycerin, which is retained with such power by the absorbent nature of the inert material that it can be kept for years under water without losing its nitro-glycerin, whilst the high

percentage of explosive gives it a greater intensity of action than is the case with the kieselguhr dynamite.

This preparation is called carbo-dynamite, and the inventor claims that it can be made absolutely uninflammable by the incorporation with it of one-fourth its weight of water, which can easily be kneaded into it, and that in this state it can still be exploded by the use of a sufficiently powerful detonator.

Dynamite No. 2 consists of nitro-glycerin absorbed by a mixture of potassium nitrate and charcoal, the whole being made homogeneous by the addition of 1 per cent. of solid paraffin or ozokerit.

Lithofracteur is composed of nitro-glycerin mixed with an equal weight of a mixture of sawdust, kieselguhr, and barium nitrate, and generally also contains a small trace of sulphur.

Carbonite consists of twenty-five parts of nitro-glycerin mixed with no less than forty parts of wood meal, and about thirty-four parts of sodium or potassium nitrate, and 1 per cent. of sulphur.

All these mixtures, unless properly protected, are liable to the great drawback of occasionally exuding nitro-glycerin, especially if water be present, and then they become highly dangerous to use, whilst another serious drawback is their liability to freeze, which will take place by continued exposure to a temperature of 4° C., or even slightly higher.

Blasting Gelatine.—The other class of dynamite explosives, namely, nitro-glycerin absorbed by an explosive agent, was invented by Mr A. Nobel, who discovered that nitrated cotton would dissolve in nitro-glycerin with the formation of a solid product. In practice, ninety-three parts of nitro-glycerin are heated in a copper water bath to about 45° C., and seven parts of nitrated cotton—a mixture of mono- and di-nitro-cellulose—stirred in gradually. As the cotton dissolves the mixture gelatinises, and on cooling solidifies.

This substance, called "blasting gelatine," is semi-transparent, of specific gravity 1·5 to 1·6, and is not altered by submergence in water. It freezes at 40° C., but, unlike kieselguhr dynamite, it is very easily exploded in this state by shock. A bullet *may* be fired through a heap of unfrozen cartridges of blasting gelatine without any explosion, whilst similarly fired through frozen cartridges it never fails in exploding them.

Gelatine Dynamite and Gelignite are prepared by adding potassium nitrate and wood meal to the blasting gelatine in varying proportions.

The addition of 4 per cent. of camphor to the blasting gelatine increases the solidity, and at the same time makes the mixture less sensitive to shock. This preparation is made and sold under the name of camphorated gelatine.

Nitro-magnite, dyna-magnite, forcite, Giant powder, Vulcan powder, Atlas powder, Judson powder, Hercules powder, and Lignin dynamite, are all modifications of the above forms of dynamite and blasting gelatine that have been used here or abroad.

We are now in a position to examine into the requirements which shall be fulfilled by a really good blasting explosive for mining work, which may be tabulated as follows:—

1. Safety in handling.
2. Safety in explosion.
3. Safety after explosion—*i.e.*, that the products of combustion shall be as little deleterious as possible.

The factors which tend to safety in the handling of blasting explosives are that the substances shall not be liable to explosion except by means of a detonator, and must not be liable to ignition by ordinary knocking about, or even by a chance spark, and also must not be liable to freeze.

When we come to examine the explosives in use for blasting purposes, we find that the mining powders are fairly

safe from these points of view, as, although many authorities state that gunpowder can be exploded by a blow, the statement is somewhat misleading. It is perfectly true that if the powder be placed upon an iron anvil and then be struck so violent a blow with an iron hammer that the force of the impact raises the temperature to the igniting point of the powder, you then have the portion so heated decomposing, but any one who has tried the experiment will realise that an accident from such a cause is practically impossible.

Experiments have been made which show that the power of bringing about such results depends a good deal upon the materials upon which the blow is struck, a blow from iron upon iron being most liable to give rise to ignition, whilst a blow from copper upon bronze is least likely; the intermediate metals show the tendency in decreasing order:— Iron upon iron, iron and brass, brass and brass, lead and lead, lead and wood, copper and copper, copper and bronze.

Such ignition cannot, however, in most cases be in any way confounded with detonation. If a thin sheet of gun-cotton be placed upon an iron anvil and be then struck a heavy blow with an iron hammer, the portion of gun-cotton struck is *ignited*, but does not communicate its combustion to the surrounding mass; whereas I think it would be found impossible to *detonate* any portion of the sheet of gun-cotton without instantaneous decomposition of the whole of the mass, but we also know perfectly well that there are many substances, such as nitro-glycerin and its derivatives, which would be detonated by a simple blow in this way, and it cannot be too strongly insisted upon that there is a very marked difference between the two phenomena.

If a 60 lb. weight, pointed at one end, be so arranged as to slide freely in a frame in such a way that its point will impinge on a rigid steel disc, it will be found that when falling from a height of from six to twelve inches, it will invariably detonate such substances as dynamite, gelignite, blasting gelatine, and carbonite. With gun-cotton or gun-cotton powders, the weight dropped from a height of two

or three feet will give a sharp explosion of the portion immediately struck, and occasionally portions of the surrounding material may be ignited, but not exploded.

If the same experiment be tried with such Sprengel explosives as roburite, it will be found that a drop varying from one foot to forty feet fails to detonate it, the only effect being that the small portion receiving the impact of the blow is decomposed, but no flame is seen, and there is no communication of the decomposition to the surrounding materials.

If a small quantity of dynamite be placed in such a position as to receive the impact of the blow, and be then surrounded with roburite, the whole of the mass is detonated, showing that true detonation, capable of being communicated to the surrounding material, has been set up; but when the roburite is so placed as to receive the full force of the blow, no explosion of the dynamite takes place, showing clearly that there has been no detonation.

The fact that such compounds as roburite or ammonite, containing ammonium nitrate as the oxidising material, can be so decomposed, is at once explained by the fact that decomposition of ammonium nitrate alone can be brought about when the heat developed by the blow reaches the same temperature at which dry powdered ammonium nitrate is broken up.

Further experiments in this direction have shown that it is perfectly impossible to detonate, or completely explode, cartridges of the ammonium nitrate explosives except by a charge of nitro-glycerin or its derivatives, or by mercuric fulminate. We may, therefore, take it that such explosives as ordinary blasting powder and the so-called Sprengel explosives, of which roburite may be taken as the type, are free from any chances of explosion by percussion, whilst nitro-glycerin and the blasting explosives obtained from its admixture with other substances are liable to this, and are rendered still more unsafe by the tendency of the nitro-glycerin to freeze at an easily reached temperature, the

necessity of thawing them before detonation being a grave source of danger.

As regards ease of inflaming by increase of temperature or by accidental spark, it is found that the nitro-compounds all have low points of ignition ranging from a few degrees below 200° C., whilst gunpowder ignites at a temperature which is generally given as from 295° to 316° C., and certainly could not inflame below 250° C., which is the ignition point of sulphur. It is uncertain whether the temperature of ignition of such safety explosives as roburite has ever been ascertained, but the fact that when a mixture of gunpowder and roburite is ignited, the roburite is scattered without ignition, certainly points to its being high.

In coming to the question of safety during explosion, we have to consider a subject of far wider and graver import, as it is upon this that the safety of the lives of thousands of miners employed in the country in winning coal from the seams largely depends.

From the time of Sir Humphrey Davy's classical researches in the early part of this century on colliery explosions, the subject has always attracted an enormous amount of attention, and has enlisted a large amount of public sympathy, and yet even at the present time there are many factors which are not fully provided against.

Until quite recently, explosions in mines were always attributed to the accidental ignition of mixtures of air and methane, to which the name of "firedamp" is given, and undoubtedly this cause is the prime factor in this class of disaster, and the introduction of such precautions as safety lamps at once brought about a considerable reduction in the number of explosions taking place. Many disasters, however, still continued to occur under apparently mysterious circumstances, the conditions being such that any large proportion of methane in the air of the mine appeared practically impossible. Investigations of such explosions showed that coal dust, in a dry and finely powdered condition, had generally been present in the mine at the time

of the explosion, and the coked residue of this dust was found afterwards on the surfaces exposed to the explosive wave. Years of experimental investigation by scientific men of the greatest ability proved the fact that air containing so small a proportion of methane as to be itself perfectly non-explosive, becomes a good explosive when holding dry and finely divided coal dust in suspension; and within the last few years explosions have taken place in mines, which have always been celebrated for their freedom from any trace of methane. Further experiments have been made by Mr H. Hall and Mr W. Galloway, who have shown that the violent ignition of dust-laden air is possible by a blown-out shot, even if the air in the mine be free from any trace of methane.

The safety of such Sprengel explosives as roburite in handling and in use is, to a large extent, dependent upon the fact, that, when the mixture of ammonium nitrate and the nitrated organic body is ignited by ordinary flame, the ammonium nitrate requires a large amount of heat for its decomposition, in order to render the oxygen which it contains available for the combustion of the carbon and hydrogen in the organic body. The temperature of the burning substance is not sufficiently high to propagate this action throughout the mass, the result being that to cause continued combustion you must have a continuous supply of heat, or the flame first started simply dies out.

The effect of this is that, in handling, such bodies are practically non-inflammable, and when they are made to explode by detonation, a more than usually powerful detonator has to be employed, so that, although with the nitro-glycerin mixtures a charge of seven grains of mercuric fulminate is amply sufficient to produce detonation, such a body as roburite needs at least fifteen grains. Moreover, when detonation has been produced, the amount of heat absorbed by the decomposition of the ammonium nitrate causes a very considerably lower temperature of explosion, as is shown in the following table, which contrasts the

temperatures developed by the more prominent explosives :—

	Degrees C.
Blasting gelatine	3,220
Nitro-glycerin	3,170
Dynamite	2,940
Gun-cotton	2,650
Tonite	2,648
Picric acid	2,620
Roburite	2,100

The temperature at which mixtures of methane and air ignite is between 650° and 700° C., and although the temperatures of explosion are so enormously high, they only occasionally ignite an inflammable mixture of the gases, this being due to the fact that in order to ignite firedamp, not only must the temperature of ignition be reached, but it must be sustained for several seconds before the gases inflame, and as the explosion by detonation is instantaneous, ignition does not occur ; if, however, some of the charge burns instead of detonating, the gaseous mixture is fired.

Bichel has recently shown that the important factors in bringing about explosion in a gaseous mixture are (*a*) the length of the flame, (*b*) its duration, (*c*) its temperature. The ratio of the duration of the flame to the rate of detonation (called the "after-flame ratio") is an excellent indication of the relative safety of blasting explosives ; where this is high, as in blasting gelatine, the explosion is extremely likely to cause ignition of firedamp, whilst when it is low, as in the usual "safety" explosives, the risk is reduced to a minimum.

With mixtures of carbon monoxide and air, however, if coal dust be present, ignition takes place directly the required temperature is reached.

The last requirement of a perfect blasting powder is that it should emit no fumes which are noxious to health.

The true noxious vapours are those which have a definite toxic action upon the system, and of these practically the

only one evolved during explosion under pressure, or by detonation, is carbon monoxide; a reference to the table giving the products of combustion of various blasting explosives will show which are the best in this respect.

Fulminates.—Nearly all explosives are now fired by means of a cap or detonator, which generally consists of a small copper cylinder charged with one of the class of bodies called fulminates, or mixtures in which they play an important part. The fulminate generally used is mercuric

PRODUCTS OF COMBUSTION OF BLASTING EXPLOSIVES.

Powder.	Carbon dioxide.	Combustibles.	
		Carbon monoxide.	Hydrogen and Marsh gas.
Gunpowder	50·6	10·5	3·1
Blasting powder	30·1	33·7	7·9
Sprengel explosives—			
Roburite	32	Nil.	Nil.
Ammonite	33	Nil.	Nil.
Nitro-glycerin explosives—			
Nitro-glycerin	63	Nil.	Nil.
Gelignite	25	7	Nil.
Carbonite	19	15	26
Blasting powder	36·5	32·5	8·6
Nitro-cotton explosive—			
Tonite	30	8	Nil.

fulminate ($HgC_2N_2O_2$), made by acting upon mercury with nitric acid and alcohol. It may be made on a small scale

by dissolving 3 grams of mercury in 36 grams (27·7 c.c.) of nitric acid having a specific gravity of 1·36. As soon as it is all dissolved, and whilst the solution is still yellow from presence of nitrous fumes, take 34·5 grams (43 c.c.) of 90 per cent. alcohol, and add one-half; a violent action takes place, and when this ceases, the second portion of alcohol is added, and the mixture allowed to stand, when the mercuric fulminate crystallises out in small needle-shaped crystals, which have a greyish colour from the presence of a trace of free mercury.

When made on a large scale the operation is a little different, the mercury being dissolved in the nitric acid and the solution allowed to cool; the alcohol is then added in one operation, which is carried out in an open shed in a large retort, and the escaping fumes condensed and utilised. The fulminate so obtained is well washed with distilled or rain water until free from all acid, and is stored whilst still containing 20 per cent. of moisture.

The changes taking place during the formation of mercuric fulminate are not very thoroughly understood, but the general action may be looked upon as resulting in the solution of mercury in nitric acid with the production of mercuric nitrate and nitrous acid, these products further reacting with the alcohol :—

Mercuric nitrate		Nitrous acid		Alcohol		Mercuric fulminate
$Hg(NO_3)_2$	+	$2(HNO_2)$	+	C_2H_6O	=	$HgC_2N_2O_2$
		Water		Nitric acid.		
	+	$3(H_2O)$	+	$2(HNO_3)$.		

Mercuric fulminate is very heavy, having a specific gravity of 4·4, and it is easily detonated either by a blow, by friction, by touching it with a wire heated to 190° C., by an electric spark, or by contact with strong sulphuric or nitric acids, when it is instantaneously decomposed into :—

Mercuric fulminate		Mercury		Carbon monoxide		Nitrogen.
$HgC_2N_2O_2$	=	Hg	+	$2(CO)$	+	N_2

with a sharp flash and evolution of greyish fumes of mercury. The rapidity of its explosion is so great that, when exploded in contact with any easily decomposable body, the vibration which it sets up travels through the mass with the rapidity of sound and affects the whole almost instantaneously, giving rise in many cases to the most rapid form of explosion, known as detonation. Berthelot has shown that even stable gases, such as nitrogen dioxide, acetylene, and cyanogen, can be decomposed into their elementary constituents by the detonation of mercuric fulminate.

The high specific gravity of mercuric fulminate (4·4) and the rapidity of its explosion make it the best detonating medium we possess, besides which, volume for volume, it is the most powerful of the explosives.

One gram of the fulminate yields 235 cubic centimetres of gas, or 1,030 times its own volume of gas measured at normal temperature and pressure, whilst the 403 units of heat evolved expand this volume enormously, and it has been calculated that the pressure generated at the moment of explosion is over 6,000 atmospheres.

If a small train of mercuric fulminate is laid on a metal plate and some gunpowder is placed on it and the fulminate fired, the powder will be scattered but not ignited, the explosion being too rapid to communicate itself to the powder; if, however, a little finely powdered potassium chlorate is mixed with the fulminate, the flame will be increased and the powder ignited. This can be explained when it is considered that carbon monoxide, which is evolved by the decomposition of the fulminate, is oxidised to carbon dioxide by the oxygen from the chlorate, thus increasing the flame and the temperature.

Advantage is taken of this fact in the preparation of composition for percussion caps, in which the fulminate is mixed with potassium chlorate, and sometimes with antimony sulphide, glass powder being often added to increase the friction and so make the cap more sensitive to percussion. A small quantity of the mixture having been put into the

cap or detonator, a drop of shellac dissolved in spirit is added, which causes the mixture to adhere to the metal and also gives it a waterproof coating.

Nobel's detonators contain a mixture of 70 per cent. fulminate and 30 per cent. potassium chlorate; and fulminate is also employed in varying charges in all the Service fuses.

The detonator is ignited either by the insertion of a piece of slow burning fuse, or by electricity.

In the Service in firing by electricity low tension fuses are used. These consist of a small primer containing a few grains of powdered gun-cotton mixed with a little gunpowder which is in touch with a small bridge of fine platinum or steel wire connected with the ends of two wires communicating with the poles of a battery. On passing the current the wire fuses and ignites the priming mixture, which causes the ignition of the mercuric fulminate, and this in turn brings about the detonation of the explosive. For blasting purposes high tension fuses are generally employed when firing by electricity. In this case a priming mixture, composed of an intimate mixture of native antimony sulphide, copper sulphide and potassium chlorate, is ignited by means of a spark passing between the terminals of two wires connected with a magneto machine. In this case the mixture is confined in a small paper case which is inserted into the detonator.

Silver fulminate ($Ag_2C_2N_2O_2$) is made in the same way as mercuric fulminate, silver being used instead of mercury; it is, however, far more sensitive and dangerous than the mercuric salt, and is only used in small quantities for "pull" and "throw down crackers."

CHAPTER XX.

Sulphur and Sulphur Compounds.

Sulphur — Occurrence in Nature — Preparation and properties— Sulphuretted hydrogen—Preparation and properties—Combustion of sulphuretted hydrogen—Use of the compound in analysis—Preparation and properties of sulphur dioxide—Action on vegetation and life— Sulphurous acid and the sulphites—Oxidation of sulphur dioxide— Sulphur trioxide—Sulphuric acid — Manufacture of oil of vitriol— Chamber crystals—Chamber acid—Concentration of sulphuric acid— Properties and composition of sulphuric acid—The sulphates.

SULPHUR is one of the few elements found uncombined in Nature, large quantities occurring as deposits in most volcanic districts, and it was from beds of this native sulphur found in Sicily that for many years the sulphur was obtained for the sulphuric acid and gunpowder factories in this country; but the imposition of a heavy tax upon the export caused manufacturers to seek other sources of supply. At the present time most of the sulphur used in this country is obtained from iron pyrites, a double sulphide of iron and copper, which is obtained in considerable quantities in various parts of the world, and from which sulphur can be obtained by a process of distillation. The sulphides of the metals are as a rule their most common ores, and besides the enormous amount of sulphur combined as sulphide, it is also extensively distributed in combination with metals and oxygen as sulphates, such as gypsum (calcium sulphate), heavy spar (barium sulphate), Epsom salts (magnesium sulphate), etc.

To obtain sulphur from the mixture of marl, limestone or gypsum with which it is found native, a heap is generally made and some of the sulphur kindled, which by its combustion melts the remainder, and on choking out the fire the melted sulphur runs from the bottom of the heap; or the

crude mixture may be heated in iron vessels by superheated steam which melts the sulphur, causing it to flow away from the impurities with which it was mixed, and it is then run into wooden moulds.

When iron pyrites is heated out of contact with air, it gives off one-third of its sulphur, a reaction which may be represented by :

Iron pyrites		Triferric tetra-sulphide		Sulphur.
$3FeS_2$	=	Fe_3S_4	+	S_2.

The purification of the crude sulphur is effected by distillation, a type of plant commonly used for the purpose being shown in Fig 47.

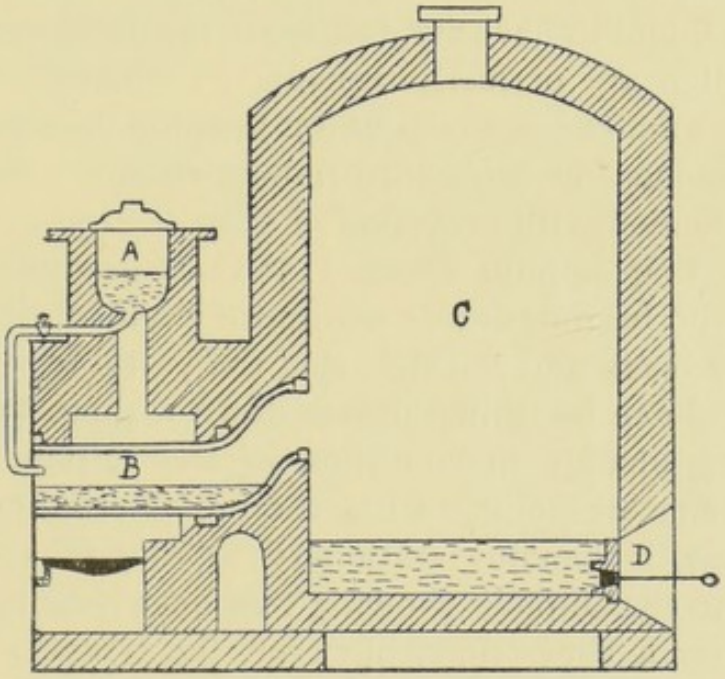


Fig. 47.

The crude material is melted in the pot (A) by the waste heat from the fireplace below, and suitable quantities can be run from time to time into the retort (B), from which it distills as vapour into the large condensation chamber (C). The first quantities of vapour passing into a cool chamber condense in a fine crystalline form (*flowers of sulphur*), but as the chamber becomes hot the whole of the sulphur passing into it condenses as a liquid which is run off by means of

a suitable plug (D) into cylindrical wooden moulds, forming *roll sulphur.*

Sulphur is remarkable for the number of different forms in which it can exist and the changes which it undergoes when heated.

Modifications of Sulphur.—At very low temperatures sulphur is nearly white, but at ordinary temperatures it has a straw yellow colour; when heated to 115° C. it melts to an amber coloured liquid, which is as fluid as water, and on allowing this to cool a crust forms on the outside of the mass. If holes are broken in this crust, and the still fluid portion is poured out from the interior, the remaining sulphur is found to have crystallised in needle shaped oblique prisms which are perfectly transparent when freshly made, but which soon become opaque on keeping, due to the mass having become converted into minute rhombic octahedra, a change attended with evolution of heat.

On heating sulphur above 115° C., it gradually darkens in colour and becomes more and more viscid, until at 180° C., it is nearly black and so thick that the vessel in which it has been melted can be turned upside down without any running out. Some change in condition of the sulphur evidently occurs about this point, as, if a thermometer is immersed in the sulphur, it remains stationary although heat is being poured into the sulphur, showing that heat is being rendered latent; after a short time, however, the temperature again begins to rise, the viscid sulphur becoming again more and more liquid, until at 250° C. it can again be freely poured out, although it is not so liquid as at 115° C. If sulphur liquefied at 260° C. is poured in a thin stream into a large vessel of water, it forms an elastic semi-transparent mass, very much resembling indiarubber; but this plastic form is not permanent, and on keeping gradually becomes yellow and brittle, being reconverted to the crystalline condition, and if the mass be broken up and examined under a magnifying glass the particles will be seen to be octahedral in form.

This change from the plastic to the crystalline form is attended with evolution of the heat rendered latent at 180° C., and the two forms of sulphur exhibit such wide differences in their behaviour that they are looked upon as allotropic modifications of the element. Plastic sulphur is only partly soluble in carbon disulphide, but both the crystalline varieties readily dissolve, and if the solvent is allowed to spontaneously evaporate, the sulphur is left in octahedral crystals of the same form as that in which it is found native. The crystalline sulphur soluble in carbon disulphide has been shown to be electro-negative, whilst the insoluble forms of sulphur are electro-positive. On continuing to heat sulphur above 260°, no further change takes place until 444° C. is reached, when it boils and is converted into vapour.

Three chief forms of sulphur are described—the octahedral, the prismatic, and the plastic or "*amorphous*" (*i.e.*, without crystalline form), while the fact that it forms two distinct kinds of crystals causes it to be classed with those substances which are called "*dimorphous*" (having two crystalline forms). Sulphur has an atomic weight of 32. The existence of various forms of sulphur may to a certain extent be explained by the presence of a varying number of atoms in the molecule, and this idea is supported by the density of sulphur vapour, which at 500° C. is 96, but steadily diminishes with increase of temperature above 700° C. and becomes constant at 1,000° C. when it is 32. At 500° C. therefore the molecule of sulphur must contain six atoms instead of two, and it is quite possible that at lower temperatures a further increase in the number of atoms in the molecule may take place.

Sulphur in its combining power very much resembles oxygen, and it will enter directly into combination with all the non-metals, with the exception of nitrogen, and with most of the metals.

Compounds of Sulphur.

Hydrogen Sulphide or Sulphuretted Hydrogen (H_2S) was discovered by Scheele in 1777, and exists free in Nature in the gases evolved from volcanoes, in certain mineral waters, such as those of Harrogate, and is formed when organic substances containing sulphur undergo putrefactive decay, hence its presence in sewer gas, stale eggs, etc.

Sulphuretted hydrogen can be made by the direct combination of its constituents, the gas being produced when hydrogen is passed over or through boiling sulphur; the method usually employed for its preparation, however, consists of decomposing a metallic sulphide with an acid.

When ferrous sulphide (made by fusing together sulphur and iron) is acted upon by dilute sulphuric or hydrochloric acid, the gas is evolved in abundance, with formation of a sulphate or chloride of the metal, the action taking place in the cold:

Ferrous sulphide		Sulphuric acid		Ferrous sulphate		Hydrogen sulphide.
FeS	+	H_2SO_4	=	$FeSO_4$	+	H_2S.

This method is usually adopted in making the gas for laboratory use; but since the iron sulphide invariably contains particles of metallic iron, hydrogen always contaminates the gas. Pure sulphuretted hydrogen can be obtained by heating together antimony sulphide and hydrochloric acid.

Antimony sulphide		Hydrochloric acid		Antimony chloride		Hydrogen sulphide.
Sb_2S_3	+	$6(HCl)$	=	$2(SbCl_3)$	+	$3(H_2S)$.

Properties.—Sulphuretted hydrogen is a colourless gas, having a sweet taste and the odour of rotten eggs, and when present in the air in any quantity is very poisonous. Under a pressure of 17 atmospheres, or at $-74°$ C., it may be condensed to a colourless liquid which freezes at $-86°$ C. The gas can be decomposed by heat and is freely soluble in water, which dissolves 4·37 times its bulk of the gas at 0° C. It has a feeble acid reaction, and burns in oxygen or air. If the

supply of oxygen is abundant, the sulphuretted hydrogen burns forming water and sulphur dioxide :—

Sulphuretted hydrogen		Air		Water		Sulphur dioxide		Nitrogen.
H_2S	+	$3(N_4+O)$	=	H_2O	+	SO_2	+	$6N_2$.

If, however, the supply of air is small and the quantity of oxygen therefore limited, the hydrogen burns forming water, and sulphur is deposited.

The gas is decomposed by chlorine, bromine or iodine, with deposition of sulphur :—

Sulphuretted hydrogen		Chlorine		Hydrochloric acid		Sulphur.
$2(H_2S)$	+	$2(Cl_2)$	=	$4(HCl)$	+	S_2

It is also decomposed by nitric and sulphurous acids.

The tarnishing of silver in the air of towns is due to the traces of sulphuretted hydrogen present, for which silver has a great affinity, combining with it to form black silver sulphide.

The action of sulphuretted hydrogen on solutions of metallic salts is of great value in analysis, and it is for this purpose that the gas is chiefly used. By its aid the metals are separated into three main groups:—1. Metals, the sulphides of which are insoluble in dilute hydrochloric acid ; 2. Metals which form sulphides soluble in dilute hydrochloric acid, but insoluble in neutral or alkaline solutions ; and 3. Metals which form sulphides soluble in water.

Composition.—The composition of sulphuretted hydrogen can be ascertained by heating metallic tin in a known volume of the gas, when the tin combines with the sulphur forming a solid sulphide, whilst the liberated hydrogen occupies the same volume as the gas taken :—

Sulphuretted hydrogen 2 vols.		Tin		Stannous sulphide		Hydrogen 2 vols.
SH_2	+	Sn	=	SnS	+	H_2

therefore, like steam, sulphuretted hydrogen contains its own volume of hydrogen.

The molecular weight of the gas is 34 and its density 17.

An aqueous solution of sulphuretted hydrogen has the same chemical properties as the gas itself, and in many cases is a very convenient solution for use in analysis, but it must be remembered that a solution of the gas rapidly oxidises, the oxygen originally dissolved in the water and absorbed from the air, combining with the hydrogen, whilst sulphur is precipitated.

Sulphuretted hydrogen can at once be detected by its fœtid odour, and by its turning a piece of paper moistened with lead acetate solution black, owing to the formation of black lead sulphide.

The Oxides of Sulphur.

Sulphur combines with oxygen in two proportions to form sulphur dioxide (SO_2) and sulphur trioxide (SO_3).

Sulphur Dioxide, sulphurous anhydride, or sulphurous acid as it is sometimes called, has been known from the earliest times, Homer and Pliny mentioning the irritating nature of the fumes given off by burning sulphur, whilst its properties were investigated by Stahl and by Priestley in 1774, the latter demonstrating its true composition by the combustion of sulphur in oxygen. Like sulphuretted hydrogen, it is found free in the gases issuing from volcanoes, and is always formed when sulphur or sulphur compounds are burnt in air or oxygen :—

Sulphur		Oxygen		Sulphur dioxide.
S_2	+	$2O_2$	=	$2SO_2$.

Preparation.—When the gas is required pure, it is prepared by heating a metal such as mercury or copper with strong sulphuric acid, when :—

Copper		Sulphuric acid		Copper sulphate		Sulphur dioxide		Water.
Cu	+	$2(H_2SO_4)$	=	$CuSO_4$	+	SO_2	+	$2(H_2O)$.

In the same way when strong sulphuric acid is heated with carbon or organic matter, sulphur dioxide is evolved, but in this case carbon dioxide is formed at the same time.

Carbon		Sulphuric acid		Carbon dioxide		Sulphur dioxide		Water.
C	+	$2(H_2SO_4)$	=	CO_2	+	$2(SO_2)$	+	$2(H_2O)$.

Properties.—It is a colourless gas, having a strong, pungent odour and an acid taste and reaction; it is freely soluble in water and in alcohol, and can be reduced to a liquid by a pressure of three atmospheres, or by a temperature of —18° C. and can be solidified at —76° C. Liquid sulphur dioxide will dissolve phosphorus, sulphur and iodine. Sulphur dioxide has a molecular weight of 64 and a density of 32.

Nearly all classes of coal contain small traces of sulphur, which, during combustion, is converted into sulphur dioxide and escapes into the air, and when present in even small traces, acts mostly injuriously upon vegetable life, one part in 10,000 of air being fatal to plants, whilst four parts in 10,000 render air irrespirable.

The gas does not burn or support combustion; indeed, its power of extinguishing fire has led to its use in several of the so-called "grenades" and "fire-extinguishers," and a handful of sulphur thrown on the fire in the grate is one of the oldest and best known remedies for a chimney on fire.

Moist sulphur dioxide has a strongly acid reaction, and its solution in water may be looked upon as a sulphurous acid (H_2SO_3), as although this compound has not been isolated, yet when the solution is acted upon by bases, hydrogen is replaced by the metal of the base, and the class of salts called sulphites is obtained.

Sulphurous acid		Sodium oxide		Sodium sulphite		Water.
H_2SO_3	+	Na_2O	=	Na_2SO_3	+	H_2O.

Sulphurous acid when left exposed to air gradually takes up oxygen and becomes sulphuric acid (H_2SO_4), and this tendency to undergo oxidation renders sulphurous acid a powerful reducing agent.

Bleaching.—Moist sulphur dioxide or sulphurous acid is also a powerful bleaching agent, but does not so completely destroy the colouring matter as in the case of bleaching by chlorine, for the colour may in many cases be restored by acting upon the substance with a stronger acid or an alkali, an example of this being the turning yellow of blankets, the

wool of which has been bleached with sulphurous acid. It is largely used for bleaching straw, wool, and silk, and is also employed as a deodoriser and as an antiseptic to prevent fermentation and decay.

Sulphur Trioxide.—Under ordinary conditions sulphur dioxide will not directly combine with more oxygen, but if a mixture of sulphur dioxide and oxygen be passed over heated platinum or platinised asbestos, the strong surface action exercised by the platinum causes combination to take place, and dense white fumes of sulphur trioxide (SO_3) are formed. The trioxide is more conveniently prepared by warming Nordhausen sulphuric acid, a fuming acid made by distilling ferrous sulphate, and which consists of sulphur trioxide dissolved in sulphuric acid. Under the influence of heat the sulphur trioxide is driven off, and may be condensed in a cooled receiver.

Nordhausen acid		Sulphuric acid		Sulphur trioxide.
$H_2S_2O_7$	=	H_2SO_4	+	SO_3.

Sulphuric trioxide is a white silky crystalline body, having a specific gravity of 1·95 and melting at temperatures varying between 15° C. and 32° C., according to its crystalline condition; when exposed to air it yields dense white fumes, and absorbing moisture, rapidly becomes liquid. At a high temperature it is decomposed into oxygen and sulphur dioxide. When free from moisture it is not acid to dry litmus, but becomes acid immediately on absorbing moisture. On bringing it in contact with water it combines with it energetically, giving off great heat and hissing as if red hot iron had been plunged into the water, instantly forming sulphuric acid (H_2SO_4), a method now largely employed for the commercial production of sulphuric acid.

Sulphur trioxide		Water		Sulphuric acid.
SO_3	+	H_2O	=	H_2SO_4.

Sulphuric acid, hydrogen sulphate or oil of vitriol (H_2SO_4) is the most important of the acids.

It is used to an enormous extent in the arts and manufactures; indeed, so many industries are dependent upon it

that Liebig has said with considerable truth that "the civilisation of a country may be roughly gauged by the amount of sulphuric acid manufactured in it."

The present method of manufacturing sulphuric acid may be said to date from 1786, when Dr Roebuck made the acid by burning sulphur with saltpetre in leaden vessels and condensing the fumes in water.

The principle of the method at present employed is the same as that of Roebuck's process, and is that whilst sulphur dioxide is not able, even in presence of water, to rapidly absorb oxygen from the air, it can readily take it from some of the oxides of nitrogen, which, in turn, can again take oxygen from the air, and may in this way be made the medium for rapidly oxidising sulphur dioxide in the presence of water, with formation of sulphuric acid. The manufacture of sulphuric acid therefore involves four distinct processes: (*a*) the generation of sulphur dioxide in large quantities, (*b*) the constant production of small quantities of oxides of nitrogen, (*c*) the generation of steam, (*d*) provision of large chambers in which these various gases can interact with the formation of sulphuric acid.

The usual arrangement in a modern sulphuric acid works is illustrated in a diagrammatic manner in Fig. 48. Iron pyrites is thrown into heated chambers (A) to which there is easy access of air, which maintains the combustion of the sulphur present in the pyrites to sulphur dioxide. This gas, together with air and excess of nitrogen, passes through the tower (E), (to be described later) along the large main (*e*), near the bottom of which another smaller pipe (*b*) leads in the gases from the nitre pots (B). These pots are situated over a smaller series of pyrites burners, the hot gases from which circulating around them generate nitric acid from a mixture of nitre (sodium nitrate) and sulphuric acid.

The sulphur dioxide and nitric acid interact with the production of sulphuric acid and nitrogen tetroxide.

Sulphur dioxide		Nitric acid		Sulphuric acid		Nitrogen tetroxide.
SO_2	+	$2HNO_3$	=	H_2SO_4	+	$2NO_2$.

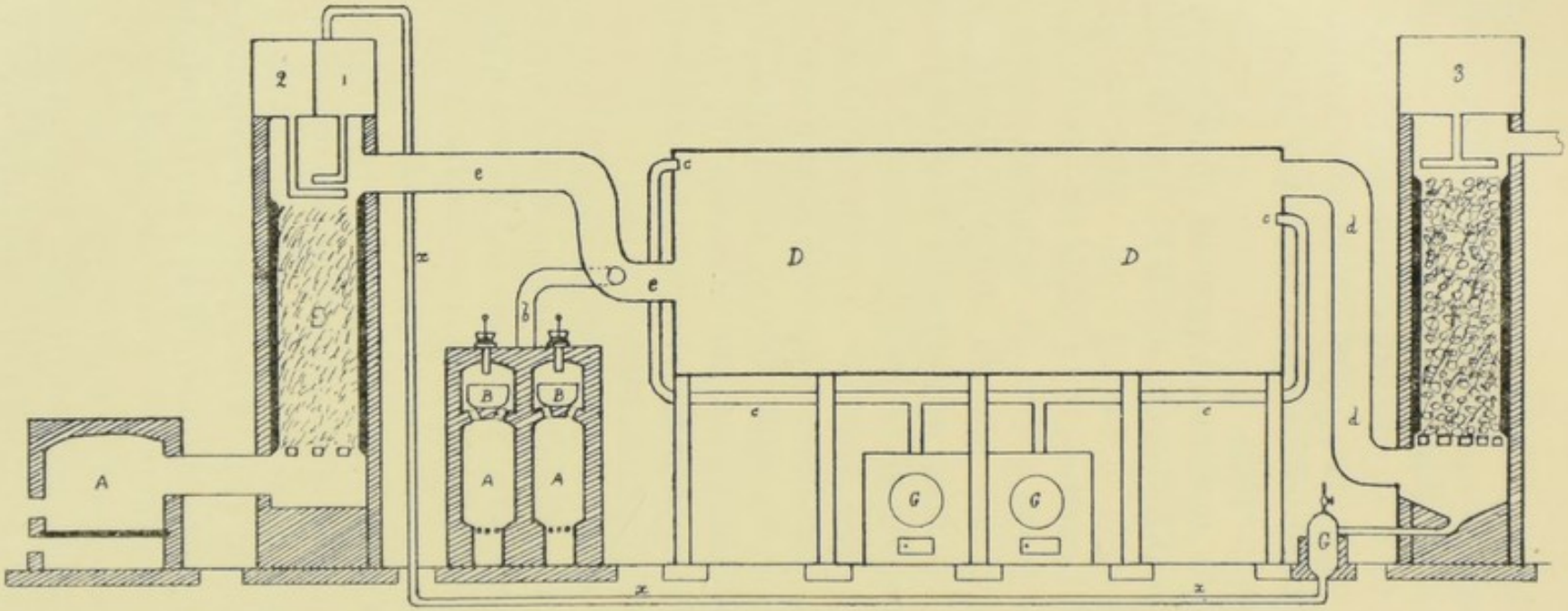


Fig. 48.

DIAGRAM OF SULPHURIC ACID PLANT.

A A. *Pyrites burners.*
B B. *Nitre pots.*
C C. *Boilers.*
D D. *Lead chamber.*
E. *Glover's Tower.*
F. *Gay Lussac Tower.*
x x. Pipe conveying acid to Tank 1.
c c. Steam Pipes.
2. *Chamber acid Tank.*

A mixture of sulphur dioxide, oxides of nitrogen, oxygen and nitrogen (derived from the air) is sent into the large lead lined chamber (D) where it meets with a plentiful supply of steam generated in the boilers (C) and delivered by small pipes (*c c*). In most modern works three of these large lead lined chambers are used, the gases passing through each in succession, steam being blown into each chamber. Here the gases interact with the formation of sulphuric acid, which condenses on the walls of the chamber. This acid is known as "*chamber acid*," and contains from 62 to 70 per cent. of sulphuric acid.

The gases escaping from the chamber by the flue (*d*) should be free from sulphur dioxide, but will contain considerable quantities of oxides of nitrogen which have been added in excess of the amount required, and to absorb these the escaping gases are passed upwards through a brick tower, called the "*Gay Lussac*" tower (F), which is filled with coke, and down this cold strong sulphuric acid flows from the tank 3. The nitrous fumes are absorbed by the acid, producing nitro-sulphonic acid.

The nitrogen oxides absorbed in this way can be recovered by causing the hot gases from the pyrites burner to act upon the acid, this being accomplished in the "*Glovers*" or "*denitrating*" tower (E), already referred to. This is filled with flints, and the acid charged with nitrogen oxides is forced by air pressure in (G) through the pipe (*x x*) into a tank (1) situated at the top of the tower. The second tank (2) contains "chamber" acid, and the mixed acids flowing down over the flints meet the hot ascending gas current, the acid from the Gay Lussac tower becoming denitrated, whilst at the same time the weak chamber acid is considerably strengthened by evaporation of water. Such an arrangement permits of very economical working.

Chemical Reactions during the Manufacture.—It has already been shown that the gases entering the chamber are a mixture of sulphur dioxide, nitrogen tetroxide, oxygen and

nitrogen (from the air), and here they meet with an excess of steam. The net result is the formation of sulphuric acid, but intermediate products are undoubtedly formed, and on this point divergent views are held. Should a deficiency of steam be present, a compound nitro-sulphonic acid—which may be regarded as sulphuric acid, $SO_2{<}^{OH}_{OH}$, in which one OH group has been replaced by NO_2, giving $SO_2{<}^{OH}_{NO_2}$ separates as white crystals known as "*Chamber crystals.*" The formation of this body must therefore be looked upon as one of the intermediate reactions.

Sulphur dioxide		Nitrogen tetroxide		Steam		Nitro-sulphonic acid		Nitrogen dioxide.
(1) $2SO_2$	+	$3NO_2$	+	H_2O	=	$2SO_2OH.NO_2$	+	NO

When this nitro-sulphonic acid meets with sufficient water, it undergoes decomposition with the formation of sulphuric acid and the liberation of a mixture of nitrogen di- and tetroxides.

Nitro-sulphonic acid		Steam		Sulphuric acid	Nitrogen dioxide		Nitrogen tetroxide.
(2) $2SO_2OH.NO_2$	+	H_2O	=	$2H_2SO_4$	+ NO	+	NO_2.

The nitrogen dioxide formed in accordance with equations (1) and (2) now takes up more oxygen from the air forming nitrogen tetroxide, which reacts again in accordance with equation (1).

Nitrogen dioxide		Oxygen		Nitrogen tetroxide.
(3) NO	+	O	=	NO_2.

The further course of the reactions in the acid chambers may be looked upon as a continual taking up of oxygen from the air by the nitrogen dioxide, and reduction of the nitrogen tetroxide formed by the sulphur dioxide and water, with formation of sulphuric acid and liberation of nitrogen dioxide, which is again ready to perform its function as a carrier of oxygen from the air to the sulphur dioxide and water. The water needed in the reaction is either blown into the chambers in a fine spray or as steam, and condensing, carries down the sulphuric acid to the floor of the chambers.

It is evident that, theoretically, the small amount of oxides of nitrogen first introduced should be able to convert an unlimited amount of sulphur dioxide into sulphuric acid, but in order to supply the oxygen necessary to the reaction, very large quantities of air must be drawn into the chambers, and the residual nitrogen must be removed, and the constant removal of the nitrogen from the chambers carries away a large percentage of the nitrous fumes, and necessitates their constant renewal.

The acid formed in the chambers is not allowed to attain a higher specific gravity than 1·55, as above this point of concentration it would absorb the nitrous fumes. After a preliminary concentration in the denitrating tower, it is run into leaden evaporating pans, and flame and hot air are allowed to play over the surface of the acid, water being evaporated and the specific gravity of the acid raised to 1·71, beyond which it is impossible to concentrate it in leaden vessels, as the hot acid would attack the lead. This strength of acid is sold for many manufacturing purposes and is technically known as B.O.V. (brown oil of vitriol), the colour being due to the presence of small quantities of carbonised organic matter.

Further concentration is effected in glass or platinum stills, until dense fumes of sulphur trioxide begin to escape, when the acid is drawn off and has now a density of 1·84.

Properties.—The concentrated sulphuric acid is a heavy, oily liquid, having no smell and an intensely corrosive action; it boils at 388° C., and at this temperature gives off clouds of white fumes; it has a great affinity for water, and when mixed with it evolves great heat and combines forming definite hydrates. If left exposed to air it rapidly increases in volume from the absorption of water vapour from the air, and this property makes it valuable as a desiccating (drying) agent, as substances containing moisture can be placed over a pan or dish of the acid under an air-tight glass shade, the acid drying the air in the confined space and so promoting

evaporation from the substance to be dried. Similarly, gases which are not acted upon by the acid can be effectually dried by passing them through tubes containing (ignited) pumice stone saturated with the strongest acid, a large surface thus being presented to the passing gases. This affinity for water is also shown in the action of the strong acid on substances of organic origin, containing besides carbon, oxygen and hydrogen in the proportions necessary to form water, when the combination of the hydrogen and oxygen is determined by the presence of the acid, and in many cases the carbon is liberated. The action is well illustrated by pouring an equal volume of the strongest sulphuric acid into a saturated sugar syrup, when the sugar is decomposed, the hydrogen and oxygen extracted as water by the acid, and a spongy mass of carbon occupying many times the bulk of the original liquid is obtained.

Sugar		Sulphuric acid		Dilute acid		Carbon.
$C_{12}H_{22}O_{11}$	+	xH_2SO_4	=	$xH_2SO_4,11(H_2O)$	+	12C.

Action on Fabrics.—Even when very dilute, sulphuric acid has a powerful "rotting" action on all textile fabrics, for if too dilute to do much damage at first, it gradually becomes more concentrated by evaporation of the water, and attacks the fibre. Dropped upon black or dark coloured fabrics, dilute sulphuric acid gives a red stain, which, however, can be removed by neutralising the acid with ammonia, and then sponging with a little water to remove the salt formed. Hydrochloric acid stains can be removed in the same way, but nitric acid gives a yellow stain which cannot be got rid of.

At a red heat the vapour of sulphuric acid is decomposed into steam, sulphur dioxide and oxygen, and this has been proposed as a method for the preparation of oxygen, as it can readily be freed from the sulphur dioxide by washing with an alkaline solution.

With the exception of gold and platinum all the metals are acted upon by boiling concentrated sulphuric acid, a

sulphate of the metal being formed and sulphur dioxide liberated.

Mercury		Sulphuric acid.		Mercuric sulphate		Sulphur dioxide		Water.
Hg	+	$2(H_2SO_4)$	=	$HgSO_4$	+	SO_2	+	$2(H_2O)$.

When unsized paper is soaked in a cold mixture of two volumes of concentrated sulphuric acid and one volume of water, it is converted into a substance called "vegetable parchment," which must be freed from acid by well washing with water; it is a tough translucent substance much used for covering jam pots, and other purposes, for which animal parchment was at one time employed.

The large and important class of salts called sulphates consists of the acid radicle (SO_4) in combination with metals, and inasmuch as on analysis sulphuric acid is found to contain its constituents in the proportion—

Hydrogen 2
Sulphur 32
Oxygen 64

and as the hydrogen can be replaced in two stages by a monad metal forming two classes of salts corresponding to the formulæ:

$NaHSO_4$ (Sodium hydrogen sulphate),
Na_2SO_4 (Sodium sulphate),

it is evident that the formula for sulphuric acid will be H_2SO_4.

When 98 parts by weight of sulphuric acid are converted into vapour, the vapour is found to occupy four volumes instead of two, but this is due to the dissociation (temporary decomposition) of the molecule into water vapour and sulphur trioxide.

Sulphuric acid		Water vapour		Sulphur trioxide.
H_2SO_4	=	H_2O	+	SO_3
2 vols.		2 vols.		2 vols.

Sulphuric acid and its salts, when in solution, may be recog-

nised by their giving a white precipitate with soluble barium salts; this precipitate is barium sulphate, which is practically insoluble in all acids.

Sulphur forms many other compounds of great scientific and industrial importance, but which do not come within the scope of the present work.

CHAPTER XXI.

THE HALOGENS

Chlorine—Preparation of the gas—Deacon's process—Properties of chlorine—Bleaching action dependent on moisture—Hydrochloric acid gas—Preparation and properties—Effect of hydrochloric acid gas on vegetation—Chlorides—Chlorine monoxide—Hypochlorous acid—Bleaching powder—Hypochlorites and chlorates—Potassium chlorate—Percussion caps—Friction tubes—Coloured fires—Bromine and iodine—Preparation and properties—Bromides and iodides—Fluorine—Isolation of fluorine—Fluor-spar—Hydrofluoric acid—Etching on glass—Gradations of chemical and physical properties in the halogens.

CHLORINE.

CHLORINE gas was discovered in 1774 by Scheele, and its elementary character was proved by Thénard and Davy in 1809-1810.

It is never found free in Nature, but abundantly in combination with sodium and other metals, and is found in all animal secretions.

Preparation.—The gas is most easily prepared by heating together a mixture of black oxide of manganese (the mineral pyrolusite) and strong hydrochloric acid, the reaction taking place in two stages—

Pyrolusite Hydrochloric acid Manganese tetrachloride Water.

$$MnO_2 + 4(HCl) = MnCl_4 + 2(H_2O),$$

Manganese tetrachloride, only existing at low temperatures, breaks up on warming into manganous chloride and chlorine gas.

Manganese tetrachloride Manganous chloride Chlorine.

$$MnCl_4 = MnCl_2 + Cl_2.$$

This is the method by which Scheele first prepared chlorine and it is still employed as the most convenient laboratory method for making the gas. When used on a manufacturing

scale the manganous chloride is again converted into the black oxide by treating with lime, which forms calcium chloride and manganese oxide (MnO), the latter being oxidised to the black oxide (MnO_2) by mixing with more lime and blowing air through the mixture (Weldon's process).

It can be prepared from common salt by mixing the salt (sodium chloride) with pyrolusite and sulphuric acid and warming the mixture:

Sodium chloride		Pyrolusite		Sulphuric acid
$2(NaCl)$	+	MnO_2	+	$2(H_2SO_4)$

Sodium sulphate		Manganous sulphate		Water		Chlorine.
$= Na_2SO_4$	+	$MnSO_4$	+	$2(H_2O)$	+	Cl_2.

On a manufacturing scale it is now largely prepared by "Deacon's process." A mixture of air and hydrochloric acid gas is passed over heated firebricks saturated with copper chloride or sulphate, when the alternate formation and decomposition of copper chloride gives chlorine gas. The final action may be represented as:

Hydrochloric acid		Air		Water		Nitrogen		Chlorine.
$(2HCl)$	+	(N_4+O)	=	H_2O	+	$2N_2$	+	Cl_2.

The chlorine obtained is mixed with twice its volume of nitrogen, but for the processes in which it is employed this does not matter.

Properties.—Chlorine is a yellowish-green gas which is volume for volume 35·5 times heavier than hydrogen; it has an insupportable odour, and when inhaled in even very minute traces causes great irritation of the mucous lining of the throat and lungs, air containing 5 per cent. of it rapidly proving fatal to animals.

It can be liquefied under a pressure of six atmospheres at 0° C. At ordinary temperatures, water dissolves a little more than 2·5 times its volume of the gas, and if the solution be cooled down to 0° C., crystals of a solid hydrate separate from the solution, their composition being ($Cl_2.10H_2O$).

Chlorine gas is not combustible in air or oxygen, and

will only support the combustion of certain metals, or substances rich in hydrogen, combining with the hydrogen of the body to form hydrochloric acid whilst the carbon is deposited, in some cases spontaneous combustion taking place, as when blotting-paper moistened with turpentine is plunged into the gas.

Chlorine does not combine directly with either carbon or oxygen; phosphorus catches fire spontaneously in it, forming chiefly phosphorus trichloride (PCl_3), and sulphur will burn feebly in it; whilst selenium, boron and silicon will combine with it when heated.

Chlorine has an intense affinity for hydrogen and the metals, a mixture of equal volumes of chlorine and hydrogen combining with explosion when subjected to direct sunlight; whilst many metals, like antimony or copper, in a fine state of division, spontaneously ignite when thrown into the gas, chlorides of the metals being produced.

When a solution of chlorine in water is exposed to daylight it rapidly loses its characteristic yellow colour and become colourless, oxygen being at the same time liberated, an action due to the chlorine under the influence of light decomposing the water:—

Water		Chlorine		Hydrochloric acid		Oxygen.
$2(H_2O)$	+	$2Cl_2$	=	$4(HCl)$	+	O_2.

Bleaching.—The affinity of chlorine for hydrogen makes chlorine a very powerful oxidising agent, as when it comes in contact with any moist substance which can be readily oxidised, the chlorine combines with the hydrogen of the moisture, forming hydrochloric acid, whilst the nascent oxygen combines with the oxidisable substance.

This explains why it is that moist chlorine will bleach many colouring matters, whilst the dry gas has no effect upon them; the bleaching action of chlorine being an oxidation at the expense of the oxygen of the water present. Colours bleached by chlorine are destroyed, and cannot, as in the case of bleaching by sulphur dioxide, be restored.

Compounds of Chlorine.

Hydrochloric Acid (HCl).—The formation of this gas by the direct combination of hydrogen and chlorine has already been referred to. So great is the affinity of the two elements for each other, that if they are mixed in equal volumes, and exposed to any light rich in the chemically active rays which are found at the violet end of the spectrum, such as direct sunlight, the light from burning magnesium, or the flash obtained by igniting a mixture of carbon disulphide vapour and nitrogen dioxide, the two gases combine with explosion, whilst even in diffused daylight they gradually combine without explosion, in each case forming their own volume of hydrochloric acid gas. A mixture of the two gases, however, may be kept for an indefinite period in the dark, but will combine when brought into the light, or under the influence of heat or an electric spark.

Hydrochloric acid is found in volcanic gases, and also occasionally in the spring waters of volcanic districts, whilst its salts are amongst the most important natural compounds.

Preparation.—For laboratory use it is always prepared by acting upon salt with sulphuric acid, when:

Sodium chloride		Sulphuric acid		Sodium hydrogen sulphate		Hydrochloric acid gas.
$NaCl$	+	H_2SO_4	=	$NaHSO_4$	+	HCl,

an interchange taking place between the sodium and one atom of hydrogen of the sulphuric acid, with formation of hydrochloric acid gas and sodium hydrogen sulphate.

In preparing the gas in this way it is found convenient to fuse the salt before using it, in order to reduce the surface exposed, and thus prevent the excessive frothing which attends the use of ordinary table salt.

At temperatures which can be safely employed in a glass flask the above reaction takes place, but at a higher temperature, such as is attained in the salt cake furnace of the soda manufacturer, both atoms of hydrogen in the sulphuric acid

can be replaced by sodium, and double the volume of hydrochloric acid gas is obtained:

Sodium chloride Sulphuric acid Sodium sulphate Hydrochloric acid.

$$2(NaCl) + H_2SO_4 = Na_2SO_4 + 2(HCl).$$

The gas so obtained must be collected over mercury or by downward displacement, as it is so intensely soluble in water that it would be impossible to utilise it for its collection. The molecular weight of the gas is 36·5 and its density 18·25.

Properties.—It is a transparent, colourless gas with a suffocating odour and acid taste; it forms dense fumes on escaping into the air. These fumes are due to the gas attracting moisture from the air and condensing it, the gas itself being extremely soluble in water.

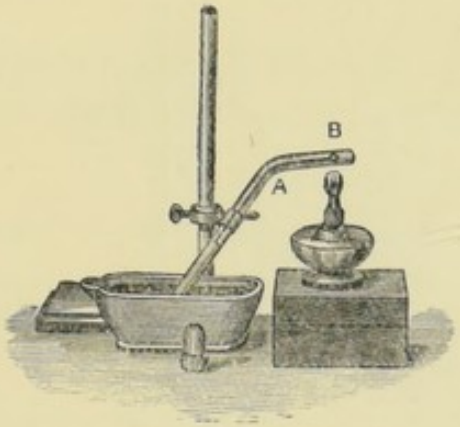


Fig. 49.

Hydrochloric acid gas can be condensed to a liquid by a pressure of forty atmospheres, and the anhydrous liquid has few of the properties of the solution of the gas in water; it has little or no action upon the metals, it hardly affects dry litmus, and has no action upon calcium carbonate or on quicklime.

Composition.—The composition of hydrochloric acid gas can be proved by confining a known volume of hydrochloric acid gas over mercury in a bent tube (A, Fig. 49), and passing up into it a pellet of potassium on the end of a platinum wire (B). The potassium at once commences to absorb the chlorine of the hydrochloric acid gas, combining with it to

form potassium chloride; and if the potassium be gently heated by a spirit-lamp flame to prevent any absorption of hydrogen, exactly half the gas will disappear, leaving only pure hydrogen behind. Another proof is that if saturated hydrochloric acid solution is decomposed by a galvanic current in a Hofmann's electrolytic apparatus (Fig. 50), using carbon electrodes, equal volumes of hydrogen and chlorine will be evolved.

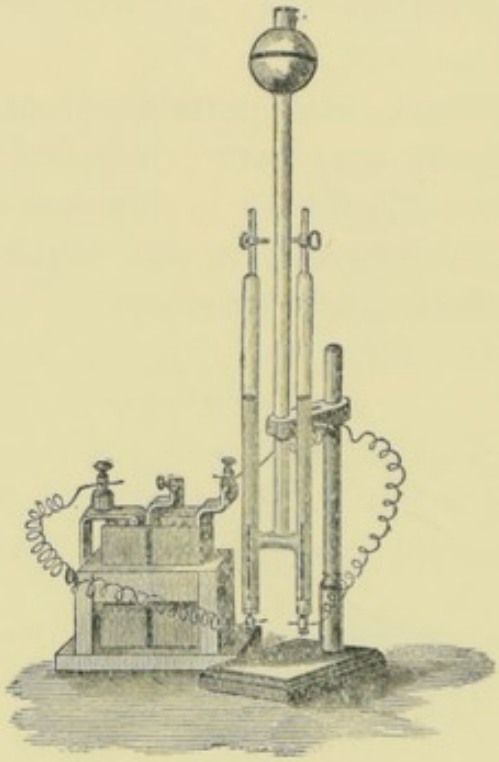


Fig. 50.

Commercial Hydrochloric Acid.—The liquid hydrochloric acid of commerce, called *muriatic acid*, or *spirits of salt*, is a solution of the gas in water. One pint of water at ordinary temperature will absorb nearly 500 pints of hydrochloric acid gas, forming $1\frac{1}{3}$ pint of the solution, having a specific gravity of 1·21.

If the strongest acid, having a specific gravity of 1·21, is cooled down to – 18° C., it deposits crystals having the composition $HCl.4(H_2O)$.

This acid is produced in enormous quantities in the alkali works, where common salt is decomposed by sulphuric acid as a preliminary step in the manufacture of sodium carbonate.

When this gas is present in the air in even small traces (1 in 25,000) it has a most destructive effect upon vegetation, causing the leaves to quickly wither and shrivel up, an effect which is supposed to be due to the attraction which the acid gas has for moisture. The effect of traces of this gas in the air may be seen in the pottery districts, where large areas are practically denuded of vegetation by the hydrochloric acid evolved during the process of salt glazing. As a consequence the alkali maker is compelled by Act of Parliament to condense the hydrochloric acid gas evolved, otherwise it would escape into the air, and wither up all the vegetation in the neighbourhood. The gas is condensed by making it pass up a tower containing lumps of coke, over which water is slowly trickling down; the water dissolves the hydrochloric acid gas, and the solution is drawn off at the bottom of the tower.

Pure hydrochloric acid solution is colourless, but the crude acid nearly always has a yellow colour, due to the presence of iron.

Chlorides.—Most of the metals, with the exception of gold and platinum, are acted upon by hydrochloric acid, forming a chloride of the metal, which is also obtained when a metallic oxide is acted on by the acid. The molecule of hydrochloric acid only containing one atom of hydrogen, no acid chlorides can be formed.

Chlorides in solution can be detected by their forming a white precipitate with soluble silver salts, which is insoluble in nitric acid but soluble in ammonia, whilst all chlorides when heated with manganese dioxide and sulphuric acid evolve chlorine.

In its great affinity for the metals, chlorine resembles oxygen, and as a rule, the more closely elements resemble each other the less will be their affinity for each other, and chlorine cannot be made to directly combine with oxygen although by indirect processes it forms several oxides.

Chlorine Monoxide.—If dry chlorine gas be passed over

dry precipitated mercuric oxide, a substance called chlorine monoxide passes off and may be condensed as a red liquid in a tube surrounded with ice and salt.

Mercuric oxide		Chlorine		Mercuric oxychloride		Chlorine monoxide.
$2(HgO)$	+	$2Cl_2$	=	$HgO,HgCl_2$	+	Cl_2O.

This liquid boils at + 19° C., and any elevation of temperature causes it to explode; it is rapidly absorbed by water, and the solution is supposed to contain hypochlorous acid, which, however, has not been isolated, although its salts are well known in an impure condition.

Chlorine monoxide		Water		Hypochlorous acid.
Cl_2O	+	H_2O	=	$2(HClO)$.

Bleaching Powder.—The most important compound of chlorine is "bleaching powder," the "chloride of lime" of the oil shops. This is made by taking freshly burnt quicklime, free from iron, and slaking it, sifting to remove lumps, and spreading it in thin layers on stone shelves fitted in a stone, brick, or sometimes lead chamber, the shelves being so arranged that they are open alternately back and front, so that gas passing through the chamber traverses the surface of each shelf; small openings with glass doors are made in the side of the chamber, so that the operation can be watched and the lime raked over once or twice during its conversion into bleaching powder. Chlorine gas is now generated in a stone "still," and the gas is made to pass over the slaked lime, care being taken to keep the temperature as low as possible, as the heat, which would be developed if the absorption went on too rapidly, would reduce the strength of the bleaching powder owing to the formation of calcium chlorate instead of calcium hypochlorite. The operation is continued for about thirty-six hours, by which time it is complete, and the bleaching powder contains from 30 to 39 per cent. of chlorine which can be rendered available for bleaching purposes.

Dry bleaching powder consists mainly of a substance intermediate in composition between calcium chloride

(Cl-Ca-Cl) and hypochlorite (ClO-Ca-OCl), namely calcium chloro-hypochlorite (Cl-Ca-OCl).

It derives its value as a bleaching preparation from the ease with which it parts with a portion of its chlorine, the moisture and carbon dioxide of the air quickly bringing this about when the material is left exposed.

When acted upon by water, calcium hypochlorite is formed, together with calcium chloride.

Calcium chloro-hypochlorite		Calcium chloride		Calcium hypochlorite.
$2Ca(OCl)Cl$	=	$CaCl_2$	+	$Ca(OCl)_2$.

The bleaching action results from the decomposition of this calcium hypochlorite with dilute acids, hypochlorous acid being first liberated, which then undergoes further decomposition with the liberation of chlorine.

Calcium hypo-chlorite		Hydrochloric acid		Calcium chloride		Hypochlorous acid.
$Ca(OCl)$	+	$2HCl$	=	$CaCl_2$	+	$2HClO$
$2HClO$	+	$2HCl$	=	$2H_2O$	+	$2Cl_2$.

In using it on a large scale a solution of the bleaching powder in water is taken, and the fabrics to be bleached are dipped into it, and after being allowed to soak for some hours, are then transferred for a short time to a tank containing very dilute acid, by which the chlorine is liberated in the material itself. When the bleaching is completed, which may require two or three dippings, the articles are well washed and boiled in a dilute solution of sodium carbonate, to remove the colouring matter rendered soluble by the chlorine, and to get rid of all traces of free acid, which, if allowed to remain, would render the fabric rotten.

Bleaching powder is of value as a disinfectant, breaking up moisture, and thus oxidising and destroying organic germs; it also decomposes noxious gases, like sulphuretted hydrogen, taking the hydrogen to form hydrochloric acid and depositing the sulphur.

Potassium Chlorate $KClO_3$.—If chlorine gas is passed into

cold dilute potassium hydroxide solution, chlorine is absorbed, and a mixture of potassium chloride and hypochlorite is formed which is technically known as "Eau de Javelles," and which was the first artificial bleaching agent used.

Potassium hydroxide		Chlorine		Potassium chloride		Potassium hypochlorite		Water.
$2KOH$	+	Cl_2	=	KCl	+	$KClO$	+	H_2O.

If this solution be boiled, the hypochlorite breaks up into potassium chloride and chlorate :—

Potassium hypochlorite		Potassium chloride		Potassium chlorate.
$3(KClO)$	=	$2(KCl)$	+	$KClO_3$.

Potassium chlorate may be formed in one operation by passing chlorine into a hot strong solution of potassium hydroxide:—

Potassium hydroxide		Chlorine		Potassium chloride		Potassium chlorate.		Water.
$6(KHO)$	+	$3Cl_2$	=	$5(KCl)$	+	$KClO_3$	+	$3(H_2O)$.

If this solution be concentrated and allowed to stand, the potassium chloride, which is soluble in three times its weight of cold water, remains in solution, whilst the chlorate, requiring sixteen times its weight of cold water to dissolve it, separates out in tabular crystals.

On a manufacturing scale a paste of potassium carbonate and slaked lime is saturated with chlorine, and treated with boiling water, which dissolves out the calcium chloride and potassium chlorate formed, and the former salt being very soluble in water, the chlorate is easily separated by crystallisation.

Potassium chlorate ($KClO_3$) is derived from an acid called chloric acid ($HClO_3$) by replacing the atom of hydrogen by potassium, and in the same way the class of salts called chlorates may all be built up.

The chlorates, like the nitrates, are all strong oxidising agents acting, however, at lower temperatures, because they part with their oxygen more easily; the oxidation by

potassium chlorate is also much more violent than the action of the nitrate, as the chlorate is one of the few compounds which give out heat during decomposition instead of absorbing it, and for this reason potassium chlorate is called an "endothermic" compound, this property enhancing the rapidity and vigour with which the salt acts.

A unit weight of potassium chlorate evolves during decomposition enough heat to raise 39 unit weights of water 1° C., hence we say it gives out 39 thermal units. At high temperatures potassium chlorate acts violently upon combustible bodies, and it has been already seen that it is the source from which oxygen gas is obtained.

A few grains of sulphur mixed with potassium chlorate and rubbed in a mortar detonates violently, and before the introduction of mercuric fulminate this mixture was used for percussion caps, for which, however, it was ill adapted, as it caused serious corrosion of the nipple of the gun.

A mixture of antimony sulphide and potassium chlorate will detonate when struck with a hammer, and is used in friction tubes for firing cannon. Friction tubes consist of a quill tube filled with powder, in the upper part of which a small rasp surrounded by the mixture is fixed, and on rapidly pulling this out by means of a cord the friction fires the mixture, which in turn ignites the powder. For military use the tube is of copper.

Potassium chlorate has been employed as an ingredient of explosives, but many compositions in which it plays a part are liable to spontaneous combustion, added to which its effects are so uncertain and violent that it is rarely licensed as an explosive in England.

Bromine (Br=80) and Iodine (I=127).

The elements bromine and iodine so strongly resemble chlorine in all their properties that the three are classed together with fluorine, these elements being commonly called "*the halogens*" or salt producers, from the fact that when an atom of one of them exists in combination with an atom

of potassium or sodium, the compound strongly resembles sodium chloride or common salt in properties.

The principal source of sodium chloride is sea water, and the salts of bromine and iodine are also obtained from it.

Bromine, was discovered in 1826 by Balard, who obtained it from the solution left after concentrating sea water and crystallising out the sodium chloride, and at first, supposed it to be a compound of iodine and chlorine. Like chlorine, it never occurs free in Nature, and its salts are found in company with the chlorides in sea water, and more plentifully in the waters of many mineral springs.

Bromine is now almost entirely prepared from the mother liquors obtained after crystallising out the potassium salts which occur in large deposits as *Carnallite* (KCl, $MgCl_2$, $6H_2O$), at Stassfurt. The present process is a continuous one, the solution containing the bromides (mainly as magnesium bromide), passing downwards through a tower filled with balls, to give a large liquid area, and meeting an ascending current of chlorine, which replaces the bromine, forming magnesium chloride.

Magnesium bromide Chlorine Magnesium chloride Bromine.

$$MgBr_2 + Cl_2 = MgCl_2 + Br_2.$$

The bromine is condensed in a suitable apparatus, the last traces which escape condensation being removed by passing over moist iron. The bromine is afterwards purified by distillation.

Properties.—Bromine and mercury are the only two elements liquid at ordinary temperatures.

The vapour has an excessively corrosive and irritating smell and acid taste, and is an active poison. Volume for volume bromine vapour is eighty times as heavy as hydrogen. Liquid bromine boils at 63° C. and solidifies at – 20° C., and is soluble in water, 34 parts of water dissolving one of bromine.

The vapour of bromine, like chlorine, only supports the

combustion of substances rich in hydrogen, and it also bleaches certain colours by oxidation in the presence of moisture.

Hydrobromic Acid.—Bromine combines with hydrogen to form hydrobromic acid (HBr), but the tendency to combine is much feebler than is the case with chlorine, the mixed gases having to be passed through a red hot tube to make them unite.

Hydrobromic acid forms the class of salts called bromides, much used in medicine and photography, but for other purposes it is of but little practical use, and the same remark applies to the compounds formed by bromine and oxygen.

Iodine was discovered in 1812 by Courtois, and like bromine it occurs chiefly in sea and certain mineral spring waters. Sea water only contains about one part of iodine compounds in 250,000 parts of water, but seaweeds during their growth collect the traces from the sea water, and when the weeds are collected and burnt, the iodides are found in the ash. On the coast of Scotland and the neighbouring islands, enormous quantities of seaweed are collected and burnt, and the ash which is called "kelp" is then exhausted with water, and on evaporating the solution potassium sulphate crystallises out; this is removed, and on further concentration and cooling a crop of crystals of potassium chloride, together with sodium sulphate, chloride and carbonate, is obtained.

The mother liquor, which contains bromides as well as iodides, is then mixed with sulphuric acid and is put into a retort, manganese dioxide is added, and the retorts are heated, when the iodine distils over as a violet vapour, which is condensed in cooled receivers as a greyish-black shining solid, crystallising in metallic looking scales.

Potassium iodide		Manganese dioxide		Sulphuric acid	
$2(KI)$	+	MnO_2	+	$2(H_2SO_4)$	=
Manganous sulphate		**Potassium sulphate**		**Water**	**Iodine.**
$MnSO_4$	+	K_2SO_4	+	$2(H_2O)$	+ I_2.

When no more iodine distils over, more manganese dioxide is added and the temperature raised, when the bromine present in the liquid distils over.

Practically all the iodine at the present time is obtained from crude Chili saltpetre (*Caliche*), which contains notable quantities, chiefly as sodium iodate. By successive crystallisations the sodium nitrate is removed, leaving a mother liquor which contains about 20 per cent. of sodium iodate. To recover the iodine from this, a solution of sodium hydrogen sulphite (obtained by passing the sulphur dioxide, obtained on burning crude sulphur, into a solution of sodium carbonate) is added, when a somewhat complex change takes place as represented by the following equation :—

Sodium iodate	Sodium hydrogen sulphite	Sodium hydrogen sulphate	Sodium sulphate	Water	Iodine.

$$2NaIO_3 + 5NaHSO_3 = 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2.$$

The iodine is allowed to settle, is washed and purified by distillation.

Properties.—The iodine so obtained is purified by resublimation, and is generally found in rhomboidal plates, having a lustre like graphite. It melts at 113° C., and boils at 200° C., being converted into a magnificent violet vapour, which is 127 times heavier, bulk for bulk, than hydrogen. It is but little soluble in water, 7,000 parts only dissolving one of iodine, but is readily soluble in alcohol, ether, carbon disulphide, or the alkaline iodides. Iodine and the iodides are much used in medicine and photography, but neither the element nor its compounds with hydrogen or oxygen have many practical applications.

Iodine has not so strong an affinity for hydrogen or the metals as either chlorine or bromine, both of which will turn it out of combination. Of these three elements, chlorine has the strongest affinity for hydrogen and the metals, and iodine the feeblest, bromine being intermediate in its affinity. This order is reversed in their combinations with oxygen, iodine being the strongest, and chlorine the weakest.

The fact that iodine can be liberated from its compounds by the addition of a drop of chlorine water can be utilised as a very delicate test for the iodides. If an iodide is mixed with a dilute solution of starch no change in colour takes place, but if a drop of chlorine water be now added, the iodine will at once be liberated and blue iodide of starch will be formed, even if the quantity of iodine present be exceedingly small.

Fluorine (F = 19).

The compounds of this element have been recognised as containing it since the close of the last century, but its affinity for nearly all other substances is so great that, in spite of the many attempts to isolate it, it remained unknown in the free state until 1887, when it was obtained by Moissan by electrolysing pure hydrofluoric acid, in which potassium hydrofluoride had been dissolved to render it a better conductor of electricity, a platinum U tube being employed, (Fig. 51). An electrode of platinum-iridium alloy was used

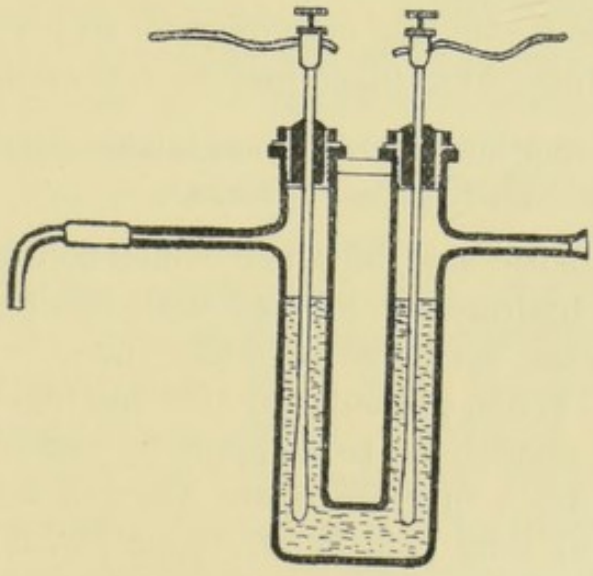


Fig. 51.

as the positive pole, whilst the negative consisted of platinum only; the U tube was provided with stoppers of fluor-spar, and platinum delivery tubes were used for the gaseous products. Under these conditions, and at a temperature of

−23° C., fluorine was obtained as a colourless gas which decomposes water, liberating oxygen and combining with the hydrogen to form hydrofluoric acid; when brought in contact with hydrogen gas it exploded, even in the dark, and combined with all the elements with combustion, oxygen and carbon alone being unaffected by it.

Fluorine occurs in Nature chiefly in combination with calcium as calcium fluoride (CaF_2), found in enormous quantities as fluor or Derbyshire spar, which forms crystals belonging to the cubical system, and is often very beautifully coloured by traces of metallic oxides.

Hydrofluoric Acid.—Fluor spar has been used from the earliest ages as a flux in metallurgical processes, and rather more than a century ago it was discovered that when it was heated with sulphuric acid, fumes were given off which had the property of rapidly corroding glass, and these fumes were afterwards shown by Gay-Lussac and Thénard to consist of a compound containing hydrogen united with the then not yet isolated element fluorine.

This method is still that employed for its preparation, and the reaction which takes place may be represented as:—

Calcium fluoride		Sulphuric acid		Calcium sulphate		Hydrofluoric acid.
CaF_2	+	H_2SO_4	=	$CaSO_4$	+	$2(HF)$.

The hydrofluoric acid obtained, which contains one part by weight of hydrogen combined with nineteen parts by weight of fluorine, forms dense white fumes when in contact with air. When prepared by this method the escaping vapour can be condensed to a liquid by passing it through a tube cooled by a mixture of ice and salt, and the liquid so obtained was long considered to be liquid hydrofluoric acid, but is, in reality, a concentrated solution of hydrofluoric acid gas in water.

The anhydrous acid may be obtained from this by distilling it with phosphorus pentoxide, the liquid boiling at 19·5° C., and when perfectly anhydrous has little or no action on glass, but in solution, or in the presence of moisture, it

rapidly attacks it, dissolving out some of the silica from it and forming a compound called silicon fluoride.

Hydrofluoric acid, in many of its properties, bears a strong resemblance to hydrochloric acid, but its action upon glass and substances containing silica distinguishes it from all other compounds.

In consequence of this property, it cannot be prepared in vessels of glass or porcelain, and retorts of lead or platinum are usually employed in its production, whilst it must be kept in bottles of lead or india-rubber.

Etching on Glass.—It is largely used for etching patterns upon glass, and for this purpose may be used either as vapour or solution, the latter being preferable, as it is much more manageable. In order to etch a drawing upon glass, the surface of the glass is first coated with a thin film of wax, either by warming the glass and brushing over it some melted wax, or else by brushing over it a solution of wax in some volatile solvent. The pattern, etc., to be etched is then drawn upon the wax with a sharp pointed tool, care being taken to remove the wax and expose the surface of the glass in the places to be etched, and a wall of wax having been built round the side of the plate, the solution of hydrofluoric acid is poured over it, and attacks the exposed glass, whilst it has no action on the wax. The acid is left on the plate for from five minutes to half an hour, according to the strength of the solution, the depth to which the etching has gone being ascertained by drawing the point of a needle across one of the lines. When etched to a sufficient depth, the acid is washed off with water, and the wax removed by scraping and washing the plate with turpentine.

In using hydrofluoric acid, care must be taken to avoid its contact with the skin, as it produces very painful wounds. Hydrofluoric acid in solution dissolves all the metals with the exception of gold, platinum, and mercury; silver and lead forming fluorides of the metals soluble in water.

The fluorides of the alkalies slowly corrode glass when

left in contact with them, and liquids for drawing or writing on glass can be prepared by mixing a solution of ammonium or potassium fluoride with sulphuric acid.

The four elements, fluorine, chlorine, bromine, and iodine, exhibit a gradual difference in properties and in their power of combining with other elements, fluorine having the greatest affinity for metals and iodine the least. The stability of the compounds formed in combining with oxygen is in reverse order, iodine forming the strongest compound, whilst fluorine is the only element which does not combine with oxygen, and this gradual gradation of affinity is also accompanied by a gradation in physical properties.

	Fluorine	Chlorine	Bromine	Iodine.
Atomic weight	19	35·5	80	127
Physical state	gas	gas	liquid	solid.
Colour ...	colourless	yellow	brown	black.
Boiling point		− 33°	+ 63°	+ 200°
Fusing point			− 7°	+ 113°

CHAPTER XXII.

SILICON AND ITS COMPOUNDS.

Silicon—Silicon hydride—Silica or silicon dioxide—Occurrence and importance in Nature—Silicic acid—Dialysis—Silicates—Glass—Composition of glass—Manufacture of glass—Silicate of alumina—Clay—Pottery—Porcelain—Stoneware—Bricks—Building stones—Decay of building stones—Granites—Sandstones—Limestones—Dolomite—Mortar—Cements—Silicon tetrafluoride—Hydrofluosilicic acid—Boron.

SILICON (Si=28).

QUARTZ was believed to be an element until, in 1813, Sir Humphrey Davy succeeded in decomposing it, and demonstrated that it was the oxide of an element called silicon, which can be obtained by acting on a compound called potassium silicofluoride at a high temperature with sodium or potassium, either of which combine with fluorine to form a fluoride, whilst the silicon is set free, and on treating the mass with water the fluorides are dissolved, the silicon being left as a brown amorphous powder.

Potassium silicofluoride		Potassium		Potassium fluoride		Silicon.
K_2SiF_6	+	$2K_2$	=	$6(KF)$	+	Si.

Silicon is not acted upon by any acid except by hydrofluoric, with which it forms silicon fluoride, hydrogen being evolved:

Silicon		Hydrofluoric acid		Silicon fluoride		Hydrogen.
Si	+	$4(HF)$	=	SiF_4	+	$2H_2$.

It burns with considerable brilliancy in air or oxygen gas, forming silica (SiO_2), which fuses on its surface and stops the combustion. Silicon has an atomic weight of 28.

If the potassium silicofluoride is fused with potassium and zinc, the silicon as it is liberated, dissolves in the molten zinc, and on cooling deposits in the mass as black shining crystals.

These can be separated from the zinc by acting upon the mass with hydrochloric acid and afterwards separately with nitric and hydrofluoric acids, which dissolve the metal but leave the crystals of silicon unaltered.

The crystals consist of black shining octahedra, having a specific gravity of 2·49, and are excessively hard. They will not burn in oxygen and are unaffected by acids, except a mixture of hydrofluoric and nitric acids. When heated in chlorine gas, silicon forms a chloride, and nitrogen also enters into direct combination with silicon at high temperatures to form silicon nitride.

In many of its properties silicon very closely resembles carbon, but unlike carbon it only forms one compound with hydrogen, which catches fire spontaneously on coming in contact with air.

Silicon hydride (SiH_4) or siliciuretted hydrogen is prepared by fusing anhydrous magnesium chloride with sodium silicofluoride and sodium, together with a flux of salt. The mixture is heated until the sodium flame ceases to be visible, and on allowing the mass to cool, and breaking it out of the crucible used, a grey mass of magnesium silicide is found at the bottom, with a layer of fused chloride and fluoride of sodium above it. If the magnesium silicide is now roughly powdered and is treated with dilute hydrochloric acid, silicon hydride is evolved which fires spontaneously on contact with air and burns with a bright flame, giving off white fumes consisting of silica.

Silica (SiO_2), also called silicic acid and silicon dioxide, is by far the most important compound which this element forms, and constitutes a large portion of the crust of the globe. The purest form of silica is called rock crystal, from its transparency, and occurs crystallised in six-sided prisms generally terminating in six-sided pyramids. These crystals, coloured by certain metallic oxides, form various precious stones such as the amethyst, jasper, agate, catseye, onyx, opal, chalcedony, carnelian, etc. Silver sand is nearly pure silica, whilst the

ordinary forms of yellow sand are silica coloured with iron.

Flint is a form of silica found in the chalk formation, and silica is one of the chief constituents of many forms of rock. Most forms of silica are intensely hard, rock crystal scratching glass nearly as easily as the diamond; and all ordinary natural forms of silica are insoluble in water. Silica, however, is found dissolved in certain springs, whilst its presence in straw, bamboo canes, and other vegetable fibres, shows that under some conditions it must be soluble.

If silica is fused with sodium carbonate, a glassy mass called sodium silicate is formed which is soluble in water, and if hydrochloric acid is added in excess to the solution, a semi-solid gelatinous mass of silicic acid is obtained; if, however, instead of adding strong hydrochloric acid to the solution of sodium silicate, the sodium silicate be poured into a dilute solution of hydrochloric acid, this silicic acid will remain in solution together with sodium chloride and hydrochloric acid.

Dialysis.—The mixture is then placed in a vessel having a bottom made of vegetable parchment, and this is floated on a bowl of clean, pure water. Under these conditions it is found that substances like salt or hydrochloric acid will undergo a process of diffusion through the vegetable parchment, and will mingle with the water in the bowl, whilst other substances, like silicic acid, are unable to penetrate the parchment, and remain behind in the floating vessel.

This method of separating certain substances is called "dialysis," and the floating vessel with the vegetable parchment bottom is called a "dialyser."

Crystallisable soluble substances like sodium chloride have the power of diffusing through parchment, and are called "*crystalloids*" to distinguish them from substances like silicic acid, gum, gelatine, albumen, starch, etc., which cannot pass through the parchment, and which are called "*colloids.*"

Treating the mixture of silicic acid, sodium chloride and hydrochloric acid in this way, the sodium chloride and hydrochloric acid diffuse out into the pure water, and water diffuses into the silicic acid, and if the water in the bowl be frequently changed, in a few hours a perfectly pure aqueous solution of silicic acid will remain in the dialyser.

If this solution be allowed to concentrate over sulphuric acid in a vacuum, it is converted into a gelatinous mass when it contains about 14 per cent. of silicic acid, and this shrinks and gives off more moisture until a glass-like mass having the composition (H_2SiO_3) is left. This substance will not again dissolve in water, is but slightly soluble in hydrochloric acid, and if it is heated so as to expel all water, it becomes totally insoluble in the acid.

When sand is fused with various metallic oxides or carbonates, combination takes place, and the compounds known as silicates are formed, very few of which in composition show that they are formed from the acid (H_4SiO_4), most of them being irregular combinations of the metallic oxide with SiO_2.

Glass is a mixture in varying proportions of silicates of potash, soda, lime, lead oxide, baryta, magnesia, and alumina. If silica, which occurs nearly pure in Nature as silver sand and quartz, is fused at a high temperature with sodium carbonate, a glassy mass of sodium silicate is obtained; but this is slowly acted upon and dissolved by water, and is, therefore, useless as glass, for it would be incapable of resisting the moisture in the atmosphere; but if a small quantity of lime or oxide of lead is fused with it, a glass is obtained which will resist almost entirely atmospheric influences.

The readiness with which glass will fuse depends upon the silicates it contains, the presence of lead, for instance, causing the glass to melt at a lower temperature than a glass containing lime.

Plate glass and ordinary window glass consist chiefly of silicates of lime and soda.

Bohemian glass is a double silicate of potash and lime, the more fusible kind required for making ornaments, vases, etc., containing also silicate of alumina. Flint glass, of which tumblers, wine glasses, etc., are made, consists of a double silicate of potash and lead; it is called flint glass because the silica used in its composition consists of ground flints.

Window glass is made by fusing together at a high temperature 100 parts of sand with about 35 parts of sodium carbonate and 35 parts of chalk (calcium carbonate). The sand, which is silicic acid, expels the carbon dioxide as gas from the sodium carbonate and calcium carbonate, and silicates of sodium and calcium are formed.

On the manufacturing scale this is done by heating the ingredients together to a temperature just short of fusion in a fireclay crucible, which causes the carbon dioxide to be slowly evolved, and prevents frothing over when complete fusion is reached. This first process is called "fritting," and when it is completed the temperature is raised and fusion takes place, the escape of the last portions of carbon dioxide keeping the liquid in agitation, and helping to promote the mixture of the ingredients.

Sometimes sodium sulphate is used instead of the carbonate, but it is then necessary to add a small proportion of charcoal to reduce the sulphur trioxide to sulphur dioxide, which is more easily expelled as gas. The molten mixture is kept for some time in the fused state, so that the air and carbon dioxide bubbles may have time to escape, and the foreign substances, consisting of undecomposed materials and impurities, may rise to the surface as a scum. The temperature is then allowed to slowly fall, and the glass assumes a pasty consistence, in which state it may be readily shaped at pleasure into the required form. The workman then plunges an iron tube into the mass, and by taking it out, allowing it to slightly cool and redipping, he collects a quantity of about seven to nine pounds weight, which is rolled into a pear-like shape on an iron plate. By blowing

down the tube whilst causing it to rotate, this is blown out into a large flask-shaped bulb, on the bottom of which another rod, also tipped with molten glass, is attached, and the neck of the flask is then detached from the blowing tube and is held in an opening of the furnace called the nose hole, where it soon begins to melt. The workman then causes the rod with the flask attached to revolve rapidly, when by centrifugal force the flask opens, and is transformed into a flat circular sheet of what is known as crown glass. At one time all window glass was made in this way, but the method is now nearly abandoned, as the glass so produced can only form panes of very limited size, in consequence of the central lump and of the circular form of the plate.

Sheet glass, which has almost completely taken the place of crown glass, is made by blowing a long spheroidal bottle, which, when the ends are cut off, leaves a large cylinder of glass. This is split down one side by touching it with a wet rod, and is then again softened in the furnace, and spread out flat upon an iron plate, giving a sheet of glass, which is less brilliant than crown glass, and the surface being wave-marked, has to be worked up by grinding and polishing.

Plate glass, which is now most used, is formed from a mixture of 300 parts of pure silver sand, 100 parts of sodium carbonate, 15 parts of lime, and 300 parts of broken fragments of glass called "cullet," and a little white arsenic. The mixture when fused and converted into glass is poured on to a heated metal table and is spread out to the required thickness by means of a heavy metal roller, and is afterwards placed in the annealing oven, where it remains for a week or a fortnight.

The annealing oven is first heated to a dull red heat, and after all air openings have been closed it is allowed to slowly cool down to the temperature of the surrounding atmosphere. The plates are then taken out, ground true and polished, and are fit for use.

The process of annealing is of the greatest importance,

for glass allowed to cool too rapidly is liable to crack and fly to pieces.

The glass of which wine bottles are made is of the commonest description, consisting of silicate of lime mixed with the silicates of the alkalies, and of iron and alumina, and it is to the iron present that it owes its dark colour.

When glass has been heated to the softening point and is kept at that temperature for some time without fusion, and then allowed to cool, it is found to be converted into a white opaque mass much resembling china, which is called "Réaumur's porcelain." This change is called "devitrification," and is due to the crystallisation of the silicates contained in the mass. Many materials are used to colour glass; in painted glass the colouring matter is merely laid on and then burnt into the surface of the glass, whilst in stained glass the colouring matter is mixed with the ingredients during manufacture. The ornamentation of cut glass is effected by grinding it, and designs are etched upon it by means of hydrofluoric acid, which dissolves out the silica from the glass, in this way eating into it.

Clay.—One of the most important natural silicates is aluminium silicate, which is the basis of all clays, and also occurs in a more or less pure condition in slate, pumice stone, and fuller's earth.

Clay varies very much in composition, china clay or kaolin being nearly pure hydrated aluminium silicate, whilst the commoner kinds of yellow clay contain considerable quantities of iron. The plastic properties of the different kinds of clay render it specially adapted for moulding into various forms; its use for the manufacture of pottery dates from a very early period in the world's history.

Pottery.—If a well kneaded specimen of clay be chosen it may be readily moulded into any required form, but when heated it has the property of shrinking; so that on baking the vessel would crack and lose its shape. To obviate this it is mixed with a certain proportion of sand, chalk, or bone

ash, which prevents shrinkage, but renders the baked vessels very brittle; to overcome this difficulty, some "felspar" (a silicate of alumina and potash) is added, which fuses at the temperature employed in baking the ware, and thus forms a cement, binding the particles of infusible clay into a compact mass. The vessel made of this mixture, when baked, retains its shape and does not crack, but it has the disadvantage of being porous, and is therefore unfit for ordinary use. To prevent this it must be glazed, that is, coated with some easily fusible material, which will form a thin coating of glass on the surface.

Porcelain.—In the manufacture of porcelain, 62 parts of kaolin, 4 parts of chalk, 17 parts of sand, and 17 parts of felspar are ground to the finest possible powder in water, and are allowed to stand until the coarser particles have settled down to the bottom of the grinding vat. The creamy fluids containing the finer particles in suspension are mixed in the proper proportions, and are allowed to settle; the sludge deposited at the bottom is drained until it reaches the right consistence, and is then thoroughly mixed and kneaded. The paste so prepared is now ready for making porcelain, but it has been found that it improves greatly by keeping for a considerable space of time in a damp place, the organic impurities which it contains being destroyed. Before the paste is used for moulding, it is again worked up and kneaded by hand.

The moulds used in the process of shaping are always made of a porous material, capable of absorbing the moisture from the clay, generally plaster of Paris. When the pattern is very complex, the mould is made in several pieces, but for round objects it is made in two parts. When the paste has been sufficiently dried by the absorption of its moisture by the mould, the latter is removed by separating its two halves, leaving the work complete. The articles are then air dried, and afterwards packed in cylindrical cases of refractory clay, which are arranged in a furnace or kiln

and baked, the temperature being allowed to rise very gradually.

When sufficiently baked, the "biscuit porcelain," as it is now called, has to be glazed, and this is done by dipping it into a very finely ground mixture of felspar and quartz, suspended in vinegar and water. The porous ware absorbs the water, and leaves a coating of felspar and quartz on its surface, which on heating a second time in the kiln, fuses and forms a glaze, partly penetrating the ware, and partly remaining as a varnish on the surface. It is very important that the glaze employed should have the same rate of expansion with heat as the porcelain ; otherwise, as it cooled, the glaze would crack.

In colouring wares of this kind, if a uniform tint is required, the materials for producing it are mixed with the glaze ; but coloured designs are painted upon the ware after glazing, and are generally composed of coloured glasses, ground with turpentine, which colours, when again heated in the kiln, fuse into the glaze.

Stone ware is a much coarser description of porcelain, containing both iron and lime, to the presence of which it owes its colour and fusibility, and it is covered with a glaze of sodium silicate which is produced by the process known as "salt glazing." The articles are coated, by dipping, with a thin film of sand, and are then intensely heated in the kiln, into which some damp salt is thrown. The water present is decomposed, its hydrogen taking the chlorine from the salt to form hydrochloric acid, whilst its oxygen combines with the sodium of the salt to form sodium oxide, which, coming in contact with the silica on the surface of the ware, forms a glaze of sodium silicate.

Staffordshire ware, of which common plates, etc., are made, is manufactured from a description of white clay of less value than kaolin ; it is mixed with ground flints, and is fired at a high temperature, and after being dipped in a highly fusible glaze, consisting of lead oxide, ground flints, and a little clay, it is again fired at a lower temperature.

Earthenware vessels and pipes are made from common clay, mixed with a certain proportion of marl and sand, and they are glazed with a mixture of from four to five parts of clay with six to seven parts of lead oxide.

Bricks are also made of common clay, mixed when necessary with sand, and they, as in the case of common earthenware, owe their colour to the iron which they contain.

In choosing building materials, those substances should be employed which offer the greatest resistance to atmospheric influences.

The causes which tend to produce decay in building materials are two: First, the disintegrating action of rain and frost; and secondly, the solvent action on certain ingredients of the materials exercised by carbon dioxide and acid impurities dissolved in rain water, or suspended in the moisture present in the air as fog or mist. As a rule, these two factors of decay act together; the weathering action first rendering the surface of the stone rough and porous, and this gives a coign of vantage for the lodgment of the rain with its gaseous impurities, which, dissolving out carbonates of calcium and magnesium, further disintegrates the surface, and causes scaling and pitting of the stone.

This being the case, it is evident that the smoother and harder the surface of the materials employed the less rapid will be the decay; and also that the vertical walls of a building, as they allow the water to freely run off from their surface, will be less exposed to these actions, and will therefore resist them better than ledges and horizontal surfaces, which, holding water, will be acted upon to a greater extent.

This is fully borne out by experience, and in buildings of sandstone and limestone it is nearly always found to be these portions which are first attacked.

It has been noticed that many of the ancient monuments of Greece and Egypt, even now, show but slight traces of decay as compared with the buildings to be found in this country, and the difference is partly due to the greater

resistance afforded by the surface of the materials used, and to an even greater extent, to the much smaller quantity of rain which falls in those countries and to the purity of the atmosphere.

The building stones used in this country are :—

1. Granite.
2. Sandstone or freestone.
3. Limestone.
4. Magnesium limestone or dolomite.

Granite is by far the most lasting of the building stones, and consists of from 65 to 80 per cent. of silica, which seems to act as a cement in building together mica and felspar, the whole mass being of a crystalline character. The chief granite yielding districts of England are Devon, Cornwall and Cumberland, whilst Scotland and Wales also furnish large quantities. The Devon and Cornwall granite has been largely used—Westminster, Waterloo and London bridges, the Thames Embankment, the London docks, Keyham docks and the Portland breakwater being built of it ; whilst in Scotland, the Aberdeen and Peterhead quarries supply some of the most valuable stone.

The fine surface and power of resisting disintegration possessed by granite, render it the best building stone we possess, but owing to its great hardness it is so difficult to work that it is only employed for massive and simple work, where great resistance to wear and tear is required.

The Sandstones consist essentially of particles of silica, *i.e.*, sand which has been probably formed by the disintegration of older rocks, and has collected in deposits, becoming consolidated into a hard mass by the carbonates of calcium and magnesium, the percentage of silica present varying from 84 to 93 per cent., whilst the carbonates binding it together vary from less than 1 per cent., up to nearly 13 per cent.

The sandstones are largely used for building purposes in

Scotland, where they are employed to a great extent, especially in Glasgow and Edinburgh, but carbon dioxide dissolved in rain water is able to rapidly dissolve out the cementing carbonates, and so cause disintegration of the surface.

The Limestones are perhaps those most generally in use, and consist of calcium carbonate, with small and varying quantities of other substances, such as silica and alumina, and their power of resisting the atmospheric influences entirely depends upon their density and compactness of structure.

Marble, which is the most compact form of limestone, will resist the action of the atmosphere for centuries, whilst the more porous kinds are rapidly acted upon.

Portland stone, of which St Paul's is built, is, next to marble, the most durable, and Bath stone also resists atmospheric action for a considerable period.

Dolomite, or magnesium limestone, is a double carbonate of calcium and magnesium, and is much used because it is easily sawn into blocks, and can be readily carved; but it is also readily acted upon by the water and carbon dioxide in the air. The magnesium limestone, of which the Houses of Parliament are built, contains about 50 per cent. of calcium carbonate, 40 per cent. of magnesium carbonate, and some silica and alumina.

In manufacturing towns much damage is caused by the sulphuric acid in the air, formed by the combustion of coal containing small traces of sulphur.

Mortar is a mixture of one part of freshly-slaked lime with two of sand, mixed with water to the consistence of a thin paste; and the hardening of mortar at first depends upon the conversion of some of the lime into carbonate by the absorption of carbon dioxide from the air; whilst, after the lapse of a considerable time, a still further hardening takes place, due to the formation of calcium silicate.

Cements or hydraulic mortars are made by heating together very finely divided chalk and clay, when carbon dioxide is expelled and silicates of calcium and aluminium are formed, together with a compound of alumina and lime; when this cement is mixed with water, combination takes place, the cement setting as a hard mass of hydrated double silicates, upon which more water has no effect.

In the manufacture of Portland cement, instead of ordinary clay, river mud is used.

Silicon Tetrafluoride.—When silica or silicates are acted upon by hydrofluoric acid, or by a mixture of fluor-spar and concentrated sulphuric acid, a gas is evolved which fumes in air and has a pungent odour. This gas is a compound of silicon and fluorine, and may be looked upon as being silica in which the two atoms of oxygen have been replaced by four atoms of fluorine. It is called silicon tetrafluoride.

Silica — Hydrofluoric acid — Silicon tetrafluoride — Water.

$$SiO_2 + 4(HF) = SiF_4 + 2(H_2O)$$

or—

Silica — Calcium fluoride — Sulphuric acid — Calcium sulphate

$$SiO_2 + 2(CaF_2) + 2(H_2SO_4) = 2(CaSO_4)$$

Silicon tetrafluoride — Water.

$$+ SiF_4 + 2(H_2O).$$

Hydrofluosilicic Acid.—When brought in contact with water, it at once undergoes decomposition with formation of silica, which is deposited, whilst an acid containing hydrogen, silicon and fluorine, called hydrofluosilicic acid, is formed :—

Silicon tetrafluoride — Water — Hydrofluosilicic acid — Silica.

$$3(SiF_4) + 2(H_2O) = 2(H_2SiF_6) + SiO_2.$$

This acid is prepared most conveniently by heating together a mixture of sand, fluor-spar, and sulphuric acid in a stoneware bottle, and leading the silicon tetrafluoride pro-

duced through a wide delivery tube, dipping into a small cup of mercury placed at the bottom of a vessel of water, thus guarding against obstruction of the exit tube by silica. Each bubble of gas as it passes up through the mercury is decomposed immediately it comes in contact with the water, and after a few hours the water becomes thick with the gelatinous mass of separated silica, and if this be filtered off, the clear filtrate will contain the hydrofluosilicic acid (H_2SiF_6).

Boron (B=11)

Boron is an element which closely resembles silicon; it is obtained from boracic acid by fusing it with potassium as a brown amorphous powder, which on fusion with aluminium, combines with some of it and forms octahedral crystals resembling the diamond in hardness and power of refracting light. Boron differs from most of the other elements in combining directly with nitrogen when heated to redness in the gas, forming a nitride.

In certain parts of the volcanic districts of Northern Italy, jets of steam issue with considerable violence from the ground, and are found to contain a compound of hydrogen, boron and oxygen, called *boracic acid*, which can be obtained in the crystalline form, having the composition (H_3BO_3). It is largely used for antiseptic purposes, as it prevents decay and putrefaction.

Boracic acid forms a few salts, the most important of which is sodium biborate or borax ($Na_2B_4O_7$), which is used to a considerable extent for cleaning metallic surfaces, from which, when fused, it has the power of dissolving metallic oxides, and also for glazing certain kinds of stoneware.

CHAPTER XXIII.

PHOSPHORUS.

Extraction of phosphorus from bones and mineral phosphates—Properties of phosphorus—Red phosphorus—Matches—Wax vestas—Safety matches—Phosphuretted hydrogen or phosphine—Calcium phosphide—Holmes' light—Phosphorus trioxide—Phosphorus pentoxide—Metaphosphoric, pyrophosphoric, and orthophosphoric acid—Arsenic—Oxides of arsenic—Arseniuretted hydrogen—Marsh's test—Testing for arsenic—Reinsch's test.

(P=31)

OWING to its intense affinity for oxygen, phosphorus is never found free in Nature, but occurs in large quantities combined with metals of the alkaline earths, the commonest being tricalcium phosphate $Ca_3(PO_4)_2$. By the disintegration of the minerals containing phosphates, the latter pass into the soil, and are absorbed by plants, appearing principally in the seed. The minerals phosphorite, coprolite, and apatite, also contain phosphorus. In the animal kingdom, the element appears to be a very necessary ingredient in the brain and other centres of nervous action; in bones about 60 per cent. of the total weight consists of mineral phosphate, and it is from the ashes of burnt bones that phosphorus itself is usually obtained.

The following analysis of the bones of oxen gives a fair idea of the general composition:—

Animal matter	30·58
Calcium phosphate	57·67
Magnesium phosphate	2·07
Calcium fluoride	2·69
Calcium carbonate	6·99

Phosphorus was probably discovered in the seventeenth century by Brandt, who obtained it by heating the residue

left after the evaporation of urine with sand. Later on Gahn discovered the existence of calcium phosphate in bones, and Scheele showed how phosphorus could be obtained from this substance.

The bones are heated with water under pressure, which dissolves out the ossein or soluble organic matter, and this is either purified for domestic or photographic use, or sent into the market as glue. The mineral matter left is heated to redness in the air, and the white ash remaining is called bone ash, and consists chiefly of tricalcium phosphate. Bone ash is also obtained by calcining animal charcoal after its decolorising power has been exhausted to such an extent that it cannot be sufficiently revived by re-burning.

Manufacture of Phosphorus.—Bone ash and mineral phosphates containing as little iron and alumina as possible, are used as the crude material, and after being ground to a fine powder, this is treated in a mixer with sulphuric acid of 1·55 specific gravity, until the whole of the lime is converted into calcium sulphat e with liberation of phosphoric acid :

Tricalcium phosphate		Sulphuric acid		Calcium sulphate		Phosphoric acid.
$Ca_3(PO_4)_2$	+	$3H_2SO_4$	=	$3CaSO_4$	+	$2H_3PO_4$.

The phosphoric acid is then filtered off and concentrated by steam evaporation to a syrup, which is mixed with sawdust, coarsely powdered charcoal or coke, and is dried at a dull red heat in a cast iron vessel. This heating converts the phosphoric acid into metaphosphoric acid by driving off one molecular proportion of water.

Phosphoric acid		Metaphosphoric acid		Water.
H_3PO_4	=	HPO_3	+	H_2O.

The dried mixture is then distilled in fireclay retorts, about three feet long and eight inches in diameter ; two inch iron pipes are luted into the mouths of the retorts and are made to dip under the surface of water.

At a white heat, the reduction of the metaphosphoric acid takes place:—

Metaphosphoric acid		Carbon		Carbon monoxide		Hydrogen		Phosphorus.
$4HPO_3$	+	$12C$	=	$12CO$	+	$2H_2$	+	P_4.

The phosphorus vapour distilling over in the atmosphere of carbon monoxide and hydrogen is condensed to the solid state in the water.

The introduction of the electric furnace has now considerably modified the process of manufacture, and is used at some of the largest works for the continuous production of phosphorus.

The calcium phosphate either as mineral or bone ash is mixed with carbon and a flux, and is then fed in through a hopper to a closed chamber lined with refractory fire brick, where the mixture is acted upon by the arc, the phosphorus distilling off through an outlet pipe to the condenser, whilst the slag is from time to time tapped and run off. This process gives a considerable saving, as the use of sulphuric acid is done away with, handling of the materials is reduced to a minimum, and the concentration of the phosphoric acid is rendered unnecessary.

Purification.—The phosphorus so obtained is generally very impure, and is again melted under warm water to which four per cent. of potassium bichromate is added, and the mixture well stirred; dilute sulphuric acid is then added, and the chromic acid so liberated oxidises the impurities and causes them to separate, leaving the phosphorus nearly pure and colourless.

Sometimes also purification is effected by redistilling the phosphorus from iron retorts at as low a temperature as possible.

The melted phosphorus is cast into sticks under warm water, or if for match manufacture into cheese-shaped masses.

Properties.—The phosphorus so obtained is almost colour-

less and transparent, but when exposed to light it gradually acquires an opaque red coating, partly due to its conversion into a suboxide of phosphorus, and partly to the formation of the red variety of the element.

Phosphorus melts at 44° C., and it has an intense affinity for oxygen, inflaming at a temperature of 60° C., and for this reason has to be kept under water. It is soluble in carbon disulphide and also in chloride of sulphur. If the solution in disulphide be allowed to stand in contact with air, the solvent evaporates off, and leaves the phosphorus in so fine a state of division that it spontaneously ignites.

Red Phosphorus.—If ordinary phosphorus be kept at a temperature of 230° C. for some hours in an atmosphere incapable of acting chemically upon it, such as of nitrogen or carbon dioxide, it gradually changes to a dark red mass, having the same chemical composition, but totally distinct in all its properties from yellow phosphorus. It undergoes no change when exposed to air or light, and may be heated to 250° C. before it ignites, at which temperature it is reconverted into ordinary phosphorus. Unlike the ordinary phosphorus it is insoluble in carbon disulphide, unattacked by chlorine or iodine at ordinary temperatures and non-poisonous.

The density of phosphorus, as vapour, is 62, and its molecular weight is therefore 124, but it can be proved from its hydrogen compounds that the atomic weight of the element is 31. It follows therefore that the molecule consists of four atoms, and inasmuch as dissociation does not take place even at 1040° C., it is evident that the molecule has this composition. Phosphorus enters largely into the composition of the paste with which lucifer matches are tipped.

Matches.—In the manufacture of lucifer matches, even-grained white pine is taken and is dressed and sawn into blocks of the required size, which are then split up by machinery into splints twice the length of the matches to be made; these are then wound round and round, by machinery,

with a thick woollen or leather band, which leaves an inch of splint projecting at each end, and the thickness of which separates the splints one from the other. Several thousand splints having been in this way rolled up into a firm compact bundle, not unlike a small millstone in size and shape, they are passed on to a man who places them on a flat metal plate, and pats the projecting ends with a flat wooden tool until the ends are all level. The bundles are then passed with one set of ends downward, over hot plates to warm the wood, and are dipped in shallow pans containing melted paraffin wax; the bundles are next turned over, passed on over more hot plates, and the other ends dipped. By the time the bundles are taken from this department to the portion of the factory where they are to be tipped with the phosphorus composition, the paraffin has hardened, and they are ready for the next process. This consists of tipping them with the match composition, made by mixing phosphorus and either potassium nitrate or chlorate, red lead, lead dioxide, or manganese dioxide, together with gum or glue enough to make a thin paste, to which sometimes some colouring matter, such as vermilion or Prussian blue, is added.

In such a composition, there is present the highly inflammable phosphorus and a compound containing oxygen, and friction is sufficient to set up chemical action between the two—the heat evolved by the combination of the phosphorus and oxygen to form phosphoric pentoxide being sufficient to inflame the paraffin or sulphur on the splint, and this in turn ignites the wood.

The amount of phosphorus present in the mixture varies very much according to the method employed in mixing it with the composition—in some cases not more than 5 per cent. being present, while sometimes the quantity rises to 30 per cent. Too much phosphorus in the mixture is to be avoided, as besides being costly, it defeats its own purpose by producing a large quantity of the pentoxide, which coats the end of the match, and so retards and even prevents ignition of the splint.

In England, potassium chlorate is generally used as the oxidising agent, such mixtures generally exploding slightly when the matches are struck, whilst on the Continent nitrate of potassium or lead and a little red lead or lead dioxide are often used instead, these matches igniting quietly and being known as "silent matches."

If phosphorus, even in the red form, is mixed with potassium chlorate, it forms a most dangerous explosive, which detonates violently on subjection to the lightest friction or blow, but in the match mixture, the particles of phosphorus and chlorate are coated with the glue used, and are thus preserved from intimate contact until friction is applied.

The match mixture is spread as a thin paste on tables made of iron, and heated by steam, the depth of mixture being gauged by a thin rim over which a flatting tool is passed. The ends of the splints already coated with paraffin are dipped in the mixture, and the wheels of splints are strung on spindles in small fireproof chambers to dry, a rapid draught of warm air being created by revolving fans. When dry the bundles are unrolled by machinery and taken to the "boxing" benches, where women take a handful of the matches, cut them in half by means of a sharp-hinged knife, and pack them into the boxes with marvellous rapidity.

At this stage of the operations, firing of the matches often takes place during frosty weather, when the air is crisp and dry, but under ordinary atmospheric conditions the loss from this cause is very small.

Safety Matches.—Bryant & May's "safety matches" contain no phosphorus in the head of the match, the tipping mixture consisting of antimony trisulphide, potassium chlorate and powdered glass, mixed into a paste with glue.

This mixture will explode when struck a sharp blow, and will ignite when subjected to very great friction, a long steady stroke across a sheet of glass being sufficient to ignite the safety matches, but they are not sufficiently sensitive to ignite with ordinary friction, doing so at once, however, when

rubbed against the composition on the side of the box, which contains amorphous phosphorus mixed with glass.

The manufacture of safety matches is in all respects the same as that described above, with the exception of the composition of the mixture used for the tips.

Wax Matches.—In the manufacture of wax vestas, cotton is wound off from the hank, and is passed in bundles of about a dozen strands through a melted mixture of stearin, containing either paraffin wax or gum dammar to harden it; the cotton is passed through several times until it has taken up the required amount of the wax mixture, and is then made uniform in size, and polished on the outside by passing through a warm metal plate pierced with holes of the required size.

At Messrs Bryant & May's manufactory, 800 miles of this taper can be made in a day.

The taper is passed on to the cutting machine, where in one operation it is cut to the required length for the matches, and clamped in frames with thin wooden battens between the rows, each frame holding 7,200 matches; the frames are taken to the dipping table, dipped in the mixture, dried in racks in fireproof chambers, and are then ready to be unpacked from the frames and put in the boxes.

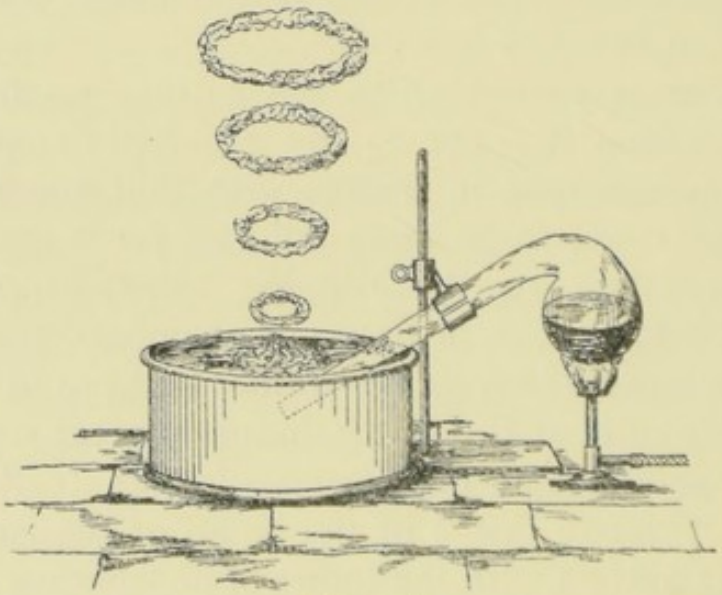
In all accounts of the match industry great stress is laid upon the painful and disfiguring diseases (called by the operatives "Phossy Jaw") of the bones of the face induced by constant contact with the fumes of phosphorus in a match factory, but of late years it has been found that attention to cleanliness of person amongst the operatives does away, to a large extent, with what undoubtedly was a great evil, and in such factories as Messrs Bryant & May's, where scrupulous cleanliness is enforced, it has practically disappeared. Red amorphous phosphorus, as it does not give off fumes, tends to reduce the danger, but in nearly all factories a larger quantity of ordinary than red phosphorus is still used.

Many attempts have been made, from time to time, to do away with the use of phosphorus in matches, but the action of the compounds used (which generally contain antimony sulphide and potassium chlorate as a basis) is not sufficiently certain to lead to their general adoption.

Compounds of Phosphorus.

Phosphorus does not directly combine with hydrogen, but by indirect means three compounds can be obtained, only one of which, however, is of any practical importance.

Hydrogen Phosphide (PH_3), phosphuretted hydrogen or phosphine, consists of hydrogen and phosphorus combined together in the proportion of thirty-one parts by weight of phosphorus to three of hydrogen, to which the formula (PH_3) has been assigned.



(Fig. 52).

A few pieces of ordinary phosphorus are placed in a retort (Fig. 52), which is then entirely filled with a solution of sodium hydroxide; if its mouth be placed under the surface of water and the retort and its contents heated, a gas is evolved, which, having filled the neck of the retort, escapes a bubble at a time, and each bubble as it comes in contact with air spontaneously inflames with a flash of white light and formation of rings of smoke, consisting of phosphorus

pentoxide, formed by the combustion of the phosphorus with the oxygen of the air. If instead of allowing the gas to escape into air it is collected in a cylinder over water, it will be seen to contain some oily drops, and also will deposit a yellow solid on the side of the cylinder. The liquid and solid are the other two "phosphines," the liquid having the composition (P_2H_4), and the solid the probable composition (P_4H_2), and it is to the presence of the liquid compound that the spontaneous inflammability of the phosphuretted hydrogen is due.

The formation of the gas may be represented as follows :—

Phosphorus	Sodium hydroxide	Water	Sodium hypophosphite	Phosphuretted hydrogen.

$$P_4 + 3(NaHO) + 3(H_2O) = 3(NaH_2PO_2) + PH_3.$$

If the evolved gas is passed through a tube cooled by a freezing mixture, the liquid phosphine (P_2H_4) condenses, and the phosphuretted hydrogen loses its power of igniting spontaneously. The liquid phosphine can also be removed by employing an alcoholic solution of potash, instead of an aqueous solution, when it is absorbed and kept back by the alcohol.

When quicklime and phosphorus are heated to bright redness in an air-tight crucible, or the vapour of phosphorus is passed over heated quicklime, a dark brown solid is obtained containing calcium phosphide. If this substance be thrown on to water, it decomposes with formation of liquid phosphine.

Calcium phosphide	Water	Calcium hydroxide	Phosphine.

$$2CaP + 4H_2O = 2Ca(HO)_2 + P_2H_4.$$

The liquid phosphine is very unstable and at once splits up into the solid phosphine and phosphuretted hydrogen, which ignites on coming into contact with the air.

Calcium phosphide rapidly deteriorates when exposed to air, being partially decomposed by the moisture present in it. This substance is used in "Holmes' lights," which consist of sealed cartridges containing calcium phosphide. To use

them the seal is torn off and they are attached to the buoy or other object, the position of which is to be made visible when in the water. The water decomposes the phosphide, and the flash of the burning phosphuretted hydrogen reveals the whereabouts of the floating object at night, whilst the heavy white smoke serves as a guide by day.

Phosphuretted hydrogen is a colourless gas with a very disgusting odour, resembling putrid fish. Its molecular weight is 34 and density 17.

In composition it resembles ammonia gas, and forms compounds analogous to those of ammonium. For instance, it combines with hydrogen iodide (HI) to form phosphonium iodide (PH_4I), corresponding to ammonium iodide (NH_4I).

Oxides of Phosphorus.—Phosphorus forms two well-defined oxides, viz. :—

Phosphorus trioxide, P_2O_3.
Phosphorus pentoxide, P_2O_5.

Phosphorus trioxide is a white, deliquescent powder formed by the slow oxidation of phosphorus in a limited supply of dry air. If the trioxide be heated to a high temperature in a sealed tube, it forms phosphorus pentoxide and phosphorus.

The trioxide dissolves in water to form phosphorous acid :—

Phosphorus trioxide		Water		Phosphorous acid.
P_2O_3	+	$3(H_2O)$	=	$2(H_3PO_3)$.

The solution is a very powerful reducing agent.

Phosphorus pentoxide (P_2O_5) is formed when phosphorus is burnt in dry air or oxygen ; it is a white flaky solid having an intense avidity for moisture. If left exposed to air, it rapidly deliquesces, and is used as a dehydrating agent, as it will abstract moisture from nearly all bodies which contain it, even sulphuric and nitric acids being dehydrated by it.

It may be sublimed unchanged, and when heated

with charcoal it breaks up into phosphorus and carbon monoxide.

Phosphoric Acids.—The pentoxide combines with water in three proportions, forming:

Metaphosphoric acid, $P_2O_5.H_2O = 2(HPO_3)$
Pyrophosphoric acid, $P_2O_5.2(H_2O) = (H_4P_2O_7)$
Orthophosphoric acid, $P_2O_5.3(H_2O) = 2(H_3PO_4)$.

Of these three acids the most important is orthophosphoric acid, or ordinary phosphoric acid (H_3PO_4). It is tribasic, and forms three classes of salts, as:

Monosodium orthophosphate = NaH_2PO_4
Disodium orthophosphate = Na_2HPO_4
Trisodium orthophosphate = Na_3PO_4.

The atoms of hydrogen can also be replaced by different monad metals as in microcosmic salt, which is hydro-ammonium sodium phosphate ($H.NH_4.NaPO_4$).

If orthophosphoric acid be heated to 215°, two molecules lose one molecule of water, and pyrophosphoric is formed, thus:—

Orthophosphoric acid		Water		Pyrophosphoric acid.
$2(H_3PO_4)$	=	H_2O	+	$H_4P_2O_7$.

This acid is tetrabasic, and forms four series of salts with monad metals.

If the orthophosphoric acid be heated to redness, one molecule of the acid loses one molecule of water, and metaphosphoric acid is formed, thus:—

Orthophosphoric acid		Water		Metaphosphoric acid.
H_3PO_4	=	H_2O	+	HPO_3.

This acid is also prepared by dissolving the pentoxide slowly in water. It is monobasic and forms only one class of salts. All these acids are deliquescent and very soluble in water. They are distinguished by the following tests:—

Orthophosphoric acid, when neutralised, gives a white

precipitate with barium chloride, and a yellow one with silver nitrate. Neither the acid nor any of the salts coagulate albumen.

Pyrophosphoric acid does not coagulate albumen, and gives white precipitates with silver nitrate and with barium chloride, only in neutral solutions.

Metaphosphoric acid coagulates albumen, and gives a white precipitate with barium chloride or silver nitrate.

Chlorine readily combines with phosphorus to form the *trichloride* (PCl_3). It is a colourless fuming liquid, decomposed by water into phosphorus and hydrochloric acids:—

Phosphorus trichloride		Water		Hydrochloric acid		Phosphorous acid
PCl_3	+	$3(H_2O)$	=	$3(HCl)$	+	H_3PO_3.

The trichloride readily absorbs chlorine to form *phosphorus pentachloride* (PCl_5), which is a yellowish crystalline solid. If this substance be exposed to moist air, it forms phosphorus oxychloride ($POCl_3$).

Arsenic (As=75)

Is often classed amongst the metals on account of its lustre and other physical properties which it possesses. It is incapable of forming a base with oxygen, and the general character of its chemical combinations justifies its consideration with the non-metals. Being a complete analogue of phosphorus, it is best studied after that element.

The element is found in combination with iron as mispickel ($FeS_2.FeAs_2$), also as realgar (As_2S_2), and yellow orpiment (As_2S_3). The ore is roasted, and the fumes of arsenic trioxide are collected and reduced with charcoal in covered crucibles, arsenic subliming in the upper part of the apparatus.

Arsenic oxidises slightly in moist air, is very brittle and crystalline. At 180° C. it volatilises without fusion, and its vapour density is twice as great as its atomic weight, consequently its molecule is assumed to contain four atoms

instead of two. The vapour has the peculiar odour of garlic.

Oxides. — On heating, arsenic readily combines with oxygen to form the *trioxide* (As_2O_3). Arsenic trioxide dissolves to a small extent in water to form arsenious acid (H_3AsO_3), but this is not known in the free state. It combines with metals to form arsenites.

If arsenic or the trioxide be warmed with nitric acid, the *pentoxide* is formed (As_2O_5). This oxide combines with three molecules of water to form arsenic acid (H_3AsO_4), which forms salts called arsenates, corresponding to the phosphates.

Arsenic trioxide, or white arsenic, is employed in the manufacture of glass, in the preparation of colouring matters, as a constituent of sheep dipping compositions, fly papers, vermin killers, and in arsenical soap, which is used for the preservation of skins and natural history objects.

Commercial white arsenic is a fine white powder so closely resembling flour in appearance that it has occasionally been substituted for it, with disastrous results. It is however, so heavy (sp. gr. 3·8) that it can easily be distinguished from flour, and under the microscope is seen to consist of glassy crystalline fragments.

White arsenic is, fortunately, only very slightly soluble in water; a cold saturated solution only containing 2·5 grams of the oxide in a litre of water. In event, then, of the oxide being thrown into water, but little dissolves; and if the mixture be stirred and swallowed, the insolubility of the oxide aids the treatment by antidotes, the chances of success being greater than in the case of easily soluble metallic poisons. The smallest dose, attended with fatal results, is about two grains.

The employment of arsenic as a constituent of green colouring matter is now, happily, to a great extent, a thing of the past; but it has been recklessly employed in wall papers, lamp shades, and even as a colouring matter for confectionery.

If zinc, alloyed with arsenic, be acted on by dilute sulphuric acid, the hydrogen given off is mixed with an excessively poisonous gas called *arsenuretted hydrogen* (AsH_3). This gas is readily decomposed on heating, arsenic being deposited. It burns with a livid flame forming arsenic trioxide and water. If a cold surface be depressed on the flame, so as to lower the temperature of the gas, a mirror of arsenic is obtained (Marsh's test).

If arsenious acid be distilled with strong hydrochloric acid, *arsenious chloride* is obtained ($AsCl_3$). This affords an excellent method of determining the presence of arsenic in certain cases, the material being boiled with strong hydrochloric acid in a retort, the distillate is diluted with water and sulphuretted hydrogen gas passed through. If any arsenic be present, a yellow precipitate of the sulphide (As_2S_3) will be obtained. This method, however, is useless in determining the presence of arsenic when mixed with organic matter, on account of the frothing up of the mixture when boiled. The simplest way is to acidify with hydrochloric acid, place in the mixture a sheet of clean copper on which a narrow strip of platinum foil has been wound, and warm gently. If any arsenic be present, it will be deposited on the copper. To determine its presence the copper is carefully wiped and dried, and heated in an open tube. The arsenic will oxidise to trioxide, and the crystals formed can be dissolved and tested in the usual way (Reinsch's test).

CHAPTER XXIV.

The Metals.

Metallic properties—Occurrence of metals in Nature—Processes by which the common metals are obtained from their ores—General properties of the metals: lustre, colour, tensile strength, elasticity, malleability, ductility, specific gravity, conduction of heat and electricity, fusibility—Structure of metals: Fracture, micro-structure—The effect of heat and mechanical treatment on structure—Classification—The Periodic system.

THE elements are for the sake of convenience divided into two groups, the non-metallic elements and the metallic; but it must be clearly borne in mind that no natural line of demarcation of this kind exists, and that the properties of the elements exhibit a gradual transition from those elements which are unmistakably non-metallic in their characteristics to those which have equally definite metallic properties, so that with some elements, such as arsenic, a certain amount of doubt exists as to which division they should belong.

Physically, metals are recognised by their lustre and power of conducting heat and electricity, whilst the chemical definition of a metal is "*an element capable of forming a base by union with oxygen.*"

Nearly all the metals used in the arts and manufactures are found in Nature combined with other substances; indeed, gold and platinum, both of them rare metals, which have very little affinity for other elements, or compounds, are the only exceptions to this; the remaining metals, although small quantities may be sometimes found uncombined, practically exist only in combination. If we take a piece of iron and expose it to the action of moist air, the iron rusts, that is, becomes finally converted into a compound of iron

with the oxygen of the air, called oxide of iron; the whole of the original metal being eaten away if exposed for a sufficiently long period. Again, if we leave a silver vessel exposed to the air, it slowly becomes tarnished, due to the formation of sulphide of silver on its surface, caused by traces of sulphuretted hydrogen in the atmosphere. It is therefore evident that our ordinary metals are in a more or less reactive condition, and, if left to themselves, are ready to unite with certain other substances to form compounds; and it is for this reason that these metals are not generally found in a pure state in Nature.

The native compounds of the metals we call "minerals" or ores, and the art of extracting metals from their ores we call "metallurgy."

The principal ores are, as a rule, oxides, sulphides, carbonates, arsenides and silicates of the metals, and have most of them been formed at a high temperature. These compounds hardly ever occur in a separate state, but are more or less mixed with other minerals, and in nearly all metallurgical operations, the ore from which the metal is to be extracted has to undergo several mechanical operations in order to free it as far as possible from these extraneous matters, before it can be subjected to the particular chemical operations which isolate the metals from the elements with which they are combined.

In all the metallurgical processes which are here considered the chemical actions taking place are aided by the action of heat, and these actions may be divided into two classes, roasting and smelting. The *roasting* may be either (*a*) *roasting and reducing*, as when oxide of iron is heated to a temperature short of its melting point in contact with gases capable of abstracting its oxygen and leaving metallic iron; or (*b*) *roasting and oxidising*, as when sulphide of copper is roasted in a current of air, when the oxygen of the air converts the sulphur into sulphur dioxide, and the copper into oxide of copper. The reducing or oxidising nature of the action is determined by the kind of furnace

used and the proportions of air, fuel and ore taking part in the operation.

In roasting operations the temperature employed is not allowed to rise to the melting point of the materials used; but in *smelting*, sufficient heat is generated to melt the substances. In the liquid state they then react upon one another, forming new compounds, and in some cases liberating the metal, as when oxide, sulphide and sulphate of lead are melted together and produce metallic lead with liberation of gaseous sulphur dioxide.

By the term "oxidation" we imply an action in which the oxidisable element or compound combines with the element oxygen, as when iron rusts, or carbon burns in oxygen gas; while the term "reduction" means the abstraction of oxygen or some element resembling oxygen in its behaviour, such as sulphur, from a compound; as, for instance, when copper oxide is heated in a stream of hydrogen gas, the hydrogen takes the oxygen from the copper oxide to form water and "reduces" the copper oxide to metallic copper.

In all metallurgical processes the most valuable reducing agent in use is carbon, the solid itself reducing many metallic oxides when heated in contact with them, whilst a still more powerful effect results from its partial combustion to carbon monoxide, this gas having great reducing properties. Not only therefore does carbon, in the form of coke, charcoal, or coal, supply the necessary heat to carry on the process, but it also plays an effective chemical part.

General Properties of the Metals.—With the exception of mercury, all the metals are solid at ordinary temperatures; most of them have definite crystalline structures, and are possessed of a certain power of reflecting light called metallic lustre, which, however, they exhibit only when in compact masses and not when in a fine state of division.

For a metal to exhibit lustre in a high degree, it follows that its surface must not easily be acted upon by the

atmosphere, thus gold, platinum and highly burnished steel have a high lustre, whilst such metals as lead have but little lustre.

Colour is also an important characteristic of metals, and determines mainly their use for certain purposes; for example, the great advantage in coins of having marked differences in colour, and again for ornamental work in metals.

However, practically all metals in common use derive their great value from their more purely mechanical properties; their strength; the ease with which they can be worked to the desired shape; their fusibility, and such properties; and for most purposes strength must be the first consideration.

When a piece of metal is subjected to a stretching force (*stress*), a certain amount of extension (*strain*), is produced, this being proportional to the stress up to a certain point. If the stretching force is no longer applied, the metal returns to its original dimensions, that is, it has *elasticity*. After reaching this *limit of elasticity*, the strain increases in greater rapidity than the stress, and now on releasing the metal from the tension it no longer attains its original dimensions, in fact it has become permanently distorted. Further stretching leads to actual rupture of the metal, and the stress applied, in tons per square inch, to bring about this result is taken as the measure of the *tensile strength* of the metal. Between the point when permanent distortion and actual rupture occurs, there may be a short or long period depending greatly on the particular metal. A metal which goes on stretching for some time before rupture is said to have high extensibility, for example copper, a property which permits of much work being done on the metal by hammering, rolling, etc., whilst hard steel, although having high tensile strength, has little extensibility, consequently it cannot be *appreciably* beaten out or rolled when cold.

A large number of factors influence the actual tensile strength of any metal, such for example as the amount of

work which has been done on it, and therefore values for the tensile strength must not be regarded as fixed points in the same way that the melting point may be. For instance, cast copper has a tensile strength of about eight tons, whilst that of sheet copper amounts to some fifteen tons, and of copper wire to twenty-eight tons.

The tensile strength also is largely influenced by the presence of foreign substances; thus with steels it increases with the increase of carbon present, but the actual effect of various other elements it is more convenient to consider when dealing with the properties of the individual metals.

The Malleability is a measure of that property which certain metals possess of being rolled or beaten out into sheets, and will naturally be largely dependent on the extensibility of the metal. The influence of temperature on malleability is very great, thus zinc is not malleable at ordinary temperatures, but can readily be rolled at 150° C.; again ordinary brass is malleable at the normal temperature, but Muntz metal, containing a higher percentage of zinc, must be rolled hot.

A metal is said to be *ductile* when it can readily be drawn down into wire, a condition which will mainly depend on the softness of the metal and on its tensile strength, since it has to resist the pull necessary to draw it through die plates of diminishing section. A metal, therefore, which is extremely malleable (soft) may not possess the necessary strength to permit of it being drawn into wire, for example lead. Iron or mild steel, on the other hand, although not particularly soft, have such high tensile strength that they may easily be drawn down very fine, a process which greatly increases the tensile strength, thus a piano wire of 0·0284 inches diameter had a tensile strength equivalent to 211 tons per square inch.

The *Specific Gravity* of metals varies greatly and is frequently a determining factor in their suitability for many purposes, thus the high specific gravity of gold enables a high value to be attained in a small compass in coinage,

whilst the low specific gravity of aluminium, combined with its relative strength, gives the metal many advantages for certain special purposes, examples of which are its use in the framework of balloons and for overhead conductors for high voltage currents, it being extensively employed for this latter purpose in the big power works at Niagara.

Any treatment of the metal which tends to bring the particles closer together, such as rolling, hammering or pressing, will naturally increase the specific gravity.

The specific gravity of the metals as compared with water varies considerably, lithium being the lightest, whilst osmium and iridium are the heaviest.

SPECIFIC GRAVITIES OF COMMON METALS.

Lithium ...	0·50	Cobalt	8·5
Potassium ...	0·86	Cadmium ...	8·6
Sodium ...	0·97	Copper	8·9
Calcium ...	1·58	Bismuth	9·8
Magnesium ...	1·75	Silver	10·5
Aluminium ...	2·56	Lead	11·4
Barium ...	3·75	Mercury	13·59
Antimony ...	6·7	Gold	19·3
Zinc	7·1	Platinum ...	21·5
Tin	7·3	Iridium	22·4
Iron	7·8	Osmium	22·4

Metals may be divided into two groups according to their specific gravities, those below five being called the "light metals," whilst those above are called the "heavy metals." The light metals generally exhibit considerable chemical energy and oxidise readily, forming strong basic oxides, whilst the heavy metals are less energetic and form weaker basic compounds.

The metals are all conductors of heat and electricity, two properties in which they are in somewhat close agreement, as will be seen from the table below. The high conductivity of copper makes it particularly valuable for electrical purposes, but here the influence of even traces of impurity is

very great. The resistance increases rapidly with rise of temperature, and the converse is true with lowering of temperature, in fact at extremely low temperatures, such as that of boiling liquid air, all pure metals become practically ideal conductors, but this does not apply in the case of alloys.

CONDUCTIVITY OF THE COMMONER METALS FOR HEAT AND ELECTRICITY.

Metal.	Heat.	Electricity.
Silver	100	100
Copper	73·6	77·4
Gold	53·2	55·9
Tin	14·8	17·0
Iron	11·9	14·4
Lead	8·5	7·7
Platinum	8·4	10·5
Bismuth	1·8	1·2

The Fusibility of metals and alloys is of great practical importance, since those which can be brought readily to the liquid condition may be employed for the production of castings, as with iron, brass, gun-metal, etc., whilst the ready fusibility of the alloys containing tin and antimony, together with the slight expansion they undergo on setting, render them extremely valuable for type in printing. On the other hand, the high melting point of platinum is of the greatest value, since it enables crucibles, etc., of this metal to be employed in the laboratory without fear of fusion: and again, to cite a more common example, the infusibility of wrought iron makes it the best of all the common metals for use as fire bars.

All metals are fusible, but their points of fusion vary very widely, as shown in the following table:—

Melting Point of Common Metals.

Metal.	Melts at °C.	Metal.	Melts at °C.
Mercury ...	−39	Aluminium ...	654
Potassium ...	+62	Silver	962
Sodium	97	Gold	1065
Tin	232	Copper	1085
Bismuth ...	270	Cast iron ...	1150
Cadmium ...	321	Nickel	1484
Lead	327	Wrought iron ...	1500
Zinc	419	Platinum ...	1780
Antimony ...	630	Iridium	1950

Structure of Metals and Alloys.

It is at once apparent that many of the physical properties of the metals will, to a large extent, be dependent on their actual structure, and it can readily be shown by even a superficial examination that many mechanical operations have a profound influence on the structure. Although in accordance with our usual system of classification all metals, with the exception of mercury, are regarded as solids, the fact must not be overlooked that metals generally do not exhibit that extreme rigidity which is associated with the ideal solid, for in all of them a certain amount of internal movement or "flow" can be brought about, depending on their "extensibility." Lead, for example, is commonly "squirted" under a pressure of some thirty-three tons to the square inch, behaving as a viscous fluid, and further examples of this flow are seen in the striking of medals, in planing, polishing and "spinning."

The appearance of the fractured surface of a bar of metal has always been the worker's guide to the quality of the metal and the timing of the operations involved in its production, and the fracture is a rough indication of the

molecular arrangement in the metal. Zinc, for example, exhibits a highly crystalline fracture, whilst that of hard steel shows an extremely fine grain; wrought iron, on the other hand, having a fibrous fracture.

The structure as exhibited by the fracture will be greatly influenced by the treatment to which the metal has been subjected. Slow cooling, allowing as it does the particles to arrange themselves, generally tends to the production of a coarse fracture, a fact well illustrated in the differences observed in the case of a large casting, the more solid parts of which having taken the longest time to cool, develop a relatively coarse structure, as shown by the fracture. When metal is "chilled" in casting, the outer portion will exhibit a fine fracture.

The introduction of the microscope into the study of the structure of metals by Dr Sorby in 1864, marked a period of great advance in metallurgy generally, and now the microstructure of metals forms an important branch of the study, and has done much to throw light on many hitherto obscure problems. For the purpose of examination, the metal is first highly polished, in which process frequently considerable structure becomes visible, since the softer portions are more readily rubbed away, but generally it is necessary to further develop the structure by suitably etching away certain constituents, or staining them in a characteristic manner.

Under suitable treatment most pure metals exhibit a definite crystalline structure, thus with copper (Plate I.), silver (Plate II.), lead, tin and zinc well developed crystals may be obtained.

The effect of working and heat treatment is well shown in the case of brass, such as that employed for production of cartridge cases, which contains 70 per cent. of copper and 30 per cent of zinc. Plates III. to VI. show the structure of such brass after subjecting to varying heat treatment. Starting with the metal which has been rolled as hard as possible, it exhibits practically no structure (Plate III.).

On heating up to a bright red and quenching, the structure is well developed, consisting of polyhedral grains (Plate IV.). If the metal is maintained at different temperatures short of its melting point, definite crystalline structure is developed, the size of the crystals depending on the temperature and length of time the metal is maintained at this temperature (Plates V. and VI.). The metal is now thoroughly annealed; mechanical work upon it results in the breaking down of the crystalline form, portions of the crystals interlocking, as it were, with each other, giving increase in tensile strength, the metal at the same time becoming hard, and ultimately all trace of crystalline form is lost. If the metal is not again annealed further working is impossible without cracks and flaws being developed. Such a crack is shown between the grains in Plate VII.

If the metal is raised to just on its fusion point, the crystalline form is entirely changed, and in Plate VIII. will be seen to consist of a fern-like structure, termed "dendritic," which, of course, will be that characteristic of cast brass. In the specimen illustrated, the fern-like crystals were easily seen with the naked eye.

The effect of annealing on gun-metal is also shown in Plate IX.

In most alloys we have more than one definite constituent present, and although chemical analysis can show the actual amount of each element present, it leaves us quite in the dark as to the manner in which these elements are associated. Here the microscope comes to our aid and we are able to differentiate between the various constituents themselves. This is of special importance in the case of alloys containing an "eutectic" (*see* Alloys), for the influence of eutectics is often considerable, and although their presence can be detected in other ways, the microscope affords by far the simplest method.

The segregation of certain constituents, often the eutectic itself, is a matter of considerable importance, and is readily seen under the microscope. A comparison of the structure

of Muntz metal (Plate X.), (63 Cu : 37 Zn), with that of the brass, will show clearly the two distinct constituents of the former. The existence of these two constituents, one of which is relatively rich in copper, the other in zinc, has been shown to have a great influence on the deterioration of such metal, since in the presence of an exciting liquid they form a galvanic couple, which results in the corrosion of the portion richer in zinc. Again in the case of cast iron, this frequently undergoes rapid attack, especially when exposed to the action of acid waters in mines, and the course of this attack along the graphite plates present is easily seen under the microscope.

An interesting case of the light microscopic investigation throws upon practical questions is afforded in the case of anti-friction metals. By simply polishing on a yielding material, hard matrices, often of a beautiful crystalline character, are revealed, these being embedded in a mass of a softer constituent. There can be little doubt but that the value of these metals is greatly dependent on this physical structure, the harder portions carrying the shaft in a yielding body of the material, and wear of this softer part will readily permit of a film of lubricant being maintained.

Undoubtedly the most interesting and valuable work in this field has been done in connection with iron and steel; in conjunction with accurate temperature measurements, by means of a Le Chatelier thermojunction, usually of platinum with platinum-rhodium (10 per cent). We are now able to fully understand the important changes taking place during the whole heat-treatment steel undergoes, such as hardening, annealing and the restoration of "burnt" steel.

Like a mineral, steel may be regarded as built up of certain definite constituents, which by suitable etching and staining, may readily be identified under the microscope. As to the actual composition of some of these substances, much difference of opinion exists, but this in no way affects the general deductions which may be drawn as to their influence. The whole question is so intimately connected

with the condition of the carbon in the steel, that its detailed discussion must be deferred till this is dealt with, only pointing out at the present that the work has had a most important influence on the whole method of treating steel during its production, for it has clearly shown the manufacturer what a very great influence even a few degrees of difference in temperature may have on the properties of the material.

Classification of the Metals.

Various systems of classification of the metals may be adopted, but for scientific purposes it is most convenient to classify all elements according to the various groups they form, in accordance with the Periodic Law. If the elements are arranged in the order of their atomic weights, it will be found that at certain regular intervals there is a recurrence in chemical and physical properties; in other words, *the properties of the elements are functions of their atomic weights.* If then the elements be tabulated in the order of their atomic weights, dividing them into periods where recurrence of properties are found, then they will be found arranged in well defined families, the members of which exhibit close similarity in properties.

Taking the first fourteen elements, after hydrogen, for example, we shall have the following:—

Li=7	Be=9	B=11	C=12	N=14	O=16	F=19
Na=23	Mg=24	Al=27	Si=28	P=31	S=32	Cl=35·5

With these, there is a reappearance of properties at each *eighth* element, and, moreover, definite progression in properties as we pass horizontally along the elements. Lithium and sodium on the one hand, and fluorine and chlorine on the other, are strikingly similar. The former are strongly electro-positive; the latter as strongly electro-negative. The valency of the elements in the first column is I.; in the second, II; in the third, III.; in the fourth, IV.; in the fifth,

III.; in the sixth, II.; in the seventh, I.; a progressive increase and decrease. Not only have the elements in a group similar properties, but their compounds are very similar.

It was found that if the elements were arranged strictly according to their atomic weights that certain discrepancies occurred in the properties of elements which would fall in the same group. This might arise from two causes; inaccurate determination of the atomic weight or the existence of an undiscovered element, in which case a gap would occur. Mendeléeff, who elaborated this Periodic arrangement, indicated certain elements, which, failing to comply with the requirements, should have different atomic weights to those accepted at the time, and re-determinations of these atomic weights proved the accuracy of his prediction. Further, he predicted exactly the properties, atomic weights, etc., of unknown elements which should occur to fill certain gaps, and in some cases these elements have been found, and fulfil in every detail their anticipated properties.

Clearly such a system of classification is of great value, in that it enables a control, within limits, of the atomic weights of known elements, and further is of advantage in pointing out the probable existence of hitherto undiscovered elements.

Since it is not within the scope of the present volume to deal with the whole of the metals, but only with those more generally employed, it is impossible to adhere to this systematic classification; therefore the metals have, as far as possible, been arranged in the order of their industrial importance. The full systematic arrangement according to the Periodic system will, however, be found in the Appendix.

CHAPTER XXV.

Iron and Steel.

Ores of iron—Production of iron in the blast furnace—Preparation of the ore, the furnace charge, construction of the furnace, working—Reactions in the furnace—Pig iron—Cast iron—Malleable castings—Wrought iron—The puddling process—Treatment of puddled iron for production of bar iron—Steel—Cementation process—Crucible steel—Case hardening—Armour plate—The Bessemer process, acid and basic—Open Hearth process, acid and basic—Ingot steel—Properties of iron and steel—Influence of other elements—Carbon—Saturated, unsaturated and super-saturated steel—Micro-constituents—Hardening of steel—Phosphorus, sulphur and silicon—Special steels—Manganese steel—Nickel steel—Chrome steel—Tungsten steel—Self-hardening steels—Vanadium steel—Compounds of iron.

Iron (Fe=56).

IRON is by far the most important of the metallic elements; its strength with comparative lightness, its fusibility in certain forms, the possibility of welding masses of it together, and the hardness which can be imparted to it, make the applications of the metal extremely varied. Further, the comparative ease with which the metal may be reduced from its ores, and the wide and abundant distribution of these ores, make the first cost of the metal very low.

Metallic iron is met with in the form of meteorites, metallic masses which occasionally fall upon the earth from unknown sources, and which generally contain small quantities of other metals, such as nickel, cobalt, chromium, etc.

The chief native compounds which are sufficiently abundant to make them valuable as a source of the metal are:—

		Percentage of iron in pure ore.
Magnetic iron ore	Fe_3O_4	72
Specular iron ore / Red hæmatite	Fe_2O_3	70
Brown hæmatite	$2(Fe_2O_3).3(H_2O)$	60
Spathic iron ore	$FeCO_3$	48
Clay ironstone	$FeCO_3$, mixed with clay,	17 to 48
Iron pyrites	FeS_2	46

These ores all contain certain quantities of foreign impurities, some of which, like sulphur and phosphorus, are nearly always present and exert a deleterious influence on the metal obtained from them. The magnetic iron ore, specular ore, and red hæmatite are the purest ores, and it is from these, therefore, that the best iron is obtained, whilst the difficulty in separating the sulphur prevents iron pyrites from being used as a source of the metal.

Magnetic and specular iron ore, however, do not exist in sufficiently large quantities in England for them to be much used, and the density of the red hæmatite offers considerable obstacles to its easy reduction, so that the most commonly used ores in this country are the brown hæmatite, the spathic iron ore, and the clay ironstone; in spite of the low percentage of metal present in the latter ore, it is the one from which by far the largest proportion of iron is made in this country.

Production of Pig Iron in the Blast Furnace.—Many simple forms of furnace have been employed in the production of iron, which, by varying the working conditions, may be obtained in almost any of its well recognised forms, but for all practical purposes we may regard the pig iron as produced in the ordinary practice of smelting in the blast furnace as the parent body from which all the different grades are obtained, ranging from wrought iron, which is nearly free from carbon, to a high carbon steel.

The reduction of a simple oxide of iron by means of charcoal in a suitable small furnace is an easy operation, the iron so produced being of remarkable purity, and charcoal iron is still produced for special purposes in this way. The majority of the iron ores are, however, not in bulk the simple bodies represented by the preceding formulæ, but contain varying amounts of foreign mineral matter which complicate the process of production. These foreign bodies have to be converted into fusible compounds termed "*slags*" to facilitate their removal and the separation of iron. Slags are essentially silicates consisting of a basic portion (CaO, Al_2O_3, etc.), with silica (SiO_2) as the acid radicle. The production of a slag fusible at a low temperature is the first essential of blast furnace practice. The ore may contain an excess of silica, in which case before smelting it is necessary to add some basic substance, such as lime (CaO), termed a "*flux*," to form the fusible silicate (slag). On the other hand a basic ore will require an acid flux, (SiO_2).

Ferrous oxide (FeO) readily forms a very fusible slag with silica, and this would lead to great loss of iron, which has to be carefully guarded against.

Preparation of the Ore.—In the case of the purer ores, the hæmatites and magnetites, no preliminary treatment is required, but poor clay ores are frequently washed, or in some cases "weathered" in order that the sulphur present as pyrites may be largely oxidised and washed away. Ores containing carbon dioxide require a preliminary calcination, which drives off water and carbon dioxide, rendering the ore more porous, and at the same time converting any ferrous oxide (FeO) into ferric oxide (Fe_2O_3), an important consideration in view of the ease with which the former combines with silica to produce the fusible slag already mentioned.

Charge for the Furnace.—This may conveniently be divided under three headings :—

(*a*) The ore or a mixture of ores.
(*b*) The fuel, usually specially prepared coke.

(*c*) The flux, which as already pointed out, depends on the nature of the ore. Frequently the blending of a clay ironstone (acidic), with a calcareous ore (basic) is all that is needed.

In general terms we may say that for the production of one ton of metal a solid charge of some three tons of ore, fuel, and flux will be required.

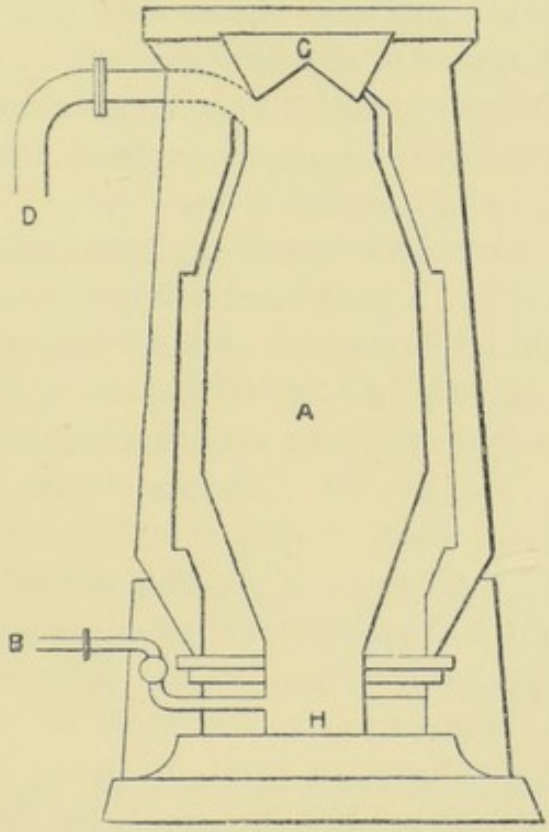


Fig. 53.

The Blast Furnace is usually built up of wrought iron plates riveted together and lined with a thick layer of fire-brick slabs, the whole being supported on a ring carried by iron pillars, to allow free access to the portions around the hearth. The height and capacity of the furnaces varies greatly, those in the Cleveland district averaging from 80 to 90 feet, with a cubic capacity of some 30,000 feet. Considerable diversity of opinion exists as to the best proportions of the relative parts, but the central portion or *body* is invariably cylindrical (A, Fig. 53), tapering inwards at the top to the

throat, and similarly at the bottom forming the *bosches*, which terminate in the *hearth* (H), the size of which largely influences the output of the furnace.

At one time the top of the furnace was always open, the gases produced in the furnace being burnt there on coming in contact with the air. The utilisation of these gases was first introduced in 1845, the usual arrangement for collecting them being shown at (C), where there is a cup-shaped opening, closed by an inverted cone, kept in position by a balanced lever arm. On shooting a charge on to this cone it is depressed, allowing the charge to pass into the furnace, when it again rises into its proper position, causing the gases to pass away through a suitable flue (D).

The temperature of the escaping gases varies between 150° and 270° C., and they are utilised after combustion for heating up the hot blast stoves, raising steam, and in many modern works directly in suitable gas engines. The blast is supplied from a main (B) to a ring running round the hearth from which it is delivered into the furnace through the "*twyers*," which are water cooled, probably six of these being arranged around the hearth in suitable positions. The air is supplied at about 5 lbs. pressure from blowing engines, these frequently having a capacity of 25,000 cubic feet per minute.

For certain classes of iron the blast is used cold, but a very great improvement in blast furnace practice resulted from the introduction of the hot blast by Neilson in 1829, the output of a particular furnace being greatly increased, the fuel consumption diminished, whilst at the same time certain classes of coal could be used directly in the furnace without previous coking. Two stoves are built close to each blast furnace, these being arranged with a suitable checker-work of firebrick; through one of these the hot waste gases are being led with the air necessary for combustion, thus heating up the one stove, whilst the air blast is being forced through the other stove in the reverse direction, taking up the heat from the hot firebrick within. Control over the temperature of the blast is now usually maintained by a

suitable self-recording pyrometer, the valves controlling the stoves being operated to reverse the gas and air current, when the temperature of the blast has reached the minimum permissible. The initial temperature of the blast is frequently above 800° C.

The furnace, when once "blown in," is kept in blast for years, the ore, flux and fuel being regularly charged in proper proportions, control of which is maintained by regular analysis of the metal and slag. In most modern forms of furnace a "closed" hearth is employed, the molten iron settling to the bottom, and over it the fused slag, which flows away continuously through a suitable *slag-notch.* The metal is tapped every twelve hours, being run off through sand channels into sand moulds, placed at right angles to the channels, where it solidifies into "pigs," which are ⊔-shaped in section, and weigh from 1 to 1½ cwts. each.

A high average output for an English hot blast furnace may be taken as 1000 tons weekly, whilst in American practice 2500 tons is common.

Reactions in the Blast Furnace.—These may be most conveniently divided under two heads; (*a*) those changes taking place in the ascending gas current; (*b*) those in the descending charge.

(*a*) The oxygen of the blast on entering at the twyers, at once combines with the carbon of the fuel forming carbon dioxide; this at the very high temperature becomes dissociated into carbon monoxide and oxygen, the latter combining with a further amount of carbon forming more carbon monoxide.

Carbon		Oxygen		Carbon dioxide.
C	+	O_2	=	CO_2.
Carbon dioxide		Carbon monoxide		Oxygen.
CO_2	=	CO	+	O.
Carbon		Oxygen		Carbon monoxide.
C	+	O	=	CO.

This is clearly shown by the fact that neither free oxygen nor carbon dioxide is found in the ascending gases a short distance above the twyers.

As the gas current ascends, carbon dioxide is found in increasing quantities, and this is believed to be due mainly to the decomposition of carbon monoxide into carbon dioxide and *free carbon* when in contact with hot spongy iron, the particles of the latter becoming impregnated with carbon.

Iron		Carbon monoxide		Iron		Carbon		Carbon dioxide.
Fe	+	2 CO	=	Fe	+	C	+	CO_2.

Near quite the upper part of the furnace, the exact locality varying with the conditions, the carbon monoxide reduces the iron oxide, forming carbon dioxide and metallic iron.

Iron oxide		Carbon monoxide		Iron		Carbon dioxide.
Fe_2O_3	+	$3CO$	=	Fe_2	+	$3CO_2$.

Certain subsidiary changes in the gases also go on at the same time; thus in the body of the furnace carbon dioxide is constantly combining with more carbon to form carbon monoxide, and again when carbonates are present (as when mes tone is used as a flux), carbon dioxide is evolved in the higher parts of the body. In general, a high percentage of carbon monoxide must be maintained in the furnace for the successful production of iron.

(*b*) Considering the solid material as it is situated in the furnace during actual working, we have in the upper part reduction of the iron oxide by carbon monoxide, the breaking up of carbonates into oxides with evolution of carbon dioxide, and still lower the deposition of carbon from carbon dioxide on the surface of the iron, all these changes being completed within thirty feet of the throat. Throughout the body of the furnace little further change occurs, but on reaching the high temperature zone above the twyers, fusion rapidly takes place, the whole flowing down into the hearth, where the iron separates as a layer beneath the slag. In this hot zone any ferrous oxide is reduced by carbon, and it is entirely in this zone that silicon and phosphorus are set

free from their compounds by carbon, to afterwards appear in the metal, on which, as will be seen later, they exercise a marked influence.

Pig Iron.

The material as obtained from the blast furnace is known as "*pig iron*"; after re-melting and casting it is known as "*cast iron*," though no chemical difference is to be found between them.

In each case a considerable quantity of carbon is present, the actual amount as well as its condition (whether free or combined) depending on the other elements present. Pure molten iron can dissolve about 7 per cent. of carbon, the maximum in pig or cast iron being about 4·5 per cent. (Howe). Chromium and manganese increase the amount of carbon iron can dissolve.

When the molten iron solidifies, the dissolved carbon may be thrown almost completely out of solution as plates of graphite, or it may remain almost wholly in the combined state, when the iron will be white, the rate of cooling and the presence of other elements (especially the latter) having a marked influence on the condition of the carbon. Slow cooling and the presence of silicon and aluminium set the carbon free, producing a soft grey iron, whilst rapid cooling and the presence of sulphur, manganese and chromium produce a hard white iron.

Pig iron is commercially graded according to the appearance of its fracture, the greyest iron (containing most free carbon) being termed No. 1, whilst the hard white iron is the last of the series. The general classification in this country is:—

No. 1
No. 2
No. 3
No 4 (Foundry)
No. 4 (Forge)
Mottled
White.

The influence of the working conditions in a blast furnace

on the quality of the iron will be very great; for example, any working conditions which tend to leave much silicon in the iron will produce also a grey iron, whilst conditions favourable to the retention of sulphur will produce a white iron. Now silicon is produced in greatest quantity when high temperatures are attained, that is when the fuel bears a high ratio to the ore, hence low ore-burdens tend to produce high quality grey irons rich in silicon; whilst low fuel consumption will tend to produce a poor white iron rich in sulphur.

The differences existing between grey and white pig iron are very marked.

Since grey cast iron is nearly pure iron with free carbon distributed throughout it, it is comparatively soft and can be easily worked; it has a higher fusing point than white iron, but when fused is more liquid, and when used for castings expands at the moment of solidification.

White iron has a higher specific gravity than the grey, and is excessively hard and brittle; it fuses at a lower temperature than the grey iron, but is never so liquid or so well adapted for taking castings as the grey.

If molten grey iron is suddenly cooled, the graphite which has redissolved in the liquid metal has not time to separate, and the casting becomes in consequence extremely hard and of the appearance of white iron. This is taken advantage of in "*chill casting*," by which shot and shell cast from grey iron have the apex and outer skin of metal made as hard as steel by casting them in iron moulds. The hard material so produced is very brittle, but since the interior portion has cooled more slowly, this interior consists of tough grey iron, which gives it any necessary support. Great judgment is needed in selecting a suitable iron for chilling, one which gives a slightly mottled fracture when cast in sand being best.

Cast Iron.—This is the cheapest form in which iron can be commercially applied, its great value being due to the

ease with which it can be melted and the exactness with which it takes the form of the mould, since on solidifying slight expansion takes place.

As compared with cast steel it has the following advantages: less cost in production of the moulds, smaller losses in casting, and further the castings do not require the careful annealing which steel castings must undergo.

An iron simply containing carbon, which may be termed "pure cast iron," is quite unsuitable for casting purposes, the small amounts of other elements present in ordinary cast iron, notably silicon, conferring upon the metal its much desired characteristics. "Pure cast iron" lacks fluidity, and castings in it contain many blow-holes.

It is seldom that one class of iron is employed for castings, since the desired amounts of those constituents which tend to produce good results can only be obtained by blending, whilst further the use of mixed irons places the iron-founder in a more independent position as regards supplies.

The metal is usually melted down in a cupola with about one quarter of its weight of fuel, when the iron undergoes certain changes, the silicon being reduced, owing to oxidation, whilst the sulphur is increased, since a certain amount is generally absorbed from the fuel. Further, the total amount of carbon is somewhat reduced, whilst the alteration in the silicon and sulphur both tend to the production of white iron having the carbon in a combined condition, hence the metal becomes harder. A soft grey iron, in fact, is considerably improved in strength.

Care has to be exercised in the selection of a metal suitable to the size of the casting it is intended to produce, a coarse grained iron, in a large casting, developing a still coarse grain in slow cooling, hence weakness, whilst the same iron might be well suited for small castings, where the rapid cooling of the metal produces a closer grain.

The influence of foreign elements on the properties of cast iron is very marked. Silicon prevents the formation of

carbon monoxide, the main cause of "blow-holes," and so produces sounder work, besides increasing the fluidity of the metal. For very fine work, where strength is not of prime importance, a fair amount of phosphorus may be present, since it promotes fluidity and diminishes shrinkage. With less than 1 per cent of phosphorus, the accompanying weakness is more than counterbalanced by the greater soundness of the castings. Manganese is frequently employed as a softener for hard irons, counteracting as it does the tendency of sulphur to keep the carbon in a combined state.

In regard to mechanical properties, cast iron may be obtained which offers greater resistance to crushing than any other material, special irons showing a crushing strength of little less than 100 tons per square inch, though the average for British irons is about 40 tons (Turner). A tensile strength of 10 tons per square inch may readily be obtained, and as high as 21·2 tons has been recorded. The average transverse strength may be taken as 20 cwts., though South Staffordshire founders have obtained iron standing 40 cwts. with fair regularity (Turner).

Malleable Cast Iron. — Although castings in ordinary foundry iron may be so cheaply produced, their value is greatly discounted for many purposes by the lack of strength of the material. White cast iron is by nature brittle, whilst grey iron containing large plates of graphite offers lines of cleavage along which a break readily occurs. White cast iron can, however, in small masses be converted into a tough malleable substance by prolonged heating, usually with some gentle oxidising substance, a process first described by Réaumer in 1722. Under proper treatment, the carbon which in the original casting is wholly in a state of combination, becomes converted into a specially fine-grained form of graphite, a certain portion of it at the same time being oxidised, so that the malleable iron obtained always contains less total carbon than the original. At the same time the sulphur present passes out into the surrounding oxidising

material, and it may be the loss of this sulphur which largely determines the appearance of the carbon in a free condition in the malleable iron.

Prolonged heating alone, the metal being protected from the action of hot gases by surrounding it with any inert material, will also bring about dissociation of the carbon-iron compound, but better results are obtained by using a gentle oxidising body such as hæmatite ore, and hence this is now universally employed.

The most successful results are obtained with special hæmatite iron which has been freed from silicon, and containing about 3 per cent. of carbon, mainly combined. The castings are made in green sand, being afterwards thoroughly cleaned, when they are packed into iron boxes and surrounded with hæmatite broken down to a coarse grain. If all the hæmatite be fresh, it exerts too powerful an oxidising action and the malleable casting is uneven in quality, hence it is usual to employ some old ore with a proportion of new. The charged boxes are then closed and heated up for several hours, the length of time being determined by the size of the castings. When cooled down the castings show a fine grey fracture ; they may be easily worked with a file and are fairly malleable. Malleable cast iron, however, cannot be welded, and it is liable to suffer from defects, owing to blow-holes in the original casting.

Wrought Iron.

The large quantities of foreign matter present in cast iron diminish its toughness and tensile strength, and render it unfit for use in many applications of the metal, and in order to give it the property of toughness, it is converted into a purified form called "wrought iron." This may be regarded as commercially pure iron, but it is always associated with small quantities of slag, which, from the subsequent rolling the metal undergoes, confers upon it a fibrous texture to which the special properties of wrought iron may be ascribed.

Wrought iron melts at a very high temperature (hence its use for furnace bars, etc.), but before melting passes through a pasty stage which permits of its being welded. When cold it is ductile (distinction from cast iron), whilst if heated and suddenly quenched it cannot be appreciably hardened (distinction from steel). It is prepared from cast iron by removing the impurities with which the latter is associated, such as carbon, silicon, phosphorus, etc. This purification is based on the fact that when cast iron is heated in contact with oxide of iron, the carbon and silicon combine with the oxygen of the oxide of iron, carbon monoxide being evolved as a gas, and the silicon combines with the oxygen to form silica, which unites with another part of the oxide of iron to form a slag; this being very fusible, can easily be separated from the metal. Bessemer first introduced his process with the view of producing soft wrought iron by a simpler process than that of "puddling," but the metal so obtained, being free from slag, had not the fibrous character necessary in wrought iron, and so the process is now entirely employed in the production of steel, which, however, may contain so little carbon (mild steel) as to approach wrought iron in this respect.

Several direct methods of producing wrought iron from the ore have been tried, but far the greater part of this material is produced by the "*puddling process.*" At one time the pig iron was always treated by the "dry" puddling process, which involved the use of white pig, since this could be obtained as a pasty mass, the surface of which was oxidised by the excess of air in the furnace, this oxide being well worked into the mass by the workman to carry the oxygen necessary for the oxidation of sulphur, silicon, etc., to all parts. When only grey pig iron was available, it was necessary to first convert it into white iron in a "finery." It will be noted that the necessary oxygen had to be first absorbed by the pasty iron from the air. A great advance on this method was introduced by Hall in 1830, when he employed oxides of iron produced in other ways for the

oxidation of the impurities, carrying out the process with the iron in a fluid condition, instead of a pasty one. The carbon monoxide produced by the interaction of the iron oxide and carbon of the pig caused violent boiling, hence this "wet" process came to be known as *pig-boiling*.

Reverberatory furnaces are employed in both puddling processes, that for pig-boiling having a bed consisting of cast iron plates, which are "fettled" with suitable basic slags, some consisting of the roasted slag obtained during the working of the process, and a certain portion, above this in the lower part of the bed, of "hammer slag." The essential point is that the molten iron has always below it free oxides of iron from which the impurities in the iron may draw oxygen to assist in their oxidation. The process is usually conducted in four stages:—

1. The furnace having been heated up, has a charge of from $\frac{1}{2}$ to 1 cwt. of hammer slag thrown into it and then some $4\frac{1}{2}$ cwts. of broken pig iron, which is slowly allowed to melt down, the molten iron and slag being well mixed. At this stage the silicon is mainly oxidised together with much of the manganese, and normally about half the phosphorus originally present is removed.

2. The whole having become fluid is now kept in this condition for about half an hour, with constant rabbling, when the remaining silicon and manganese are oxidised, and also a considerable amount of the phosphorus.

3. The temperature is now reduced and the mass well rabbled to bring the oxide of iron into intimate contact with the molten metal. The carbon is rapidly oxidised with the evolution of carbon monoxide, which gives the metal the appearance of "boiling." Quantities of slag (*tap cinder*) are produced, and flow out into suitable trucks, this cinder being frequently calcined to be afterwards employed in fettling the furnace.

The violence of the reaction will have ceased in about half an hour, and the metal "comes to nature," showing the process to be complete.

4. All that now remains is for the workman to raise the temperature sufficiently to thoroughly soften the pure pasty iron in the furnace, in order that he may work it into "blooms" of a size suitable for the subsequent treatment.

The changes brought about may be briefly summarised. Silicon and manganese are almost completely oxidised and removed in the slags. Of the phosphorus originally present some 75 to 80 per cent. will have disappeared and possibly 50 per cent. of the sulphur, whilst the carbon will have been reduced from some 3 per cent. to less than one-tenth of this quantity.

Gas-fired puddling furnaces on the regenerative principle are now extensively used, and when the success of the Bessemer process was assured, large numbers of patents were taken out for furnaces in which the puddling process was carried out mechanically, it being hoped to thus stave off the threatened extermination of the process. Few of these mechanical appliances have remained in use, and since the character of puddled iron is much superior for special purposes to the soft iron which can be produced by the Bessemer process, the manufacture by "puddling" still holds its own.

Treatment of the Puddled Iron.—The blooms obtained are far from uniform and are impregnated with large quantities of slag. To remove this, it may be hammered or squeezed. The hammering was formerly entirely performed by "*helves*," a type of heavy hammer, usually weighing some six tons, which was raised by four cams on a rotating axle and allowed to fall on the bloom below. Steam hammers are generally employed at the present time, since greater masses of metal can be worked under them, the process is quicker, and commoner irons can be manipulated under the varying blows of a steam hammer. With the helve the blow is fairly uniform, and it is impossible to work a red-short iron (containing much sulphur) under it, so that the helve is still employed for the production of high-class irons. The slag forced out of the blooms is termed "hammer slag," and is

charged into the puddling furnace (see p. 447). The hammered iron is now taken to the rolls and after passing through the first pair is termed "No. 1 iron," or puddled bar. This is far from uniform, containing considerable quantities of slag. To produce greater homogeneity the bars are cut into short lengths, "piled" together in bundles and reheated, when they are again hammered to weld them together, and passed through the rolls, giving "No. 2" or "merchant" bar. By again repeating the process a still better quality iron (No. 3) is obtained. Compound bars can be obtained by suitable selection of the irons and arrangement of the short bars in the pile, thus the centre bars may be of high tensile strength, whilst the outer bars may be of a tough iron.

Wrought iron is of a very fibrous nature, is ductile, fusible only at very high temperatures. In a dead soft condition it is employed in dynamos, motors, etc. The tensile strength may vary from 18 to 30 tons, and it is usual to specify for 17 to 26 tons, according to the size and quality required.

Steel.

The cheap production of steel which has been rendered possible during the last sixty years through the inventions of Bessemer and Siemens has had an enormous influence on the whole commercial development of the world, and it is almost impossible to mention any great industry which has not benefited by the introduction of this material in a cheap form. For constructional work, for ship-building, rails, guns, and a thousand other industries, it has proved invaluable. Before the announcement of Bessemer's great discovery at Cheltenham in 1856, the total steel produced in this country was 51,000 tons (1855), the price being about £50 per ton, whilst Sheffield alone produces some 830,000 tons annually at a price of £4 and upwards (Roberts-Austen).

The first boiler in which Bessemer steel-plates were employed was constructed in 1860, and steel rails were tried

about the same time, and found to outlast in many cases twenty iron rails. In 1863 two steel barges were built, and in 1864 a 400-ton paddle-steamer, to be followed shortly after by a ship of 1250 tons (Turner).

Before the introduction of the mild steels produced by the Bessemer and Open Hearth processes, the definition of steel was a simple matter. On the one hand we had wrought iron containing less than 0·2 per cent. of carbon, which could not be hardened on quenching, yet could be welded and forged hot; and on the other hand, cast iron containing from 2·5 to 4 per cent. of carbon; a material which could not be forged hot and could only be employed in the form of castings. Between these two varieties of iron we had steel, which could be forged hot and whose special characteristic was that it could be hardened on quenching, such steel containing an amount of carbon intermediate between that in wrought and cast iron. That steel could be made by dissolving wrought iron in molten cast iron was shown by Réaumer in 1722.

Much of the steel produced by modern methods contains so little carbon that it cannot be appreciably hardened by quenching, in fact it only differs from wrought iron in the absence of a fibrous structure, and in having been cast whilst in a molten state. Harbord defines such steel as "purified pig iron in which the carbon and other impurities present have been reduced to such a point that the ingot cast is capable of being forged or rolled into blooms, slabs, etc."

Production of Steel.—Since ordinary steel is an intermediate body between pig iron and wrought iron, its production would be a fairly simple matter if, in the puddling of iron, the process could be stopped before the whole or nearly the whole of the carbon had undergone oxidation. *Puddled steel* was produced in this way from an iron containing much carbon and manganese, the latter serving to protect the carbon from too rapid oxidation, but clearly the great difficulty of knowing exactly the right point at which to

check the process in order that the desired quantity of carbon might remain in the product was very great, and so the process never became general. It is usual to completely oxidise out the carbon and produce wrought iron, afterwards treating the bars by the *cementation process* in such a way that the requisite amount of carbon is taken up by the pure iron. It was by this process that practically all steel was produced before the introduction of the Bessemer and Open Hearth processes, and for many purposes, such as cutlery, tools, etc., steel is still largely produced by cementation.

The process depends on the fact that at a high temperature iron in contact with carbonaceous matter absorbs a certain amount of carbon, the quantity being largely dependent on the length of time the materials are kept in contact at the requisite temperature. Carbon monoxide was at one time supposed to play an important part in the process, but since if pure iron and carbon be heated together in a vacuum the carbon is found to penetrate the iron, producing steel, and again if cylinders of pure iron are shrunk on to hard steel cores and heated out of contact with air, diffusion of the carbon into the soft iron is easily seen, it may be assumed that diffusion is what actually occurs in practice.

The cementation furnace has in the interior two rectangular pots, which are usually some 12 feet in length and 3 feet in cross section, which are heated by fires below, the heat being uniformly distributed by suitable flues. For the manufacture of the highest quality steel, Swedish iron is employed, hammered bars being preferred to those which have been rolled. A layer of charcoal is placed in the bottom of the pot, and then the iron bars are laid in with spaces between each bar, another layer of charcoal and more bars being added until the pot is full; the top is then well covered with the sediment from grindstone troughs, termed "wheel swarf," which fuses and protects the contents from oxidation. There is a hole at the end of each pot, in order that a trial bar may be withdrawn and examined to see how the carburisation is progressing.

The furnaces are slowly heated up and maintained at a temperature somewhat over 1000° C. for several days, according to the carbon content required in the finished steel, when the furnaces are allowed to cool down slowly. The bars of steel obtained are, from their appearance, termed *blister steel*, the blisters being produced by the interaction of the carbon with small quantities of slag present in the original bar, with the production of carbon monoxide. It is highly important that air shall not reach the bars during the process, for it leads to the oxidation of the carbon in the outer layers (aired bars).

As might be expected, the amount of carbon in the outer portion of the bar will be much greater than in the interior; in fact, if the process is only carried on a few days for the production of mild steel, the interior portion will still be soft iron. With an "aired" bar, on the other hand, the outer layers are practically free from carbon.

The cemented bars are afterwards made up into faggots, heated (with suitable precautions to prevent oxidation) and drawn out under the hammer, thus producing *shear steel.* Occasionally these bars of shear steel are folded on themselves, reheated and hammered to produce *double shear steel.* The material is afterwards drawn down into suitably thin form for cutlery and other purposes.

Crucible Steel.—Shear steel is naturally anything but uniform throughout, and a great advance was made in the production of steel when Huntsman (1740) introduced the melting down and casting into suitable ingots of the shear steel. For this purpose crucibles or pots are employed which hold about 56 pounds of the broken up shear steel, and this is melted down in a special furnace.

For mild steels fireclay pots are employed, since their use does not lead to the introduction of more carbon, whilst for the harder steels it is usual to employ pots made by mixing Ceylon graphite with fireclay. In melting, the amount of carbon present is generally re-

duced, and the use of pots containing carbon minimises this loss.

The molten steel is poured into cast iron moulds, and when more than 1 per cent. of carbon is present a hollow "pipe" is left at the top of the mould. After removing the "pipe" until sound metal is reached, the ingot is reheated and rolled or forged to the desired section.

The percentage of carbon in crucible steels ranges from 0·5 to 2 per cent., the amount or "temper" varying with the particular work which the steel is being prepared for, thus "razor temper" indicates 1·5 per cent. of carbon; "chisel temper," 1 per cent.; "die temper," 0·75 per cent.

Case Hardening and Armour Plate.

The case hardening of iron and the production of armour plate are but special applications of the process of cementation. In both it is desirable to leave a tough interior or backing of soft steel, whilst the surface shall be capable of being rendered exceedingly hard.

For the former the articles, having been machined to the approximate requirements, are packed into iron boxes with material to supply the requisite carbon, some of which it is desirable to have as hydrocarbon vapours, charred leather or material to which a certain amount of oil has been added, being excellent for the purpose. The box is then closed with a lid, which is luted into place, and the whole raised in temperature. The depth to which the carbon penetrates depends on the time the materials are kept heated in contact with each other. The contents of the boxes are now turned out into water, a sieve being usually placed a few inches below the surface to catch the cemented articles, which by this treatment become hardened. Various colours can be given to the pieces according to the height from which they are allowed to fall into the water, owing to more or less oxidation in their passage through the air. Any slight distortion is removed by grinding.

Armour Plate.—The face hardening of mild steel for use as armour plate was first introduced by Harvey, hence the process is frequently termed "Harveyising." The metal now employed is open hearth steel, usually containing both nickel and chromium. The steel is prepared in large ingots, the bottoms and tops of which are removed, for reasons explained later, and the ingots are then thoroughly worked under powerful hydraulic presses into slabs, and finally rolled to the desired thickness; the rolled plates being larger than the required size of the finished plate, a considerable amount of "scrap" is cut off.

For the carburising a special furnace is employed, the bed of which can be run in and out on a tramway. The iron body of the car has a firebrick covering of some thickness, and above this firebrick is built up so as to leave a number of flues running the long way of the furnace. The first plate is now placed so that it rests on these piers of firebrick, then a thick layer of carbonaceous material is spread on it, and finally the upper plate is laid on. In this way the carbonaceous material lies between the two plates and is under considerable pressure, which materially assists in the process. Firebrick walls are now built up at the sides and a thick layer of sand covers in the top. When in the furnace, the burning gases from the producers pass above the upper plate and are drawn back underneath the lower plate through the flues provided. The plates are maintained at a high temperature for some seven to fourteen days, when they are allowed to cool down.

After carburising, the plate being still soft, it is bent to the required shape, and undergoes a further heating to above the recalescence point, being then oil quenched, and, finally, reheated to below the recalescence point. This treatment has been shown to considerably increase the tensile strength and elastic limit of steel.

Any drilling, etc., on the face of the plate must be carried out before the final hardening. The whole success of the plate depends now on its being properly hardened, a

process requiring great experience to obtain the best results. The plate is reheated in a gas-fired furnace in such a way that, whilst the face attains a temperature well above the recalescent point, in order that quenching may harden it, the back portion of the plate is kept below this point, hence preserving the advantages derived from the preceding heat treatment.

Water is then forced at considerable pressure from suitable jets both against the front and back of the plate, hundreds of tons of water being required for the larger plates. The hardened surface may be from 1 to 1½ inches in depth, this depending upon the temperature and length of time the plate was in contact with the carbon.

The net result is the production of a plate having an extremely hard but tough face, whilst the back of the plate is soft but has high tensile strength and elasticity.

The Beardmore process consists in running high carbon steel into a horizontal mould, the bottom of which is cooled by air channels. The steel in contact with the bottom of the mould quickly sets, but whilst the upper layers are still fluid, a mild steel is poured in so that it flows evenly over the surface of the hard steel, with which it forms a perfect union. Such plates have resisted Krupps' projectiles under Admiralty requirements. Krupps, again, are understood to have employed rich hydrocarbon gases for carburisation; but so far as the authors can ascertain, the older process, as first described, is practically the only one at present extensively employed.

The Bessemer Process.

This has proved to be one of the most important inventions in metallurgy, and its influence on the extended use of steel has already been referred to. The oxidation of carbon and other constituents in pig iron by blowing air upon the molten metal was known for generations, and employed in the old "finery" hearth. Bessemer's original idea was to

blow air through the metal and so prepare it for use in the puddling furnace; he does not at first appear to have recognised the possibility of producing such a high temperature that the oxidation could be carried to completion, whilst the heat developed maintained the metal in a fluid condition. The practically pure iron thus obtained only required the addition of carbon in suitable quantities to convert it into varying grades of steel.

The process is carried out in a "converter" (Fig. 54), con-

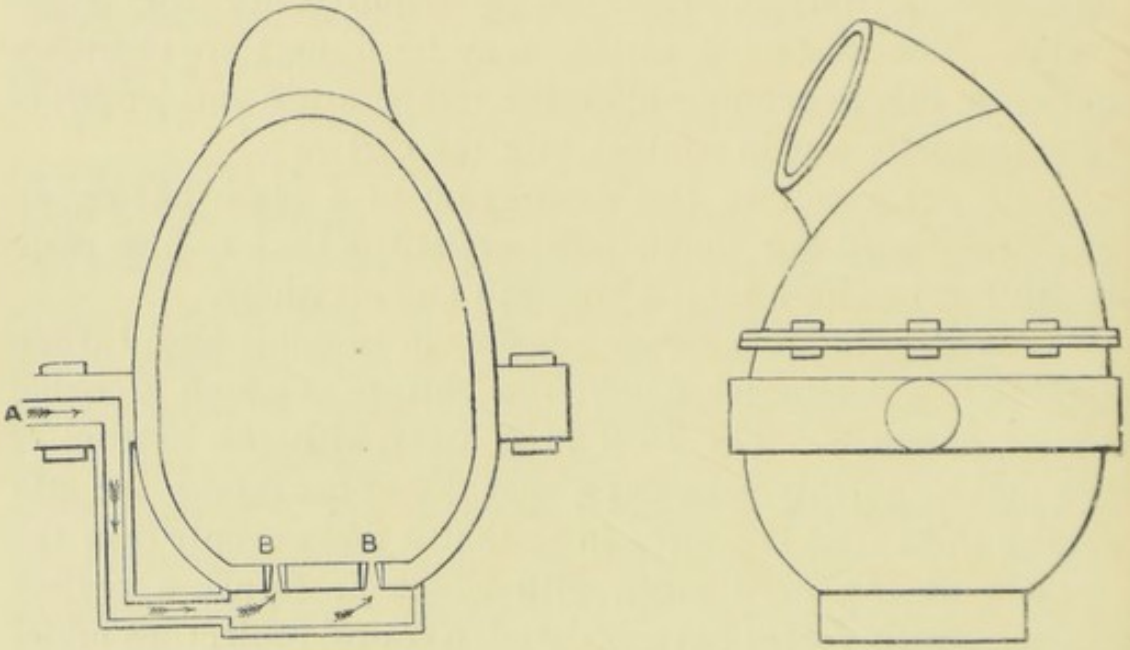


Fig. 54.

sisting in the most modern forms of three portions; the bottom section, which is easily removable, the body and the nose. Since the bottom section will only stand from twelve to fifteen "blows," whilst the upper portions will last several months, it is a great advantage to have the former easily replaceable. The whole converter is built up of either mild steel or wrought iron plates, and is lined with a fireclay lining, "ganister," a special form of clay, being usually employed. The converter may have the nose either situated eccentrically (as illustrated) or concentrically.

The converter can be rotated on trunnions, the air blast being conveyed down one arm (A) at a pressure of 20 to 25 lbs. into the blast box at the bottom of the converter, whence

it is delivered through fireclay twyers (B) in the bottom of the vessel. There are several of these twyers arranged in the bottom, each having from twelve to eighteen holes in it.

When charging, the nose of the converter is turned down in order that the twyers may be above the level of the molten iron which is poured in, sometimes from the blast furnace direct or a suitable mixer which may hold iron from several furnaces, so ensuring uniformity in the charge; or from a special cupola in which the pig is melted down. The blast is now turned on and the converter rotated to a vertical position. The flame is at first small, practically only manganese and silicon undergoing oxidation, and then rapidly increases in size as the carbon becomes burnt to carbon monoxide, giving a violent "boil," quantities of metal and slag being ejected. The flame then quickly drops, indicating the completion of the "blow," which usually takes about twenty minutes.

The iron is practically free from silicon, carbon, etc., and the charge has now to be "finished" by suitable "additions," depending on the class of steel it is desired to produce. Manganese is absolutely necessary to make the steel workable, and to introduce this, together with the requisite carbon, either *ferro-manganese* or *spiegeleisen* is added. These are manganese-iron alloys produced by specially smelting manganiferous iron ores in the blast furnace. Their composition is approximately:—

	Ferro-manganese	Spiegeleisen.
Manganese	... 70 – 80	... 10 – 45 per cent.
Carbon	... 6	... 5 „

To introduce into the steel the requisite amount of manganese, less ferro-manganese is required, hence less carbon is at the same time introduced. Ferro-manganese is therefore added in lumps for mild steel. On the other hand, for hard steel where more carbon is required, spiegel is employed, and since the quantity added is greater, it is always melted first. When the charge has had time to

properly mix it is poured into the casting ladle, which, being mounted on a suitable rotating platform, can be brought successively over the ingot moulds. The more modern practice is to swing the casting ladle over the first of a series of cars into which the metal is run (car casting), a second car being pushed forward to replace the first when full, and so on.

Basic Bessemer Process.—The acid Bessemer process is only suitable for the treatment of iron containing but little phosphorus and sulphur, since it does not eliminate these undesirable elements, hence until Thomas and Gilchrist introduced their basic method in 1878, the pig irons available were somewhat limited. Enormous quantities of good steel are now produced by the basic method from phosphoric irons.

The whole success of the process depends upon getting the phosphorus into combination with a suitable base (usually lime) in the form of phosphate, in which condition it occurs in the "basic slag" produced. This slag has proved a valuable asset, since it is largely used as a manure. Silica in any quantity is undesirable in the slag on account of its acid properties, hence whilst a silicious pig iron is requisite for the acid Bessemer process, the quantity of silica present in pig iron for the basic process should not exceed 1 per cent., whilst the phosphorus may be present in considerable amount in order to develop the heat necessary for success.

The converters are of the concentric type and are of larger capacity than those employed in the acid process. The lining is of calcined dolomite, a calcium-magnesium carbonate. To form the basic slag, 3 to 4 cwts. of lime are thrown into the converter per ton of metal, which is afterwards run in and the blow commenced. There is little difference observed in the appearance at the mouth of the converter until the flame "drops," and up to this point manganese, silicon and carbon have alone been oxidised. The blow is now continued for some three or four minutes longer

—the "after blow," and it is during this period that the phosphorus is oxidised to phosphorus pentoxide, which combines with the lime forming calcium phosphate ($Ca_3P_2O_8$). The point at which this is completed is determined by taking a sample of the metal, cooling it and fracturing.

The addition of ferro-manganese for recarburising may take place in the converter, but spiegel must only be added to the metal in the ladle when it is free from slag, otherwise the phosphorus is again reduced by the considerable amount of carbon added, and passes back into the metal.

The Open Hearth Process.

Steel made by this process has proved the only serious competitor to that produced by the Bessemer process, and open hearth steel is generally preferred to the same class as prepared in the converter. There is not the same risk of over-oxidation, and throughout the production repeated samples can be examined which makes the product a more reliable material.

Siemens conceived the idea of oxidising the impurities in pig iron by the addition of iron ore, whilst in France, Martin worked out a process by which the silicon, carbon, etc., in the pig were partially oxidised, but mainly diluted, by the addition of wrought iron or mild steel scrap. The great difficulty was to maintain a sufficiently high temperature for the reaction, and this Siemens overcame by the introduction of gas firing on a "regenerative" system, by which both the combustible gases and the air needed for their combustion are raised to a high temperature before combination.

The common practice of to-day is to employ both ore and scrap, the whole being melted down in a large rectangular hearth (A, Fig. 55) lined with either silica bricks and sand or basic material, for the process may be either "acid" or "basic," just as in the case of the Bessemer process. The large hearths employed by many firms have a capacity of 45 tons. These are generally built on independent founda-

tions from the regenerators (B,B′,C,C′) and opening at either end of the hearth are the gas and air ports, the air ports being slightly in excess of those for gas. The gas from the producer is led through the gas regenerator B, whilst the air supply is heated up in C, the combustible and the supporter of combustion not meeting until they arrive at the furnace proper. The hot products of combustion, after passing over the hearth, are drawn through the other

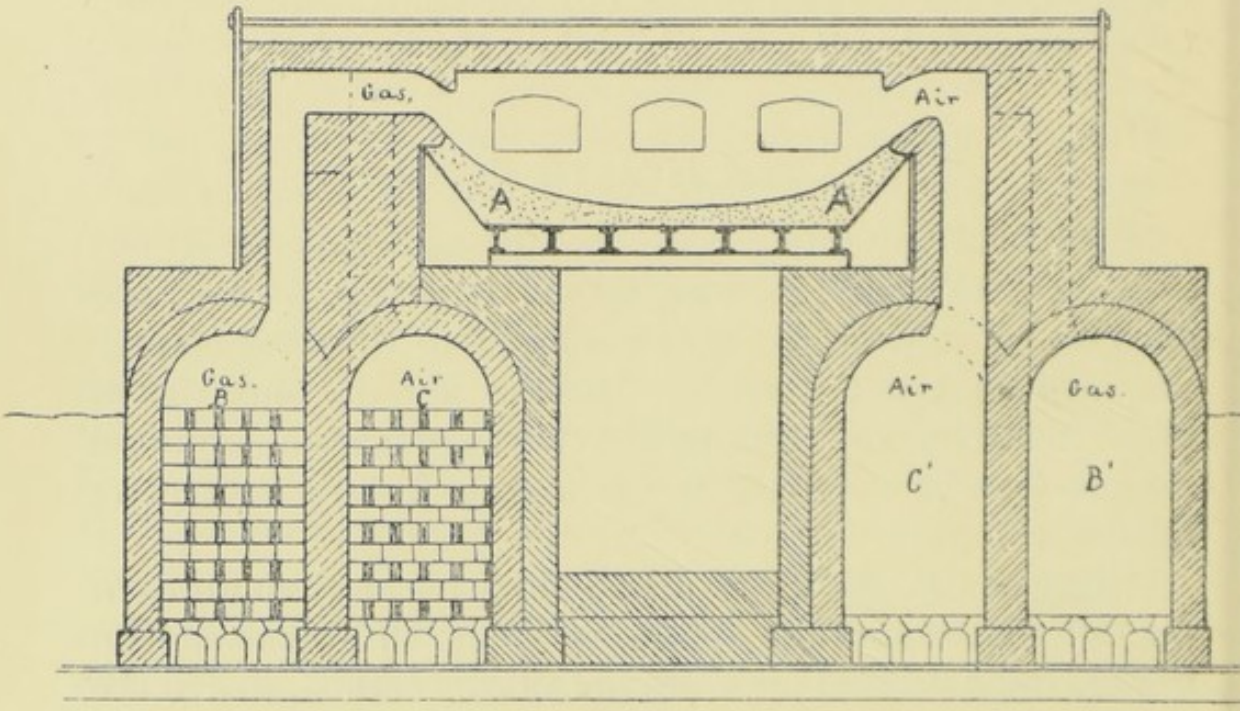


Fig. 55.

pair of regenerators B′, C′, heating them to the requisite temperature, when the controlling valves are reversed, and the gas and air currents sent through in the opposite direction.

The charge varies greatly with the nature of the pig, the scrap available, etc., but usually some 75 to 80 per cent. of pig is charged into the furnace, and 20 to 30 per cent. of heavy scrap charged on top of it, when the whole is slowly melted down, some of the impurities undergoing oxidation. Pure hæmatite is now thrown in, causing the liquid to undergo a violent boiling, due to the oxidation of the carbon with the evolution of carbon monoxide.

$$3C + Fe_2O_3 = 2Fe + 3CO.$$

In this way the carbon is reduced until the metal is "dead soft," a few pigs of iron are thrown in to keep up a gentle "boil" and then the furnace is tapped, the necessary "additions" of ferro-manganese for mild steel being made to the stream of metal as it flows to the casting ladle. If spiegeleisen is employed for hard steels, it is charged into the furnace and well rabbled in. Pig iron, or a mixture of pig and spiegel, is also employed in recarburising for high carbon steels.

The acid open hearth process does not remove any of the phosphorus or sulphur from the metal, therefore great attention has to be paid to the selection of suitable pig iron, since the amount actually present becomes somewhat greater in the process.

In the *basic open hearth* process it is necessary to maintain a basic slag. The lining of the hearth is usually dolomite, and a little lime and ore is first charged, then the pig and scrap, with an occasional shovelful of lime and ore.

Recarburisation must in this case be effected in the tapped metal, since the introduction of carbon, in the presence of the basic slag, would reduce the phosphorus and cause it to pass back into the steel, just as in the basic Bessemer process.

The subsequent treatment of steel after it is tapped from the furnace has an enormous influence on its value. Great trouble arises with low carbon steels, owing to the amount of gases, chiefly carbon monoxide, which are dissolved, causing general unsoundness in the ingots, since these dissolved gases are liberated at the moment of solidification. In some cases, known in the works as "wild heats," the liberation of gas is so copious that the metal boils over. Generally speaking, even the best ingots have small "blow-holes," but since the inside surfaces are clean, they are readily united when properly worked under the hammer or press.

Naturally, any substances which will cause the molten steel to dissolve less gas, or which will be acted on by

dissolved gas, will tend to promote soundness in the castings, effects well known to be brought about by silicon and aluminium, the addition of a few ounces of the latter per ton being now common practice.

Fluid compression is also used to attain the same object, the metal being poured into suitably strong moulds, and whilst still fluid, placed in a hydraulic press. Quantities of gas are forced out, and the resulting ingot is much sounder; but after working ingots of the same steel, pressed and unpressed, of course no difference would be expected in them, one great advantage, however, is that a much larger portion of the ingot is available for use if produced under pressure.

With high carbon steels, blow-holes or "honey-combing" do not occur, but owing to the great contraction of such steel in cooling, the ingot is always found to have a conical hollow, extending for some distance downwards from the top, termed a "pipe." Owing to this and the recurrence of slag in the upper parts, much metal has to be sacrificed, and at the bottom of the ingot, due to chilling, the metal is also unsatisfactory, so that the Admiralty require that 30 per cent. from the top and 3 per cent. from the bottom shall be removed from ingots.

With large ingots, trouble arises from the separation of certain portions rich in sulphur and phosphorus, and further from the expansion of the metal after it has set, due to recalescence.

Steel castings are liable to fracture from the shrinkage on solidification, which amounts to some $\frac{3}{16}$ths of a linear inch per foot, and in any case the casting will have developed considerable internal stresses, which must be removed by proper annealing.

The steel ingots are first worked up under the steam hammer or powerful hydraulic presses, some of the latter, such are used for armour plate, giving a pressure on the metal of between 5 and 6 tons to the square inch, the whole press being capable of exerting a pressure of over 12,000 tons.

Metal is more thoroughly worked through under the press than under the hammer, and larger masses can be dealt with.

The hammered or pressed metal is then finished off, as may be required by machining, rolling, drawing, etc., into the thousand various forms in which it is employed.

Properties of Iron and Steel.

Pure iron is a soft malleable metal of considerable tensile strength. Its specific gravity is 7·88, and it fuses at about 1600° C. In the presence of moisture and air it readily rusts, and decomposes water at its boiling point with the formation of triferric tetroxide (Fe_3O_4). It dissolves in hydrochloric and sulphuric acids, with the production of ferrous salts. With nitric acids its reactions are somewhat remarkable. When the acid is fairly strong, no action takes place, the metal being termed "passive," and even on the addition of water there is no sign of chemical activity. If now the surface be scratched, at once violent action is set up. With dilute nitric acid a ferrous salt is formed and hydrogen liberated, but with strong acid a ferric salt and nitrogen dioxide are the products.

Wrought iron more nearly approaches pure iron in its composition and properties than any other commercial form of the metal. Like the pure metal, it cannot be hardened by quenching.

If a rod of practically carbonless iron be taken, having a small hole bored in it into which a thermo-junction may be inserted, and the metal be slowly and regularly heated up in a furnace, certain well-marked periods of rest are observed during the heating, and corresponding points also in the cooling; and well defined changes in physical properties occur at these points. This is generally regarded as indicating certain allotropic changes in the iron, but as the subject is so closely connected with the influence of carbon on iron, the further consideration of the question will be dealt with later.

Influence of Other Elements on Iron.

Carbon.—This element has by far the greatest influence on the properties of iron, determining as it does the capability of the metal to be hardened and tempered, its power of becoming permanently magnetised, its melting point and tensile strength, in fact all those properties associated with the different classes of iron and steel.

In a fused condition carbon can dissolve to the extent of 7 per cent. in iron, but on solidifying, a certain proportion is thrown out, so that the maximum found in solid iron is 4·6 per cent. This carbon may be free, as in grey cast iron, where it occurs mainly as plates of graphite, or it may be in combination as a definite carbide (Fe_3C), as in white cast iron. Certain elements have great influence in determining its condition; thus silicon causes it to separate "free," whilst sulphur maintains it in combination. Other elements influence the amount of carbon which iron is capable of retaining, thus manganese considerably increases the amount.

Within limits, the amount of carbon is proportional to the hardness it is possible to impart to a steel, and likewise to its power of retaining magnetism. The tensile strength is also greatly increased with increase of carbon present.

The very important influences of this element were not understood until the question came to be studied by careful temperature measurements, aided by microscopic examination of the various specimens which had been subjected to well ascertained thermal treatment. As already mentioned, pure iron on cooling, say, from 1000° C., does not do so with complete uniformity, certain well-marked periods occurring, during which the process is much retarded, showing that some internal molecular change evolving heat is taking place. Similar points are observed during heating up, these being denoted by Ac, whilst those on cooling (which usually occur some 30 degrees lower) by Ar (from *arrêter*). With

practically carbon free iron, the following are the observed temperature checks:—

Ar3	860° C.	Pronounced check.
Ar2	750° C.	Slight check.
Ar1	660° C.	Almost imperceptible check.

The first two points agree with certain well marked changes in the physical properties of the iron. At Ar3 there is a sudden change in the rate of variation of electric resistance, and at Ar2 we have the reappearance of magnetic properties, which above this point have disappeared. Since Ar1 is almost unnoticeable with carbonless iron, but rapidly increases in importance with increase of carbon, it is undoubtedly connected with changes in the condition of the carbon.

With low carbon steels, all three points are observed, Ar1 being more definite and Ar3 less marked. With further increase of carbon Ar3 as an individual point disappears, and there are now well marked checks at Ar2 and Ar1. Still further increase in the carbon results in only one big check being observed, corresponding with Ar1, so much heat being frequently evolved that the metal visibly heats up again, giving the well-known phenomenon of *recalescence*.

The well marked checks Ar3 and Ar2 in the case of pure iron can only be due to molecular change in the metal, and most authorities are agreed that they indicate allotropic conditions, thus below Ar2 the iron is said to be in the α condition, between Ar2 and Ar3 in the β condition, and above Ar3 in the γ condition.

Recalescence is therefore to be primarily ascribed to change in the condition of the carbon ("hardening" to "cement"), possibly the effect being accentuated by allotropic change in the iron itself, the temperature at which this occurs being lowered by the presence of carbon, until it coincides with the change of the carbon condition.

The effect of these points, especially Ac1 and Ar1, upon the hardening and tempering of steel is of the greatest

importance, and has been very carefully studied. Steel quenched above Ar1, is hard, whilst if allowed to fall below this "critical point" it is not hardened on quenching. Great structural change is also brought about in steel when, for example, hard steel is heated up above Ac1, all previously existing structure is obliterated, and according to Brinnel and Sauveur, just at this point the metal has the finest structure it is capable of assuming.

It is found that steel containing 0·89 per cent. of carbon is perfectly uniform throughout, no matter how it is cooled; such steel is therefore termed *saturated;* below this percentage it is *unsaturated*, and above it *supersaturated.* With such steel recalescence is well marked, that is as the steel cools down to the point Ar3, 2, 1 (where they all merge) the steel again gives out so much heat that it becomes visibly brighter. If the steel is quenched above this point it is hard, if below it is soft. Under low magnification saturated soft steel shows only one constituent, termed from its pearl-like appearance, *pearlite.* With higher powers this is seen to normally consist of alternate layers of free iron (*ferrite*) and a carbide Fe_3C (*cementite*), and with 0·89 per cent. of carbon the pearlite agrees with $21Fe + Fe_3C$. When *quenched* the mass consists entirely of *hardenite*, the composition of which is an open question, but is probably represented by $Fe_{24}C$. The appearance of this constituent varies considerably; when highly heated and quenched rapidly, it has an interlaced structure showing a large number of triangles, and was regarded as due to a special constituent characteristic of hard steels, "Martensite," but Arnold has recently shown that martensite must not be regarded as a constituent, but only as a structural form, and it is not indicative of hard steel, such structure having been found in soft varieties.

The case of unsaturated and supersaturated steels remains to be considered. With the former there is an excess of iron over that required to produce pearlite ($21Fe + Fe_3C$), and hence when slowly cooled, a mixed structure of free ferrite and pearlite will be observed. When quenched from

above the critical point, the pearlite will have been converted into hardenite, which appears associated with free ferrite.

Slowly cooled supersaturated steels show a mixture of pearlite with free cementite, whilst if quenched from well above the recalescent point with the utmost rapidity the structure will appear to be that of hardenite, almost free from cementite, the latter being retained in "solid solution," since it dissolves in hardenite at about 900° C. If the quenching is less rapid the amount of free cementite increases, until if quenched just above the recalescence point the whole excess of cementite will be found rejected.

The transformations in different steels may be summarised as follows :—

SATURATED STEEL.

Soft.	Hard.
Pearlite { Ferrite, Fe_{21} / Cementite, Fe_3C.	Hardenite, $Fe_{24}C$.

UNSATURATED.		SUPERSATURATED.	
Soft.	Hard.	Soft.	Hard.
Ferrite, x.	Ferrite, x.	Pearlite, x.	Hardenite, x.
Pearlite, y.	Hardenite, y.	Cementite, y.	Cementite, y.

The amount of y in each case will increase with increase of carbon.

The hardening of steel is the maintenance of an unstable condition in the cold of that condition in which the metal was at a high temperature. Several theories have been built up upon the thermal measurements and micro-structure, and considerable diversity of opinion exists on the question of the actual changes involved. From soft steels the definite carbide Fe_3C. has been isolated, it not being attacked by dilute acids. On the other hand the carbon in hard steels yields hydrocarbon gases when treated with dilute acids. This and other evidence shows that the carbon is in a different

condition in hard steels to that in which it exists in soft steels. Again the influence of possible allotropic forms of iron being present in hard steel, maintained in this condition by the presence of carbon in some form, must not be overlooked. It is certain that pearlite (the mixture of ferrite and cementite), on raising to Ac3, 2, 1 (where they agree), undergoes a change, most probably owing to the formation of $Fe_{24}C$ (hardenite), which is maintained in this condition on quenching. It is highly probable that this is a carbide of the β form of iron and not of the α form in which the original ferrite existed. Heating to even 400° C. causes some of the hardenite to again change into pearlite, a change which occurs in "tempering" steel, and this change is always complete when Ac1 is reached.

Phosphorus, Sulphur, and Silicon. — Both the former elements have great influence on the quality of iron and steel, and as already mentioned, the Bessemer process could only be applied to iron free from phosphorus until the introduction by Thomas and Gilchrist of the basic method, which permitted its elimination. Sulphur again is so objectionable that every care has to be taken to avoid its introduction, principally through the fuel in smelting, so that for the best qualities charcoal is employed, whilst coking the coal, thereby eliminating much of the sulphur, is general practice.

Phosphorus generally makes iron "cold short" (brittle when cold), and very liable to fracture under shock. In tool steel it seriously interferes with proper tempering, and a fine cutting edge cannot be obtained with such steel.

The influence of phosphorus is considerably modified by the amount of carbon present, and generally in mild steels very erratic behaviour is noticed, so that well under 0·1 per cent. is all that can be allowed in such steel. With the high carbon steels this element should be almost entirely absent.

It has been shown that if an ingot of steel is allowed to partially solidify and is then submitted to hydraulic pressure, the metal extruded is much richer in phosphorus than

the average content of the original steel; in other words, there is a "phosphorus eutectic," and the presence of this causes distinct segregation of metal rich in phosphorus.

In cast iron the element is not so objectionable, since it promotes soundness in the casting and hence greater combined strength.

Sulphur.—This renders iron "red short" (incapable of being worked at a red heat without cracking), and when much is present the iron has no welding property.

The "red shortness" in the case of steel is at once detected by the bad rolling qualities of the metal, but this is very largely counteracted by manganese.

Silicon may render iron both "cold short" and "red short," but the actual amount causing these effects depends on the amount of carbon present, a small amount of carbon may carry with it far more silicon without ill-effect than a higher proportion of carbon. Its effect in causing carbon to separate in the form of graphite in pig iron has already been mentioned. Generally speaking, the amount of this element ever likely to occur in mild steel will never be sufficient to have injurious effects. Its presence in small amounts in molten steel promotes soundness in the ingots.

The important influence which varying amounts of other metals have on steel has within recent years received much attention, and most valuable materials for certain special purposes have been the outcome of these researches, notably the steels suitable for armour piercing projectiles, armour plates, and the "self-hardening" steels now coming into such general use. Although these may be looked upon as true alloys, yet they are of such a special class that it is desirable to deal briefly with their properties under "steel," rather than under "alloys" generally.

In the first place a clear distinction must be drawn between the influence of other metals when the quantities present are merely those incidental to the production of the steel, and those special alloys in which the foreign metal has

been purposely added in suitable proportions to produce certain results.

Manganese was the first metal to be largely introduced into the metallurgy of steel, Heath having noticed in 1839 the improvement effected by its presence in small amounts.

Manganese has been termed the "physic" of the steel-maker, its greatest use in small quantities being for counteracting the bad effects of sulphur, and at the same time it facilitates the removal of some of this element. It will be remembered that manganese, either as spiegel or ferro-manganese, is commonly added to the steel produced by either the Bessemer or open hearth processes, the finished metal containing from 0·3 to 1·0 per cent. In addition to its effects when sulphur is present manganese causes slags to be more fusible, and therefore more easily worked out of the metal.

Its general effect in mild steel is to increase tensile strength. Less manganese is usually found in high carbon steels than in mild steels, and its presence in any but small quantities is undesirable, since the steel is liable to fracture on quenching.

Above 2 per cent. will justify the metal being classed as *manganese steel*, but when less than 7 per cent. is present the metal is worthless on account of its brittleness. Between 7 and 20 per cent. we have the valuable manganese steel, a material of extraordinary strength and toughness. The influence of heat treatment on manganese steel is remarkable. Heated to about 1000° C. and quenched, the metal is soft and capable of being worked. On now heating to a bright red and cooling in air the metal is hardened. Two other remarkable points which are closely connected with this may be mentioned. Manganese steel is practically *unmagnetisable*, and further if the cooling curve be taken for such steel, *no recalescence check* is observed, as with ordinary steel (p. 465). These facts point to the conclusion that manganese permanently retains iron in the β condition.

Although the material is so valuable, its use is limited, owing to the difficulty of working it.

Nickel.—The introduction of this metal was made by Riley in 1889, and it has proved a most valuable alloy, being very tough and having great power of resisting shock, properties which make it particularly suitable for armour plate, propeller shafts, gun steel, etc. Some nickel steel gun forgings showed an increase of 10 per cent. in tensile strength, and an increase of about 25 per cent. in elastic limit over ordinary steel for the same purpose. The presence of nickel enables iron to take up a greater amount of carbon, hence such metal may be rendered extremely hard, but its greatest effect appears to be in toughening the steel.

The maximum tensile strength and elastic limit is obtained with 20 per cent. of nickel. For many purposes, where hardness together with toughness is required, chromium as well as nickel is added, the chromium together with carbon giving the metal special hardness.

Chromium without much carbon has little influence on iron, but with about 1 per cent. of carbon and about 3 per cent. of chromium a metal very suitable for armour piercing projectiles is obtained. The maximum amount of chromium which can be employed is under 5 per cent. Chrome steel is difficult to work hot and to weld, owing to the formation of chromium sesquioxide (Cr_2O_3).

Aluminium.—The use of this metal in promoting soundness in steel castings has already been referred to (p. 462) and since the metal acts much as manganese does in regard to sulphur it is now being employed to correct for sulphur in cases where it is not desired to introduce carbon to the metal, as must inevitably be the case when spiegel or ferromanganese is employed.

Aluminium has no effect on the hardening properties of steel. Like silicon, it tends to the liberation of carbon as graphite.

Tungsten is now a metal of great importance in the production of "self-hardening" steels, and since it greatly improves the steel in its power of retaining magnetism, tungsten steel is being employed for permanent magnets.

On iron it has little influence, but on steel it confers great hardness, but such steels must not be quenched, otherwise they crack. By heating to nearly a welding heat and cooling in an air blast, great hardness may be obtained. Tungsten steel is fragile, and therefore only suitable for tools where no "jarring" is likely to occur in their use. *Mushet* or self-hardening steel contains from 5 to 8 per cent. of tungsten, the carbon ranging from 1·5 to 2·3 per cent.

Self-hardening Steels. — These in addition to tungsten generally contain small amounts of chromium and molybdenum, with usually under 1 per cent. of carbon. Ordinary hard carbon steel begins to undergo softening, that is the hardenite present begins to change into pearlite, at a little over 400° C., hence the speed at which tools of such steel can work is low on account of the heating. Many of the newer "self-hardening" steels can be used at a low red heat without losing their hardness and cutting properties, a fact which is rapidly having a great influence on workshop practice and machinery. At the Paris Exhibition (1900) such tool steel was shown in operation taking cuts on mild steel at the rate of 150 feet per minute, 60 feet on medium steel, and 15 feet on very hard steel. The time saved in the shops by such practice is enormous, and naturally the general introduction of high speed machinery, of a heavier type than that commonly employed, suitable for this class of tool, is only a question of time. The success of many of these special steels lies, not so much perhaps in their composition, but in the heat treatment to which they have been subjected. Usually this consists in heating up to quite high temperatures (well over 1000° C.), and then allowing the material to cool down slowly and regularly whilst the surface is protected from atmospheric oxidation.

The composition of some English high speed tools was approximately between the following limits:—

	Carbon	Chromium	Tungsten.
Minimum	0·6	2·5	9·5 per cent.
Maximum	1·0	7·0	23·0 „

Vanadium, a somewhat rare element, is now being employed for the production of steels suitable for special purpose, and owing to the very small quantities of vanadium required, such steel compares well in the matter of price with nickel steels. It is found advantageous to use chromium in conjunction with vanadium, open hearth steel forming the basis. Most of the chrome-vanadium steel is employed in the motor industry, since it offers great resistance to shock and alternation of stress. It will possibly find extended use for connecting rods, etc., in marine engines.

The ordinary type contains roughly 1 per cent. of chromium and 0·15 per cent. of vanadium. Such steel when rolled has a tensile strength of some fifty tons; it can be bent double cold, and offers great resistance to alternations of stress, to fatigue and torsion. The best results, in respect to the latter qualities, are obtained by annealing at a full cherry red when the tensile strength, etc., is somewhat reduced, though still equal to 3 per cent. nickel steel.

Special chrome-vanadium steels are now being made to resist torsion, for springs, and for case-hardening, where a particularly tough core is desired.

Compounds of Iron.

Iron forms three well defined oxides:—

Ferrous oxide (FeO);
Triferric tetroxide (Fe_3O_4);
Ferric oxide (Fe_2O_3);

and in addition may exist in combination as FeO_3 forming

ferrates, the oxide and these salts being analogous to chromium trioxide (CrO_3), and the chromates.

Ferrous and ferric oxides alone form salts when treated with acids, the oxygen being replaced by proportionate amounts of various acid radicles, giving two distinct series of salts :—

	Ferrous salts (FeO)	Ferric salts. (Fe_2O_3)
Chlorides ...	$FeCl_2$ or Fe_2Cl_4	$FeCl_3$ or Fe_2Cl_6
Sulphide ...	FeS	Fe_2S_3
Sulphate ...	$FeSO_4$	$Fe_2(SO_4)_3$
Nitrate ...	$Fe(NO_3)_2$	$Fe(NO_3)_3$
Carbonate ...	$FeCO_3$	Not known.

Ferrous salts are generally unstable, showing a marked tendency to pass into the ferric condition ; when in solution ferrous salts are readily converted into ferric salts by the action of an oxidising agent, such as nitric acid. Similarly chlorine will convert ferrous chloride into ferric chloride.

Oxides.—Ferrous Oxide (FeO) is extremely unstable, and when slightly warmed in air at once takes fire, forming ferric oxide.

Ferric Oxide (Fe_2O_3), forms one of the chief sources of iron (p. 435). It is largely employed as *rouge*, for polishing purposes, also as a colouring material for glass, porcelain, etc., and in paints (Venetian red).

Ferric oxide is readily prepared by heating either of the sulphates, the oxalate or hydroxide.

Triferric tetroxide (Fe_3O_4) is also a valuable ore of iron (magnetite), and is frequently termed magnetic oxide of iron, since masses of it occur naturally having strong magnetic properties (lode-stone).

It is the oxide formed when steam is decomposed by red hot iron, or when iron burns in oxygen. Since it is intermediate in composition between ferrous and ferric oxide, it may be regarded as FeO, Fe_2O_3.

Hydroxides.—All the oxides may be obtained associated with water in the form of hydroxides.

Ferrous Hydroxide $Fe(HO)_2$ is obtained as a white precipitate when potassium hydroxide is added to ferrous salts in solution, but all the materials must be free from dissolved oxygen, otherwise the substance rapidly undergoes oxidation. The dry hydroxide, obtained in an atmosphere free from oxygen, absorbs this gas so rapidly when exposed to air that considerable heat is developed.

Ferric Hydroxide $Fe_2(HO)_6$ is easily prepared by adding either ammonia or potassium hydroxide solutions to ferric salts. The colour of the precipitate varies somewhat with the conditions of preparation, the usual colour being reddish brown.

When iron rusts in moist air, the ultimate hydroxide formed has the composition $2Fe_2O_3, 3H_2O$.

Chlorides.—Ferrous chloride ($FeCl_2$) may be obtained in solution by the action of hydrochloric acid in iron, whilst if chlorine be passed over an excess of iron, the chloride may be obtained by sublimation as colourless crystals. It has the composition Fe_2Cl_4 at low temperatures, but dissociates into $2FeCl_2$ on heating.

Ferric Chloride ($FeCl_3$) is a yellow solid which can be easily fused. Below a full red heat, the vapour density shows it to have the composition Fe_2Cl_6, but above this, it dissociates into $2FeCl_3$. Ferric chloride is largely employed in the laboratory.

Ferrous Sulphate ($FeSO_4$) usually crystallises with seven molecules of water, and in this form is known as *green vitriol.* On exposure to air, the crystals readily lose some of their water and become covered with a white powder, consisting of the less highly hydrated salt. By heating ferrous sulphate, it yields Nordhausen sulphuric acid ($H_2SO_4.SO_3$) and ferric oxide.

CHAPTER XXVI.

COPPER (Cu = 63).

Occurrence and ores of copper—Metallurgy of copper—The Welsh process—Production in the blast furnace—Bessemerising copper mattes—Extraction from spent pyrites—Commercial copper—Electrolytic refining—Properties of copper—Compounds of copper.

COPPER has been known from earliest times, being used in the form of an alloy "bronze," for making tools and weapons long before any methods were discovered for the extraction of iron from its ores. It derives its name from the island of Cyprus. It is found native in the metallic form in Wales, Cornwall, and more abundantly in Siberia and South America.

Next to iron, copper is the metal of greatest industrial importance, and of the "common" metals its market price is second only to that of tin. It owes its general application to its extreme malleability and ductility, and for electrical purposes its high conductivity is of great value. Its application in the form of alloys is very great.

It occurs native in large quantities in the neighbourhood of Lake Superior and also in New Mexico, and the copper produced by smelting the former deposit rivals the best that can be obtained by smelting ores. It is also found native in small quantities in Wales, Cornwall, Siberia and Chili.

The most important ore of copper is "copper pyrites," which is a double sulphide of copper and iron, which, when pure, may be represented as (Cu_2S, Fe_2S_3); it is nearly always, however, mixed with arsenical pyrites and other minerals, the percentage of copper which it contains varying considerably. The rich Bratzberg ore from Norway con-

tains as much as 23 per cent. of the metal, whilst the ordinary grey Cornish ore contains about 6 per cent.

Amongst the other less important ores of copper are malachite, a basic cupric carbonate [$CuCO_3.Cu(HO)_2$], red copper ore or cuprous oxide (Cu_2O), and black oxide (CuO) found in the north of Chili.

Metallurgy of Copper.—This is generally a very complex process, for the ores are so highly laden with foreign bodies extremely detrimental to copper, that their complete elimination is a matter of very great importance. Further, the amount of earthy matter usually present with the ore, leads to complications.

The different methods of obtaining the metal may be divided into two main classes :—

(*a*) Those which depend on the reducing action of copper sulphide ;

(*b*) Those in which reduction is effected by carbon monoxide.

The Welsh Method, as practised in the district around Swansea, is dependent on the former, and by this method by far the largest proportion of the world's copper is produced. The process is very complicated, but certain main factors will indicate the general bearing of each stage.

1. In a mixture of copper and iron sulphides, under suitable conditions the iron sulphides will be oxidised in far greater ratio than the copper sulphide.

2. Cuprous oxide (CuO), and ferrous oxide (FeO), readily form fusible slags with silica (SiO_2).

3. That at a high temperature a mixture of copper sulphide and oxide interact with the production of the metal.

First process.—This is intended to expel, as far as possible, volatile substances, such as arsenic, antimony, etc., and then to oxidise, as fully as possible, the iron sulphide.

Copper pyrites		Oxygen		Copper sulphide	Ferrous oxide		Sulphur dioxide.
$Cu_2S.Fe_2S_3$	+	$4O_2$	=	Cu_2S +	$2FeO$	+	$3SO_2$.

In practice some of the iron sulphide escapes oxidation, whilst a little of the copper sulphide becomes oxidised (Cu_2O).

To accomplish this, charges of from 3 to $3\frac{1}{2}$ tons of ore are roasted in a reverberatory furnace with free access of air for twelve hours.

The roasted ore averages some 10 to 13 per cent. of copper.

Second process.—To form a slag by the combination of the ferrous oxide with silica which can be withdrawn, thus concentrating the copper sulphide. Slags from the fourth process are added, in order that the copper in them may be recovered.

The roasted ore is heated in another reverberatory furnace (*ore furnace*), so constructed, that a temperature sufficient to bring about fusion is attainable, silica being added to form the slag. The mass when fused evolves sulphur dioxide and the slag separating, permits of the *coarse metal* being run off.

The coarse metal contains from 30 to 40 per cent. of copper.

Third process.—To oxidise the remainder of the iron sulphide the granulated coarse metal is roasted as in the first process.

Fourth process is intended to bring about practically the same result as in the second process, namely the removal of iron as silicate. Slags from the fifth and sixth processes are added to recover the copper from them.

After fusion the matte produced (*fine metal*) contains from 60 to 80 per cent. of copper, whilst the slags contain from 3 to 4 per cent. of the metal. If there is over 75 per cent., free copper, as "*moss*," is seen.

As already mentioned, the slag from this process being rich in copper, goes back to the second process.

Fifth process.—The fine metal is nearly pure copper sulphide (Cu_2S). In this process, a portion must be converted by oxidation into a mixture of cuprous oxide (Cu_2O) and cupric oxide (CuO), when on raising the temperature it will react with the remaining sulphide to produce the metal.

Copper sulphide		Cuprous oxide		Copper		Sulphur dioxide.
Cu_2S	+	$2Cu_2O$	=	$6Cu$	+	SO_2.

Copper sulphide		Cupric oxide		Copper		Sulphur dioxide.
Cu_2S	+	$2CuO$	=	$4Cu$	+	SO_2.

To bring about these changes, the metal is heated without fusion, with plentiful air supply for four hours, the excess of air is now shut off by dampers, and the temperature raised until the mass fuses, when vigorous action sets in, *blister* copper containing about 98 per cent. of the metal remaining, the slags containing 17 to 20 per cent.

Sixth process.—The blister copper contains such impurities as sulphur, arsenic and iron, and this process is intended to finally oxidise these, so that they may be removed as slag. Since a considerable quantity of the copper is also oxidised, the slag is very rich in copper, and is returned for treatment in the fourth process.

After roasting for some hours to bring about the oxidation, the metal is melted and well rabbled, the slag being removed. Cuprous oxide is formed, and being dissolved in the molten copper, renders it "dry." To remove this oxide, the metal is stirred with a green wood pole (poling), when the hydrocarbon gases evolved reduce the oxide, producing *tough pitch* metal. 30 to 40 per cent. of copper is found in the slag.

Production of Copper Mattes in the Blast Furnace.—Great advances have been made in America in the production of copper mattes directly in suitable blast furnaces. The richer sulphide ores may be charged directly into the furnace, but

the poor ores are generally first crushed and washed to remove earthy matter. A suitable mixture of the ore with slags from subsequent processes is made, so that the matte produced may contain about 30 per cent. of copper, 2 to 3 cwt. of coke per ton being necessary for smelting.

The furnaces are from 6 to 10 feet high, made of iron and provided with a water jacket. The hearth is usually oblong or rectangular and must not exceed 4 feet across, otherwise the blast from the twyers will not pass through the fused matte. The air blast is supplied at from 1 to 1½ inches of mercury. As the matte is produced it passes to the lower part of the hearth together with the slag, but the two are generally allowed to flow out into a fore-hearth of special pattern, being divided into two chambers by a partition, one chamber having about twice the capacity of the other, the two communicating by a hole at the bottom of the partition. The larger chamber goes under the tap hole of the furnace, the hole in the partition being temporarily closed. A mixture of matte and slag collects and the former settles to the bottom. When nearly full the second chamber is put into communication with the first, and matte only flows into it. The process is now continuous, for matte free from slag continually passes into the smaller chamber from which it overflows into suitable moulds, whilst the separated slag overflows similarly from the larger chamber.

The matte produced may then be treated by the Welsh method.

Bessemerising Copper Mattes.—The success of the Bessemer process in the case of iron naturally led to its being tried for the oxidation of copper mattes, and although many difficulties had to be overcome, notably that of maintaining a sufficiently high temperature, the process is now being largely worked, and its success greatly simplifies the production of the metal.

One of the most successful converters is in the form of a cylinder, open at the ends and capable of being turned on

its long axis in order that slag and the metal may be poured from a suitable spout. Twyers pass at an angle through the walls and lining, being so placed that by rotation of the cylinder they may be either below or above the surface of the metal in the converter. A very thick siliceous lining has to be employed, as this is the only source of silica present to flux out the iron compounds.

Care has to be taken that the matte contains about the right amount of copper, which should be between 50 and 55 per cent. The molten matte is charged in with the twyers well above the level it will rise to, then the blast is turned on and the converter turned to deliver the blast through the matte. The reactions which ensue are :—

(*a*) Oxidation of iron sulphide and formation of an iron slag which is poured.

Iron sulphide		Oxygen		Ferrous oxide		Sulphur dioxide.
$2FeS$	+	$3O_2$	=	$2FeO$	+	$2SO_2$.

(*b*) Partial oxidation of the copper sulphide to oxide :—

Copper sulphide		Oxygen		Cuprous oxide		Sulphur dioxide.
$2Cu_2S$	+	$3O_2$	=	$2Cu_2O$	+	$2SO_2$.

(*c*) Interaction between the copper oxide and sulphide, with the production of the metal, exactly as in the fifth stage of the Welsh process where "blister" copper results :—

Copper oxide		Copper sulphide		Copper		Sulphur dioxide.
$2Cu_2O$	+	Cu_2S	=	$6Cu$	+	SO_2.

Even in South Wales the Bessemer converter is replacing the older reverberatory furnace, the usual practice being to charge with $7\frac{1}{2}$ tons of fluid matte, containing 45 per cent. of copper, and to reduce the metal in six "blows."

Extraction of Copper from Spent Pyrites.—A great deal of copper and silver is obtained from the pyrites after it has been roasted for the production of sulphur dioxide in the manufacture of sulphuric acid (p. 367). It is estimated that half a million tons are employed annually in this industry, and since much of it averages 3 per cent of copper in addi-

tion to silver, the extraction of these metals from what would otherwise be a waste product is of considerable importance.

The method usually employed is a "wet" one, the ore after grinding being mixed with common salt (NaCl) and roasted. The copper sulphide becomes oxidised to sulphate, and then this interacts with the sodium chloride, forming copper chloride.

Copper sulphide + Oxygen = Copper sulphate.

$$CuS + 2O_2 = CuSO_4.$$

Copper sulphate + Sodium chloride = Copper chloride + Sodium sulphate.

$$CuSO_4 + 2NaCl = CuCl_2 + Na_2SO_4.$$

Any silver present is also converted into silver chloride. The mass is now extracted with hot water in vats with false bottoms, when the copper and silver chlorides pass into solution, the latter dissolving in the brine, since it is not soluble in water alone.

Several methods may be employed for recovering the silver; one involves its deposition on copper plates immersed in the solution, another its conversion into silver iodide by the addition of zinc iodide, the copper afterwards being recovered by passing the solution on to iron scrap where it is deposited. The copper so obtained is very impure (*cement copper*) and is usually purified electrolytically.

Commercial Copper.—The most common impurities are iron, arsenic, antimony and bismuth, whilst occasionally sulphur, tin and lead are present. Since these have a marked influence on the properties and value of the metal, brief reference must be made to their effect.

The presence of iron, whilst increasing the tensile strength, makes the metal harder and hence impairs its malleability and ductility.

The effect of arsenic is most pronounced, and copper obtained from ores, such as some of the Spanish ores, is quite unfitted for electric conduction, some specimens only having one-seventh the conductivity of pure copper. The effect of arsenic on the mechanical properties is not great,

and where the metal has to stand high temperatures arsenic is frequently added.

The influence of most impurities on the electric conductivity of copper is very great, and Sir Wm. Preece has stated that a cable made of the pure copper now employed will carry twice the number of messages that a similar cable made of less pure copper would carry in the early days of submarine telegraphy.

Bismuth, besides seriously impairing the quality of copper, also injuriously affects its conductivity, and, according to Lord Kelvin, 0·1 per cent. in a cable would render it useless.

Electrolytic Refinement of Copper.—A considerable amount of copper is now sent in to the market after refinement by electro-deposition, cement copper especially being treated in this manner. By a suitable adjustment of current and strength of solution very pure copper indeed can be deposited, though the process is of necessity a slow one. The crude copper plates form the anodes in a bath containing copper sulphate with sulphuric acid, and sheets of pure copper the kathodes. On passing the current copper goes into solution, a like amount being simultaneously deposited at the kathode, whilst at the same time iron, nickel and zinc also dissolve, but with suitable current are not deposited. In acid solution neither gold nor silver dissolve, and they remain on the surface of the anodes as a slimy deposit which can subsequently be treated for their recovery.

Properties.—Copper has a specific gravity of 8·92; it melts at 1085°C., and expands as it solidifies; it is very malleable, and can be beaten out to thin leaf, or drawn out into wire. In tenacity or strength it ranks next to iron, but it is very inferior to it; a copper wire, one-tenth of an inch in diameter, will only support between 380 and 390 lbs., whilst a similar iron wire will carry just over 700 lbs. It is a good conductor of heat and electricity.

When copper is in the molten state it can absorb various

gases, such as carbon monoxide, which escape as the metal solidifies, rendering the mass porous; consequently, pure copper is rarely used for castings.

Copper is very largely used in alloys with other metals, these being dealt with in the special chapter on alloys.

Copper resists the action of pure water or dry air, but when exposed for any length of time to moist air, the surface first becomes dimmed by a thin coating of copper oxide, and this then takes up carbon dioxide from the air and is converted into a basic copper carbonate, often erroneously called "verdigris." This action has occasionally led to very serious results from the use of copper vessels for culinary purposes; clean bright copper surfaces are not affected by the preparation of food in contact with them, but the oxide or carbonate is readily dissolved by such substances, and is a virulent poison.

Of the three common acids, nitric has by far the most violent action on copper; when concentrated the attack is very brief, since the nitrate formed on the surface protects the metal from further attack. On the addition of water the action becomes very vigorous, since the film of nitrate dissolves in the water, leaving a fresh surface of the metal exposed, when nitrogen dioxide is set free. In the cold sulphuric and hydrochloric acids have little or no action, but on warming the former produces copper sulphate with the evolution of sulphur dioxide, and the latter, when boiled with finely-divided copper, forms cuprous chloride (Cu_2Cl_2) hydrogen being evolved.

Finely divided copper has the peculiar property of forming a compound with nitrogen tetroxide (Cu_2NO_2), which decomposes with water.

Compounds of Copper.

Oxides.—Two well defined oxides are known, cuprous oxide (Cu_2O) and cupric oxide (CuO).

Cuprous Oxide is found as the mineral cuprite.

If a cupric salt be boiled with a reducing agent, such as grape sugar, in the presence of an alkali, a red powder is obtained consisting of cuprous oxide (Cu_2O). This oxide is very unstable. It is dissolved by melted glass, and imparts to it a ruby colour. The cuprous compounds are generally colourless and insoluble in water ; readily soluble in ammonia and hydrochloric acid, absorbing oxygen rapidly and yielding cupric compounds.

Cupric Oxide is formed as a black film on the metal when it is heated in the air, or by igniting the nitrate. This oxide readily dissolves in acids, forming cupric salts. From the ease with which it parts with oxygen when heated in contact with organic bodies, it is largely employed in analytical work.

Hydroxide $Cu(HO)_2$.—By adding potassium or sodium hydroxide to a cupric salt, a greenish blue precipitate of cupric hydroxide forms, which is converted into the black cupric oxide when the solution is boiled.

The hydroxide is soluble in ammonia to a deep blue solution, which under proper conditions will dissolve cellulose, whilst under other conditions it converts it into a parchment-like substance (*vegetable parchment*).

Chlorides. — Two chlorides, corresponding to the two oxides are known.

Cuprous Chloride (Cu_2Cl_2) is obtained when the metal or cuprous oxide is dissolved in hydrochloric acid. It is a white crystalline body, insoluble in water, but readily soluble to colourless solutions in hydrochloric acid or ammonium hydroxide. The former is largely employed in gas analysis for the absorption of carbon monoxide, with which it forms a compound, $Cu_2Cl_2.CO.2H_2O$. The ammonia solution turns rapidly blue on exposure to air, owing to absorption of oxygen.

Cupric Chloride ($CuCl_2$) is prepared by dissolving cupric oxide in hydrochloric acid. It forms blue crystals ($CuCl_2.2H_2O$) which are soluble in alcohol.

Copper Nitrate.—[$Cu(NO_3)_2.3H_2O$] is readily formed by dissolving copper in nitric acid and crystallising. It is an oxidising substance, and as such is used in dyeing.

Copper Sulphate or blue vitriol ($CuSO_4.5H_2O$) is obtained on a large scale by roasting copper pyrites and extracting the mass with dilute sulphuric acid.

This salt on being heated loses its water and becomes white. This anhydrous salt is sometimes used to abstract the last traces of water from alcohol and other organic liquids.

Sulphate of copper is much used by the dyer and calico printer; besides which, it is employed as the source of copper in the electrotype process, and also in certain forms of galvanic battery.

CHAPTER XXVII.

LEAD (Pb=206·5).

Lead—Metallurgy—Softening crude lead—Recovery of silver from lead—Properties of lead—Compounds of lead—White lead—Tin—Metallurgy—Properties of tin—Compounds of tin—Zinc—Metallurgy—Belgian process—Silesian process—Properties of zinc—Compounds of zinc—Cadmium—Mercury.

LEAD is probably never found free in Nature. Its principal ores are galena (PbS), which is very widely distributed throughout the world, including many parts of the British Isles; and the carbonate ($PbCO_3$) or white lead ore found in Spain, and near Aix-la-Chapelle.

Metallurgy.—The chemical principles involved in the reduction of the metal from the sulphide are similar to those in the production of copper, namely, roasting to convert some of the sulphide into oxide and then fusion, in order that the oxide and sulphide may interact to produce the metal.

Lead sulphide + Oxygen = Lead oxide + Sulphur dioxide.

$$2(PbS) + 3O_2 = 2(PbO) + 2(SO_2).$$

Lead oxide + Lead sulphide = Lead + Sulphur dioxide.

$$(2PbO) + PbS = 3Pb + SO_2.$$

At the same time some of the lead sulphide becomes oxidised to the sulphate, which is also capable of mutual reduction with the lead sulphide.

Lead sulphide + Oxygen = Lead sulphate.

$$PbS + 2O_2 = PbSO_4.$$

Lead sulphate + Lead sulphide = Lead + Sulphur dioxide.

$$PbSO_4 + PbS = 2Pb + 2(SO_2).$$

The process adopted to bring about these reactions varies greatly with the locality, the method common in this country being that in which the operations are carried out in a

suitable reverberatory furnace, having a depression in the bed for the molten metal to run into.

There are really four stages in the treatment of each batch of ore. During the first the ore is gently roasted together with skimmings from a subsequent stage, which interact, causing lead to flow out, and the metal separated at this stage carries with it considerable quantities of silver.

The temperature is now raised, when the metal is rapidly produced. The slag is thickened, by the addition of lime, raked out of the hollow and spread well over the hearth. The temperature is still further raised, more lime being added. Some of the lead oxide will have combined with silica to form a fusible slag, which is decomposed by the lime, and the lead oxide so liberated can then react with more of the lead sulphide.

In the final "heat," the highest temperature is attained, and the metal is tapped out into an iron pot, the slag being further thickened with lime, and since it carries a considerable amount of lead, this is afterwards recovered on the "slag hearth."

On the Scotch hearth, the ore is charged on to the fuel (usually a mixture of peat and coal) and an air blast is used, but the reactions are very similar to those just described. The process is only capable of dealing with small quantities of the ore at a time, but it is a continuous one, the reduced metal constantly flowing away through a suitable channel in an iron plate in front of the furnace.

Blast furnaces of the type described under copper (p. 480) are now largely employed for extracting lead. Carbon from the fuel is capable of effecting the reduction of lead oxides, but is ineffective with the sulphide, as is usually the case with partially roasted galena. In this case a rich iron ore is usually mixed with the charge, when at the temperature of the furnace, iron is reduced, and this interacts with the lead sulphide, liberating the lead.

In all lead smelting operations a great deal of dust and

fume is produced, and long flues have to be provided, in order that the dust and fume may settle out.

Softening Crude Lead.—Owing to the presence of small amounts of copper, iron, antimony, etc., the lead obtained by either of the above processes is rendered hard and quite unsuitable for many purposes. To soften the metal quantities up to 150 tons are melted in a special reverberatory furnace—the "calcining furnace"—a plentiful supply of air being admitted, when a rich dross collects, owing to oxidation of the impurities, this dross being constantly removed. The operation is continued until a sample shows the metal to have been sufficiently softened. In the later stages much lead undergoes oxidation, but the metal is easily recovered from this dross.

Recovery of Silver from Commercial Lead.—Before the year 1833 the only method of obtaining the silver from lead, in which it nearly always occurs in fair amount, was that of cupellation. Since the amount which could be economically extracted had to exceed 8 oz. per ton, much of the old lead used for roofing and other purposes contained quantities of silver which could now be profitably extracted.

The first and most important method for de-silverising lead was due to Pattinson, advantage being taken of the fact that when an alloy of lead-silver is cooled, pure lead crystallises out, leaving as a mother liquor the richer *eutectic alloy* (see "Alloys"). A series of iron pots are employed, each heated by a separate fire, and the lead containing small quantities of silver is melted in the centre pot. On allowing to cool, the mass being repeatedly stirred, crystals of nearly pure lead separate, and are ladled into the next pot with a perforated iron ladle. When a definite fraction has been thus removed, the richer lead-silver alloy is transferred to the pot on the left. Lead containing approximately the same amount of silver as that already transferred is added in each case, in order that the charges operated on may be about the same, when the melting and cooling process is repeated. It

will be seen that the lead practically free from silver is being gradually worked in one direction, while the richer alloy, becoming richer and richer in silver at each pot, is being worked in the other direction. In this manner the amount of silver per ton of lead may be raised to several hundred ounces per ton. The eutectic alloy contains about 800 ounces of silver per ton, but in practice it is not usual to work the process beyond 500 ounces to the ton. To recover the silver the rich alloy is then submitted to cupellation.

The Parkes process depends on the superior attraction for silver which molten zinc has over lead. By adding zinc to the lead, on cooling the two metals almost completely separate, the zinc as an upper layer carrying with it nearly all the silver. By distilling the silver-zinc alloy (containing some lead) with lime and coal the zinc is recovered, and the silver is afterwards obtained from the remaining lead by cupellation.

Properties.—Lead is bluish-white or grey in colour; it is extremely malleable and ductile, but is of slight tenacity; it is so soft that it may be easily cut with a knife, and leaves a mark if rubbed on paper. Lead expands greatly when heated, and does not on cooling always return to its original dimensions. It melts at 327°, and partially volatilises at a bright red heat. The metal slowly oxidises in moist air, and, consequently, clean surfaces soon tarnish. Lead in contact with aërated water soon becomes oxidised, forming the white hydrated monoxide $Pb(HO)_2$, which is slightly soluble in water; the corrosive action is increased if ammonium salts are present, but is retarded by the presence of sulphates, phosphates and carbonates, owing to the formation of insoluble salts which coat the surface of the metal with a thin film, and protect it from further action. A large excess of carbon dioxide will, however, even then, increase the solvent action. For some waters this action prevents lead being used either for storing or distribution, as the dissolved lead salts are very poisonous, and act as a cumulative poison in

the system. Lead cisterns should never be used for storing rain water. Lead is employed in several alloys, which will be described in a subsequent chapter.

The high specific gravity as well as the fusibility of lead recommend it for the making of projectiles for small arms. Rifle bullets are made of very pure soft lead, in order that they may easily take the grooves of the rifle. In rifled ordnance, where iron projectiles are used, the surface of the shell is thoroughly cleansed, dipped into a solution of sal ammoniac, next into melted zinc, and is then coated with metallic lead; the coating of zinc causing a firm adhesion between the iron and the lead. Bullets intended to be discharged from smooth-bore small arms, are hardened by the addition of antimony, in order to give them greater penetration. In the manufacture of small shot for fowling pieces, the lead is alloyed with about 5 per cent. of arsenic, which enables the lead to take a spherical shape when the melted metal is dropped through a colander into water. It is necessary, however, to cool down the drops before they fall into the water, and this is accomplished by allowing the molten metal to drop through the air from a height of 100 to 150 feet, according to the size of the shot. It is probable that the presence of arsenic diminishes the power of the liquid lead to contract as it cools after the outer surface has solidified. The shot are dried on a hot plate, and polished by friction in a revolving drum containing a small quantity of plumbago.

Lead is easily dissolved by dilute nitric acid, but the action of strong nitric acid is stopped by a coating of nitrate of lead in fine crystals. Dilute hydrochloric and sulphuric acids do not attack lead, but when hot and concentrated readily form the chloride and sulphate of the metal.

Compounds of Lead.

Oxides.—Oxygen combines with lead in five proportions, three only of the oxides being important. *Lead monoxide*

(PbO) is formed by the oxidation of metallic lead in air; at a moderate heat a yellowish powder, called *massicot*, is obtained; at a higher temperature, a reddish powder, which yields a crystalline mass called *litharge*, when fused. This oxide is the only one that forms salts; the salts of lead being easily obtained by acting on the oxide with the corresponding acid, *e.g.*:—

Lead oxide		Acetic acid		Lead acetate		Water.
PbO	+	$2(HC_2H_3O_2)$	=	$Pb(C_2H_3O_2)_2$	+	H_2O.

Lead oxide		Nitric acid		Lead nitrate		Water.
PbO	+	$2(HNO_3)$	=	$Pb(NO_3)_2$	+	H_2O.

The monoxide is largely used in the Arts in the manufacture of lead pigments, of lead plaster, of flint glass, etc.

Red Lead or *Minium* (Pb_3O_4) is a bright red heavy powder, prepared by prolonged heating of the monoxide at a dull red heat in a current of air. It appears to be a compound of two molecules of monoxide and one molecule of dioxide of lead; for if red lead be acted on by nitric acid, the acid dissolves out the monoxide to form lead nitrate, and the dioxide is left as a brown powder. Red lead is largely used as a pigment, and in the manufacture of glass. It is frequently adulterated with brickdust, oxide of iron, etc.

The *dioxide*, or *lead peroxide* (PbO_2), is best prepared from red lead, as stated above:

Red lead		Nitric acid		Lead nitrate		Lead dioxide.
Pb_3O_4	+	$4(HNO_3)$	=	$2[Pb(NO_3)_2]$	+	PbO_2

Water.

$+ 2(H_2O)$.

The dioxide is left as a dark brown heavy powder. When heated strongly it gives off half its oxygen, and the monoxide is left.

If heated with hydrochloric acid, lead chloride and chlorine gas are formed:

Lead dioxide		Hydrochloric acid		Lead chloride		Chlorine		Water.
PbO_2	+	$4(HCl)$	=	$PbCl_2$	+	Cl_2	+	$2(H_2O)$.

White Lead.—The most important salt of lead is the basic carbonate [$2PbCO_3.Pb(HO)_2$] known as *white lead.* It is a very heavy powder, almost insoluble in water, but is more soluble if carbon dioxide be dissolved in the water. It is much used as a pigment, and possesses special advantages as such, on account of which, in spite of its very poisonous character, and that it is blackened by sulphuretted hydrogen, it has not been superseded by zinc white (ZnO) or baryta white ($BaSO_4$). White lead has the property of combining to a certain extent with oils and varnishes, and gives the paint the property of what is known as covering well. A great deal depends, however, on the way the white lead is prepared. (*See* Pigments.)

Lead Chloride ($PbCl_2$) is always formed when a chloride is added to a strong solution of a soluble lead salt :

Lead nitrate		Sodium chloride		Lead chloride		Sodium nitrate.
$Pb(NO_3)_2$	+	$2(NaCl)$	=	$PbCl_2$	+	$2(NaNO_3)$.

The precipitated lead chloride is a heavy white crystalline substance, soluble in hot water. A number of oxychlorides are known, some of which are of value as pigments, *e.g.*, Pattinson's white oxychloride ($PbCl.OH$), and Turner's patent yellow ($PbCl_2.7PbO$), sometimes called "Paris" patent or mineral yellow.

Lead salts are easily distinguished by their turning black when brought into contact with sulphuretted hydrogen gas ; in fact, a most minute trace of this gas is easily detected by holding a piece of moistened lead paper (made by wetting blotting paper with a solution of lead acetate) in the gas, the blackening being due to the formation of black sulphide of lead.

Tin ($Sn=118$).

Tin has been known and used from the earliest times. Pliny relates that the Phœnicians were in the habit of trading both with Spain and Great Britain for tin. In this country

it still occurs abundantly in Cornwall, and is also found in considerable quantities in Malacca, India and Mexico. Its chief and only important ore is tinstone (SnO_2).

Production.—The tinstone as found in England is nearly always mixed with a large quantity of foreign substances such as quartz, earthy matters, pyrites, etc., and whilst the extraction of the metal is simple, the ore being readily reduced by carbon, in order to remove these it has first to undergo a series of preliminary operations.

The purer portions are picked out by hand and are put on one side, whilst the residue is crushed in stamping mills, and the lighter portions consisting of the earthy impurities are washed away by exposure to a stream of water. This also gets rid of some of the pyrites, as the tinstone being very hard remains in larger pieces than the more friable sulphides ; and as the specific gravity of the tinstone is 6·5, which is far higher than that of any of the substances mixed with it, it is possible to successfully treat even the poorest ores by this process.

The washed ore is now roasted to expel arsenic and also to break up any of the mixed sulphides of iron and copper (pyrites) which may remain in it. These latter are left as iron oxide and sulphide and sulphate of copper, and on allowing the roasted ore to stand exposed to the action of air and moisture, the copper sulphide is converted into soluble sulphate which can be removed by washing with water.

The ore so treated now contains from 60 to 70 per cent. of tin, and the metal is obtained from it by mixing it with one-sixth of its weight of charcoal and a small quantity of lime ; the mixture is then carefully heated in a reverberatory furnace. The carbon unites with the oxygen of the ore and escapes, while the metal separates :

Tinstone		Carbon		Carbon monoxide		Tin.
SnO_2	+	$2C$	=	$2(CO)$	+	Sn.

The temperature is then raised, and the added lime forms a slag with any siliceous matter that may have been present in

the ore, and this collects on the top, the metallic tin sinking through it, and being drawn off from the bottom. This metal is cast into ingots, and is purified by the operations of *liquation* and *poling*. The ingots are heated up in a reverberatory furnace, care being taken that the temperature does not rise too high, when the metal fuses and flows away from the impurities, which have a higher melting point. The metal now requires to be exposed whilst in the molten condition to the oxidising action of the air, for the remaining impurities to be oxidised. This is usually accomplished by holding down in the metal logs of wet wood, the steam and gases which are evolved serving to violently agitate the metal and so expose a great surface. The longer this process takes the purer the resulting metal, the best metal being known as "grain tin" from the fact that it occurs in irregular crystalline fragments, which are produced by allowing ingots heated to just below the melting point to fall from a height, when they readily break up.

Properties.—Tin is a somewhat soft, malleable metal. It emits a peculiar sound (*creaking* or *cry*) when bent, owing to its crystalline structure. It has the lowest melting point of any of the metals in common use, about 232° C. On exposure to damp air it is scarcely altered, and one of its greatest uses is in the production of *tin plate*. It is also used in many alloys, such as gun-metal, solder, pewter, etc.

The action of acids on tin is variable. Strong hydrochloric acid attacks it, forming stannous chloride ($SnCl_2$), and liberating hydrogen. Dilute sulphuric acid has little action on it. With nitric acid much depends on the strength of the acid and conditions under which it acts. Thus strong nitric acid scarcely acts at all; on diluting, somewhat violent action sets in, and if the temperature is allowed to rise, a yellowish insoluble body, metastannic acid, is obtained, but if the solution is kept quite cold it remains clear.

Compounds of Tin.

Oxides.—Tin forms two oxides—stannous oxide (SnO) and stannic oxide (SnO_2), and in the same way forms two classes of salts, in one of which it behaves as a dyad, whilst in the other it is tetrad.

Stannous oxide dissolves in sodium hydroxide, forming a salt, *sodium stannite*, whilst the compound from stannic oxide is *sodium stannate* ($Na_2SnO_3 . 4H_2O$). Both these salts are extensively used by the calico printer.

Chlorides.—Stannous Chloride ($SnCl_2$) is also much used for calico printing, and is prepared by dissolving tin in hydrochloric acid.

Stannic Chloride ($SnCl_4$) can be obtained by heating tin in a current of dry chlorine gas, or boiling stannous chloride with aqua regia.

Sulphides.—Stannous Sulphide (SnS) is readily obtained by heating the metal with sulphur. When sulphuretted hydrogen is passed into solutions of stannous salts, a hydrated form of this sulphide is precipitated as a dark brown mass, readily soluble in sodium hydroxide and strong hydrochloric acid. As prepared from its elements, it is a dark grey crystalline powder, not very soluble in hydrochloric acid.

Stannic Sulphide (SnS_2) is used for decorative purposes under the name of mosaic gold, and is prepared by subliming a mixture of tin amalgam with sulphur and sal ammoniac, when the mosaic gold is left in the form of beautiful yellow scales.

Zinc (Zn=65).

Zinc.—Metallic zinc is never found native; it occurs in combination with sulphur as *zinc blende* (ZnS), and as carbonate of zinc in *calamine* ($ZnCO_3$).

Zinc blende, or *black jack* as it is called by the miners, is

found in considerable quantities in this country, but calamine is imported principally from Spain and the United States.

Production.—The metallurgy of zinc is very simple, since the metal is easily reduced from its oxide by heating with carbon; the zinc being volatile then distils off, and can be condensed in suitable receivers. The temperature at which reduction of the oxide takes place is well above the boiling point of the zinc.

The first step therefore in the production of the metal from either calamine or zinc blende, is to convert these into the oxide, for zinc sulphide is unreduced by carbon at any temperature. With calamine, simple treatment in a kiln, much after the manner of preparing lime from limestone, is all that is necessary. In the case of the blende, this must be roasted in a reverberatory furnace with free access of air, when the sulphur is wholly removed as sulphur dioxide, zinc oxide being left behind.

Calamine — Carbon dioxide — Zinc oxide.

$$ZnCO_3 = CO_2 + ZnO.$$

Zinc blende — Oxygen — Sulphur dioxide — Zinc oxide.

$$2(ZnS) + 3O_2 = 2(SO_2) + 2(ZnO).$$

This zinc oxide is then mixed with finely powdered coal, and is heated in fireclay retorts, when, at a red heat, the metallic zinc distils over and is condensed.

Zinc oxide — Carbon — Carbon monoxide — Zinc.

$$ZnO + C = CO + Zn.$$

In all the processes for extracting zinc, the general chemical reactions are the same, but different forms of furnace, retorts and receivers are employed.

Belgian process.—The process mostly used in this country is known as the "Belgian process," in which the oxide mixed with coal is charged into fireclay cylinders about 4 ft. 6 in. long and 8 in. diameter, closed at the one end. Such

cylinders hold about 1 cwt. of the mixed ore and coal and from forty to eighty of these retorts are arranged in tiers over the same fire (Fig. 56). Fireclay receivers from 2 to 3 ft. long (B) are now luted on, and distillation commenced.

The flame of carbon monoxide soon makes its appearance at the mouth of the tube, and shortly acquires a

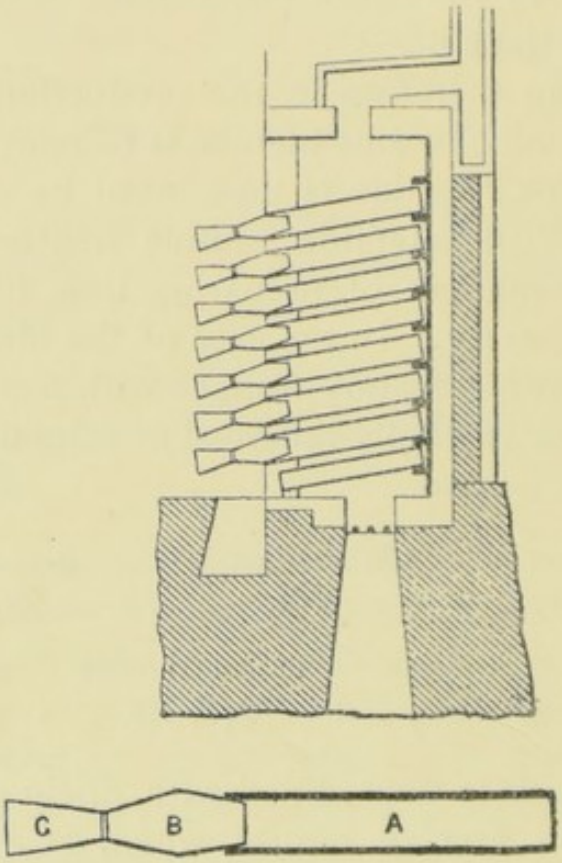


Fig. 56.

characteristic bluish-white colour, indicating that the metal has commenced to distil off. The greater part of the zinc condenses in the fireclay condenser (B), but in order to catch any which passes this point, an iron cylinder (C) is attached. About every two hours this cylinder is taken off and the mixed dust of zinc and its oxide cleared out, the workman at the same time removing the metal condensed in B with an iron ladle.

About 3 or 4 cwt. of coal is required to produce the metal from 1 cwt. of ore by this process, and the loss of zinc usually

amounts to over 10 per cent. The time occupied in working through a charge is about twelve hours.

Silesian process.—In this process the mixture of ore and coal is thrown into muffles about 4 to 5 ft. long, with flat bottoms, a number of these being arranged in pairs in one furnace, the grate of which runs along between the closed ends. Condensation is now usually effected in three long horizontal tubes, connected alternately at the ends, so that the vapours circulate properly through them.

The shape of the muffles used in this process offers certain advantages over the Belgian retorts, and these are sometimes used in conjunction with similar condensing arrangements to those in the latter process, giving to the compound method the term Belgian-Silesian process.

The remelted zinc is generally cast into slabs or ingots which are commercially termed *spelter*.

It has been proposed to use the mixture of zinc and oxide obtained in the condensing cones as a basis for paint intended for iron work.

Both at the ordinary temperature of the air and high temperatures, zinc is so brittle that it cannot be rolled, but at a temperature between 100° and 150° C., it becomes sufficiently malleable to permit of it being rolled down to quite a thin foil. Above 200° C. it is so brittle that it may be pounded in a mortar.

Properties.—Zinc is a bluish-white, hard, lustrous metal. At ordinary temperatures zinc is brittle, but when heated to about 150° C. it is both malleable and ductile. It melts at 412° C., and volatilises at 1040° C. Its specific gravity is about 7·0, varying from 6·8 to 7·1. Zinc undergoes very little change in air, but in contact with water charged with carbon dioxide it becomes coated with a film of oxycarbonate of zinc. When strongly heated in air or oxygen it burns with a bluish-white flame, forming zinc oxide. One of the chief applications of zinc is for coating iron, in order to protect the latter metal from the corrosive action of moist

air. Iron so coated is called "Galvanised Iron," and when exposed to air the outer surface of the zinc becomes converted into zinc oxide, which slowly forms a basic carbonate by absorbing carbon dioxide, and this thin film, not being porous, protects the metal below it from further action.

Compounds of Zinc.

Oxide (ZnO).—Only one oxide of zinc is known. This body is a white powder, formed by burning the vapour of the metal in air, and is used as a pigment (Chinese white). The colour not being affected by impurities in the air, especially sulphuretted hydrogen, it is frequently used in the place of white lead.

Hydroxide [$Zn(HO)_2$] is formed when ammonia is added to a solution of a zinc salt. By adding sodium or potassium hydroxides, the same precipitate is formed, but in each case dissolves in excess of the reagent forming compounds of the type $Na_2O.ZnO$.

Chloride ($ZnCl_2$) is readily produced by the solution of the metal in hydrochloric acid. It is a white deliquescent solid, and is used as a caustic. It is also used as a disinfecting agent (Sir W. Burnett's fluid) to absorb the offensive gases emitted by organic matter during putrefactive decay, such as ammonia gas and sulphuretted hydrogen. The chloride is also used to clean metallic surfaces which are to be soldered together.

Sulphate ($ZnSO_4.7H_2O$) is similarly produced by the action of sulphuric acid on the metal. This salt is isomorphous with magnesium sulphate (Epsom salts), and this has led to fatal mistakes, the former salt being poisonous. In small quantities it is used in medicine as an emetic.

Sulphide (ZnS) when found native is black, owing to the presence of sulphide of iron. When prepared in a pure

state, either by precipitation from a soluble zinc salt with an alkaline sulphide, or by fusing together zinc dust and sulphur, it is quite white, but turns yellow if heated.

Cadmium (Cd = 112).

This metal is always found in small quantities associated with zinc in its ores, and strongly resembles zinc in its physical and chemical properties; it melts at 228° C., and is converted into a vapour at 860° C.

The metal itself is employed in many fusible alloys, but its chief use is in the form of the sulphide, of which the pigment "cadmium yellow" consists. *Cadmium sulphide* (CdS) is easily precipitated by passing sulphuretted hydrogen through an alkaline solution of one of its salts. The *iodide* and *bromide of cadmium* are used in photography.

Mercury (Hydrargyrum, Hg = 200).

Mercury, also called quicksilver, occurs chiefly as sulphide in the mineral *cinnabar* (HgS), from which the metal is obtained by roasting; the sulphur burns off, and the mercury vapour is led along cool passages where it condenses. Mercury is the only metal which is liquid at ordinary temperatures. It is almost silver white, of bright metallic lustre, and extremely mobile. It freezes at −40° and boils at 357·5°, but volatilises at all temperatures. Metallic mercury is used for the manufacture of thermometers, barometers and other physical apparatus; for the collection of certain gases, the preparation of mirrors, and for the extraction of gold and silver from their ores.

All the ordinary metals with the exception of iron and platinum dissolve in mercury, yielding alloys which are known as *amalgams*. These amalgams are liquid at ordinary temperatures if the mercury is in excess, but are otherwise solid or semi-solid.

There are four general methods for preparing amalgams :—

1. Bringing the metal and the mercury together under ordinary conditions.

2. By adding mercury or a sodium or zinc amalgam to a saturated solution of a salt of the metal, when part of the mercury goes into solution, and the remainder combines with the liberated metal. By this method amalgams of calcium, chromium, iridium, iron, osmium, palladium, strontium, nickel and cobalt can be prepared.

3. The metal, such as copper, is placed in a solution of a mercury salt.

4. The metal is placed in contact with mercury and dilute acid, as in the amalgamation of zinc.

In the manufacture of mirrors, the under surface of the glass is covered with an amalgam composed of one part of lead, one of tin, two of bismuth and four of mercury. The excess of mercury is drained off, and after the lapse of a few weeks a solid metallic coating is left on the glass containing about 20 per cent. of mercury. For electrical purposes an amalgam of one part of zinc, one of tin and three parts of mercury is employed, whilst in dentistry, amalgams of mercury with gold, zinc or cadmium, are used.

Compounds of Mercury.

Mercury forms two classes of compounds, namely, *mercurous* and *mercuric*. The mercurous are the most unstable, and have a great tendency to break up, forming the higher compound and metallic mercury.

Oxides.—Mercurous Oxide (Hg_2O), is a black heavy powder, easily decomposed into mercury and mercuric oxide by heat or light, and is prepared by precipitating a mercurous salt with sodium hydroxide.

Mercuric Oxide, or red oxide of mercury (HgO), is a red crystalline solid when prepared by heating mercury in air for some hours to a temperature near its boiling point. If

this red oxide be heated to a higher temperature, it splits up again into oxygen gas and mercury. When the oxide is prepared by precipitating a mercuric salt with sodium hydroxide, it comes down as a yellow amorphous powder, and being in a finer state of division, is chemically more active than the crystalline variety.

Chlorides.—The most important salts of mercury are the chlorides. To prepare these, mercuric sulphate is taken; this is obtained by boiling mercury and sulphuric acid together:—

Mercury		Sulphuric acid		Mercuric sulphate		Sulphur dioxide		Water.
Hg	+	$2(H_2SO_4)$	=	$HgSO_4$	+	SO_2	+	$2(H_2O)$.

Mercuric sulphate is formed and sulphur dioxide gas is given off. The mercuric sulphate is crystallised out and ground up with sodium chloride, and the mixture heated up in a retort. The *mercuric chloride* ($HgCl_2$) or corrosive sublimate, as it is sometimes called, distils over and sodium sulphate is left behind. Mercuric chloride is a crystalline salt, soluble in water, very poisonous, and is used as an antiseptic.

Mercurous Chloride, or calomel (Hg_2Cl_2), is a white salt insoluble in water and dilute acids, readily decomposed by alkalies. It is prepared in the same manner as mercuric chloride, only to the mixture of mercuric sulphate and sodium chloride some metallic mercury is added and an intimate mixture made. The mixture is distilled, calomel comes over, and is condensed in an atmosphere of steam, this causing the powder to fall in a fine state of division.

Mercuric sulphate		Sodium chloride		Mercury		Mercurous chloride		Sodium sulphate.
$HgSO_4$	+	$2(NaCl)$	+	Hg	=	Hg_2Cl_2	+	Na_2SO_4.

Calomel is largely used in medicine, and consequently great care must be taken to ensure the absence of corrosive sublimate, the presence of which may be readily tested by

placing some calomel moistened with alcohol on a polished knife blade, which will be blackened by the slightest trace of corrosive sublimate.

Iodides.—The iodides of this metal may be easily prepared by treating a soluble mercurous or mercuric salt with potassium iodide, and are recognised by their characteristic colours, *mercurous iodide* (Hg_2I_2), being yellowish green, and *mercuric iodide* (HgI_2), a brilliant scarlet; the latter salt is, however, soluble in excess of either potassium iodide or the mercuric salt. An alkaline solution of mercuric iodide in potassium iodide is known as Nessler's solution, and is a delicate test for ammonia both free and combined.

Nitrates.—The nitrates are readily prepared by dissolving mercury in nitric acid. If the mercury be in excess, *mercurous nitrate* [$Hg_2(NO_3)_2$], is formed; if the acid be in excess, *mercuric nitrate* [$Hg(NO_3)_2$], is formed. Both these salts are soluble in water.

Sulphide.—Mercuric sulphide (HgS), may be precipitated by sulphuretted hydrogen from solution of a mercuric salt as a black precipitate, and is insoluble in nitric acid. The native sulphide, *cinnabar*, is red, and when ground to a fine powder constitutes the pigment vermilion.

The brilliant colour can be produced from the black variety artificially by two distinct processes. In the dry process, mercury and sulphur are heated together and the black mass formed is then sublimed, and the vermilion is ground under water. The wet process consists in digesting amorphous mercury sulphide with an alkaline sulphide, great care being taken to regulate the temperature. A brilliant vermilion may also be prepared by heating freshly precipitated "white precipitate" with ammonium polysulphide at a temperature of 45° C.

If ammonia solution be added to a metallic salt, the oxide of that metal is generally precipitated, but with the

salts of mercury this is not the case, for if a solution of mercuric chloride be added to ammonia, an *amido* compound is formed, in which one atom of the chlorine is replaced by the amidogen group (NH_2), and has the formula ($HgCl.NH_2$); the common name for this substance is *white precipitate.*

CHAPTER XXVIII.

Aluminium—Production in the electric furnace—Properties and compounds—Gold—Parting of gold and silver—Silver—Cupellation—Properties and compounds—Photography: Wet process—Dry plate process—Development—Printing—Toning—Platinotype, ferrotype and carbon processes—Platinum.

ALUMINIUM (Al=27).

ALUMINIUM is one of the most abundant elements; it is never found in the free state, but occurs chiefly as silicate and oxide in felspar and all the older rocks, also in clay, marl, slate, and cryolite (a double fluoride of aluminium and sodium found in Greenland in large quantities).

Although aluminium occurs so abundantly in Nature, yet only during recent years has it been possible to produce it on anything like an extensive scale. Even at the highest temperatures attainable in an ordinary furnace, carbon or other reducing agents fail to free it from its compounds. The first commercially successful method was that of Deville, in which he reduced the double chloride of aluminium and sodium ($Al_2Cl_6.2NaCl$) by means of metallic sodium, but such a process was necessarily very costly, and now the metal is entirely produced by electrolysis.

Production. — The electric furnace (Fig. 57) consists of a rectangular box with a carbon lining, which forms the negative pole, and the positive pole is made up of a number of carbon rods about 3 inches in cross section, separated from each other and held in a suitable holder of copper.

A fused bath of cryolite ($Al_2F_6.6NaF$) and fluor spar

(CaF_2) is first prepared by packing this mixture around the carbon rods, an arc being then struck and the poles gradually parted, so that the whole mass is gradually brought to fusion, the carbon anode dipping into this liquid bath.

The material to be reduced is now added in the form of pure alumina (Al_2O_3), which dissolving in the bath, undergoes electrolysis, the fused aluminium sinking to the bottom as it is set free, where means are provided for its removal.

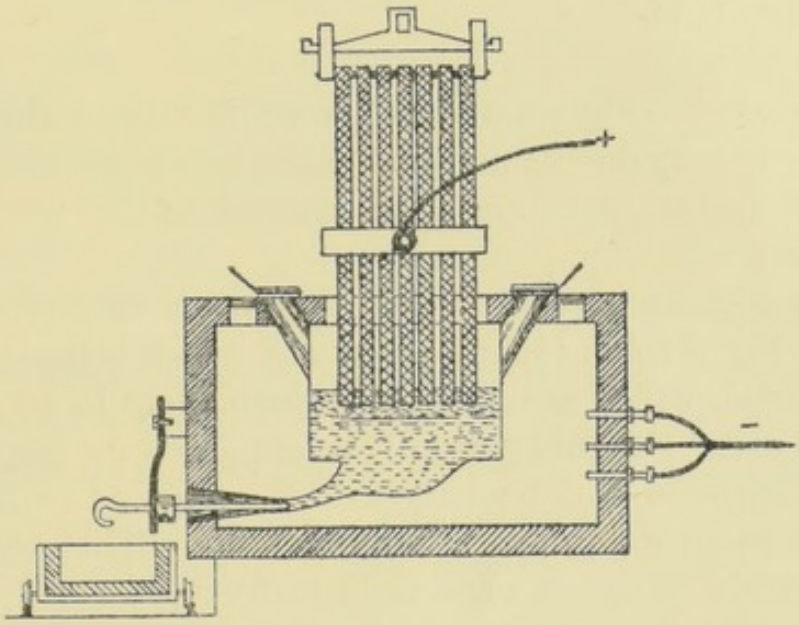


Fig. 57.

Fresh alumina is charged in from time to time, so that the process is a continuous one.

Care has to be taken in the preparation of the aluminium oxide employed. This is carried out by taking a variety of clay known as "*bauxite*," which contains from 30 to 50 per cent. of alumina, together with iron, silica, etc., and roasting this with "soda ash", so producing sodium aluminate ($Al_2O_3.3Na_2O$), carbon dioxide escaping during the process. On extracting the mass with water, the sodium aluminate goes into solution, leaving behind the iron oxide. On passing carbon dioxide through this solution aluminium

hydroxide is precipitated, and from this water is easily driven out, leaving the oxide.

Sodium aluminate		Water		Carbon dioxide	
$Al_2O_3.3Na_2O$	+	$3H_2O$	+	$3CO_2$	=
Sodium carbonate		Aluminium hydroxide.			
$3Na_2CO_3$	+	$Al_2(HO)_6$.			

Even by this process the production of the metal is slow, for only about one ounce of aluminium is obtainable per E.H.P. per hour.

Properties.—The pure metal is white, with a slight tinge of blue; is very ductile and malleable, and possesses a bright metallic lustre that does not tarnish in air at ordinary temperatures.

The specific gravity of cast aluminium is 2·58, but after hammering or rolling increases to 2·68, and it is the lightest of those metals which are sufficiently permanent in air to allow of their use. For this reason it is employed for purposes for which lightness and tenacity are of value, as in beams of delicate balances, optical instruments, etc. The metal itself is extremely sonorous when lightly struck.

Nitric acid has little action on the metal, and sulphuric acid only attacks it when heated. Hydrochloric acid and the alkaline hydroxides readily dissolve it with the evolution of hydrogen.

Aluminium is used to some considerable extent in alloys and in the production of steel (p. 462). It is also finding extensive use in a mixture of metallic oxides with the finely divided metal, under the name of *thermit*. When combustion is started by means of a fuse, a very high temperature is reached, oxygen from the metallic oxide combining with the aluminium. The material has been applied for work which must be done *in situ*, such as welding rails, repairing propeller shafts, etc.

Compounds of Aluminium.

Aluminium Oxide (Al_2O_3).—Aluminium forms but one compound with oxygen, called alumina. In the natural crystallised state it constitutes, according to its colour, various precious stones, such as the sapphire, ruby, amethyst, corundum and emery. Combined with silica and silicates of various metals it forms the garnet, emerald, topaz, beryl, and the splendid blue mineral known as lapis lazuli. Alumina combined with silica forms clay.

Hydroxides.—Three of these are known, a monhydrate ($Al_2O_3.H_2O$), a dihydrate ($Al_2O_3.2H_2O$) and a trihydrate ($Al_2O_3.3H_2O$) the latter being easily obtained by adding ammonium hydroxide to a solution of an aluminium salt. It is readily soluble in hydrochloric acid and sodium or potassium hydroxide, forming the aluminates ($Al_2O_3.K_2O$).

The Alums.—One of the most important classes of salts of this metal is the alums. These consist of double sulphates of triad metals such as aluminium with the sulphates of the monads. For instance, potash alum has the formula ($Al_2(SO_4)_3.K_2SO_4.24H_2O$), and can be formed by mixing, in proper proportions, solutions of aluminium sulphate and potassium sulphate and crystallising.

Very frequently ammonium sulphate (from gas liquor) is used instead of the potassium salt, in which case ammonia alum is formed $(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$.

Alum is a white crystalline body, soluble in water, and has an astringent taste. Its solution has an acid reaction. It is largely used as a mordant to fix colouring matters on calico, the aluminium hydroxide combining with certain organic colouring matters to form insoluble "lakes."

Gold (Aurum, Au = 197).

Gold is found most widely diffused in nature, but in small quantities only. It occurs chiefly in the metallic (native)

form, but occasionally combined with other elements, especially tellurium. It is also found mixed with iron, lead, zinc and silver ores. In the native form it is principally obtained from the quartz veins in some of the older rocks or from alluvial deposits. Owing to the simplicity of the metallurgical treatment, it is found profitable to work with rock containing as little as one ounce, or even less, of gold to the ton, and in the case of alluvial deposits as low as a few grains to the ton.

The alluvial deposits may exist as surface gravel beds called "shallow placers," or as "deep leads," which occur at greater depth, and are probably the beds of ancient rivers. In the Transvaal, "banket reefs," or inclined seams of gravel cemented together, have been worked to a considerable depth.

In the metallurgical treatment of the ordinary alluvial deposits, the sand is simply washed away by the action of running water, and the heavier gold remains behind. With the rock or cement, the latter is pulverised to a powder by means of "stamps." The finely divided powder after being passed through a sieve is carried by a current of water over the surface of amalgamated copper plates. By this means any gold that may be in the rock is dissolved by the mercury, and remains behind, whilst the powdered rock is washed away. After a time the mercury is collected, squeezed through a leather bag, and the solid amalgam remaining is heated in a retort. The mercury distils over, and is used again, whilst the gold remains behind.

The extremely valuable nature of the metal naturally makes it essential that with any process the losses shall be as small as possible, and the commercial success of most mines depends upon the care taken in recovering the last traces of the gold. The washings from the amalgamated plates are run into settling tanks, in the first series of which the coarser particles, "tailings," subside, whilst in the last tanks a fine mud, known as "*battery slimes*," settles out.

One of the most successful methods of recovering the

gold from the tailings is the cyanide process largely worked in South Africa. In this the precious metal is dissolved in large vats having a false bottom, to allow the weak solution of potassium cyanide to slowly percolate through. The gold is then replaced from the double cyanide of gold and potassium by means of metallic zinc.

Another process depends on the conversion of the gold into chloride ($AuCl_3$) by the action of chlorine gas. Since sulphides of other metals would also be attacked and pass into solution, pyritic ores must first be roasted to convert them into oxides which are not capable of being attacked by chlorine. The metal is precipitated as a soft brown powder by means of ferrous sulphate solution.

Ferrous sulphate		Gold chloride		Ferric chloride		Ferric sulphate		Gold.
$6(FeSO_4)$	+	$2(AuCl_3)$	=	Fe_2Cl_6	+	$2Fe_2(SO_4)_3$	+	Au_2.

The precipitated gold is collected and refined by melting under a mixture of borax and nitre. Gold has little affinity for oxygen, and the oxides of gold can only be formed indirectly. This property of gold of resisting the action of oxygen in the air and not rusting, classes it as one of the noble metals.

Many copper ores contain considerable quantities of silver and small quantities of gold, which however it pays to extract. By suitable treatment most of the copper is extracted, leaving an alloy of silver with a fair quantity of gold and still a little copper. The various methods of separating the gold and silver are known as "parting," and three of these may be briefly referred to:—

(*a*) "Parting" by strong sulphuric acid, with which the granulated ore is heated, the silver and copper being converted into sulphates, the gold being left unattacked. From the solution silver is recovered by precipitation with copper or zinc.

(*b*) By strong nitric acid, whereby the silver is converted into the nitrate, from the solution of which it is precipitated as

chloride by the addition of salt, this chloride being further reduced to produce metallic silver by the hydrogen evolved when zinc and sulphuric acid are in contact with the silver chloride.

(*c*) By passing chlorine gas into the molten alloy covered with borax, when the less precious metals are first attacked forming chlorides, the commencement of the attack of the gold being evidenced by the appearance of orange vapours, when the chlorination is stopped. For success with this process, the amount of silver should be small.

Gold is now generally purified by passing chlorine through it when in a molten condition, in the most recent practice the gas being led into the crucible through a tube made of fused quartz.

Properties.—Gold possesses a bright yellow colour by reflected light, and is the most malleable of all metals; if beaten out into thin sheets it transmits green light. It is not acted on by any single acid (except selenic), but dissolves in the presence of free chlorine, and in nitro-hydrochloric acid. Gold is nearly as soft as lead, so that it cannot be used for coinage in the pure state, the standard gold of our country being an alloy of eleven parts of gold to one of copper. For jewellery, pure gold is regarded as of 24 carats. An 18 carat gold, therefore, contains $\frac{18}{24}$ or three-fourths its weight of gold.

One of the most curious compounds of gold is fulminating gold. This is prepared by acting on the trioxide (Au_2O_3) with aqueous ammonia in excess, a yellow brown powder is obtained which, when dry, explodes very readily when heated to 100° or struck by a hammer. The composition of this substance is not accurately known, but it is no doubt an ammonium compound, in which part of the hydrogen of the ammonium is replaced by gold.

By adding a mixed solution of stannous and stannic chloride to a solution of gold chloride, a purple precipitate is obtained, which is called the "Purple of Cassius." The

precipitate dissolves in melted glass, imparting to it a magnificent red tint; it is also used for painting on porcelain.

Silver (Argentum, Ag = 108).

Silver occurs both native and as sulphide in silver glance (Ag_2S), as chloride in horn silver (AgCl). Large quantities are obtained from galena, the ore of lead, which contains traces of this metal. Sea water also contains minute traces of silver.

The oldest method of obtaining silver consisted in fusing the ore with lead, when the latter metal dissolved out the silver, which was recovered by "cupellation." In this process advantage is taken of the ready oxidation of lead to litharge at high temperatures the silver remaining unoxidised. The process is usually carried out in a special type of reverberatory furnace, having an almost elliptical hearth, suitably hollowed, the material employed for lining it being bone-ash. A strong current of air is forced over the molten alloy and the lead slowly oxidised, the melted oxide being driven out of the cupel by the blast. Since in the last stages the litharge carries with it much silver, it is usual to stop the first cupellation before loss of the precious metal takes place, and to subject the much richer alloy to a further cupellation, reserving the litharge so produced for future reduction and recovery of the silver it contains. The amount of silver per ton of lead must exceed 8 ozs. for the cupellation method to be economically carried out.

Silver is also extracted by amalgamation with mercury, the latter being afterwards distilled off.

Properties.—Silver is the whitest of all metals, and admits of the highest polish. It is the best conductor of heat and electricity. It is very ductile, and so extremely malleable that it can be beaten out into leaves that transmit a bluish light. Silver melts at 962°, and possesses the remark-

able power of absorbing oxygen from the air while it is liquid, and giving off the gas again when it is solidifying. When a mass of molten silver is allowed to cool, the film of solid metal which is formed upon its surface is burst in several places by the escaping oxygen, forming beautiful cones. This phenomenon is called "spitting," frequently causing a loss of the metal. Silver is rarely used in the pure state, as it is too soft, and is therefore generally alloyed with other metals, chiefly copper. English standard silver is an alloy containing 7·5 parts of copper to 92·5 of silver. A beautiful alloy is produced by adding a small proportion of silver to aluminium. The properties of aluminium silver are similar to those of aluminium, but its hardness and elasticity are considerably increased, while its colour is identical with that of silver. The alloy being capable of taking a high polish and not being liable to oxidation renders it particularly useful for general use in lieu of silver itself.

Silver is extensively used for coating other metals by electro-deposition; the object to be plated being placed in a bath consisting of silver chloride dissolved in a solution of potassium cyanide, the object is connected with the negative pole of a battery, the positive pole being connected with a silver or platinum plate and immersed in the bath opposite the object to be plated. Silver is also employed for silvering mirrors and reflectors. A flask or globe may be easily silvered by taking a solution of silver nitrate, adding two or three drops of ammonia, then potassium hydroxide, and lastly a solution of grape sugar in alcohol. On warming the contents of the flask gradually, the silver is reduced by the grape sugar, and deposits as a brilliant mirror on the inside of the flask.

On treating galena, all the silver present in the ore will be contained in the lead produced from it, and, if present only to the amount of a few ounces to the ton of lead, it may be profitably extracted by Pattinson's process (*see* p. 489).

Compounds of Silver.

Oxides.—Silver does not combine readily with oxygen, and on this account is useful for coating other metals and for coinage, the tarnishing of silver being due to the presence of sulphur compounds in the air, which coat the silver with a film of the sulphide. Two oxides of silver are known ; both are, however, very unstable, hence they are powerful oxidising agents. The *monoxide* (Ag_2O) is prepared by precipitating a solution of silver nitrate with alkaline hydroxides; a brown earthy powder is obtained, excessively soluble in ammonia, and this solution evaporated at a gentle heat yields crystals, probably of the composition ($AgNH_2$), which are most violently explosive at the slightest touch.

If silver monoxide be acted on by hydrogen peroxide, oxygen is given off, and metallic silver left.

Silver monoxide		Hydrogen peroxide		Silver		Water		Oxygen.
Ag_2O	+	H_2O_2	=	Ag_2	+	H_2O	+	O_2.

Silver Dioxide (Ag_2O_2) is a brown powder produced by the action of ozone on silver.

Nitrate.—Silver Nitrate ($AgNO_3$) is one of the most important salts of the metal. It is formed by dissolving silver in nitric acid, the salt crystallising in plates that contain no water. It melts at 193° without decomposing, and solidifies to a crystalline mass on cooling, known as lunar caustic. The salt is used as a cautery, also for marking inks and in hair dyes.

Halogen Compounds. — Silver combines with the halogens, chlorine, bromine and iodine, forming salts having the composition respectively represented by AgCl, AgBr and AgI. These are all insoluble in water, but completely soluble in sodium hyposulphite. These salts are easily prepared from silver nitrate by precipitation with the chloride, bromide, or iodide of potassium.

Photography.

The three halogen compounds show, in a marked degree, the action of light on silver salts, namely, their instability under the action of white light. Certain parts of the spectrum, the blue end especially, have the power to decompose them, with the formation of subsalts, and for this reason they have been employed most successfully in the processes of photography.

On studying the various parts of the solar spectrum, we find that different parts of it exhibit different properties, *e.g.*, the most refrangible or blue rays possess physical properties which readily start and support chemical action; whereas the rays at the red end do not possess this property; or, if so, only in a very slight degree. The red end of the spectrum, on the other hand, has greater illuminating power than the blue end. The rays at the blue end are termed the actinic rays. If such be allowed to fall upon a mixture of the two gases, hydrogen and chlorine, they combine and explosion takes place; whilst with certain compounds, such as the iodide, bromide and chloride of silver, decomposition takes place, small quantities of lower compounds being formed, and giving a dark colour to the salt which was originally white, or very pale yellow. It was upon this fact that in a paper read before the Royal Society in January 1839, Fox Talbot based his process of "photogenic drawing," which consisted of coating writing paper with a solution of salt, and this, after drying, was brushed over with a solution of silver nitrate, forming silver chloride; on the surface so prepared he placed lace, ferns, etc., and by exposing to light the uncovered portions were blackened, whilst those parts protected from light by the substance remained white. That is, he produced an outline of the object in white on a black ground, and he found that if now he dissolved away the undecomposed silver salts, and having dried his impression, used it to place over a second piece of prepared paper, he

was able, on exposing once more to light, to obtain the outline in black on a white ground.

These two prints he respectively named the *positive* and *negative*, names which we use to the present time.

The silver salts most commonly used in photography are the chloride, iodide, and bromide, and these are all combinations in which one atom of the metal silver is combined with one atom of the non-metals, chlorine, bromine, or iodine; when light acts upon these, some of the chlorine, bromine, or iodine, as the case may be, is liberated, and a silver compound is left containing only one half as much of them as the salt originally taken, and these "subsalts" being all dark coloured form the original image.

Silver chloride undergoes this alteration with considerable rapidity, silver bromide much more slowly, and silver iodide not at all, unless some substance be present which will take up the iodine as it is liberated; and this may be effected by adding to the silver iodide a little silver nitrate and gallic acid, which also renders the decomposition of the chloride and bromide much more rapid.

Silver chloride		Silver sub-chloride		Chlorine.
$2(AgCl)$	=	Ag_2Cl	+	Cl.
Silver bromide		Silver sub-bromide		Bromine.
$2(AgBr)$	=	Ag_2Br	+	Br.

A dark coloured compound will be formed by any of these mixtures after long exposure to light, but when only exposed for a short time, the amount of the original compound decomposed is so small that it is not visible to the eye, and in order to make it visible, it has to undergo a process known as "developing." The latent image may be rendered visible by taking advantage of the fact that the small quantity of subsalt of silver formed during the brief exposure, although present in such minute quantity as to be invisible, yet can exercise sufficient chemical attraction upon metallic silver in the nascent state as to cause it to be deposited from a de-

composing solution of a silver salt upon those portions of the plate where the subsalt has been formed.

Where the light has fallen most strongly upon the original sensitised material, there then will be the largest amount of the subsalt, and when immersed in the developing solution this will have the greatest attraction for the depositing metal, and at these spots the darkest image will be found.

In the developing solution is present some substance with a strong attraction for oxygen, which will tend to cause the separation of finely divided silver. The solution of silver is already present in the wet processes, and in the old dry processes is added to the oxygen-absorbing substance, which as a rule is pyrogallic acid or ferrous sulphate together with some acetic acid and alcohol, the acetic acid controlling the reduction of the silver nitrate.

In the early stages of photography, metallic plates were used to form the background for the thin film of silver salt, and then gradually paper began to be used, but the surface was too rough and uneven to receive sharp images, and the desirability of having a transparent background at once suggested glass; the trouble being, however, to form a thin coherent film of the silver salt on its surface. This was got over, in 1851, by the discovery of the collodion process which consists of dissolving an inferior kind of gun-cotton, called collodion cotton (*see* p. 298), in a mixture of ether and alcohol, and allowing the solution to flow evenly over the face of a sheet of glass; the solvents evaporate and a transparent film is left on the surface of the glass. In the collodion is dissolved a little iodide and bromide of potassium, and it is now rendered sensitive by immersing it in a solution of silver nitrate, when iodide and bromide of silver form in the pores of the collodion—the plate is then exposed, and the latent image developed by the reducing action of pyrogallic acid or ferrous sulphate solution.

The developed image being a metallic image will be permanent, but in order to prevent its being rendered indis-

tinct by the undecomposed silver salts undergoing further decomposition, their removal is now necessary. To do this advantage is taken of the solubility of the undecomposed silver salts in sodium hyposulphite or thiosulphate, so that by soaking the plate in a solution of this salt, called the *fixing bath*, the image is rendered permanent.

This constitutes the old *wet plate* process, in which the plate has to be prepared, sensitised, exposed, and developed within a very short period, unless it be specially prepared and protected. Within the last few years, however, a great advance has been made by the introduction of the so-called *dry plate* process, in which the collodion is replaced by *gelatine*.

Dry Plate Process.—Such plates can be kept for months without deteriorating, and the development can be delayed after exposure to any convenient time. The plates also are much more rapid than those prepared by the collodion process (the ordinary gelatine plates being from ten to thirty times, whilst special plates are made from seventy to 196 times as rapid). The preparation of dry plates requires some care, and of course all the operations must be conducted in a non-actinic light.

If potassium bromide be dissolved in water, and a solution of silver nitrate is now added, the precipitate rapidly settles to the bottom, and on stirring it up, it again settles when left at rest; if, however, a small quantity of gelatine is added to the water in which the potassium bromide is dissolved, the precipitate of silver bromide formed on adding silver nitrate does not settle, the colloid gelatine keeping it in suspension. If more gelatine were now added, an emulsion could be formed with which plates could be coated, but the action of light upon them would be excessively slow, and in order to make them more sensitive, the original liquid with its small trace of gelatine is warmed for some time with a little ammonia at 35° C., or boiled with a small quantity of hydrochloric acid; this causes the particles of silver bromide

to aggregate into larger masses of definite form, a change which can be seen by transmitted light. The silver bromide when first precipitated is orange by transmitted light, but as the warming proceeds, it gradually becomes lighter and acquires a blue tint which finally becomes grey; it should be stopped when the blue tint is reached, as at that point it is most sensitive, and if the required amount of gelatine be now added, a highly sensitive emulsion is produced, which sets on cooling. The potassium bromide, when acted upon by the silver nitrate, gave, by double decomposition, silver bromide and potassium nitrate, and the next step is to remove this latter salt which is in solution, and which, when a plate was coated with the emulsion, would crystallise out and spoil the surface. This is done by breaking up the gelatine by pressing it through fine canvas or a syringe with holes in the bottom, and then dissolving out the potassium nitrate by repeated washings with pure water, which dissolves the nitrate and leaves the gelatine and silver bromide undissolved.

The gelatine with its silver bromide is now melted, and a small quantity of alcohol, not exceeding 10 per cent., is added to make it flow evenly over the surface of the glass, together with a minute quantity of chrome alum, which has the effect of rendering the gelatine after drying on the plate much more insoluble in warm liquids, preventing its softening in warm weather, and also checking the so-called "frilling" or puckering of the film of gelatine when immersed in liquids.

The glass plates after having been thoroughly cleaned, best by soaking in chromic acid, washing well with distilled water and drying, are now coated evenly with the emulsion and are placed in a perfectly horizontal position to set, care being taken that the air is dry and free from dust. When dry they are ready to be placed in the dark slide and transferred to the camera.

Developing.—The plate having been exposed to light, and

having received the image, is now ready for the second process, called "developing."

Many substances are used in solution as developers, amongst them the following:—

1. Ferrous oxalate, made by adding one part of a saturated solution of ferrous sulphate to three parts of a solution of neutral potassium oxalate.

2. Alkaline pyrogallate, in which pyrogallic acid is dissolved in the presence of some alkaline substance such as ammonia or sodium or potassium carbonate.

3. Alkaline hydroquinone.

All these three solutions are powerful reducing agents, and rapidly absorb oxygen. In order to check any too rapid action, and to prevent any of the unexposed salts of silver being reduced, a little potassium or ammonium bromide is added, and this acts as a "restrainer" and helps to prevent the plate from becoming "fogged," as it is termed.

The plate which has been exposed is now taken to the dark room and placed in one of the above developers; in a short time the image will begin to appear, and gradually gains in strength until all detail shows itself, provided the plate has been properly exposed, the exact time to stop development only being acquired by experience. The image now consists of silver reduced from the bromide. The developing solution is washed from the plate by water, and the unacted on compounds of silver are removed by immersing the plate in a solution of sodium thiosulphate, until the lighter portions of the image are quite clear. The plate is now washed for some time in order to remove all soluble salts from the film and thus render it permanent. As before mentioned, all these operations must be conducted in a non-actinic light. If one of the gelatino-bromide plates be exposed to the action of a spectrum, and then be developed, we find that the reduction only occurs in those portions that have been exposed to the green, blue and violet rays; the red, orange and yellow rays having little or no effect. Therefore, all preparation of emulsion, coating or

developing a plate must be done in darkness or by means of a light protected by yellow or red medium, such as ruby glass or an orange-coloured cloth called "golden fabric."

Printing.—Having obtained the negative in which the lights of the original picture are reversed, it is easy to produce any number of positives by means of one of the many printing processes now in use. The simplest and most general method adopted is by employing a sensitised paper prepared as follows:—

The paper is floated on a mixture of albumen and ammonium chloride, thus producing what is generally known as albuminised paper; so prepared it will last for an indefinite period, and is not sensitive to light; in order to render it so, it is floated on a 10 per cent. solution of silver nitrate, which forms in the albumen silver chloride and silver albuminate; the paper after flotation is hung and dried, the sensitising and drying being carried on in yellow light. When dry, it is cut up to the required size and exposed under the negative; those portions of the negative which are opaque allowing no light to pass through, the silver salts beneath remain undecomposed, the transparent portions of the negative allow the light to pass through, and there a darkening takes place; in this way, therefore, we have the image of the original produced in its proper gradation of light.

The next step is to remove all soluble salts by washing in ordinary water, and to tone the print.

If the undecomposed silver salts were removed by fixation, a disagreeable foxy red print would result; and in order to avoid this, recourse is had to what is called "toning," which consists simply in gilding the reduced silver in the image, by immersing the print in a solution of sodium acetate, gold chloride and water. The resulting colour will depend upon the time the print is kept in the solution, and also on the salt used in conjunction with the gold, the tungstate, phosphate and borate of sodium, all giving

different tints if used instead of the acetate. The print having been toned, is now rinsed in clean water and is transferred to a fixing solution, which is a 20 per cent. solution of sodium thiosulphate in water; in this the print is allowed to soak for fifteen minutes so as to ensure the complete solution of the undecomposed silver salts—after this all soluble salts are eliminated by thorough washing in running water. and the print after drying is ready for mounting.

Various other printing processes are also used, *e.g.*, platinotype and ferrotype photographs are made by taking advantage of the fact that ferric salts are converted by light into ferrous salts, and that these, when placed in a bath of potassium chloro-platinite, reduce the salt, and platinum is deposited in a fine black powder on the portions of the exposed paper where the ferrous compounds have been formed.

In the ferrotype process, the paper with reduced iron salt is placed in a bath of potassium ferricyanide, which gives a deep blue colour with the reduced iron salt.

In the so-called carbon process, advantage is taken of the fact that a mixture of gelatine and potassium bichromate becomes insoluble on exposure to light. If then a piece of paper be coated with a film of this mixture (the gelatine being coloured by suspending some pigment such as lamp-black in it) and be exposed under a negative, where the light has penetrated, the gelatine will become insoluble, and on immersion in hot water the unacted on portions will dissolve away and leave behind a positive picture composed of gelatine, rendered visible by the colouring matter suspended in it.

Platinum (Pt=194·5).

Platinum is only found native, that is in the metallic condition, but always alloyed with other metals. Its chief sources are the Ural Mountains, but it occurs also in very small quantities in Peru, California, etc.

The present method of working up platinum is to melt

the ore in a very powerful furnace, using the oxy-hydrogen blowpipe. In this way an alloy of platinum, iridium and rhodium is formed, the other constituents or impurities of the ore being absorbed by the lime of the crucible, or volatilised by the intense heat. This alloy is more useful than pure platinum, being harder and less easily attacked by acids than the pure metal.

Platinum is a white metal, does not tarnish in the air, is extremely infusible, and can only be melted by means of the oxy-hydrogen blowpipe. It also resists the action of any single acid, but dissolves in aqua regia, or chlorine water; for this reason platinum vessels, wire and foil are much used in the laboratory. Caustic alkalies, silicon, phosphorus and carbon, however, attack the metal at high temperatures; also several metals, such as lead and antimony, form fusible alloys with the platinum. Vessels made of this metal should therefore never be brought in contact with these substances at an elevated temperature.

Molten platinum, like silver, has the power of absorbing oxygen and of giving it off again on solidifying. At a red heat the metal is readily permeated by hydrogen, but not by oxygen and the other gases. Another remarkable property this metal has, is the power to condense gases on its surface; this power, however, depends greatly on the physical condition of the metal. In a very finely divided state, as in the form of spongy platinum, or in the form of platinum black, many gases and vapours unite with the oxygen of the air, in their presence even at ordinary temperatures.

Platinum is tetravalent and combines with chlorine to form platinum tetrachloride ($PtCl_4$), a brownish red deliquescent salt, soluble in alcohol and ether, and is remarkable for the ease with which it forms double chlorides with the chlorides of the alkalies and alkaline earth metals and with the chlorides of many vegetable alkaloids. For this reason it is used to determine quantitatively the amount of potassium and ammonium present in different compounds. The double chloride of potassium and platinum has the formula ($PtCl_4.2KCl$).

CHAPTER XXIX.

Nickel—Production and properties—Cobalt—Manganese—Chromium—Chromium salts and chromates—Antimony and its compounds—Bismuth—Bismuth compounds.

NICKEL (Ni=58·5).

THIS metal is nearly always found associated with cobalt. The most important ore is nickeline (NiAs), whilst considerable quantities are found as a silicate of nickel and magnesium in New Caledonia. A magnetic pyrites containing nickel is also worked in Pennsylvania. Canada and Norway contribute largely to the supply of nickel, which, since the extensive introduction of nickel steel, has become a metal of great importance.

Metallurgy.—The first step in the production of the metal is the concentration of the metal into a "matte," from which it can afterwards be reduced.

The usual process is to roast the ore and then reduce it in a blast furnace, lime and slag being added. The ore usually averages from 2 to 4 per cent. of nickel, and after smelting the amount is between 15 and 30 per cent. The matte is now treated much as iron is in the Bessemer process, when sulphur, arsenic and iron are oxidised.

There are many methods, both wet and dry, by which the matte may be treated, in order to obtain the metal, one of the most recent and successful being that introduced by Mond. When the metal in a fine state of division is heated to about 80°C. in presence of carbon monoxide, nickel carbonyl [$Ni(CO)_4$] is obtained, which is volatile. The stream of carbon monoxide carrying with it nickel carbonyl is then led

through a series of tubes heated to 180°C., when the carbonyl is decomposed and pure nickel is deposited.

Nickel carbonyl		Nickel		Carbon monoxide.
$Ni(CO)_4$	=	Ni	+	4CO.

The carbon monoxide is then available for further use.

Properties.—Nickel is a steel-like metal capable of taking a high polish. It is not oxidised in air at ordinary temperatures, but on heating is slightly attacked. The melting point is somewhat uncertain, but it is slightly lower than that of iron. Acids attack it with fair ease.

The metal is largely employed in steel for armour plates, shells, etc. (*see* p. 471), and in the form of alloys. Since the metal so well withstands the action of the atmosphere it is extensively used for plating steel for bicycles and other purposes.

Nickel forms at least two definite oxides (NiO) and (Ni_2O_3). From the former all the salts of nickel may be regarded as derived, the chloride ($NiCl_2$) and the sulphate ($NiSO_4$) being the most common.

Cobalt (Co=59).

Cobalt occurs in the metallic state in meteoric iron, also is found combined with arsenic as Speiss cobalt ($CoAs_2$) and cobalt glance (CoAsS). This metal resembles iron in colour, but melts at a somewhat lower temperature, and has nearly double the tenacity of iron. It is only slightly malleable, but is very ductile. It is not acted on by dry air, but oxidises rapidly at a red heat. The metal dissolves in acids to form cobaltous salts, which are soluble in water, forming red solutions.

Cobalt		Hydrochloric acid		Cobalt chloride		Hydrogen.
Co	+	2(HCl)	=	$CoCl_2$	+	H_2.

This salt crystallises in dark red prisms with six molecules of water ($CoCl_2.6H_2O$) which lose part of their water

when heated to 120° and become blue ($CoCl_2.2H_2O$), becoming anhydrous at 140°. By writing with a dilute solution of cobaltous chloride on paper, the writing after drying at the ordinary temperature becomes almost totally invisible; on warming the paper the writing becomes dark blue, but fades away on cooling in moist air (sympathetic ink).

Cobalt forms several oxides, but only the cobaltous oxide (CoO), in which the metal is a dyad, yields stable salts. This oxide is extensively used to impart a blue colour to glass. Fused with an acid silicate and ground to a powder it forms the pigment "smalt." The blue colour is not affected by acids or alkalies.

MANGANESE (Mn=55).

Manganese occurs chiefly combined with oxygen as pyrolusite or dioxide (MnO_2); also as manganese spar or carbonate ($MnCO_3$), or Braunite (Mn_2O_3) and Hausmannite (Mn_3O_4).

The metal manganese is only obtained in the pure state in small quantities for scientific purposes, but it plays a most important part in the manufacture of steel and in the production of alloys, such as manganese bronze, in each case the source of the metal being either *ferro-manganese* or *spiegeleisen.*

Spanish ores containing iron and manganese can be readily reduced in the blast furnace, alloys containing as much as 70 to 80 per cent. of manganese being produced. Higher percentages entail certain difficulties in working. Ferro-manganese is usually made to contain between 70 and 80 per cent. of manganese, whilst spiegeleisen may be taken to contain anything below 40 per cent., although the usual amount lies between 5 and 20 per cent.

Manganese is a reddish-grey metal, very hard and brittle, scratching glass; but owing to its rapidly oxidising in moist air, has to be kept under naphtha. The metal combines with oxygen, forming a very complete series of oxides; the

lowest being basic and the highest acid forming, whilst the intermediate ones are neutral.

Compounds of Manganese.

Oxides.—The most important oxide is the dioxide (MnO_2). This is found tolerably pure, and is largely used in the preparation of chlorine gas (*see* Chlorine). The oxide is a powerful oxidising agent in the presence of sulphuric acid; *e.g.*, oxalic acid is completely oxidised by this mixture to carbon dioxide.

Manganese dioxide		Sulphuric acid		Oxalic acid		Manganese sulphate
MnO_2	+	H_2SO_4	+	$H_2C_2O_4$	=	$MnSO_4$
		Carbon dioxide		Water.		
	+	$2(CO_2)$	+	$2(H_2O)$.		

Manganous oxide (MnO) is a strong base, and dissolves in acids to form pink or white salts in which the manganese is a dyad. The chloride and sulphate are both used in calico printing.

Several other oxides are known.

Hydroxide.—$Mn(OH)_2$ is obtained as a white precipitate when sodium or potassium hydroxide is added to a solution of a manganese salt, but on exposure to air the precipitate quickly turns brown, owing to absorption of oxygen from the air, with the formation in the first place of Mn_3O_4 and finally Mn_2O_3.

Manganese forms two series of salts, manganous salts, such as the chloride ($MnCl_2$) and the sulphate ($MnSO_4$), and manganic salts which are not so well defined; the chloride (Mn_2Cl_6) has not been isolated but is believed to exist in solution, whilst the sulphate [$Mn_2(SO_4)_3$] is very unstable.

Chromium (Cr=52)

Chromium occurs principally as chrome-ironstone or chromite ($FeO.Cr_2O_3$), from which large quantities of chrome-

iron are obtained, to be afterwards utilised in the production of chrome steel. The chrome-iron is easily obtained by reduction in the blast furnace, though the consumption of fuel is much greater than for pig-iron.

The pure metal may be obtained by the reduction of chromium sesquioxide (Cr_2O_3) with carbon in the electric furnace, the large amount of carbon accompanying the first product being removed by subsequent fusion with lime, when calcium carbide is formed.

Properties.—Chromium is a metal harder than glass, and has a very high melting point. It combines with carbon much in the same way as iron does, the resulting body being so hard that it can only be cut by a diamond. In its other properties it closely resembles iron.

Compounds of Chromium.

Oxides.—Chromium forms two oxides, the one chromium sesquioxide (Cr_2O_3) being *basic* and from which a series of chromium salts are derived, the other chromium trioxide (CrO_3) being *acidic*, yielding an important series of salts, the *chromates*, much resembling the sulphates.

When the sesquioxide is fused with an oxidising substance, such as potassium nitrate, it is converted into a potassium salt of chromic acid (H_2CrO_4). Other powerful oxidising agents can bring about a similar change; thus if potassium hydroxide be added to a solution of a chromium salt, a chromium hydroxide is precipitated, but dissolves to a green solution in excess of the potassium hydroxide.

Chromium chloride		Potassium hydroxide		Chromium hydroxide		Potassium chloride.
Cr_2Cl_6	+	$6KOH$	=	$Cr_2(HO)_6$	+	$6KCl$.

On now adding lead peroxide and boiling, the colour of the solution changes from green to yellow, owing to the conversion of chromium hydroxide into the lead salt of chromic acid.

Chromium hydroxide		Lead peroxide		Lead chromate		Lead oxide		Water.
$Cr_2(HO)_6$	+	$3PbO_2$	=	$2PbCrO_4$	+	PbO	+	$3H_2O$.

The converse change of a compound of chromic acid to one of chromium sesquioxide may be brought about by the action of reducing agents, thus sulphuretted hydrogen brings about such reduction with the liberation of the whole of its sulphur.

By treating one molecular proportion of a chromate with half a molecular proportion of sulphuric acid, a *bichromate* is obtained, which may be regarded as a combination of the chromate group with one CrO_3 group, thus:—

Potassium chromate		Chromium trioxide		Potassium bichromate.
K_2CrO_4	+	CrO_3	=	$K_2Cr_2O_7$.

An excess of strong sulphuric acid added to a chromate or bichromate in solution, leads to the deposition of fine long red crystals of chromium trioxide (CrO_3) which is an extremely powerful oxidising agent, rapidly attacking organic matter. For this reason a mixture of sulphuric acid and potassium bichromate is frequently employed for cleansing glass apparatus in the laboratory.

Antimony (Sb=120).

Antimony is a very brittle crystalline metal, having a density of 6·7. It is rarely found native, but occurs principally as trisulphide in the ore called Stibnite (Sb_2S_3). The metal is obtained on a large scale by heating the trisulphide with half its weight of metallic iron, when ferrous sulphide and metallic antimony are obtained:—

Antimony sulphide		Iron		Ferrous sulphide		Antimony.
Sb_2S_3	+	$3Fe$	=	$3(FeS)$	+	Sb_2.

The crude metal so obtained is purified by repeated fusion with dry sodium carbonate.

Antimony undergoes no alteration in the air at ordinary temperatures, but if heated up to 450° it melts and rapidly oxidises; if heated more strongly, it takes fire and burns with a white flame, giving off dense white fumes of antimony trioxide. Antimony is not attacked by dilute hydrochloric

or sulphuric acids. Nitric acid attacks the metal, dense red fumes of the lower oxides of nitrogen are given off, and a white insoluble powder is left behind, called antimony pentoxide, but this is usually accompanied by lower oxides.

The alloys of antimony are largely used in the arts.

Compounds of Antimony.

Antimony Hydride (SbH_3) very much resembles arsenic hydride (AsH_3) being obtained as a colourless, odourless gas on treating zinc-antimony alloys with dilute hydrochloric acid. The gas burns with a bluish white flame and, like arsenuretted hydrogen, deposits the metal on any cold surface brought in the flame.

Oxides.—Antimony forms three oxides, Sb_4O_6, Sb_2O_4, and Sb_2O_5.

Antimonious Oxide (Sb_4O_6) is produced when the metal burns in air, and also when steam is passed over the heated metal.

This oxide dissolves when boiled with a solution of cream of tartar (hydrogen potassium tartrate), forming the substance "tartaric emetic," employed in medicine.

Antimony Tetroxide (Sb_2O_4, or $Sb_2O_3.Sb_2O_5$) is obtained as a yellowish white residue when the metal is treated with nitric acid. Unlike the above oxide, it is not soluble in cream of tartar.

Antimony Pentoxide (Sb_2O_5) is a light yellow powder, which on heating yields the tetroxide. It may be regarded as the anhydride of antimonic acid ($HSbO_3$), two molecules of which on losing one molecule of water would give Sb_2O_5. Since antimonic acid is obtained when nitric acid of suitable strength acts on the metal, it is often mixed with some of the anhydride.

Chlorides. — *Antimony Trichloride* ($SbCl_3$) — sometimes called butter of antimony—is formed when powdered anti-

mony is thrown into chlorine gas, or by dissolving the trisulphide in hydrochloric acid, evaporating the excess of acid, and then distilling off the antimony chloride.

Antimony trisulphide		Hydrochloric acid		Antimony trichloride		Sulphuretted hydrogen.
Sb_2S_3	+	$6(HCl)$	=	$2(SbCl_3)$	+	$3(H_2S)$.

This method is used for the preparation of sulphuretted hydrogen, when the gas is required free from hydrogen.

If a solution of antimony chloride be mixed with much water, a white precipitate of the oxychloride is obtained.

Antimony trichloride		Water		Antimony oxychloride		Hydrochloric acid.
$SbCl_3$	+	H_2O	=	$SbOCl$	+	$2(HCl)$.

The trichloride is used extensively to produce the brown surface on steel in guns, which prevents rust. Antimony pentachloride is prepared by saturating the trichloride with chlorine; it is decomposed easily by water or by heating. It is used as a chlorinator, since it readily gives up a portion of its chlorine.

Sulphides.—Antimony Trisulphide (Sb_2S_3) and *Antimony Pentasulphide* (Sb_2S_5) can be precipitated from solutions of corresponding salts by sulphuretted hydrogen. The trisulphide so precipitated is of an orange-red colour, and is employed for vulcanising caoutchouc. If this red sulphide be strongly heated it becomes permanently grey, and resembles the natural black sulphide of antimony. The native sulphide when mixed with chlorate of potash and phosphide of copper is employed in the manufacture of electric fuses.

Bismuth (Bi=208·5).

Bismuth usually occurs native and in combination with sulphur, as *bismuthite* (Bi_2S_5). To obtain the metal the sulphide is roasted in the air, and the resulting oxide reduced with charcoal. Bismuth is a reddish-white metal of specific gravity 9·9. It is permanent in dry air at ordinary

temperatures, but rapidly oxidises at a red heat. It is brittle, and may be easily pulverised. It melts at 268°, and, like water, expands at the moment of solidification. The solidified metal has a pronounced crystalline structure, taking the form of rhombohedra in shape, closely approximating to cubes. It is very soluble in nitric acid, slowly soluble in sulphuric acid, and practically insoluble in hydrochloric acid.

The metal *per se* is not used in the arts, but is employed as an admixture in various alloys, most of which are remarkable for their low melting points.

Compounds of Bismuth.

Oxides.—Bismuth forms three oxides, Bi_2O_3, Bi_2O_4 and Bi_2O_5.

Bismuth Trioxide (Bi_2O_3) is formed when the metal is strongly heated in air, and when potassium hydroxide or ammonia is added to a solution of a bismuth salt, a hydrated oxide ($Bi_2O_3.H_2O$) is precipitated.

Chlorides.—Two chlorides are known, $BiCl_2$ and $BiCl_3$.

Bismuth Chloride ($BiCl_3$) is formed when bismuth is dissolved in aqua regia, and like the nitrate and other salts, it is decomposed by much water, forming an oxychloride.

Bismuth chloride		Water		Bismuth oxychloride		Hydrochloric acid.
$BiCl_3$	+	H_2O	=	$BiOCl$	+	$2(HCl)$.

This substance is used as a pigment, and called "pearl white."

Bismuth Nitrate $Bi(NO_3)_3$ is formed when bismuth dissolves in nitric acid, and it crystallises with five molecules of water of crystallisation. These crystals are deliquescent. When water is added to the salt a basic nitrate is produced, but this readily dissolves in dilute acids.

Bismuth Sulphide (Bi_2S_3) is obtained as a dark brown powder when sulphuretted hydrogen is passed through solutions of bismuth salts.

CHAPTER XXX.

Metals of the Alkaline Earths.

Metals of the alkaline earths—Magnesium and its compounds—Calcium and its compounds—Barium—Strontium—The alkali metals—Potassium—Compounds of potassium—Sodium—Compounds of sodium—The spectroscope—Ammonium compounds.

IN this group we may place the four metals, magnesium, calcium, strontium and barium, and of these the only one which, in the metallic state, is of any importance, is magnesium, the others being oxidised by moist air with such rapidity that they can have no commercial value, and are little more than scientific curiosities. Their numerous compounds, however, are of great importance.

They all form oxides in which one atom of the metal is united with one atom of oxygen, and these oxides dissolve to some extent in water, magnesium oxide but slightly, while the solubility increases until it reaches a maximum with barium oxide. The solutions in every case are alkaline, hence the term "alkaline earths."

Magnesium (Mg = 24).

Magnesium occurs widely diffused in nature and in large quantities, especially as carbonate in dolomite and magnesite, as sulphate in Epsom salts, and as silicate in asbestos, meerschaum, talc, steatite or soap-stone, etc. It is found as sulphate and chloride in sea water.

Magnesium has only been extracted in any quantity during the last few years, a considerable demand for it having arisen in consequence of its property of burning in air with a very brilliant flame, rich in actinic or chemical rays, which make it valuable as a source of artificial light in

photography. A wire of 0·3 millimeter in diameter in burning produces a light equal to that of seventy-four sperm candles, of which six go to the pound. For signalling purposes a preparation is made by fusing together ten parts of shellac with sixty parts of barium nitrate, grinding and adding two parts powdered magnesium. This mixture when made into torches constitutes the so-called "Bengal lights."

Preparation.—The metal is prepared by heating to redness a mixture of sodium and magnesium chlorides with one-fifth its weight of metallic sodium in an iron vessel. The crude magnesium so obtained is then distilled, out of contact with air, at a white heat into an iron receiver placed directly over the crucible.

Magnesium is a white metal much resembling silver, but soon tarnishes in moist air owing to the formation of a film of oxide on the surface. It melts at about 800°, is malleable, and at a temperature of 450° can be readily worked and rolled into any form. Magnesium readily forms alloys with the ordinary metals, that with aluminium, sold under the name of "Magnalium," promising to be of considerable use.

Compounds of Magnesium.

Oxide (MgO).—Magnesium oxide or magnesia is formed when the metal is burnt in the air, or when the carbonate or nitrate is ignited. It is a white amorphous powder, almost insoluble in water (one part dissolving in about 55,000 parts of water), giving it a feeble alkaline reaction.

Magnesia formed by the prolonged ignition of the carbonate is much used in pharmacy, whilst the commoner kinds are used for the manufacture of crucibles, fire-bricks, etc., on account of their infusibility.

Chloride ($MgCl_2$).—The metal readily dissolves in dilute acids, forming the different salts. Magnesium chloride is present in sea water, and also occurs in large quantities,

combined with potassium chloride in the mineral Carnallite ($MgCl_2.KCl.6H_2O$) in the Stassfurt deposits. From this compound the magnesium chloride is separated, and is used by the cotton spinners in this country as a thread lubricator.

Carbonate ($MgCO_3$). — Magnesium carbonate, commercially known as *magnesia alba*, is prepared by precipitating a solution of the sulphate or chloride with sodium carbonate. A basic carbonate is thrown down, having the probable formula of $3MgCO_3.Mg(HO)_2.3H_2O$. A denser variety having an extra molecule of water may be obtained in the same manner, only using hot and strong solutions.

Sulphate ($MgSO_4$).—Magnesium sulphate is found native in many places, and forms the purgative principle of several spring waters, such as those obtained from Epsom, Seidlitz and Püllna. The salt is easily soluble in water, and is largely used in the cotton trade as a warp-size, also for medicinal and agricultural purposes.

Nearly all the minerals containing magnesium silicate may be recognised by their peculiar greasy feeling ; this is most marked in soap-stone.

Calcium (Ca=40).

Calcium forms a very large proportion of the Plutonic rocks, of which the earth is composed, and occurs in considerable quantities, forming whole mountain chains of limestone, chalk and gypsum. It is also found in all animals and vegetables, being absorbed by means of their food.

The metal itself is of a light yellow colour, of specific gravity 1·58, is harder than lead, and very malleable. In ordinary air it combines slowly with the oxygen, but at a red heat it fuses and burns with a brilliant light, forming calcium monoxide or lime.

Calcium		Oxygen		Calcium monoxide.
Ca	+	O	=	CaO.

Compounds of Calcium.

Oxides.—Two oxides are known, the monoxide (CaO) or *lime*, and a dioxide (CaO_2).

The former is produced in large quantities wherever limestone rocks are found, since it is extensively used in the production of mortar and bleaching powder, in tanneries, and for agricultural purposes. The limestone together with coal is thrown into suitable kilns, the type of which varies in different localities, when the heat resulting from the combustion of the coal breaks up the calcium carbonate, carbon dioxide being driven off and calcium oxide (*quick lime*) settling to the bottom of the kiln, where it is raked out from time to time.

Calcium oxide, when pure, is white, and on strongly heating emits an intense light, and is used in the form of cylinders in the oxy-hydrogen light.

Calcium Hydroxide $Ca(HO)_2$.—On exposing lime to moist air, water is slowly absorbed, forming the hydroxide, which on prolonged exposure further absorbs carbon dioxide. If freshly burnt lime is taken, and water added to it, the formation of the hydroxide takes place with such energy that considerable heat is developed, the mass swells up, and if not too great a quantity of water has been added, the mass breaks up into a dry white powder, calcium hydroxide (*slaked lime*).

Lime		Water		Calcium hydroxide.
CaO	+	H_2O	=	$Ca(HO)_2$.

Calcium hydroxide is slightly soluble in water, the clear solution obtained by allowing the excess of the hydroxide to settle is called "lime-water," and is employed medicinally and in the laboratory. It is alkaline to test paper, and on exposure to air absorbs carbon dioxide, forming a white precipitate of calcium carbonate.

Calcium hydroxide		Carbon dioxide		Calcium carbonate		Water.
$Ca(HO)_2$	+	CO_2	=	$CaCO_3$	+	H_2O.

Calcium Chloride ($CaCl_2$) can readily be obtained by the action of hydrochloric acid on the carbonate.

It combines with water to form several crystalline salts, which on heating lose water, forming a dry granular mass which is largely employed for drying gases and liquids, since it is very hygroscopic.

Ammonia gas and alcohol both form compounds with calcium chloride, so the material is unsuitable as drying agent in these cases.

Calcium Carbonate ($CaCO_3$).—Calcium occurs principally as the carbonate, and from this all the manufactured compounds of lime are prepared. The forms in which the carbonate are found are very numerous. In the amorphous state it exists as limestone and chalk; the crystalline forms being calc spar or Iceland spar, and arragonite. Marble has also a crystalline form, and sometimes is found coloured or variegated by the presence of oxides of iron and manganese. Black marble owes its colour to the presence of bituminous matter. Calcium carbonate is also the principal constituent of egg shells, the shells of fishes, and coral.

Calcium Sulphate ($CaSO_4$) occurs in nature as "anhydrite," but more generally combined with two molecules of water, as selenite, alabaster and gypsum ($CaSO_4.2H_2O$). From gypsum, the substance called *plaster of Paris* is obtained, by heating the former to a temperature between 110° to 120° C.; it then loses about three-fourths of its water and forms a substance which, on being powdered, has the property of recombining with water, forming a hard mass, which expands at the moment of setting or solidifying, and is therefore much used in taking casts.

In burning the gypsum to form "plaster of Paris" care has to be taken to avoid too high a temperature, in which case it becomes "overburnt" and to a great extent loses the property of recombining with water. An addition of a small percentage of lime to plaster of Paris (not more

than 10 per cent.) increases the rapidity of setting and makes it harder; this latter property being also induced by addition of a little solution of alum to the plaster and again burning.

Plaster of Paris must always be kept in a dry place, otherwise it absorbs water, and to a great extent loses its power of setting.

Calcium sulphate is slightly soluble in water (1 part in 400, at 35°C.), and less so in hot water. It is one of the chief causes of the permanent hardness of water, which is not removed by boiling. The presence of other salts, such as sodium and magnesium chlorides, increases its solubility in water.

Calcium Nitrate [$Ca(NO_3)_2$] is an extremely deliquescent and soluble salt, found in many well waters, and often as an efflorescence on the walls of places where there is any organic refuse. It is made artificially on the Continent for the production of nitre, by mixing organic matter, both animal and vegetable, with chalk, old mortar, etc., moistening occasionally with liquid stable manure, and exposing the mass to the air, in the dark, for two or three years. The soluble salts are then dissolved out, and consist largely of calcium nitrate. This is decomposed by adding a solution of potassium sulphate or carbonate, the corresponding calcium salt is precipitated, and the potassium nitrate crystallised out.

Calcium Fluoride (CaF_2) is found in Nature as fluor-spar; it is used as a source of hydrofluoric acid, and as a flux in many smelting operations.

Calcium Carbide (CaC_2) is a compound which is now produced on an extensive scale for the preparation of acetylene, which it readily yields on treating with water.

Calcium carbide		Water		Calcium hydroxide		Acetylene.
CaC_2	+	$2H_2O$	=	$Ca(HO)_2$	+	C_2H_2.

For the manufacture, a mixture of finely ground lime and coke is charged into an electric furnace, the bottom of

which frequently consists of a carbon plate to form one pole and a large carbon rod, capable of being raised and lowered, forms the other pole. On striking an arc and gradually raising the upper pole, the materials interact, and slowly an ingot of the carbide is built up.

Calcium oxide Carbon Calcium carbide Carbon monoxide.

$$2CaO + 6C = 2CaC_2 + 2CO.$$

Calcium carbide so prepared is a black crystalline substance. If care be taken in the proper selection of the materials as to their purity, the acetylene generated is very pure.

The salts of calcium impart a yellowish-red colour to flame. The most commercially important compound of calcium is bleaching powder ($CaOCl.Cl$), the preparation and uses of which are described under "Chlorine" (p. 382).

Barium (Ba=137) and Strontium (Sr=87).

These metals very much resemble calcium in their properties, and form salts of an exactly similar type. These have a very limited use, being mainly employed in the manufacture of coloured fires—barium salts imparting a green colour to flames and strontium salts a magnificent crimson.

The chloride and nitrate of barium [$BaCl_2$ and $Ba(NO_3)_2$] are used as laboratory reagents, and also to a certain extent the clear solution of the hydroxide [$Ba(HO)_2$], known as "*baryta water*," which serves as a more delicate test than lime-water for carbon dioxide.

Barium dioxide (BaO_2) is used extensively in the production of oxygen by Brin's process (p. 66).

The Alkali Metals.

There are five metals included in this group which strongly resemble each other in their properties; they are all silvery white, so soft that they may easily be cut with a knife, but the cut surface almost immediately tarnishes

in the air. They all decompose water at ordinary temperatures. Of these five metals the only two of practical importance are potassium and sodium.

POTASSIUM (K=39).

Potassium was not known until 1807, when Sir Humphrey Davy succeeded in breaking up potassium hydroxide by a strong galvanic current.

This element exists very widely distributed in nature, both in combination with chlorine as potassium chloride (large deposits of which, together with magnesium chloride, are found in Saxony), and with silica and alumina in the minerals felspar and mica, and it is from these minerals, by the process of disintegration, that it passes into the soil in a soluble state. All plants depend very largely on the supply of potassium salts in the soil, and when any vegetable matter is burnt, the ash is found to contain a considerable percentage of potassium in the form of carbonate.

Preparation.—Davy first obtained the metal by the electrolysis of fused potassium hydroxide, but owing to the difficulty of obtaining sufficient current, the method was not a commercial one. Within recent years, however, the development of electrolytic processes has been very rapid, and now the greater part of this metal is prepared by a method identical with that of Davy, only, of course, adapted for commercial purposes. This will be referred to in greater detail under Sodium (p. 543).

Potassium may also be obtained from the hydroxide by fusing it with a mixture of carbon and iron (which may contain some iron carbide, Fe_2C) when the carbon reduces the hydroxide in the following manner:—

Potassium hydroxide		Carbon		Potassium carbonate		Hydrogen		Potassium.
$6KOH$	+	$2C$	=	$2K_2CO_3$	+	$3H_2$	+	K_2.

Compounds of Potassium.

Oxides.—It is probable that potassium forms four oxides, but the only one of importance is the monoxide (K_2O), which is readily obtained when the metal burns in air or oxygen. It is a powerful base which readily dissolves in water, forming potassium hydroxide (KHO).

Potassium Hydroxide is formed from the monoxide by its solution in water, but is prepared on a large scale commercially by boiling together lime and a solution of potassium carbonate.

Potassium carbonate		Calcium hydroxide		Potassium hydroxide		Calcium carbonate.
K_2CO_3	+	$Ca(HO)_2$	=	2KHO	+	$CaCO_3$.

A certain degree of dilution is necessary, and when the reaction is complete the calcium carbonate is allowed to settle out, the clear liquid being afterwards concentrated in iron pans until on cooling it solidifies.

Potassium hydroxide is largely used commercially and also for laboratory purposes, such as the absorption of carbon dioxide in gas analysis.

The salts of potassium are numerous, and many of them are very important, being largely used in our manufactures. Of these may be mentioned the nitrate, or saltpetre, which has been treated at length under "Gunpowder." The chlorate and iodide have also been previously described. Potassium sulphate (K_2SO_4) is found crystallised with magnesium salts in large natural deposits forming the substance called *kainit*. The salt itself is largely used in making potassium alum.

Potassium Carbonate (K_2CO_3) was at one time the main source of potassium salts, being obtained by extraction from the ashes of wood—hence the name "potash." It is now manufactured by processes similar to those employed for the production of sodium carbonate (p. 546)

Nearly all the salts of this metal are very soluble in water.

The compounds of potassium may be recognised by adding a solution of platinum chloride to a strong aqueous solution of the salt, when a yellow crystalline precipitate is obtained on stirring the mixture; also by the violet colour which they impart to flame when a fragment is taken on a clean platinum wire, moistened with hydrochloric acid, and then heated in the inner blow-pipe flame. Potassium is one of the lightest of the metallic elements, having a specific gravity of 0·865, and an atomic weight of 39·1.

Sodium (Na=23).

Sodium very strongly resembles potassium, both in the elementary state and in its compounds, but is far more abundant in Nature, common salt, or sodium chloride, existing in enormous quantities in sea water, and also in very extensive deposits found in many parts of the world.

In warm countries sea water is run into shallow tanks, where it evaporates under the heat of the sun, and on reaching a specific gravity of 1·2 begins to deposit coarse crystals of crude sodium chloride known as "bay salt," which after being allowed to stand and drain free from the deliquescent magnesium chloride, are ready for use in the manufactures in which it is employed; whilst the "bittern" or mother liquor which has given birth to the crystals is utilised for the production of bromine.

Preparation.—As in the case of potassium, sodium is now prepared on a large scale by the electrolysis of the hydroxide under suitable conditions, the metal produced being at one time largely employed in the extraction of aluminium and magnesium. The commercial success of the electrolytic method has been mainly due to Castner. In order that the yield of metal shall be good, it is essential that the electrolysis shall take place at about 330° C., therefore means are provided for maintaining this temperature—with low currents gas heating is employed, whilst for heavy currents it is

necessary to keep the fused hydroxide down in temperature by circulating water around the iron vessel in which the action takes place. The metal, together with hydrogen, is liberated at the negative pole, and being lighter than the fused hydroxide, rises into an inverted cylinder, from which it can be ladled out with a perforated ladle which allows the fused hydroxide to run back into the furnace.

Compounds of Sodium.

The compounds of sodium are amongst the most important in nature, the chloride being essential to animal life, and being also used to a very large extent for glazing earthenware and for agricultural use, whilst sodium carbonate is of the greatest importance and use in the arts and manufactures, as well as for cleansing purposes.

Oxides.—Two of these are known, and when sodium burns in air a mixture of the two results. The peroxide (Na_2O_2) is a yellowish white body which, in contact with water, evolves oxygen (mixed with a certain amount of ozone) and forms sodium hydroxide.

Sodium oxide		Water		Sodium hydroxide		Oxygen.
Na_2O_2	+	H_2O	=	$2NaHO$	+	O.

Sodium peroxide is frequently employed for oxidising purposes, and has been used for supplying oxygen in closed spaces, such as submarines, for not only does it evolve the necessary oxygen to support life, but the sodium hydroxide produced in the process is capable of absorbing the carbon dioxide evolved during respiration.

The monoxide, Na_2O, is an amorphous grey powder which, like the corresponding oxide of potassium, readily forms the hydroxide with water.

Sodium Hydroxide (caustic soda) (NaHO).—In a pure condition this may be obtained by the action of sodium on water, the liquor remaining being concentrated in silver vessels.

A crude product is very largely employed technically, and the manufacture is one of very great importance. The solution obtained by treating the "black ash" in the Leblanc process (p. 546), and which contains sodium carbonate and sulphide, is heated and agitated with an excess of lime when the following reaction takes place:—

Sodium carbonate		Calcium hydroxide		Calcium carbonate		Sodium hydroxide.
Na_2CO_3	+	$Ca(HO)_2$	=	$CaCO_3$	+	$2NaHO$.

The calcium carbonate is allowed to settle out, the clear liquor being concentrated in iron pans, when by means of air which is blown through and the addition of sodium nitrate, the sodium sulphide is oxidised to sulphate which may be crystallised out, the mother liquor being still further concentrated until a fused mass results, which is then cast into cakes or sticks as desired.

A more modern method consists in electrolysing brine of a suitable strength, when not only can the caustic soda be obtained, but also chlorine for the manufacture of bleaching powder (p. 382). A divided cell is employed in order that the liberated elements, sodium and chlorine, may be separated as quickly as possible; the cathode is of mercury, the anode being of carbon in order that it may not be attacked by the liberated chlorine. On passing the current, sodium is liberated at the mercury cathode, where it at once forms sodium amalgam, which flows off into a separate vessel containing water. Here the sodium acts on the water, forming a solution of the hydroxide which can be concentrated.

Sodium Carbonate (Na_2CO_3).—This compound is of the greatest importance in the arts and manufactures, and its production forms one of the most important of the chemical industries. In ordinary washing soda the crystals contain 10 molecules of water of crystallisation ($Na_2CO_3.10H_2O$), but in dry air they lose water, assuming a white appearance on the surface (*efflorescence*).

Manufacture.—Up to the year 1790, Europe was almost entirely dependent upon natural sources for sodium carbonate, which was employed as one of the most essential substances in the manufacture of soap and glass, England obtaining her supplies from the ash of seaweeds collected and burnt on the Scotch and Irish coasts and called "kelp," whilst the Continental supply was derived from the ash of certain kinds of marine plants growing on the coast of Spain, which was known as "barilla."

This ash, however, only contains about one-fourth of its weight of sodium carbonate, so that this latter substance was very expensive, and the manufactures of soap and glass were very much hampered by its cost. During the French Revolution, the price of "barilla" had risen so high that a premium was offered for the discovery of a cheap method of preparing sodium carbonate, and this led to the discovery by Leblanc of a process by which it can be prepared from common salt.

Common salt (sodium chloride) is mixed with an equal weight of sulphuric acid upon the hearth of a reverberatory furnace, which converts it into sodium sulphate, at the same time expelling hydrochloric acid gas, which, if allowed to escape, would kill all the vegetation in the neighbourhood; the fumes are therefore made to pass up towers filled with coke, down which water is allowed to trickle, and as hydrochloric acid gas is intensely soluble in water, the acid is dissolved, forming the solution which is commercially known as "Muriatic Acid" or spirits of salt.

Sodium chloride		Sulphuric acid		Sodium sulphate		Hydrochloric acid.
$2NaCl$	+	H_2SO_4	=	Na_2SO_4	+	$2HCl.$

The dried sodium sulphate, called "*salt cake*," is then mixed with an equal weight of chalk (calcium carbonate) and about one-half its weight of fine coal dust, and is again heated upon the hearth of the furnace, when decomposition takes place; carbon monoxide is evolved, and a mixture of

sodium carbonate with lime and calcium sulphide is left. This mass is called "*black ash*," and it is next treated with water, which dissolves out the sodium carbonate, leaving most of the calcium sulphide behind; the solution then has air blown through it to oxidise any calcium sulphide to sulphate, which being very slightly soluble, settles out, and the clear liquid is evaporated and yields impure sodium carbonate called "*soda ash*."

Sodium sulphate	Calcium carbonate	Carbon	Sodium carbonate	Calcium sulphide	Carbon monoxide.
Na_2SO_4	+ $CaCO_3$	+ $4C$	= Na_2CO_3	+ CaS	+ $4CO$.

On dissolving the soda ash in water and evaporating to the necessary strength, crystals of washing soda containing 10 molecules of water separate out.

Several other processes have of late years come into extensive use, one of the most important being the "ammonia-soda or Solvay's process," which consists of passing carbon dioxide through a saturated brine solution, containing one-fifth its own volume of strong ammonia solution, when sodium bicarbonate is thrown down:—

Salt	Ammonium hydroxide	Carbon dioxide	Sodium bicarbonate	Ammonium chloride.
$NaCl$	+ NH_4HO	+ CO_2	= $NaHCO_3$	+ NH_4Cl.

On strongly heating the bicarbonate, it breaks up into the carbonate with evolution of carbon dioxide:

Sodium bicarbonate		Sodium carbonate		Carbon dioxide		Water.
$2(NaHCO_3)$	=	Na_2CO_3	+	CO_2	+	H_2O.

The ammonia can readily be recovered from its chloride and used for saturating fresh brine, and similarly the carbon dioxide liberated in the second reaction can be re-employed, hence the process is an extremely economical one.

The salts of sodium give no precipitates with the ordinary reagents, but may be recognised by the intense yellow colour which they impart to flame.

Spectrum Analysis.—The preceding metals all impart a particular colour to flame, but when two or more are present at the same time the colours often interfere with or mask each other, but their presence is easily detected by spectrum analysis.

When a ray of light passes obliquely from one medium to another, it becomes bent or refracted, and the amount of refraction varies according to the density of the medium. It is for this reason that a stick plunged obliquely into water appears bent, the immersed part appearing raised. Now ordinary sunlight consists of a number of beams or rays of various colours which blend together and form white light, and these rays differ in their refrangibility or bending power.

If a beam of white light be allowed to fall on the face of a wedge-shaped piece of glass, termed a prism, it will be found that after passing through the glass, it has been broken up into an oblong band, possessing all the tints of the rainbow, which is called the solar spectrum. This spectrum contains an infinite number of different tints, which merge one into the other, but it will be easy to distinguish seven principal colours arranged in the following order: violet, indigo, blue, green, yellow, orange, red—the violet being the most refrangible, and the red least.

Bunsen and Kirchhoff have, by means of an instrument called the Spectroscope, utilised this phenomenon to found the study of spectrum analysis. In the spectroscope a ray of light is projected (through a narrow vertical slit placed in the focus of a lens) on to a prism, and the refracted light is examined by means of a telescope. A scale is also provided in the instrument so as to divide off the different parts of the spectrum.

Not only white light, but most coloured light, is found to consist of rays of different refrangibility, and if an incandescent solid or liquid be examined, it will be found to give a continuous spectrum. If, however, an incandescent gas be examined, it will be found that the light emitted gives bright bands separated by dark intervals. The position of these

bright bands varies for every element; but for the same element, under similar conditions, the position is definite, so that it can be recognised by simply studying the relative position which the bands occupy.

Certain chemical substances, especially the salts of the alkalies and alkaline earths, when heated in a non-luminous flame, impart a characteristic colour to that flame, and the presence of the substance may be determined by that colour. On examining such a flame by means of the spectroscope, the detection can be made with still greater certainty and delicacy. Sodium and sodium salts impart a yellow colour to the flame, and if this be examined it will be found that the spectrum consists of two fine bright yellow lines very close together, whilst the purple potash flame gives a spectrum in which there are two bright lines—one in the extreme end of the red, and the other in the violet. If a flame tinted by a mixture of sodium and potassium salts be examined by the naked eye, the sodium will mask the colour of the potassium, whilst examination by the spectroscope shows the yellow bands due to the sodium in the proper position, and the potassium lines are as plainly seen as they would have been had no sodium been present. By this method less than $\frac{1}{180000000}$th part of a grain of sodium can be detected.

If a ray of sunlight be allowed to fall upon the slit of a spectroscope, it will be found to give a spectrum, intersected by a number of fine dark lines, some of which are more prominent than others. These lines always occupy the same relative position in the solar spectrum, and are termed *Fraunhofer's lines*, after a German optician, who first satisfactorily mapped and described them. If the position of these dark lines be compared with bright lines in the spectra given by certain metals, such as iron, magnesium, sodium, etc., it is seen that each of the bright lines of the particular metal coincides, not only in position, but also in breadth and intensity, with a dark solar line. The question at once arises, are these coincidences due to the presence of these metals in the sun? And if this is the case, why do the

lines in the solar spectrum appear dark? This can be easily explained.

We have seen that a sodium-coloured flame gives a double band of bright yellow light when viewed through the spectroscope. Now, if a bright white light is placed behind the sodium-coloured flame so that the light passes through and on to the slit, a continuous spectrum is seen, but there will be a double black band now where the yellow one was before, the yellow flame of the sodium having absorbed the yellow light in that particular part. The existence of the dark lines in the solar spectrum is probably due to passage of white light through the vapour of the metals in question, present in the atmosphere of the sun, and these vapours absorb exactly the same kind of light which they are able to emit. An accurate comparison of the Fraunhofer lines with the bright lines of the various elements has revealed the fact that iron, sodium, magnesium, calcium, chromium, nickel, barium, copper, zinc and hydrogen are present in the sun's atmosphere. The light from the fixed stars has also been investigated, and these appear to possess a constitution similar to that of the sun. The spectra of nebulæ, however, only show bright lines; hence, these consist of uncondensed, incandescent masses of vapour.

Solutions of coloured salts, and many coloured media absorb light of different refrangibility, and accordingly, when interposed between a source of white light, such as an ordinary gas flame or Argand burner and the slit of the spectroscope, give a spectrum which is marked by bands or dark lines; these are termed absorption spectra, and may be made use of in detecting certain substances. Not only coloured solutions, but water, ammonia solution and many colourless substances, will give absorption spectra if about six to eight feet of the liquid be looked through.

Ammonium Compounds.

The similarity in behaviour of the radicle (NH_4) to the metals potassium and sodium in the formation of salts has

already been pointed out. It is therefore necessary to consider the salts of this radicle with those of the two above-mentioned metals.

Ammonium Chloride (NH_4Cl) is commercially known as sal-ammoniac, and has been known from very early times. The Arabs obtained it by heating the soot deposited when camels' dung is burned. When ammonia gas and hydrochloric acid gas are brought together, dense fumes of ammonium chloride are formed. It is manufactured by passing ammonia from gas liquor into hydrochloric acid.

Ammonium chloride is a white solid, which easily volatilises, but the vapour readily dissociates into ammonia and hydrochloric acid, which, however, recombine on cooling.

Sal-ammoniac is extensively employed for use in Leclanche batteries, and in the laboratory is the common source from which ammonia gas is obtained.

Sulphides.—The normal sulphide of ammonium has the composition $(NH_4)_2S$, but this is a very unstable body, which, by the elimination of ammonia, yields the well-known stable *ammonium hydrogen sulphide* (NH_4HS). This is largely prepared for laboratory work by saturating dilute ammonia solution with sulphuretted hydrogen.

Ammonium Sulphate $(NH_4)_2SO_4$, is a salt of great commercial importance, and it is obtained largely as a by-product in the production of coal-gas, the material finding a ready sale as a fertiliser, and is much employed as a source of other ammonia salts. The method of preparation consists in passing the ammonia vapours from the ammoniacal liquors into sulphuric acid contained in lead-lined tanks, the crystals of the salt being removed by perforated ladles.

Ammonium Nitrate, NH_4NO_3, is a white crystalline deliquescent substance, readily decomposed by heat into nitrous oxide and water. The substitution of this nitrate for potassium nitrate in certain forms of powder has already

been referred to. When the material is sharply heated up, it undergoes decomposition with explosion.

Carbonate.—Three carbonates of ammonium are known. The *normal ammonium carbonate* $(NH_4)_2CO_3$ is unstable, and when dissolved in water, readily parts with ammonia, forming *ammonium hydrogen carbonate* (NH_4HCO_3). Either of these salts dissolved in ammonia solution yields a *tetrammonium dihydrogen carbonate* or *sesquicarbonate*. The relation between these three substances may be shown thus:—

Ammonium carbonate	Ammonium sequicarbonate	Ammonium hydrogen carbonate.
$(NH_4)_4.(CO_3)_2$	$(NH_4)_4.(CO_3)_2.H_2CO_3$	$(NH_4)_4.(CO_3)_2.2H_2CO_3$.

CHAPTER XXXI.

ALLOYS.

Definition of alloys—Amalgams—Properties attained by alloying—Production of alloys—Nature of alloys—Eutectics—Copper alloys—Brass—Muntz metal—Bronze (gun-metal)—Phosphor bronze—Manganese bronze—Silicon bronze—Aluminium bronze—Machine brasses and anti-friction metals—Tin alloys—Lead alloys—Shot metal—Alloys for electrical resistance.

EXCEPT for scientific purposes the quantity of metal used in the pure condition is very small. For electrical purposes both copper and very pure iron are requisite, but for most other purposes we rely on the modifying influence of other elements to produce the desired qualities. The most valuable form of iron, steel, is as we have seen dependent upon carbon for its special characters, although this is not strictly speaking an alloy, the term being better restricted to the permanent mixture of two or more metals, the term "mixture" being used in its wider sense.

An alloy has been defined by a Committee appointed by the Iron and Steel Institute as "a substance possessing the general physical properties of a metal, but consisting of two or more metals, or of metals with non-metallic bodies in intimate mixture, solution, or combination with one another, forming when melted a homogeneous mixture."

The inclusion of non-metals in the above definition is open to question, for there are several compounds of metals and non-metals which are clearly not alloys, yet which exhibit quite as many "metallic properties," and have quite as distinct metallic appearance as some undoubtedly true alloys of the brittle class, in which the metals are united in definite atomic proportions, as for example, $SnCu_3$. Man-

ganese carbide, for example, can be fused in an electric furnace, and certainly might far more readily be taken for an alloy than many of the indisputable alloys of two metals. Many authorities therefore restrict the term to metals "in intimate mixture, solution or combination." Such restriction necessarily excludes the combinations of iron and carbon in steel, the desire to include which possibly influenced the inclusion of non-metals in the first definition.

Although by this definition the mixture is homogeneous when fluid, it by no means follows that when the alloy solidifies the mixture will then have the same composition throughout, but the commercially useful alloys will vary only slightly in different parts.

Alloys containing mercury are frequently liquid or semi-solid, and all mercury alloys are termed *amalgams.*

It is probable that metal was first employed in the form of the alloy "bronze," and the brass of the Old Testament and the brass armour of the Greeks is well known to have been the copper-tin alloy we now term bronze. Iron might also have been employed at very early times, but owing to its rapid rusting, most of the early iron implements, etc., would be lost, which is not the case with bronze, the latter being relatively permanent.

By alloying metals we are able to obtain some special and suitable modification of their properties, in certain cases very small amounts of other elements exercising a most unexpected influence. It may be that a soft metal requires hardening, as in the case of gold, silver and copper for coinage; these metals in their pure condition being so soft that they would be unable to resist the wear in exchange. Generally speaking, the alloy of any two metals has a lower melting point than that of either constituent, a fact taken advantage of in the preparation of solders. Again, various alloys are made with the object of producing metal of a particular colour, nickel to brass for instance, imparting to it a silvery nature.

It is not possible to get any pair of metals to alloy; they

may in the molten condition form a homogeneous fluid, but on setting may almost entirely separate. A mixture of lead and zinc may, for example, be poured into a cylindrical mould, but on examining the cast rod, almost pure lead will be found in the bottom portion and pure zinc in the upper. Aluminium and bismuth are another pair of metals which cannot be alloyed.

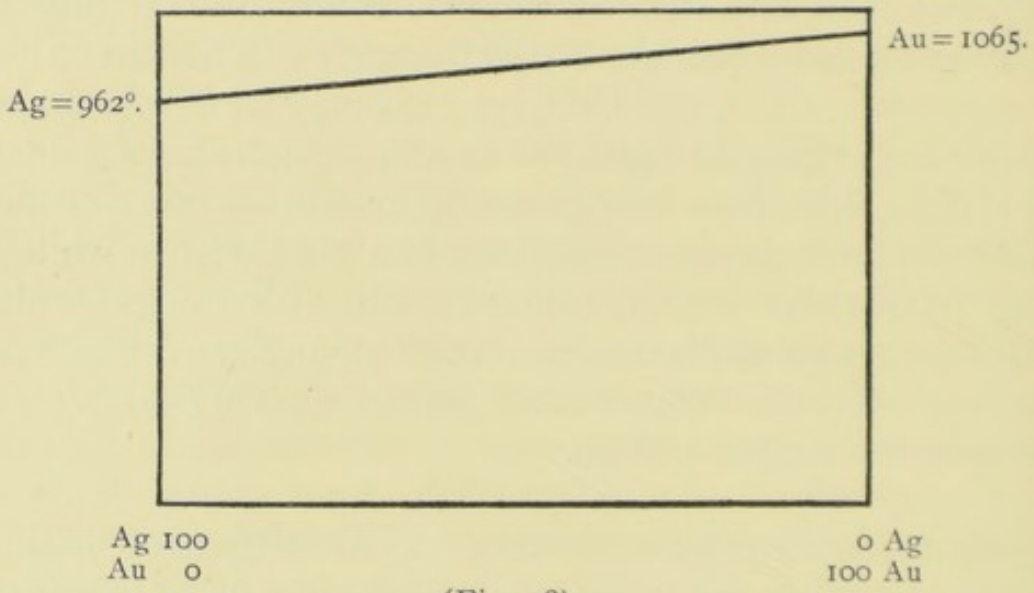
The characteristic property by which chemists classify the elements into non-metals and metals is the ability of the latter to form at least one basic oxide. Some metals form only basic oxides, such as copper, whilst others form in addition oxides which are distinctly acidic. The two oxides of chromium, Cr_2O_3 and CrO_3 (p. 529), may be cited, and tin oxide (SnO_2) may be regarded as the anhydride of stannic acid (H_2SnO_3). Now it is generally found that metals which form only basic oxides are difficult to alloy together, whilst a metal of this class usually unites readily with a metal which may produce an acidic oxide. As an example, we may take the case of bronze, where most perfect alloying takes place between the copper and tin.

Methods of Formation of Alloys.—The most general method is that of uniting the constituents whilst in a fused condition. The usual practice is to first melt that metal which has the higher melting point, and then add the requisite amount of the other metals, these being frequently heated but not melted. This is a simple process if neither constituent is volatile, but with volatile metals, such as zinc or antimony, loss is unavoidable, and allowance must be made for this. To minimise the loss the volatile metal, in lumps, is usually plunged well below the surface of the molten metal, so that as much combination takes place as possible before the vapours can escape. Again in remelting old alloys, one constituent being volatile, loss of the latter must occur and is made good by the addition of fresh metal.

One of the most interesting methods by which alloys may be produced is due to Spring, who showed that finely

divided metals under great pressure may be caused to "flow" with the production of true alloys, although it was conclusively proved that practically no rise of temperature sufficient to produce fusion had taken place.

Alloys may also be deposited from suitable solutions by electrolysis, although great care is necessary in the adjustment of the current, otherwise one or other of the metals may be deposited in a nearly pure condition. Naturally, as the deposition is slow, the production of a skin of metal of any thickness is a tedious process.



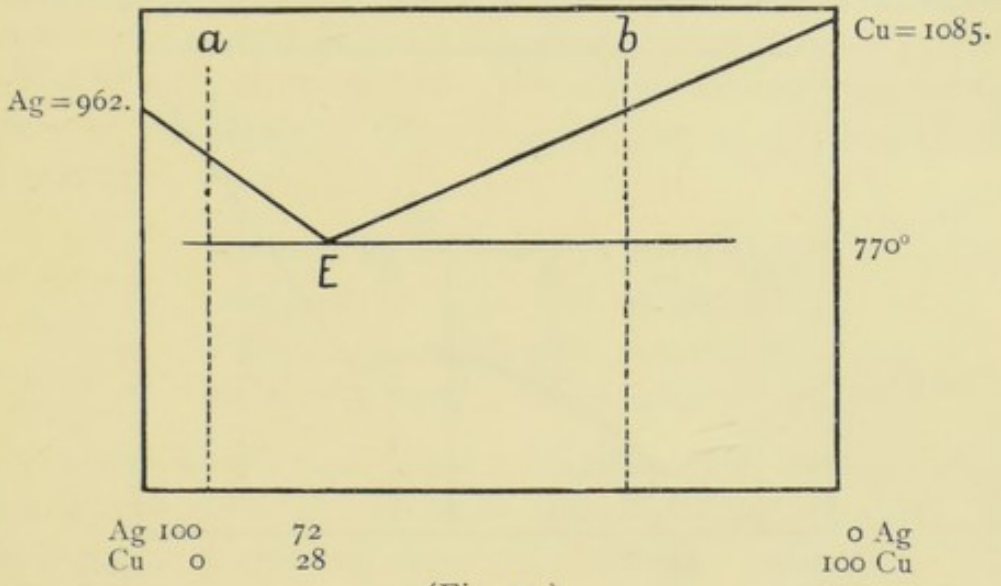
(Fig. 58).

Nature of Alloys.—Much research work on this interesting subject has been carried out in recent years, and this has shown that alloys vary very much in their nature. Some of the most valuable information has been yielded by the study of the freezing or solidifying points of the alloys, supplemented by microscopic examination. Alloys may be generally divided into three main classes, the simplest being those in which the two metals exist as a mechanical mixture, gold-silver alloys for example. In such a case if the composition of the alloy is plotted as abscissae, and the freezing points as ordinates, the line joining these points will be practically straight between the melting points of the two constituents (Fig. 58).

In certain cases it is possible to obtain alloys which

appear to be definite chemical compounds, the two metals being combined in true atomic proportions, and such alloys show under the microscope perfect uniformity. Some of these compounds can actually be separated from alloys in which they occur by suitable methods. Again, their existence is clearly indicated by the occurrence of well-defined "rests" in the cooling curves of alloys, these rests always occurring at the maxima points in the curves.

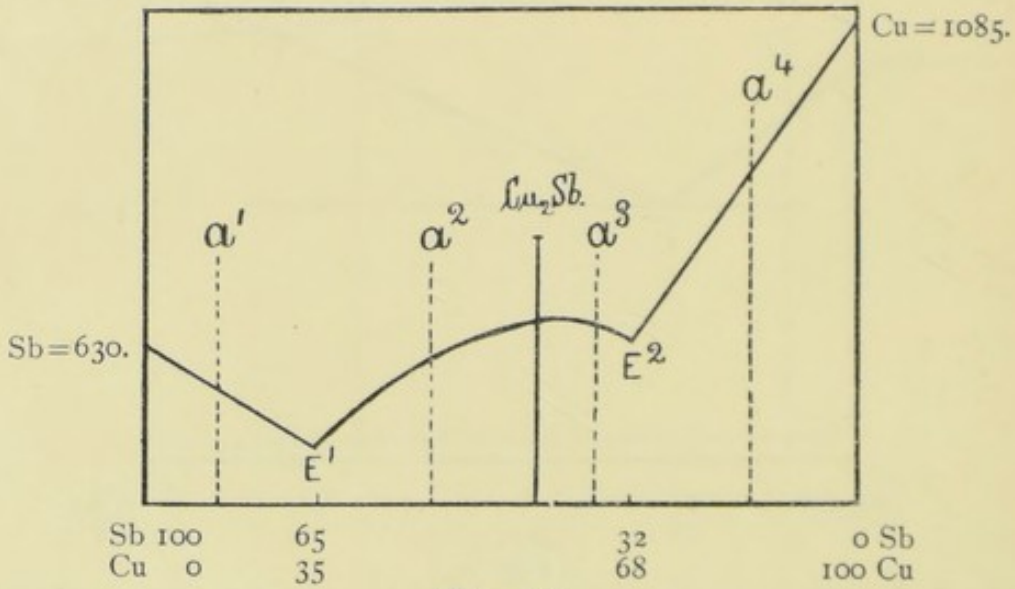
By far the largest number of alloys, however, do not fall into either of the above two simple cases, but consist of



(Fig. 59.)

what may be regarded as the solution of one substance in another, whilst all are in the solid state (*solid solutions*). The simplest case is that in which two metals are in solid solution in each other. Here we always find one alloy, the proportions of the two constituents of which are constant, though not atomic, which melts at a lower temperature than any other alloy of the series, and such alloys were termed by Guthrie "*eutectics*." The behaviour of alloys which may contain a eutectic is of great practical importance, since it frequently leads to segregation of the eutectic. The freezing point curve for the copper-silver alloys, which form no definite compound, but exist in solid solution in each other, is shown in Fig. 59.

The alloy containing 72 silver 28 copper is the eutectic, and this alloy freezes at one definite temperature, 770° C. Let us now consider the case of an alloy containing 90 per cent. of silver (shown at *a*, Fig. 59). When the fluid alloy reaches the temperature at which solidification commences, practically pure silver freezes out, and hence the alloy left is now richer in copper and has a lower freezing point, and until the metal cools further no more solidification can occur. This goes on progressively as the metal cools, nothing but silver solidifying until the eutectic composition is reached, when the eutectic alloy solidifies at a constant



(Fig. 60).

temperature. The resulting solid alloy, when examined under the microscope, will therefore show crystal grains of nearly pure silver, surrounded by the silver-copper eutectic.

On the other hand we may consider the solidification of the alloy containing 70 per cent. of copper (*b*). Here copper alone will first separate out, and, following the same changes as just described, copper continues to separate as the metal cools, enriching the still fluid portion with silver until the eutectic alloy is reached, when this solidifies. The microscope in this case would show crystal grains of copper surrounded by the eutectic.

There is reason to believe that *pearlite* behaves almost as

an eutectic in the case of iron and carbon forming soft steel, and that the two branches on either side of it represent respectively the segregation of pure iron (ferrite), and the carbide, cementite (Fe_3C.).

The nature of alloys which form definite compounds in addition is still more complex, for on either side of each compound an eutectic alloy is generally found. The alloys of copper-antimony may be briefly summarised to indicate what occurs. The freezing point curve is shown in Fig. 60.

The compound containing 55 per cent. of copper agrees with the formula Cu_2Sb. The two eutectics E^1, and E^2, contain respectively 35 and 68 per cent. of copper, and these solidify at a constant temperature. We may now summarise the nature of the alloys of other composition, as marked by the vertical lines, a^1, a^2, etc.

a^1. Metallic antimony with eutectic E^1.
a^2. Compound Cu_2Sb with eutectic E^1.
a^3. Compound Cu_2Sb with eutectic E^2.
a^4. Metallic copper with eutectic E^2.

Copper-aluminium alloys include two definite compounds and three eutectics, so that the alloys on solidification will present several more possibilities.

The formation of eutectics leads to several important considerations in practice. Since the eutectic solidifies last, it will tend to concentrate in those portions of a large mass of metal which cool last, a process well recognised as taking place with many alloys, and with large steel castings. Again, it will be the first portion of such an alloy to melt, and the process of "liquation," applied for example in the purification of tin, depends upon this property. Owing to the fairly viscous nature of metals, and their fair approximation in specific gravity, separation of the metal and eutectic into quite separate portions seldom, if ever, occurs, the first constituent to solidify remaining as separate crystal aggregates diffused throughout the still fluid portion, the latter finally setting around these. Obviously the rate of

cooling will have considerable influence on the resulting solid alloy.

There is a good deal of evidence to show that several metals in the alloyed condition are in the form of allotropes; for example, the iron, nickel and cobalt released from their respective amalgams with mercury are spontaneously inflammable, owing to the exceeding fineness of their state of division, and again, although sheet aluminium is scarcely acted on by air, yet if the surface be rubbed with mercury, it undergoes most rapid oxidation, the oxide flaking off in considerable quantity.

Copper Alloys.

Brass.

This alloy of copper and zinc is one of the most generally employed and important alloys known. The principal advantages gained by the addition of zinc are that the alloy melts at a lower temperature than copper, and is much more fluid when molten, thus allowing sound castings to be produced. Copper again works badly with cutting tools, and its softness gives it little resistance to wear, both disadvantages being overcome by the zinc.

The properties of the alloy are closely related to the amount of zinc present, and hence great variety is found in the metal as prepared for different purposes. Practically the useful limits for zinc lie between 30 and 43 per cent., although the two metals alloy in all proportions. For castings, the metal must be as fluid as possible and set "sound" with a fine grain. Standard brass for casting contains 66·6 per cent. of copper. The mechanical properties of the brass vary greatly with the condition of the metal, since on rolling or beating it becomes hard and increases in tenacity. For many purposes it requires careful annealing, which will be referred to later. The highest tensile strength is obtained with 45 per cent. of zinc, but the highest quality of brass, such as is employed for cartridge cases on account

of its great malleability, contains 70 parts of copper and 30 of zinc. Suitable brass may, with careful annealing, be rolled and beaten out to a thickness of less than $\frac{1}{50000}$ of an inch, forming the well-known imitation of gold-leaf, "Dutch metal leaf."

Brass was originally made by smelting an ore which contained both copper and zinc, but later the ore of zinc was reduced in contact with the copper, for brass was employed for ages before the existence of zinc as a metal had been discovered. Soon after the discovery of zinc the production of brass by the direct mixing of the two metals was introduced. About the year 1700 Bristol was the centre of the brass trade, but about 1740 the manufacture was introduced in Birmingham, where it became one of the principal industries.

Manufacture.—The alloying of the copper and zinc is carried out in two distinct types of furnace. For the production of relatively small quantities of high-class brass the copper is melted down in fireclay pots, heated usually on the regenerative gas principle, and then the addition of zinc is made by means of suitable proportions of scrap brass and metallic zinc, which have been previously heated up. Considerable quantities of zinc become vapourised at the high temperature requisite to maintain the copper fluid, though these losses are reduced by the first addition of scrap metal and also by the careful exclusion of air, the oxygen of which rapidly combines with zinc at the high temperature necessary; however, greater uniformity can be obtained in the product, when made in pots.

Where large quantities of brass, such as Muntz metal, are required, then the alloying is carried out on the hearth of a reverberatory furnace, although the loss of zinc is necessarily much greater, but the zinc fume is led away through suitable condensing chambers, and the metal recovered.

Great care and skill are requisite in pouring the finished metal. If it is to be employed for future castings, then it is

poured into ingot moulds, but for rolling and drawing it is cast into plates.

The composition of the brass has a very great influence on its behaviour during rolling. Above 62 per cent. of copper the metal can be rolled cold but not hot, whilst the alloys containing somewhat less than this amount (such as Muntz metal) can be rolled hot, which is desirable from an economical standpoint. During rolling the metal hardens and requires annealing, in which process it becomes black, this blackness, due to the oxides of the metals, being removed by a mixture of dilute sulphuric acid and sand. If hard sheet brass is desired, then the metal is passed again through the rolls two or three times after the final annealing, but if soft brass is wanted the annealed sheets are simply cleaned up.

During annealing the brass may suffer considerable reduction in quality if the temperature employed be too high, though to a great extent this is dependent on the purity of the metal, a good quality, 70 Cu, 30 Zn, brass suffering little nearly up to its melting point. The effect of annealing is shown in Plates III. to VIII. in the Appendix. Cast brass (Plate VIII.) has a distinct dendritic structure, but on rolling naturally the crystals themselves become greatly broken down and distorted, so that hard rolled brass (Plate III.) shows only an indefinite minutely crystalline structure. On heating to a bright heat and quenching, distinct polygonal grains are developed (Plate IV.), but if the heating be maintained for some time to a temperature of some 800° C., then a large crystalline structure is developed (Plates V. and VI.), many of the crystals having characteristic dark bands across them. If the temperature rises to the softening point, the structure is totally changed, becoming that of cast brass. The structure is closely associated with the physical properties, such as malleability and ductility, and much attention is now paid to obtaining suitable temperatures for the annealing of the brass to be employed in cartridge cases at Woolwich, pyrometers having

been installed in the annealing ovens. If tin or lead be present in the brass, great care is requisite to avoid "burning," which spoils the metal.

For certain special purposes other metals are added to brass. From 1 to 2 per cent. of lead is said to make the metal work better in the lathe or when filed, but many engineers strongly object to its addition. Tin is also added to brass, especially for use by engravers, as the metal cuts out cleaner. The metal is also of closer texture and sounder, and addition of 1 per cent. to Muntz metal constitutes "naval brass."

Muntz Metal contains more zinc than ordinary brass, the proportions usually varying between 38 and 40 per cent. The metal specified in a patent (1846) was 56 copper, 40·25 zinc and 3·75 lead, the latter being added to make the metal roll better. It was introduced as a cheaper metal than brass, both in production and in rolling, since this can be performed hot, thus leading to economical working. The metal was said to resist the action of sea-water better than copper or ordinary brass. With reference to the former, the failure of yellow metal sheathing as compared with copper has already been dealt with, the very resistance which the yellow metal offers to exfoliation preventing it throwing off barnacles, weed, etc., whilst the claim that it resists the action better than ordinary brass has been clearly disproved. Annealed Muntz metal, as seen under the microscope (Plate X.), consists of two distinct substances, one of which is richer in zinc than the other, and the researches of Arnold, Milton, and others have shown that complete removal of the zinc frequently occurs, the explanation being that the two constituents form a galvanic couple, which results in the removal of the zinc from the alloy. By substituting 1 per cent. of tin for a like amount of copper, as in "naval brass," a more homogeneous alloy, less liable to this decay is obtained, but there can be no doubt but that alloys richer in copper, which are perfectly homogeneous, resist the action of sea water better than any alloys where

two distinct constituents are found, as is the case with all brass containing less than 67 per cent. of zinc. Much trouble has been experienced in the Mercantile Marine with condenser tubes of Muntz metal, troubles not found with 70/30 brass tubes. One large mail line is employing tubes of the composition 78 Cu, 21 Zn, 1 Sn, which clearly has the advantage of homogeneity, combined with the protection afforded by small quantities of tin. Gun-metal in contact with any brass is to be avoided.

Sterro, Aich, and Delta Metal.—These are all brasses which contain iron, which imparts strength and elasticity, and considerably increases the hardness. The amount of iron which can be introduced in brass is small, and many discordant results have been obtained in practice. In Delta metal a small percentage of phosphorus is found to give great improvement. Such alloys offer special resistance to corrosion.

The approximate composition of the more commonly employed copper-zinc alloys is as follows:—

	Copper	Zinc	Other Constituents.
Best brass	70	30	—
Common brass	64	36	Composition variable.
Muntz metal	60-63	40-37	Sometimes lead.
Naval brass	62	37	1 tin.
Sterro metal / Aich's metal	60	38·5	1·5 iron, sometimes tin.
Hard solder (for iron)	57	43	—
Do. (for brass)	50	50	—

Bronze (*Gun-metal*).

The alloys of copper and tin are known under the general term of *bronze*, and since the mixture in certain well-defined proportions was formerly employed for casting ordnance, the term "gun-metal" came into general use. This alloy con-

sisted originally of copper and tin only, but at the present time it is commonly applied to strong and tough alloys which contain, in addition of copper and tin, other metals, such as zinc. Higher proportions of tin constitute "bell-metal," and with still higher proportions the white brittle alloy, "speculum-metal," is obtained.

As already mentioned, bronze has been known from very early times, its valuable property of being hardened by slow cooling and hammering, in which condition it can take a fine cutting edge, being taken advantage of by the ancients in producing weapons of war and of the chase. Some of the earliest coins are also of bronze.

The addition of tin to copper lowers its melting point and renders the molten alloy very fluid, thus enabling good castings to be made. The proportions found most generally useful are those formerly employed in the best gun-metal, viz., 90 copper, 10 tin, the strongest alloy however, being that containing 18 per cent. of tin. All the commercial copper tin alloys are subject to "liquation," and therefore variation in the composition of castings is very liable to occur.

Small quantities of zinc improve the fluidity of the metal, though it is not desirable to add more than 2 per cent. Iron, in small quantities, may also be present in metal intended for bearings, and a little lead is also said to improve the working of the metal.

The composition of the principal copper-tin alloys is as follows:—

	Copper	Tin	Other Constituents.
Bronze coins	95	4	1 zinc
Gun-metal	90	10	—
Bell metal	78 to 80	24 to 20	—
Speculum metal	67	33	—

Very great improvements have been made in recent years in the production of special bronzes of great strength and malleability, notably manganese, silicon and phosphor

bronzes. Many of the latter are found on analysis to contain very little phosphorus, but the introduction of this element during the preparation greatly improves the properties of the bronze, this being due mainly to its action upon the metallic oxides formed during the melting of the metals, the phosphorus combining with the oxygen forming the acidic oxide (P_2O_5), which combines with a further quantity of the basic metallic oxides to form easily fused slags. The alloy is generally more homogeneous than a similar alloy in the preparation of which no phosphorus has been employed. Phosphor bronze does not develop crystalline structure, and, moreover, resists well corrosive action.

Manganese Bronze.—Both iron and manganese may be added to copper or its alloys with zinc and tin, producing greater hardness and strength. Of the two metals manganese is in every way preferable, and it can be added in much larger amounts than iron. Bronzes containing manganese are made of widely varying composition. The usual method of producing them consists in first making a rich cupro-manganese alloy by reducing manganese dioxide in presence of granulated copper. In some cases a ferro-manganese alloy is made, and either of the above are added in suitable quantities to bronze containing either tin alone, or both tin and zinc.

One of the most useful alloys is that obtained by the addition of a fair percentage of manganese, together with a little iron, to an alloy of the ordinary gun-metal composition (90/10 Cu, Sn). This manganese bronze gives good sound castings of great strength, and is largely employed for ships' propellers. For this purpose it has many advantages and is now very generally employed. It is claimed for such propellers that they can be made lighter than steel ones; that they are more true, not having to undergo an annealing process as with steel, they are smoother and less liable to corrosion.

Cases have occurred where such propellers have met

with severe blows, with the result that the blade affected has been seriously bent, in one case quite double, but no sign of cracking has been observed.

Silicon Bronze has been employed with much success where wire of great strength and good electric conductivity, as for telegraph and telephone purposes, is required. The presence of even traces of phosphorus on the conductivity of copper is well known, but by using silicon this trouble is overcome, and very strong and elastic wire is obtained. The silicon acts much as does the phosphorus in phosphor bronze, combining with the oxygen of any metallic oxides, whilst any excess enters into the alloy, although in the analysis of such alloys it is unusual to find more than a trace of silicon.

Aluminium Bronze usually contains from 5 to 10 per cent. of aluminium, the remainder being copper. Many of the alloys are of the colour of gold, and much cheap jewellery is made from them, 5 per cent. of aluminium giving the best colour. Considerable heat is evolved when the aluminium is introduced into the molten copper.

The alloy containing 10 per cent. of aluminium can be beaten out with great ease when hot, the metal being very malleable and ductile, possessing tensile strength equal to mild steel (43 tons per sq. in.).

Aluminium bronze is largely made by the Cowles process in the electric furnace, alumina, generally in the form of *bauxite*, being reduced in the presence of copper. The process is interesting, as it was employed previous to the electric furnace method of producing pure aluminium (p. 506).

Aluminium bronze sometimes has zinc or ordinary brass added to it in order to produce aluminium brass, the aluminium present ranging from a little over 1 per cent. to some 3·5 per cent.

Speculum metal is an extremely hard, white and brittle alloy, capable of taking a high polish. It is chiefly employed

for reflecting purposes in optical instruments. It consists of copper and tin approximately in the ratio of 2 : 1.

The influence of temperature on the tensile strength of copper alloys is of considerable importance, and Professor Unwin carried out numerous experiments for the Admiralty to determine this. Briefly his results showed with ordinary brass, Muntz metal, and phosphor bronze, the tensile strength steadily diminished up to 260° C., and the metals had still considerable strength up to well over 300°, whilst with gun-metal the decrease in tensile strength became rapid after passing 158-175°, and in some cases at 260° C. *the metal exhibited no tenacity whatever.*

Machine Brasses, such as are employed in bearings, etc., must have certain general characters, such as resistance to wear, and properties which allow of the metal being readily prepared in the desired form for the variety of purposes for which it may be applied. The composition adopted by different makers for metal for similar purposes is so variable that it is difficult to select typical mixtures, but generally the alloys contain from 75 to 85 per cent. of copper, the remainder being tin and zinc, sometimes one preponderating, sometimes the other. One authority recommends the substitution of lead for zinc in the mixtures.

Anti-friction Metals.—Although these are all white alloys, containing but little copper, even if any is present, they may well be considered in conjunction with the above. A "liner" of soft white metal inside the ordinary "brass" is a great advantage, since suitable compositions greatly reduce the friction, and the alloys being of low fusibility are easily melted out when worn and replaced. Microscopic examination in polished specimens generally shows hard crystalline granules embedded in a soft matrix, which polishes away, leaving the harder portions in relief. Charpy has pointed out that the value of these alloys is mainly due to this structure, the harder portions acting as supports, whilst the

yielding qualities of the softer portion allow of the metal flowing to suit the bearing.

The metals usually employed are lead, tin, zinc, antimony and copper, and examples of different compositions have been collected from various sources below.

Lead	Tin	Zinc	Antimony	Copper.
88	—	—	12	—
78[1]	6	—	16	—
14	81	—	—	5
—	81	—	14	5
—	14	80	—	6
—	—	85	10	5
5[2]	19	69	3	4

Although the composition is so varied, yet it is found that quite small amounts of impurity greatly increase the friction with many of these alloys.

Tin Alloys.

Next to the alloys containing a large percentage of copper, those of tin with other metals, notably lead, are of the greatest importance. Tin alloys with lead in all proportions, the alloys being generally characterised by low fusibility, hence their general employment as "soft" solders. Three different ratios of tin to lead are commonly employed for *fine* solder, melting at 180°, 2 : 1 ; for *common* solder, 1 : 1 ; and for *coarse*, or plumbers' solder, 1 : 2. Fine solder practically agrees in composition with the only eutectic alloy occurring in the lead-tin series, hence it has a very definite setting point, which is lower than for any other proportions. On the other hand, with the ratio of 1 : 2, when the alloy first begins to set, practically pure lead crystallises, the crystals being still surrounded with the still fluid eutectic, hence the solder remains pasty for several minutes depending on the mass of metal. It is owing to this property that such solder

[1] Magnolia metal (Hiorns). [2] Babbitt's metal (Ledebur.)

can be employed for "wiped" joints, a purpose for which fine solder would be quite inapplicable, owing to its definite setting point.

Pewter originally consisted of tin-lead in the proportions of 80 : 20, but since pewter has again come into vogue, manufacturers have considerably altered its composition, each employing his own special mixture, hence there is great variety both in the metals employed and their proportions.

An alloy consisting mainly of tin and antimony, known as *Britannia metal*, is largely employed for the production of many articles, since it gives excellent castings, can be rolled or stamped, and takes a high polish. From 1 to 2 per cent of copper is usually present, together with small quantities of zinc, bismuth, or lead.

Lead Alloys.

The principal alloys containing lead, in addition to those already described, are those employed as *type metal*, the essential features requisite for such a purpose being—ready fusibility, sufficient hardness to resist wear, and well defined castings. The alloys always contain antimony, and frequently in addition tin, whilst where special hardness is required, a small quantity of copper is added.

Shot metal consists of lead to which a small quantity of arsenic (and frequently also antimony) has been added, these additions rendering the otherwise soft lead sufficiently hard for the purpose of shot. The lead is melted at the top of a high tower, and additions of suitable proportions of a richer alloy of lead with arsenic and antimony added, the alloy being then poured through a perforated iron basin, spherical drops being formed as the metal falls down the tower into water placed at the bottom. The different sizes are made by employing basins with holes of varying diameter, and also by mechanically sorting the shot.

It is essential that the alloy shall be quite fluid, otherwise the shot does not assume a spherical form.

LEAD AND TIN ALLOYS.

	Lead	Tin	Antimony	Other Constituents.
Fine solder	33·3	66·6	—	—
Common solder	50	50	—	—
Plumbers' solder	66·6	33·3	—	—
Pewter	20	80	—	—
Britannia metal	—	92	6·5	1·5 Cu
Type metal	80	—	20	—
„ „	70	10	18	2 Cu
„ „ (stereo)	82	3	15	—
Shot metal	99·7	—	—	·1 to ·3 As.

Fusible Alloys usually contain lead, tin, and bismuth, and they derive their name from their low fusibility, which may be below the boiling point of water. Rose's metal, for example, melts at 94° C., and consists of two parts bismuth, one part tin, and one part lead. Various fusing points may be obtained with different proportions of these metals, and plugs of such alloys are sometimes used in boilers to minimise the risk of explosions, since as soon as the steam reaches a temperature (owing to increase of pressure) above that desired, the plug of fusible alloy melts, permitting the steam to escape.

There are a large number of other alloys employed for special purposes, but of these only one or two call for mention. An alloy of aluminium with some 10 to 20 per cent. of magnesium, known as *magnalium*, promises to be of considerable value, since it is light, strong, and not easily tarnished.

The alloy of iron with 30 per cent. of nickel, *in bar*, is remarkable for the very slight expansion and contraction which it undergoes with change of temperature, hence it is extremely useful for such purposes as clock pendulums, etc.

Some of the most important of the rarer alloys are those which are employed for electrical resistances. The composition of the more generally employed of these is as follows :—

	Copper	Zinc	Nickel	Other Constituents.
German silver	50 to 60	25 to 15	25 to 15	—
Argentan	52	19	24	—
Platinoid	50 to 60	25 to 15	25 to 15	1 to 2 per cent. tungsten
Manganin [1]	84	—	12	4 Mn.
Rheotan [1]	84	4	—	12 Mn.

[1] Hiorns.

CHAPTER XXXII.

The rusting of iron—Action of sea water on iron and steel—Relative corrosion of iron and steel—Corrosion and pitting in boilers—Corrosion of plates—Rust cones—Corrosion of copper and its alloys—Protection of iron from corrosion—Galvanising—Tinning—Protective compositions—Corrosion and protection of interior plates—Fouling and its prevention—Copper sheathing—Anti-fouling compositions—Conditions of animal and vegetable life on a ship's bottom—Action of metallic poisons—Properties necessary in a good anti-fouling composition—Pigments—Causes which affect colour—Whites, white lead, zinc white—Blacks—Reds, iron oxide, red lead, vermilion—Yellows—Greens, copper greens, chromium green, mixed greens—Blues, ultramarine, Prussian blue, indigo—Raw and burnt umber—Sepia—Effect of light on water-colour paintings.

THE Rusting of Iron.—When iron is exposed to the action of the atmosphere under normal conditions corrosion rapidly commences, and continues at an increasing rate, until finally the whole of the metal is converted into "iron rust," consisting mainly of a mixture of ferric oxide (Fe_2O_3) and ferric hydroxide $Fe_2(HO)_6$.

Pure water alone has no action whatever on iron, even in the presence of oxygen or air, providing no trace of carbon dioxide is present. Pure dry carbon dioxide again has no effect upon the iron. Clearly then, since the admission of the minutest traces of carbon dioxide, in the presence of oxygen and moisture rapidly causes rusting, this substance must be looked upon as the fundamental agent in setting up and continuing the corrosion of iron or steel. Under all circumstances, whether the metal is exposed directly to atmospheric influences, or is submerged in water, there will always be present carbon dioxide, free oxygen and water, and hence corrosion invariably takes place, unless special means are adopted for its prevention.

Analyses of *fresh* iron rust show it to consist mainly of ferric oxide, together with ferrous oxide and ferrous carbonate. On exposure to air the two latter compounds readily undergo oxidation, with the formation of more ferric oxide and the liberation of carbon dioxide, so that it frequently happens that analyses of rust, which has been removed from the iron undergoing corrosion, show but little iron to be present in the ferrous condition.

If the dissolved oxygen is eliminated from water, and the solution is saturated with carbon dioxide at ordinary pressure, and kept from contact with the air, the carbonic acid present will act directly upon iron or steel forming ferrous carbonate and liberating hydrogen gas:—

Iron		Carbonic acid		Ferrous carbonate		Hydrogen.
Fe	+	H_2CO_3	=	$FeCO_3$	+	H_2.

This ferrous carbonate being soluble in the excess of carbonic acid present, the solution remains perfectly clear until air is admitted, when the ferrous salt at once is oxidised, and the liquid turns brown, throws down a brown precipitate, and forms a brown pellicle on its surface.

The reactions involved in the rusting of iron may therefore consist in, first, the direct action of carbonic acid (H_2CO_3) on the metal; secondly, the oxidation of the ferrous carbonate formed, into probably first of all basic carbonates and finally ferric oxide.

Ferrous carbonate		Oxygen		Ferric oxide		Carbon dioxide.
$4(FeCO_3)$	+	O_2	=	$2Fe_2O_3$	+	$4(CO_2)$.

If moisture be present in any quantity ferric hydroxide is formed:—

Ferric oxide		Water		Ferric hydroxide.
Fe_2O_3	+	$3(H_2O)$	=	$Fe_2(HO)_6$.

During these reactions the carbon dioxide is liberated in the moist metal and reacting with more oxygen from the air,

carries on the process of corrosion, which is now further accelerated by the fact that the hydrated oxide on the surface of the metal is electro-negative to the metal itself, and excited by the presence of moisture and carbon dioxide creates a galvanic current at the expense of the metal, so that the mass of rust formed being porous, the action continues until all the metal is destroyed and has returned to its natural condition of hydrated oxide.

In fresh water the corrosion which takes place on the surface of iron is due to the same cause, *i.e.*, the simultaneous action upon the metal of oxygen and carbon dioxide; if an alkali be added to the water to absorb and neutralise all carbon dioxide, corrosion is stopped, and a piece of bright iron or steel may be kept perfectly uncorroded in such a solution.

Sea water acts upon iron and steel in exactly the same way as fresh water, but the rapidity of the action is increased by the saline constituents of sea water, which undoubtedly play an important part in a more active form of corrosion, by helping to excite galvanic action between the iron in the plates and any foreign metal or impurities present, an action which is also materially aided by want of homogeneity in the metal, by particles of rust, by mill scale, by wrought and cast iron or steel in contact with each other; or even by the different amount of work, such as hammering or bending, undergone by different parts of the same plate. In all of these cases, the galvanic action set up causes rapid oxidation of the iron at the expense of the oxygen of the water, hydrogen being evolved.

Exposed iron work in a large city is subjected to the action of rain water containing sulphur acids washed from the smoke-laden air, and these seriously increase the rate of corrosion. Again, a ship with her protective composition abraded in places by contact with chains, etc., cruises on the West Coast of Africa, where the rivers sweep down large quantities of vegetable and animal organic matter to the sea, which decompose the sulphates present in the sea

water and charge the water with sulphuretted hydrogen, which attacks the exposed metal with great rapidity.

These local causes of corrosion, however, have only to be taken into consideration where they occur, and do not affect the general question.

Relative Corrosion of Iron and Steel.—One of the most important questions of the present day is, does steel corrode more quickly than iron? A very valuable research by Andrews[1] shows conclusively that there is a greater tendency to corrosion on the part of all steels than wrought iron, when exposed to the action of sea water. The composition of some of the best known brands of plates was first carefully determined (*see* Table, page 577), and plates of known weight were then exposed to the action of sea water in presence of air, care being taken that no galvanic disturbances other than those set up on the surface of the plates themselves should interfere, and the plates were carefully cleaned, dried and again weighed after various periods of exposure; the loss in weight being taken as representing the loss by simple corrosion (*see* Table, page 578).

This table brings out very clearly the fact that there is a greater tendency to corrosion on the part of the various samples of steel than of the wrought iron, and also that the rate of corrosion increases very rapidly with the length of exposure, this latter being due to the fact that the oxides first formed are electro-negative to the remaining metal, so that with the formation of rust galvanic disturbances are increased on the surface of the plate, and tend to increase the rapidity of its destruction.

The probable reasons which tend to increase the rate of corrosion in steel are that it is not so homogeneous as the wrought iron, that the manganese is usually present in larger quantities and that the carbon present in combination is partly eliminated during corrosion in the form of carburetted hydrogen which tends to disintegrate the surface.

[1] Institution of Civil Engineers.

Description.	Graphitic carbon.	Combined carbon.	Silicon.	Sulphur.	Phosphorus.	Manganese.	Iron (by difference).	Total.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
Wrought iron, No. 1	—	Trace	0·206	0·024	0·454	0·396	98·92	100
„ „ No. 2 (Wortley best scrap)	—	None	0·392	0·034	0·27	0·194	99·11	100
Soft Bessemer steel	—	0·15	0·015	0·111	0·064	0·54	99·12	100
Soft Siemens-Martin steel ...	—	0·17	0·071	0·117	0·077	0·627	98·938	100
Soft cast steel	—	0·46	0·074	0·025	0·21	0·184	99·047	100
Hard Bessemer steel	—	0·51	0·068	0·113	0·087	1·153	98·069	100
Hard Siemens-Martin steel ...	—	0·72	0·08	0·102	0·143	1·239	97·716	100
Hard cast steel	—	1·407	0·121	0·056	0·08	0·36	97·976	100
Cast metal, No. 1	1·5	2·01	0·41	0·25	0·45	0·65	94·73	100
„ „ No. 2	2·62	0·67	1·94	0·09	0·95	0·52	93·21	100

Loss by Corrosion in Sea Water.

Description.	Combined carbon.	First Period.	Second period.	Third period.	Total period.
		Loss per Square Foot of Surface.			
		Bright plates exposed singly in sea water for 4 weeks.	Bright plates exposed singly in sea water for 16 weeks.	Bright plates exposed singly in sea water for 54 weeks.	Bright plates exposed singly in sea water for 114 weeks.
	Per cent.	Grains.	Grains.	Grains.	Grains.
Wrought iron	—	—	—	—	—
Wrought iron, No. 1.	Trace	34·4	114·68	169·7	318·78
Wrought iron, No. 2 (Wortley best scrap)	None	—	97·99	139·27	—
Soft Bessemer steel	0·15	34·56	108·85	158·18	301·59
Soft Siemens-Martin steel	0·17	40	125·83	155	320·83
Soft cast steel	0·46	37·76	148·65	227·74	412·15
Bessemer steel	—	—	—	—	—
Hard Bessemer steel	0·51	38·96	134·92	199·68	373·56
Hard Siemens-Martin steel	0·72	34·24	122·14	173·24	329·62
Hard cast steel	1·407	39·68	139·57	184·54	363·79
Puddled steel	—	—	—	—	—
Puddled steel (chilled)	—	—	—	—	—
Tungsten steel	—	—	—	—	—
Cast metal, No. 1.	2·01	—	160·62	254·25	—
„ „ No. 2.	0·67	—	182·7	172·73	—
„ „ No. 3.	—	—	—	—	—

A very valuable paper read before the "Iron and Steel Institute" by Mr Parker in 1881 [1] also shows that mild steels such as are now used for boilers and for shipbuilding suffer from corrosion more than the purer metal, but that the increase is not nearly so great as alarmists would have one believe. Nickel steel is not so easily corroded as the ordinary forms of steel.

Corrosion and Pitting in Boilers.—In the Navy the most important cases of corrosion are those which affect the plates and tubes of marine boilers and the plates of the bottom of vessels, and inasmuch as the causes at work in these two cases are not identical, it is better to discuss them separately.

In the marine boilers at present in use, working at pressures of from 50 to 250 lbs., serious pitting and in some cases puncturing of the plates and tubes take place, a result which, before the introduction of hydrocarbon lubricators, was largely attributed to the corrosive action of the fatty acids liberated by superheated steam from the oils and fats used for the lubrication of the cylinders, but as the corrosion and pitting has continued since these lubricants have been discarded, and as the trouble increases with the increase in the pressures employed, it is evident that some other solution of the difficulty must be sought.

The pitting and corrosion are due not to one cause only, but to several acting together.

1. Ordinary corrosion due to the carbon dioxide and oxygen dissolved in all natural water, which act but little when the boiler is in use, the gases being driven off by the steam, but which act rapidly when a boiler is out of use more especially when, as used to be the case in the Navy, the water is partially blown off and the boiler left wet and exposed to air.

The simplest cure for this is, when a boiler is at rest, to

[1] *Journal of the Iron and Steel Institute*, No. I., 1881, p. 39.

fill it quite full with boiled water to which a little lime or other caustic alkali has been added.

2. One of the causes of pitting in a boiler is the formation of spots of rust from the previous cause, which being electro-negative to the metal rapidly cause it to corrode, and it is this action, and also the galvanic action of traces of metallic impurities, which is to a certain extent prevented by zinc protectors, zinc being electro-positive to both iron and iron oxide, but for the protectors to be of any use they must be in metallic contact with the metal of the boiler.

3. The solvent action of distilled water upon metals, which, in modern marine boilers fed with condenser water and specially distilled water, rapidly attacks the plates in places where the presence of a trace of slag or other impurity renders the metal less dense or gives it a tendency to lamination. This can be avoided by using a saline solution such as the prepared sea water advocated at page 147 for the prevention of incrustation and avoiding too frequent blowing off, the action of water on iron rapidly decreasing with an increase in its density.

4. The fact that at a high temperature water is directly decomposed by iron with formation of black magnetic oxide and liberation of hydrogen:—

Water		Iron		Black magnetic oxide of iron		Hydrogen.
$4(H_2O)$	+	$3Fe$	=	Fe_3O_4	+	$4\ H_2$.

This action, which is the cheapest method of obtaining the gas, takes place at a dull red heat, and more slowly at temperatures considerably below dull red heat, which are often approached, if not reached, on the surface of tubes coated with incrustation, where the moisture present rapidly acts on the metal and ultimately pierces it.

This latter cause of pitting can only be avoided by keeping the boiler free from all incrustation by using either distilled water or prepared sea water.

Corrosion of Plates.—On the outer skin of an iron vessel

two processes of rusting are going on, the one simple corrosion on exposed surfaces of the metal, due to the presence of moisture, carbon dioxide and free oxygen, which forms a fairly uniform coating of rust on the metal, and the more local corrosion due to galvanic action, which results in pitting and uneven eating away of the plates.

Rust cones are due to the most local form of galvanic action, caused by the presence of a speck of deposited copper, lead, or other foreign metal, or even a small particle of rust or mill scale left on the surface of the iron, and covered by the compositions used as protectives and anti-foulers; as soon as the sea water penetrates these, galvanic action is set up, water is decomposed, rust formed, and the escaping hydrogen pushes up the composition, forming a blister; the hydrogen escapes and water leaks in, the action becoming more and more rapid, and the blister gradually filling with the result of the action—rust. The blister bursts, but the cone of rust has by this time set fairly hard, and continues to grow from the base, the layers of rust being easily distinguished in a well-formed cone, and when the rust cone is detached, the pitting of the metal at the base of the cone is, as a rule, found to be of considerable depth.

The speck of foreign matter which has caused this destructive action generally clings to the surface of the iron, and being at the bottom of the pitting, escapes detection and removal; and when the vessel, newly coated with fresh composition, again goes to sea, fresh corrosion will probably be set up in the same spot.

The corrosion of the plates in the interior of a vessel is a subject quite equal in importance to the external action of sea water and dissolved gases on the metal; and from the fact that certain portions of the interior plates, from their position, escape the frequent examination and attention bestowed upon the exterior, it becomes a still greater source of danger.

Corrosion, like all other forms of chemical action, is much accelerated by increase of temperature; and in the

bottom of a ship, near the furnace room and boilers, this has a considerable effect in increasing the rapidity of rusting. Also in the coal bunkers, the mere contact of moist coal with the iron plates sets up galvanic action, carbon being electro-negative to iron, and the coal dust which sifts down into the double bottoms lends its aid to the destruction of the plates; whilst if the coal contains any "pyrites," which is nearly always the case, these double sulphides of iron and copper are gradually oxidised into soluble sulphates of the metals; these, washing down into the bilge water, would at once cause most serious corrosion should they come in contact with any bare portion of the plates. Repairs to any portion of the inside plates will loosen rust and mill scale, which, finding its way into the bottom, tends to set up galvanic action; whilst the scale of copper oxide from copper and brass fittings and pipes is another great cause of danger, as the bilge water would gradually convert it into soluble salts, which will deposit their copper upon the iron wherever a crack or abrasion enables them to come in contact with it; and finally, leakages from stores and cargo are in many cases of a character highly injurious to iron.

In addition to all these sources of danger, we must remember that the interior of a vessel is the part most liable to abrasion from shifting and moving of cargo, coals, etc.

Corrosion of Copper and its Alloys.

In the presence of sea water, corrosion of copper readily takes place, owing to the direct action of the saline constituents of the water, aided by carbon dioxide. This results in the formation of a green coating consisting of the carbonate and oxychloride. The formation of this coating gave the value to copper sheathing, which it undoubtedly possessed over all other sheathings, of remaining "clean" when used on a ship, but in such cases as copper fire-mains on a ship, charged as they are with salt water under pressure,

the corrosion becomes a serious matter. A coating of one of the asphaltum compositions then is frequently employed for protection.

With copper-zinc alloys, such as ordinary brass and Muntz metal, it is frequently found that nearly the whole of the zinc in certain circumstances disappears, without any apparent alteration having taken place in the metal. The results in practice are often very contradictory, metal of the same class standing for years, whilst under apparently similar circumstances, decay may be very rapid.

Alloys of copper and zinc, containing over 67 per cent. of copper, have been shown to be homogeneous throughout, but with less copper, as in Muntz metal, two distinct constituents are present (Plate X), one relatively richer in zinc than the other. When exposed to an exciting liquid, this richer zinc alloy is attacked, the two forming a galvanic couple. Slowly the zinc is removed, this alloy becoming richer in copper. Ultimately the alloy previously richer in copper will contain more zinc than the residue from the primary attack, when it will then become the positive element in the numerous couples, and zinc will pass out of it. The ultimate result will be the almost complete removal of zinc from the alloy.

The greater the uniformity therefore which can be attained in such alloys, the less likely are they to undergo corrosion. This is frequently seen to be the case with brazed joints in tubes, the brazing, containing a higher proportion of zinc, undergoing much more rapid corrosion than the main portion of the tube.

The addition of a small quantity of tin lessens the liability to corrosion, and hence the Admiralty introduced naval brass, having practically the composition of Muntz metal with 1 per cent. of tin, for all fittings exposed to the action of sea water.

Condenser tubes are particularly liable to corrosion, which, when local, leads to serious pitting and even perforation. By employing brass containing at least 70 per cent. of copper, together with a small percentage of tin, the diffi-

culty is mainly overcome, and this composition is in accordance with the Admiralty specification for metal to be used as condenser tubes (see also p. 563).

It has been shown in the case of brass that where the metal has been bent or distorted, there the action takes place first, and with much greater vigour than elsewhere.

Pitting of condenser tubes of really good composition occasionally takes place, in many cases it being difficult to satisfactorily account for. It must be due to some purely local cause, possibly the deposition of a small speck of foreign material, or it may be segregation of some constituent of the alloy employed.

Bronze resists corrosion much better than brass, but where it has been employed in connection with copper sheathing, etc., then it is slowly corroded. Bronze, however, is very permanent when in contact with iron.

Protection of Iron from Corrosion.

The protection of iron and steel from corrosion has been attempted in two ways; either by covering the surface with some other metal not easily corroded, or which is attacked in preference to the iron; and by the application of various paints, varnishes, and the like which prevent access of the agents causing corrosion.

Metallic Coatings.—Of these the principal are zinc, tin, nickel and copper. Zinc is far preferable to the others for the reason that it maintains the iron in the electro-negative condition, undergoing itself any corrosion, hence frequently the coating lasts a comparatively short time. In the case of the other metals, so long as their surface remains intact, the protected iron will undergo no corrosion, but once the surface becomes abraded, then corrosion of the iron will take place locally at a greater rate than it would if uncoated, since it now becomes the positive metal in a galvanic couple.

Galvanising consists in covering the iron with a thin

coating of metallic zinc, the name originating from the galvanic couple so obtained.

The plates which are to be coated must first be thoroughly cleaned by pickling in either dilute sulphuric or hydrochloric acid. The commercial zinc (*spelter*) is maintained at a temperature of about 450° C. in a special tank having a "flux" box containing ammonium chloride at either end. The tank is fitted with rollers which carry the sheets through the bath of molten metal, the sheets entering and leaving through the flux boxes. The zinc readily adheres to the clean iron surface, together with a certain amount of the flux, to remove which the galvanised plates are passed through two tanks of water. The plates are finally cleaned up with sawdust and dried.

Made up articles, such as cisterns, buckets, etc., are simply dipped in the zinc bath after suitable pickling.

Zinc may also be deposited by the electrolytic method, and this is employed for certain Admiralty work, such as the framing, etc., of torpedo boats. The metal surface to be coated is first cleaned and immersed in a solution of either the sulphate or chloride of zinc. Zinc anodes are employed, but since these do not dissolve with sufficient rapidity to keep up the strength of the bath, the liquid is made to circulate through vats containing zinc dust. The Admiralty require a coating of about ·86 of an ounce to the square foot.

Instead of using a bath, a current at fairly high voltage is sometimes passed through suitable brushes saturated with the electrolyte.

Another process of considerable interest recently introduced, consists in heating the articles when they are surrounded by finely divided zinc, to a temperature below the actual melting point of the zinc. Penetration of the latter takes place, and a firm adherent coating is obtained. The process is known as *Sherardising*.

Zinc is practically the only metal which could be used to preserve the iron plates of a ship from corrosion, since it

places them in an electro-negative position, and it is therefore to zinc that inventors have turned from time to time, the chief novelties introduced being the method of attachment. As far back as the year 1835, Mr Peacock tried zinc plates on the bottom of H.M.S. *Medea*, and in 1867 Mr T. B. Daft again brought the subject forward; Sir Nathaniel Barnaby, Mr M'Intyre, and others, also suggesting various plans of attachment, whilst more recently Mr C. F. Henwood read a paper at the United Service Institute again strongly advocating zinc sheathing as attached by his system.

There is no doubt that if a surface of iron is kept in galvanic contact with zinc, and the surface of zinc exposed be of sufficient size relatively to the iron surface to be protected, it will act as a perfect protection against the more active forms of galvanic corrosion, but it will not entirely prevent the ordinary oxidation due to the dissolved gases in sea water; and it must also be remembered that the salts in sea water have a fairly rapid action upon the zinc, which, when it is increased by the galvanic action set up by the enormous surface of iron present, would destroy the zinc sheathing too rapidly to render it a practical method, several cases having occurred in which an iron ship coated with zinc plates has returned from a voyage minus a considerable portion of her sheathing. If no galvanic contact exists the zinc sheathing will last fairly well, but does not afford any protection to the iron.

Attempts have been made to galvanise the iron before the building of the ship, but Mr Mallet showed as early as 1843 that this coating was absolutely useless in sea water, as in from two to three months the whole of the zinc was converted into chloride and oxide; but used as a foundation over which the ordinary protective and anti-fouling compositions are to be painted, galvanising acts as a perfect protective, the only trouble being that it affords but little hold for the compositions which have to be put on over it, so that a galvanised torpedo boat quaking along at twenty knots requires a very adhesive composition to stick on. This ob-

jection could, however, be easily got over by a slight roughening of the galvanised surface so as to give the paints a "grip."

Tinning.—The protection of iron by coating it with tin is a very old process, and was introduced into South Wales, the centre of this important industry, as early as 1665.

At one time a specially prepared sheet iron was alone employed, but at the present time what is practically an extra mild steel is used. The success of the process depends on a thorough cleansing of the plate and the production of a fine surface by means of special rolls. The plates are first cleaned by pickling in B.O.V. sulphuric acid (p. 371), they are then annealed and rolled, afterwards undergoing a further annealing and pickling.

In the old process the plates were kept in a bath of melted tallow, and on withdrawing them from this, they were dipped in a bath of melted tin, the surface of which was protected from oxidation (p. 432) by a layer of fat; after taking out and brushing over quickly to remove any excess of tin, they were dipped in a second pot of the metal kept at a higher temperature than the first, being finally placed in a bath of highly heated tallow, when the excess of tin ran to the lower edge and was detached by a sharp blow. Such a procedure led to very uneven covering, and was, moreover, somewhat slow.

In the modern method, the plates are lowered into the tin bath, through a flux of zinc chloride containing a little ammonium chloride, and are then raised until they engage in the first of several pairs of rollers placed above each other and running in grease. These rollers have below them small troughs in which the tin squeezed off the plate collects. The speed at which the rollers travel determines the amount of metal left on each plate. By the old dipping process, about 8 lbs. of tin was required for every 1 cwt. of plates, but with the modern method the usual practice is to employ but a few ounces over 2 lbs. for the same quantity.

The tinned plates are polished up with sheepskin rubbers and bran. For certain purposes a cheaper grade of plate is made by dipping in a lead-tin bath, such plates being termed "*terne plates.*"

As long as the tin surface remains unimpaired, the iron beneath is adequately protected, but if abrasion occurs, so that the iron is exposed, local rusting is very rapid, since iron is electro-positive to the tin.

Non-metallic Coatings.—The coatings of this type which are intended to do away with corrosion, are very numerous. In addition to those still holding a place in the market, the patent list for several decades shows an enormous number which were practically still-born.

They may be divided for convenience into :—

(*a*) Oil paints.

(*b*) Pitch, asphalt, or tar.

(*c*) Varnishes, consisting of resins and gums dissolved in volatile solvents.

(*d*) Varnishes containing substances to give them body.

(*e*) Coatings of cement.

Before going into these in detail it is necessary to consider the condition of the surfaces to which they will have to be applied, and the effect this will have upon them.

Air has the power of holding water vapour in suspension, the amount so held being regulated by the temperature ; the higher the temperature the more vapour can the air hold, whilst when the air, saturated at a particular temperature, is cooled the surplus moisture is deposited. When a ship is scraped down to the bare iron in the dry dock, we have a large surface of metal which varies in temperature much more rapidly than the surrounding air, and cools much more rapidly than the stone walls of the dock; as it cools so it chills the layer of air in immediate contact with it, and causes a deposition of the surplus moisture on its surface—a phenomenon known as the "sweating of iron"—and on to this moist surface the protective composition has to be

painted. If now a quickly drying varnish is put on, the rapid evaporation of the volatile solvent causes another sudden fall of temperature—evaporation being always accompanied by loss of heat—and this fall of temperature again causes a deposition of moisture, this time on the surface of the protective, so that the coating is sandwiched between two layers of moisture, both of them probably acting deleteriously upon the resin or gum in the varnish, whilst the moisture on the iron also prevents adherence of the varnish to the metal. If, instead of a quick-drying varnish, the old-fashioned red lead and linseed oil protector had been used, the second deposition would not have taken place, but the sweating of the iron would have prevented adhesion, and, when dry, any rubbing of the coating would bring it off in strips.

The condition of the outer skin of a ship, when she is being coated with her protective composition, is one of the prime factors in the discrepancies found in the way in which compositions act; it being a very usual thing for a composition to give most satisfactory results on several occasions, and then, apparently under exactly similar circumstances, to utterly break down, and to refuse even to keep on. Too much stress cannot be laid upon the condition of the plates at the time of coating, and it is absolutely essential either to have a perfectly dry ship, or else a composition which is not affected by water.

Oil Paints.—When an old ship is broken up, the numbers are often seen on the backs of the plates, having been painted on them with white lead and linseed oil before the ship was built, and under the paint the iron is in a perfect state of preservation, the reason being that the paint was put on while the plates were hot and dry.

Boiled linseed oil, mixed with red or white lead, is amongst the oldest of the protective compositions in use, but of late years has been but little employed, since it was proved by M. Jouvin of the French Navy, and also in this

country, that compounds of lead, when exposed by the wasting of the linseed oil to the action of the sea water, are converted into lead chloride, and this is rapidly acted on by the iron, depositing metallic lead and forming iron chloride, the deposited lead carrying on the corrosion of the iron by rapid galvanic action. The drying of boiled linseed oil is due to the fact that it has in it a certain quantity of an organic compound of lead, and the drying properties are given to it by boiling it with litharge (lead oxide), so that even when red or white lead is not mixed with it, still lead compounds are present, and this action will go on to a smaller extent.

When the boiled oil dries, it does so by absorbing oxygen from the air and becomes converted into a sort of resin, the acid properties of which also have a bad effect upon iron, so that the protectives containing boiled oil are open to objection. A good example of the action of sea water on the bottom of an iron ship, coated with red lead, was afforded by H.M.S. *Nile*, which, after being painted over with coats of red lead, was allowed to remain for some months in Milford Haven, with the result that her bottom was very seriously corroded, and, on examination of specimens of rust taken from her, the crystals of metallic lead were in many cases easily identified.

If red lead is used, it can only form a ground work for an anti-fouling composition which has to protect the red lead as well as the iron of the ship from the action of sea water, and when the anti-fouling composition perishes, then serious corrosion must ensue.

Pitch, Asphalt, etc.—The second class of protectives, consisting of tar and tar products, such as pitch, black varnish, and asphalt, are amongst the best protectives, not being affected by the sweating of the plates, and forming admirable coatings. Certain precautions, however, must be taken in the case of tar and tar products, both of which are liable to contain small quantities of acid and of ammonium salts; but

if care be taken to eliminate these, and if it could be managed to apply this class of protectives hot to warm plates, the question of protection would be practically solved, bituminous and asphaltic substances forming an enamel on the surface of the iron which is free from the objections to be raised against all other protectives, that is, that being microscopically porous they are pervious to sea water. Coverings of this class are commonly employed for protecting water and gas mains, which have to be buried in the earth, and with proper care in selecting a composition, and in its application, very good results are obtained.

Simple Varnishes.—The third class of protectives consists of varnishes formed by dissolving gums or resins in volatile solvents, such as spirit, turpentine, naphtha, fusel oil, etc., and such varnishes are open to several objections—in the first place, they are acted upon by moisture, which causes a deposition of the resins or gums as a non-coherent powder, and destroys the tenacity of the varnish. The amount of action which moisture has on such a spirit varnish, depends to a considerable extent upon the proportion of resin or gum to spirit. When the solvent is present in large quantities, and the resin in comparatively small, then the moisture has apparently little action ; but it must be remembered that the drying of such protectives means the rapid evaporation of the solvent and concentration of the resin or gum, whilst the rapid volatilisation which is going on cools the hull of the ship, and causes deposition of moisture on the drying varnish with most disastrous results.

Another point which must be borne in mind is that no such varnish is impervious to gases and liquids. We are apt to think of a coating of varnish as being perfectly homogeneous; but on examining it through a microscope, it is seen to be full of minute capillary tubes, which become gradually enlarged by the action of water, and finally result in the destruction of the varnish, whilst moisture and dissolved gases find their way to the metal and carry on cor-

rosion. The application of several coats of varnish tends to diminish this evil, as in many cases the holes in the first coat will not correspond with the holes in the second, and so each succeeding coat will tend to make the protective more and more impervious. In using such varnishes, they must only be applied in favourable weather, and must be allowed to thoroughly harden before being brought in contact with the water.

Varnishes with Mineral Additions.—In the fourth class we have varnishes of this kind to which body has been given by the addition of foreign constituents, generally mineral oxides; and this class is far preferable to the last, if the solvent used is not too rapid in its evaporation, and if care has been taken to select substances which do not themselves act injuriously upon iron or upon the gums or resins which are to bind them together, and are also free from any impurities which could do so.

At present the favourite substance used to give colour and body to such varnishes is the red oxide of iron, the colour of which effectually cloaks any rusting which may be going on under it. In using the red oxide for this purpose, care should be taken that it contains no free sulphuric acid or soluble sulphates, as these are common impurities, and are extremely injurious, tending to greatly increase the rate of corrosion. The finest coloured oxides are, as a rule, the worst offenders in this respect, as they are made by heating green vitriol (ferrous sulphate), and in most cases the whole of the sulphuric acid is not driven off, as the heat necessary impairs the colour.

The best form of iron oxide to use for this purpose is obtained by calcining a good specimen of hæmatite iron ore at a high temperature. When prepared in this way, it contains no sulphates, but from 8 to 40 per cent. of clay; if the percentage does not, however, exceed 12 to 18 per cent. it is unobjectionable.

A far better substance to use for this purpose would be

the mixture of finely-divided metallic zinc and zinc oxide, which can be obtained as an impalpable powder from the cones used to close the nozzles of the retorts in the Belgian process of distilling zinc (page 497). If a good sound shellac varnish had body given to it by this mixture, which usually contains about 80 per cent. of zinc, no action would take place until the varnish had perished, and when this took place the zinc would set up galvanic action with the iron and afford the plates a further period of protection, leaving a spongy coating of zinc oxide behind on the metal, which would again tend to protect it.

Cement Coatings.—In the fifth class of protectives we have cement coatings ; but these, together with such schemes as covering the hull of the vessels with vitreous glazes, glass, etc., have of late years been entirely abandoned. The action of cement on iron, however, must later on be discussed in its important bearing on the protection of the interior portions of the hull, for which it is largely employed, its weight and the difficulty of attachment rendering it unfitted for outside work.

In selecting a protective composition for the bottom of a vessel, one of the second or fourth class should be chosen, attention being given to the points indicated, which are that in the bituminous and asphaltic compositions all the original acids must be eliminated, and that in the varnishes of the fourth group quickly evaporating solvents should be avoided, and, if possible, zinc substituted for iron oxide.

The vessel should have her plates as dry as possible during the application of the protective, and, if feasible, days on which the air is fairly dry, and a brisk breeze blowing, should be chosen. The protective should not be too thick as, if it is, it does not readily fill into inequalities in the plates ; and, if in this way any air is enclosed, change of temperature will cause it to expand or contract, thus causing a blister to form, which will fill with sea water and set up

rapid corrosion. The composition must either be elastic or else have the same rate of expansion and contraction as the iron; for, if not, the change of temperature will cause cracking and tearing of the composition with disastrous results. The vessel, if she has to be scraped down to the bare metal, must be scrubbed free from all traces of rust, and where a well adhering coating of composition exists, it should be painted over and not disturbed. In the case of a new ship, she must be pickled with dilute acid to get rid of every trace of mill scale, and then washed down with some slightly alkaline liquid to neutralise every trace of acidity, the alkali in turn being removed by clean water. Under these conditions, and given a composition with good adhering properties, but little apprehension need be felt as to the ravages of corrosion on the metal of a ship's bottom, the chief risk being from abrasion and other mechanical injury to the composition, coupled with improper constituents in the anti-fouling composition.

The protection of the interior portion of the vessel, where the plates are exposed to the corrosive action of bilge water, rendered more active by a high temperature, leakage from cargo, acids and sulphates from wet coals, and the presence of such electro-negative bodies as coal dust, scale and rust, is a matter of quite as great importance as the external protection; whilst the great risk of mechanical abrasion during coaling and shifting of cargo, as well as the difficulty of getting at the lower portions of the hold to examine the condition of the plates, renders adequate protection absolutely necessary. The corrosion found in the portions underneath the engine seats, the bunkers, and the water ballast chambers, especially near the engine room, is often very serious, and needs most careful watching, which, from the position of these parts of the vessel, it is very hard to bestow upon it.

It must also be remembered that the bilge water in a vessel is in constant motion, and that the air in these parts of

the vessel may be expected to be exceptionally rich in carbon dioxide, which is the most important factor in corrosion. Under these conditions any abraded portion would probably be continually washed over, and then exposed to the foul air, a condition of things most conducive to rapid rusting. There are three main classes of protectives for the interior of a ship—

(1) Cements.
(2) Bituminous coatings.
(3) Paints.

The first of these, the cement coatings, have many good points to recommend them, but they also have many serious drawbacks.

The rigidity, firmness of adherence and endurance, are all of them points of the greatest importance, and there is no doubt but that the silicates present in the cement in time not only bind the cement into a mass of great hardness, but also bind the cement to the iron. A thin coating of Portland cement, however, is highly porous, and can be permeated by liquids and gases. Suppose, now, that the oxidation of copper pyrites in the coal bunkers had given rise to some soluble copper sulphate which had washed down into the bilge water, this solution would soak through the capillary orifices in the cement until it came in contact with the iron below, when the copper would be deposited on the iron, and rapid galvanic action set up, the cement being loosened, and to a certain extent lifted, by the formation of rust, whilst corrosion would gradually extend under the cement, giving on the outside of the coating but little sign of the damage taking place below it.

That this is a real danger is proved by the fact that on several occasions a deposit of metallic copper has been found under the cement and in contact with the iron.

Also, the hardness and rigidity of the cement give it a tendency to crack away from the metal when any strain is thrown on the plates, or during any expansion or contraction

of the metal; whilst any repairs on the outside of the ship, such as making a boring to test the thickness of plate, replacement of rivets, etc., would undoubtedly cause a loosening of the cement coating within, and, wherever a loosening takes place, the space between the cement and the plate will quickly become a starting point for corrosion, which rapidly spreads and loosens the cement, and will only be discovered by chance.

It is for this reason that bituminous or asphaltic varnishes, freed from any trace of acid and applied hot, or sound tough paint, are preferable to cement; as, although they are not so hard, yet if serious corrosion should be set up, it is easily discovered and stopped before much damage results, whilst being impervious to moisture, deleterious solutions, either from the coal bunkers or cargo, would be prevented from acting upon the skin of the ship.

Fouling and Anti-fouling Compositions.

In approaching the subject of fouling, one is impressed with the apparent hopelessness of obtaining any reliable information from the successes or failures registered by the bottoms of the vessels in the Service, or in the Mercantile Marine. Hundreds of ships may be examined, and their condition and the nature of the compositions used upon them registered, and just as one begins to feel that the key to the mystery is within one's grasp, a whole series of results so abnormal suddenly comes to light that it seems impossible to reconcile them with previous experience. A ship may sail half a dozen times to the same waters, coated with the same composition—on four occasions she will come home clean and in good condition, whilst on the other two voyages she may accumulate an amount of weed and animal life sufficient to reduce her speed from nine knots to five. Moreover, if the compositions with which she was coated be examined, and scrapings taken from her on her return, no cause will present itself that can in any way explain the great

difference in her condition. After several years' close observation, however, certain factors begin to make themselves apparent. Some seasons of the year give rise to more fouling than others, according to the waters in which the ship has been; one also begins to realise that the amount of fouling increases enormously if the ship has been long at anchor—ships which have been lying at the mouths of rivers, although quite clean in the brackish water, foul much more rapidly on going to sea than vessels which have been cruising, or even at anchor for the same time, in salt water; and finally, certain ports and certain seas seem to exercise a deleterious effect, both as regards corrosion and fouling, which is not to be found elsewhere.

Turning back to the naval history of the past, we find that fouling is no new trouble born with the advent of our present iron monsters, but that it has been the one trouble that the combined engineering and scientific skill of many centuries has been unable to overcome.

Copper Sheathing.—With our wooden ships, metallic copper sheathing, if it were of the best kind, answered the purpose fairly well; but then the copper wasted so fast that inferior kinds and alloys were substituted to prevent the rapid loss, and, with the slowing down of the destruction of the copper, at once the trouble of fouling returned.

When a clean sheet of copper is exposed to the action of sea water, the first action is the formation of a thin film of cuprous oxide due to the action of dissolved oxygen in the water. This cuprous oxide is then converted by the carbon dioxide and salts present in the sea water into carbonate and oxychloride, both of which are practically insoluble, and form a greenish-blue deposit which peels off from the surface of the metal carrying with it any vegetable or animal germs and organisms which may have attached themselves to it, a process called "exfoliation." Sir Humphrey Davy, who first investigated this action, also found that the presence of even very small proportions of metals electro-positive to it pre-

vented this action and slowed down the wasting of the copper, but that this at once allowed fouling to take place.

If the purest copper also is not used, the scale of oxy-chloride and carbonate is more adherent; and setting up galvanic action with the still exposed metallic portions of the plate, after a short time causes it to be unevenly eaten away at these points.

When iron ships began to replace the wooden ones, as was only natural, attempts were made to utilise the metal which had before given relief; but it was quickly found that the effect of the galvanic action set up by the copper was fatal to the iron plates of the ship, and attempts were then made to sheathe the ship with copper plates in such a way that they should be insulated from the iron of the vessel. This idea has been from time to time revived down to the present day, and, indeed, is in considerable use in some foreign Services; but the difficulty of ensuring complete insulation, and the great risk of serious damage which must ensue to the iron of the hull if any injury happened to the insulating sheathing, make it a most undesirable method if any other means can be adopted to fulfil the same purpose as that for which the copper is used.

Compositions.—Early in the history of iron shipbuilding the idea was conceived of using coatings of paint, so prepared as to fulfil the same function as the copper plates had done; but from 1840, when the first paint of this kind was patented, down to the present day, when there are upwards of thirty-two different compositions in the market, very little progress has been made in their manufacture, and the best of the present compounds cannot be relied upon for keeping a ship's bottom even fairly free from fouling for periods extending over nine months.

The idea which originally led to the present class of anti-fouling compositions was that the copper salts formed by the action of the sea water on the metallic sheathing owed a

considerable portion of their value as anti-foulers to the poisonous action they exerted upon marine animal and vegetable growths; but when an observer comes to study the natural history of these lower forms of animal life and vegetation, it is gradually forced upon him that it is only in the early stages of their growth—the germ period—that metallic poisons can affect them. Seaweeds do not take in the constituents they require for their growth by means of their roots, as is, to a certain extent, the case with ordinary plants, but absorb them by means of their pores from the water itself, the root only serving to attach them to the solid they choose for their resting place; and it is also well known that when once a marine plant which has passed the first stages of existence is dislodged or torn from its support, it cannot again attach itself to anything else, whilst most of the mineral poisons have little or no effect upon their life and growth.

In the same way we find that, with the animal life found on a ship's bottom, the under-side is used to cling on with only, and not as an extractor of nourishment; and that, therefore, after the seeds and germs have once obtained a foothold on the side of the vessel, no amount of poison which can be put into a composition will have any effect upon them. Metallic poisons undoubtedly do exert an influence upon the germs in their earliest stages; but after that, they are perfectly useless as anti-foulers, and only imperil the plates of the vessel.

The germs of both kinds of growth are of necessity more abundant in the surface water near shore than in deep water, and, therefore, the period when the ship is in port is the time when the germs are most likely to make good their attachment, after which their further development is, unless other methods of getting rid of them are employed, merely a matter of time.

On examining the conditions under which a vessel is placed when coated with a composition which relies for its anti-fouling powers on metallic poisons only, we at once see

the reasons which must make such a coating of little or no avail. In the composition we have drastic mineral poisons, probably salts of copper, mercury, or arsenic, which have been worked into a paint by admixture with varnishes of varying composition, and each particle of poison is protected from the action of the sea water by being entirely coated by this vehicle; that this must be so is evident, or the composition would not have sufficient cohesive power to stick on the ship. As a rule, care is taken to select fairly good varnishes which will resist the action of sea water, for, perhaps, two or three months before they get sufficiently disintegrated to allow the sea water to dissolve any of the poison; whilst, even with the accidental or intentional use of inferior varnishes, three or four weeks will pass before any solution can take place, and any poison be liberated to attack the germs. A ship is dry docked, cleaned, and her anti-fouling composition having been put on, she goes probably into the basin to take in cargo. Here she is at rest, and, with no skin friction or other disturbing causes to prevent it, a slimy deposit of dirt from the water takes place, and this, as a rule, is rich in the ova and germs of all kinds of growth, whilst the poisons in her coating are locked up in their restraining varnish, and are rendered inactive at the only period during which they could be of any use. After a more or less protracted period, the ship puts to sea, and the perishing of the varnish being aided by the friction of the water, the poisonous salts begin to dissolve or wash out of the composition; but the germs have already got a foothold, and with a vessel sweeping at a rate of, say ten to twelve knots through the water, the amount of poison which can come in contact with their breathing and absorbing organs is evidently so infinitesimally minute that it would be impossible to imagine it having any effect whatever upon their growth. If the poison is soluble, it is at once washed away as it dissolves; if it is insoluble, then it is also washed away, but there is just a chance that a grain or two may become entangled in the organs of some of the forms of life, and cause

them discomfort. As the surface varnish perishes, the impact of the water during the rapid passage of the vessel through the water quickly dissolves or washes out the poisonous salts, and leaves a perished and porous, but still cohesive coating of resinous matter, which forms an admirable lodgment for anything which can cling to it; and by the time the vessel lays-to in foreign waters, teeming with every kind of life, the poison which would now again have been of some use is probably all washed away, and a fresh crop of germs is acquired, to be developed on the homeward voyage, and a "bad ship" is reported by the person who looks after her docking. It is evident that a poison, even if it had the power of killing animal and vegetable life in all stages, could only act with the vessel at rest, unless it were of so actively corrosive a nature as to burn off the roots and attachments of the life rooted to it; and if it did this, what would become of the protective composition and the plates of the vessel? Any poison so used must be under conditions in which it is very unlikely to be in a position to act when it might do good.

The lamentable failure of composition after composition of this kind has gradually reduced them in number to some ten or twelve in general use, and in most cases it is low price alone which keeps them in the market.

The practical proof, given by experience, that poisons alone are unable to secure a clean bottom soon led many inquirers to the conviction that it was the exfoliation in the case of copper which had acted in giving fairly good results; and in many compositions the attempt has been made to provide a coating which shall slowly wash off, and, by losing its original surface, shall at the same time clear away germs and partly developed growths, and so expose a continually renewed surface—in this way keeping the bottom of the vessel free from life. There is no doubt that when this is successfully done, a most valuable composition will result, but the practical difficulties which beset this class of anti-foulers must not be overlooked. In order to secure success

the composition must waste at a fairly uniform rate when the ship is at rest, and also when she is rushing through the water; and this is the more important in the case of Service vessels, as in many cases they spend a large percentage of their existence at anchor, or in the basins of our big dockyards. If a composition is made to waste so rapidly that it will keep a vessel clean for months in a basin, then you have a good composition *for that purpose;* but send the vessel to sea, and under conditions where you have water of a higher temperature, and the enormous friction caused by her passage through the water exerting its influence upon the composition, and you will find that the coating, which did its work well for six months at rest in the basin, will, in the course of one month under the altered conditions, be all washed away, and fouling will be set up. Noting this result, the manufacturer renders his composition more insoluble—less wasting—and so obtains a coating which, when the vessel is in motion, scales just fast enough to prevent fouling, and good results at once follow; the composition is then put on the same or other vessels, and they take a spell of rest in the basin, and bereft of the aid of the higher temperatures and the friction of the water, the composition ceases to waste fast enough, and bad results at once have to be recorded.

There is no doubt that this is the true explanation of the wide discrepancies which are found between the compositions in the Navy and the Mercantile Marine. Take any of the big lines, their steamers are running at a fairly uniform rate of speed, and the periods of inaction are as short as the desire not to waste charge on the capital they represent can make them; and under these conditions, by varying the constituents in the varnishes used for anti-fouling purposes, it is fairly easy, given the necessary data, to so constitute a composition as to secure admirable results; but when you come to apply this same coating to an ironclad, running at various speeds, and as often at rest as in motion, then you at once find that the composition you before imagined to be all that

could be desired fails just as lamentably as the tribe of anti-foulers which preceded it.

Another factor which is often overlooked, and which tends to give misleading results, is the action of brackish water which, in many cases, seems to exert a special action in keeping the bottom of a vessel clean; the fresh water having a tendency to disagree with certain forms of marine growth, whilst the salt water is apparently equally unpalatable to the fresh water forms of fouling.

In most of the compositions now in use attempts are made to combine strongly poisonous substances with exfoliating and wasting coatings, and this is done by either using metallic soaps, the basis of which is, as a rule, copper, or else by charging a perishable and easily washed off varnish with poisonous salts, consisting as usual of compounds of either copper, mercury or arsenic, and in some cases all three.

As before pointed out, the presence of these substances does not exert any deterrent action upon the fouling, save perhaps when the vessel is at rest; but they exert undoubtedly an important influence upon the rate of exfoliation, as when the perishing of the varnish exposes them they dissolve, or are washed out, and in this way tend to disintegrate and clear away the surface more rapidly, an important and decidedly useful function, but one which might be more cheaply performed by substances other than high-priced metallic poisons.

The use of metallic poisons of the character indicated throws an increased burden upon the protective composition, as should the latter become abraded by friction of chain cables, barges alongside, or any other cause, the iron of the vessel will be attacked by the metallic salts, either present in the soluble form in the anti-fouling composition, or rendered so by the solvent action of the saline constituents of the sea water, the action of the metallic salts being to rapidly dissolve portions of the iron, and to deposit the metal which they contain upon the surface of the plates, and these deposits, exciting energetic galvanic action, cause corrosion

and pitting to go on with alarming rapidity. Both mercury and copper salts are offenders in this way, but copper is by far the most objectionable, from the fact that the salts formed by the action of the sea water upon some of the compounds used in the composition are more soluble than the corresponding salts of mercury, and are, therefore, liable to be present in larger quantity, and so exert comparatively a much more injurious action on the plates.

All the time the ship is in motion the wash of the sea water will prevent the metallic poisons doing the plates or the marine growths much harm, but there is one phase of this question which has been overlooked. In certain ports there is a fashion in compositions, and most of the homes of the Mercantile Marine have some pet local composition which is largely used at the particular port. If, now, many ships are lying in a basin, taking in and discharging cargo, and if the prevalent compositions contain soluble salts of copper, it is evident that a certain quantity will go into solution in the water, which often does not undergo frequent or rapid change, and under these conditions every ship in the basin will be exposed to the same danger, and wherever an abrasion has taken place in the protectives, there copper will be deposited on the iron, causing corrosion and destruction of the plates; and it must be remembered that when the vessel is next docked and coated no amount of scraping will remove the fine particles of copper deposited in the pitted and corroded portions of the plate, and so finely divided as to be invisible to the eye, but that it will remain and carry on its destructive work under the new coatings of protective.

It is a well recognised fact that when a vessel coated with a copper compound has become corroded from failure of her protective, or from abrasion, even an entire change of composition does little or no good in stemming the tide of corrosion, until after some considerable period has elapsed, a result which is due to the same cause.

At the present time, many of the principal compositions rely upon copper in some form or other as the basis of their

anti-fouling composition, and in one which has enjoyed considerable favour finely divided metallic copper itself is used, and should a vessel coated with it, after the varnishes have commenced to disintegrate, be moored alongside an iron ship by a chain cable, or even by a wet hawser, a big galvanic couple would be formed at the expense of serious damage to any exposed iron.

Glazed Surfaces.—In the history of anti-fouling many attempts have been made to obtain highly glazed and glass-like surfaces, which it was hoped would withstand the action of sea water and afford no lodgment to marine growths; but even glass itself is slowly acted upon by sea water, and, when once roughened on the surface, will foul, while the rigidity of such coatings, and the straining and cracking consequent on unequal expansion and contraction of the plates and their coating, offers a serious obstacle to any such scheme.

The protective composition is the important composition, and care must be taken to obtain the best in the market, as if the protection is good, the plates remain uninjured even if fouling take place. The anti-fouling composition to be used with it must either be elastic, or have the same rate of contraction and expansion as the protective, and must—at any rate in the Navy—be chosen to suit the work to be done, such as contain soluble copper compounds being carefully rejected, whilst preference should be given to those which rely on exfoliation rather than mineral poisons. If a vessel is to remain at rest for a considerable period, an anti-fouling composition which exfoliates rapidly, and which also contains poisons known to act on germ life, must be used, the amount of such poison depending on the seasons and the waters in which the ship is to be; whilst if a vessel is to be continually running, then a slowly exfoliating composition must be employed, and a very small percentage of poison is all that is required, as skin friction and the comparative absence of the germs and spores in deep water will do the rest.

Pigments.

The question of colours is so closely allied to that of the various compositions and paints in use, that a few words on the nature of colour and the composition of the pigments employed will not be out of place.

All natural objects are distinguished by particular colours and when we want to artificially imitate these colours we use strongly coloured bodies, called pigments.

Theory of Colour.—When a beam of light falls on any substance, some of the coloured rays of which the beam is composed are absorbed and taken up by the substance, whilst the remaining rays are reflected back to the eye, and give the sensation of colour; for instance, a poppy looks red, because its petals have the power of absorbing all the rays, with the exception of the red rays, and these are reflected back to the eye.

A body which reflects all the rays of the spectrum in equal proportion will appear of the same colour as the light that falls upon it, that is to say white. But the majority of bodies reflect some rays in larger proportion than others, and are therefore coloured, their colour being that which arises from the mixture of rays which they reflect.

A body reflecting no light would be perfectly black.

That this is true may be seen by taking a source of light yielding only one kind of ray—called a monochromatic light; and all colours that have not the power of reflecting this particular ray appear black.

When light falls upon an opaque body, it is all either reflected or absorbed, but when it falls upon a transparent body, some of these rays are absorbed, whilst others pass through, and these are said to be transmitted.

A transparent body seen by transmitted light is coloured, if it is more transparent to some rays than to others, its colour being that which results from the mixture of the

transmitted rays. Hence, a piece of blue glass appears blue, because it allows the blue rays to pass through.

The condition or state of division of a substance has a great influence upon its colour; for instance, gold is yellow by reflected light, brown in a state of fine powder, and when beaten out into very thin leaf, by transmitted light it is green; in a still finer state, as when precipitated from dilute solutions of gold, it appears blue or purple.

Temperature also, in many cases, affects the tints of colours, and often the colour itself; for instance, if scarlet mercury iodide be heated, it becomes yellow.

But besides these influences, others of even greater importance are always at work, such as oxidation of the oil with which the colour is mixed, light, and the action of impure air; whilst in very many cases the colours used by the artist chemically act upon one another in the course of time, and entirely destroy the effect which he intended to convey.

In order to avoid as much as possible the deterioration of paintings from these and similar causes, it is of great importance that anyone using colours should have an idea of the composition and properties of the substances employed.

Whites.

White Lead or *Flake White* is a basic lead carbonate [$2PbCO_3.Pb(HO)_2$]. The Dutch method of preparation is to expose gratings of lead (as pure as possible and free from silver, which, even in small quantities, greatly impairs the good colour of white lead) to the action of the mixed vapours of vinegar (acetic acid) and carbon dioxide gas. The carbon dioxide is generated from a covering of spent tan and stable manure, the decomposition of which causes the requisite increase of temperature. The vapours of acetic acid attack the lead and form a basic acetate, which in its turn is converted into basic lead carbonate, acetic acid being liberated, and this attacks a fresh portion of lead. After these actions

have gone on for some time, the layers of basic carbonate are scraped off the gratings and ground to a fine powder. This rather clumsy process has been of late somewhat superseded by more rapid methods, in which tribasic lead acetate, formed by boiling an excess of litharge with acetic acid, is decomposed by passing carbon dioxide through it. The white lead produced in this way has a crystalline structure and does not cover so well as that obtained by the Dutch method, hence very considerable quantities are still made by the older process. White lead is very poisonous, and being a cumulative poison, painters and others often suffer from lead colic. In white lead manufactories the workmen drink water containing dilute sulphuric acid, so as to convert the lead into non-poisonous lead sulphate.

The great drawback to white lead as a pigment is that in foul air it gradually darkens. This is due to the fact that the air contains traces of sulphuretted hydrogen, which combines with the lead, forming lead sulphide—a black compound.

Lead carbonate		Sulphuretted hydrogen		Lead sulphide		Carbon dioxide		Water.
$PbCO_3$	+	H_2S	=	PbS	+	CO_2	+	H_2O.

Pictures so blackened may be partially restored by washing the surface with a solution of hydrogen peroxide, which converts the black sulphide into white lead sulphate.

Lead sulphide		Hydrogen peroxide		Lead sulphate		Water.
PbS	+	$4(H_2O_2)$	=	$PbSO_4$	+	$4(H_2O)$.

A little lead sulphide or Berlin blue is sometimes added to the commercial white lead to give it a bluish tint.

Lead Sulphate ($PbSO_4$) is used as a constituent of many white paints, but alone it has poor covering power, hence is generally mixed with zinc white, baryta, etc. Since lead sulphate is very insoluble, it is far less poisonous than ordinary white lead, and is commercially known as "non-poisonous white lead."

Lead sulphate is commonly prepared by the addition of dilute sulphuric acid to the basic carbonate. Owing to the crystalline nature of the body as thus prepared, it is greatly improved by grinding.

Sublimed White Lead is mainly composed of the sulphate, but is of very variable composition. It is prepared from the "fume" given off in the smelting of lead (p. 489), and is but little inferior to ordinary white lead, whilst it has the advantage of not turning appreciably darker when exposed to traces of sulphuretted hydrogen.

Zinc or *Chinese White* consists of zinc oxide (ZnO). It is most generally prepared by volatilising zinc from fire clay retorts and admitting air for the combustion of the zinc. The fumes of the oxide are condensed in suitable chambers.

Zinc white is an excellent pigment, mixing readily with oils and water. It is quite unacted on by the impurities likely to be present in air, being therefore very permanent. It is, however, deficient in body, and for ordinary oil-paints cannot be used alone. Generally a mixture of two parts of white lead with one part of zinc white is found most satisfactory.

Zinc Sulphide (ZnS) is also employed as a pigment. It has good body, but considerable difficulty is experienced in obtaining it as a pure white; for this reason it is usual to employ it in mixtures, as for example, with barium sulphate.

Baryta, or *Permanent White*, is barium sulphate ($BaSO_4$); it is deficient in body, but is of great use in fresco and siliceous painting. It is perfectly permanent under all conditions, and is not affected by sulphuretted hydrogen, since the barium sulphide which might be formed is also white.

Blacks.

Most of the blacks consist of carbon in a very fine state of division.

Ivory Black is practically animal charcoal, obtained by carbonising ivory cuttings.

Vine Black is a vegetable charcoal, obtained from the twigs of vines, and is given a blue-black tint by mixing it with some Prussian blue.

Lampblack is a very finely divided soot, made by burning resinous oils in an insufficient quantity of air, and condensing the smoke.

Indian ink and Chinese ink consist of lampblack, mixed with gum, shellac, a little borax and water.

All these blacks are good and permanent, and may be mixed with other pigments without fear; it is better, however, not to mix ivory black with vegetable colours.

Mineral Black (which is very little used) is black manganese oxide; it does fairly well in oils, but always has a brown tint.

Reds.

These are of two kinds:—(1) Mineral reds, like vermilion, and (2) Organic reds, like carmine, etc.

Mineral Reds.

Indian Red, Venetian Red, Light Red, chiefly consist of ferric oxide (Fe_2O_3), with an admixture of basic iron sulphates. They are directly prepared by heating ferrous sulphate (the green vitriol of commerce) with a small trace of nitric acid.

Ferrous sulphate		Ferric oxide		Sulphur dioxide		Sulphur trioxide.
$2(FeSO_4)$	=	Fe_2O_3	+	SO_2	+	SO_3.

Much of the oxide now employed is obtained as a bye-product from liquors containing iron salts, such as the acid used for pickling iron plates before tinning. By the addition of alkalies to the liquors, hydrated ferric oxide ($Fe_2(HO)_6$) is precipitated, which may then be calcined.

The peroxide is permanent under all ordinary conditions, but it must be carefully freed from all traces of acid before being applied as a paint to the surface of iron. It is much used in the protective coating for ships.

Red Ochre is a soft variety of the iron ore, hæmatite (Fe_2O_3), containing a little clay.

Red Lead or *Minium* (Pb_3O_4). This may be regarded as a compound of lead monoxide (PbO) and dioxide (PbO_2), but there is reason for believing that a portion of the monoxide exists in the free condition.

It is prepared by first calcining lead at a moderate heat, in order that whilst the lead may melt, yet the monoxide formed remains as a solid "dross." The lead monoxide first formed is of a yellow colour.

Lead		Oxygen		Lead monoxide
Pb	+	O	=	PbO.

This product is now "coloured" by heating in another furnace, with free air supply, when more oxygen is absorbed and red lead produced.

Lead monoxide		Oxygen		Triplumbic tetroxide
$3PbO$	+	O	=	Pb_3O_4.

Red lead, although much used, is very unsuitable, as it is open to all the objections of white lead, and also when mixed with oils forms with them a kind of soap, which causes the colour to lose its opacity.

When linseed oil is boiled for some time with lead oxide, it forms and dissolves some of this lead soap, and acquires the property of rapidly drying. Such oil is technically called "dryers," and is much used to mix with oil paints to cause them to quickly dry; but as it contains lead, all colours mixed with it are liable to darken in the presence of sulphuretted hydrogen.

Vermilion is the most brilliant of the mineral reds. It is mercury sulphide (HgS) and is found native as *cinnabar*.

It may be artificially prepared by precipitating the black mercury sulphide from a solution of mercuric chloride. This black sulphide on being sublimed and finely ground changes to the red variety without altering its composition. The most brilliant colour is obtained by the wet process, which consists of triturating mercury and sulphur together for some hours, and treating the black product formed with a warm solution of potassium hydroxide and water. The colour is not destroyed by any single acid or alkali. When used as a water colour it is apt to turn black in sunlight.

Chrome Red.—This pigment is a basic lead chromate [$PbCrO_4.Pb(HO)_2$], known also as Austrian cinnabar. It is best prepared by fusing the nitrates of sodium and potassium together at a low red heat, and adding gradually yellow lead chromate. After cooling, the insoluble chrome red is well washed and dried.

Organic Reds.

Madder Lake, Rose Madder, Pink Madder, Carmine Madder, are made by treating madder, the root of the "*Rubia Tinctorum,*" which has been previously washed with water, with a boiling solution of alum, filtering the red liquid, and adding some sodium carbonate, when a red precipitate of the colouring matter and alumina, which is the madder lake, separates.

Carmine derives its colour from cochineal, which contains carminic acid, and this is split up by acids into carmine red and glucose.

The common carmine is obtained by treating an aluminous solution of cochineal with sodium carbonate, the lake being precipitated.

Crimson Lake contains more aluminous base than carmine, and consequently has not such a fine colour.

Scarlet Lake is crimson lake with an admixture of vermilion.

Indian Lake and *Dragon's Blood* are obtained from certain resins.

YELLOWS.

Aureolin Yellow is made by warming a solution of cobalt with potassium nitrite in presence of acetic acid, when the yellow is precipitated; it is a rich colour, and mixes well with other pigments, but is not permanent.

Cadmium Yellow is cadmium sulphide (CdS), and is a very stable and valuable colour, being unaffected by sulphuretted hydrogen. It is best prepared by precipitating a solution of cadmium sulphate with sodium sulphide, and thoroughly washing and drying the precipitate.

Lemon Chrome, or *Baryta Yellow* is barium chromate ($BaCrO_4$); it is difficult to prepare, and the stability and beauty of colour depend on the method of manufacture. The colour is very permanent.

Chrome Yellow is a neutral lead chromate ($PbCrO_4$), and can be obtained by adding potassium chromate to a solution of lead acetate. The pigments known as *chrome orange* are mixtures of chrome yellow and the basic chromate, or *chrome red*, and are prepared by boiling chrome yellow with milk of lime.

King's Yellow, or *Orpiment*, is the highly poisonous arsenious sulphide (As_2S_3), and *Naples Yellow* contains both lead and antimony as oxides.

The Ochres are native earths consisting chiefly of alumina and silica coloured by hydrated ferric oxide [$Fe_2(HO)_6$]. They are very permanent and can be used with great safety. When heated they become brown, and are then called *sienna*.

Gamboge is a gum resin which exudes from the young shoots of the gokathu tree in Ceylon and Siam.

Yellow Carmine and *Yellow Lake* are prepared from quercitrin, a colouring matter existing in the bark of the quercitron. It is precipitated by means of alum.

Indian Yellow or *Purree* consists of an organic compound of magnesia, and is obtained from the urine of the camel.

Greens.

Among the many pigments that owe their green colour essentially to copper, the following are important:—

Bremen Green is copper hydroxide [$Cu(HO)_2$], obtained in various hues by mixing with barium sulphate.

Casselman's Green.—A basic compound formed by mixing together boiling solutions of copper sulphate and an alkaline acetate. This salt is, next to the arsenic compounds, the finest of all the colours obtained from copper.

Mineral Green, or *Scheele's Green*, is copper arsenite ($CuHAsO_3$).

Schweinfurt Green or *Emerald Green.*—This is the most beautiful, but also most poisonous of all the copper pigments. It is really an aceto-arsenite of copper and may be made by adding sodium acetate and arsenious acid to a solution of copper sulphate. It is a well-known fact that paper hangings containing this pigment, and pasted on damp walls, cause the inmates of the rooms to suffer from headaches, due probably to volatile arsenical compounds being formed.

Verdigris is a subacetate of copper. As a water colour it is very unstable.

Chrome Green, *Viridian Green*, are usually chromium oxides (Cr_2O_3), prepared by adding sodium hydroxide or carbonate to a solution of chromic chloride. Chrome greens, however, vary much in composition, in some cases consisting of the phosphate [$Cr_2(PO_4)_2$]. They have good body, and do not affect other colours with which they may be mixed.

Terre Vert, as indicated by its name, is found as a green earth, which is a very permanent green, consisting mainly of an oxide and silicate of iron.

Other greens are compounded from yellows and blues; if mixtures (such, *e.g.*, as Prussian blue mixed with raw or burnt sienna or Vandyke brown) be exposed to light, the green colour gives place to brown, on account of the Prussian blue fading. If the faded colour be then kept for some time in the dark, the colour returns.

Blues.

Ultramarine.—This is a double silicate of alumina and soda, and contains sulphur in the form of sulphide, but no definite formula has been found for it. It occurs native as "lapis lazuli." The commercial product is obtained by heating together soda, clay, sulphur and charcoal in various proportions. It is first white, but quickly turns green (green ultramarine), and when this is heated with sulphur in presence of air it becomes blue without change of composition. Ultramarine is unacted on by alkalies, but is readily decomposed by acids with evolution of sulphuretted hydrogen.

Cobalt and *Smalt Blues* are exceedingly permanent under all ordinary conditions. They are prepared by dissolving cobaltous oxide in a fused acid silicate, which yields a glass of magnificent blue colour, which is ground to a fine powder.

Cærulean Blue is a stannate of cobalt, chiefly used for scene-painting.

Prussian Blue is ferrocyanide of iron; it is made by adding a ferric salt to potassium ferrocyanide, when Prussian blue is precipitated. It is readily destroyed by alkalies. The pigment is soluble in oxalic acid and molybdic acid.

Antwerp Blue is a compound of Prussian blue and alumina, but it has been almost completely superseded by *Brunswick blue*, which is a mixture of Prussian blue and baryta.

Indigo is the blue colouring matter obtained from several species of *indigofera*. The leaves are macerated in water, when they undergo oxidation, forming a yellow solution, which, on exposure to the air, deposits indigo in the form of a dark blue powder. The pigment is soluble in Nordhausen sulphuric acid, forming a deep blue solution. For dyeing purposes the cloth is dipped in a vat containing one part of indigo, two parts of ferrous sulphate, and three parts of slaked lime, to about 200 parts of water. On exposure to air the cloth becomes permanently blue by the deposition of insoluble blue indigo. Indigo has also been prepared synthetically.

Browns.

Raw and *Burnt Umber* consists of a native ore of iron, containing a little manganese. The pigments are permanent.

Sepia is extracted from cuttlefish, and consists of carbonaceous matter and animal gelatine.

Madder Brown is extracted from the madder root, and is very apt to fade, whilst *Vandyke Brown* and the *Brown Ochres* are oxides of iron, and are quite permanent.

From a series of experiments made on the action of light on water colours, the following notes may be of interest.[1]

Paper painted with simple colours and mixtures was exposed to light under different conditions, with the following results.

Mineral colours are far more stable than vegetable colours.

The presence of moisture and oxygen is in most cases essential for a change to be effected, even in the vegetable colours. It may be said that every pigment is permanent when exposed to light "in vacuo."

The effect of light on a mixture of colours which have no direct chemical action on one another, is that the unstable

[1] "Report of the Action of Light on Water Colours," by Russell and Abney.

colour disappears, and leaves the stable colours unaltered appreciably.

Experiments also show that the rays which produce by far the greatest change in a pigment are the blue and violet components of white light, and that these for equal illumination predominate in light from the sky, whilst they are less in sunlight and in diffused cloud light, and are present in comparatively small proportion in the artificial light usually employed in lighting a room or gallery.

Experiments have also shown that about a century of exposure would have to be given to water colour drawings in galleries lighted as are those at South Kensington, before any very marked deterioration would be visible in them, if painted with any but the more fugitive colours; and that when the illumination is of the same quality as that of gas-light, or of the electric glowlight, rendered normally incandescent, and of the same intensity as that employed in those galleries, an exposure to be reckoned by thousands of years would be necessary to produce the same results.

QUESTIONS.

1. Point out the difference between physical and chemical change and illustrate your answers by examples.
2. To which kind of change do the following phenomena belong :—
   (*a*) Conversion of water into ice.
   (*b*) The rusting of iron.
   (*c*) The burning of a jet of coal gas.
3. Why do solids seldom react upon each other? Enumerate some of the causes which tend to set up chemical action, and give examples.
4. Why are iron, sulphur and oxygen called elements?
5. State the leading characteristics which serve to distinguish between a chemical compound and a mechanical mixture, and illustrate your answer by examples.
6. What reasons have we for saying that water is a chemical compound? How would you prepare oxygen and hydrogen, respectively, from steam?
7. State the main principles on which the liquefaction of a gas depend.
8. Under what circumstances can oxygen be condensed to a liquid?
9. Define the terms "molecule" and "atom."
10. Write the symbols for sulphur, silicon, silver; and write the formulæ for sulphuric acid and zinc sulphate, and the equation for the action of hydrochloric acid on chalk.
11. What is the "atomic weight" of an element?
12. How could the atomic weights of chlorine, carbon, and iron respectively be determined?
13. The molecular weight of carbon dioxide is 44; what is its density on the hydrogen scale?
14. Show how the "specific heat" of an element may be used as a guide in determining its atomic weight.
15. What do we mean by the "equivalent weight" of an element? 65 grams of zinc will expel 2 grams of hydrogen from sulphuric acid. What is the equivalent weight of zinc?
16. How can it be proved that the molecule of hydrogen contains two atoms?
17. The density of a gas on the hydrogen scale is 22. What will be the weight of 22·32 litres of this gas at normal temperature and pressure?
18. How much zinc and how much sulphuric acid must be employed to generate sufficient hydrogen to fill a balloon with capacity of 1,250 litres? At. Wts: Zn. = 65; S = 32; O = 16.
19. Explain fully what is meant by the density of a gas.
20. What precautions must be observed in comparing the weights of equal volumes of gases?
21. What is meant by normal or standard temperature and pressure?

22. If the pressure remains constant, to what temperature must the air in a vessel be heated so that half may be expelled?

23. A room contains 560 cubic feet of air at 5° C. and 762 m.m. How much air will be driven out at 12° C. and 750 m.m.?

24. Write out the formulæ for the chlorides, nitrates, sulphates and phosphates of potassium, calcium, and bismuth respectively.

25. What do you understand by "empirical," "molecular," "graphic," and "constitutional" formulæ? Give examples.

26. Give two methods for the preparation of hydrogen. What precaution must be observed in preparing and collecting it?

27. Enumerate some of the more characteristic properties of hydrogen.

28. Describe the effect of hydrogen on sound.

29. Give examples to show that hydrogen in combination can, in some cases, be replaced by metals and also that, under certain conditions, metals can be turned out from their compounds and be replaced by hydrogen.

30. State Graham's Law for the diffusion of gases. What are the relative rates of diffusion of carbon dioxide, oxygen, air, and hydrogen?

31. Why was varnished silk unsuitable for balloons to contain hydrogen? How are military balloons at present constructed?

32. Describe how the heat evolved by the action of zinc on dilute sulphuric acid can be converted into electricity.

33. By what experiments could you prove that when a plate of zinc and a plate of copper are placed in dilute sulphuric acid and are in metallic contact a current of galvanic electricity is produced?

34. How do you explain the rapid falling off of the current in a simple voltaic combination?

35. Describe and explain the methods employed in the following cells to prevent this falling off (*a*) Daniell, (*b*) Varley-Daniell, (*c*) Menotti, (*d*) Leclanché, (*e*) Grove?

36. Why is Daniell's battery not used for firing fuses? What advantages has the Leclanché battery?

37. For what purpose is the Menotti cell mostly used?

38. How is the internal resistance of a Leclanché battery intended for firing purposes made as low as possible?

39. Explain the chemical actions taking place in a "bichromate cell," and illustrate your answers by equations. Why must sulphuric acid be used in excess in charging this form of cell?

40. Describe what happens when a current is passed through acidulated water using lead electrodes.

41. Explain fully the action and changes taking place in a secondary battery.

42. Explain the terms "electrolysis," "electrolyte," and "electrode." Describe what happens when a galvanic current is passed through a solution of sodium sulphate?

43. The same current is passed through three cells containing respectively—sodium chloride, copper sulphate and silver nitrate; explain the decomposition taking place in each cell. What ratio by weight do the copper and silver deposited bear to each other and to the zinc used up in each cell of the battery?

44. Explain the process of electro-plating.

45. What is the use of zinc protectors on ships' bottoms?

46. Give two methods for the preparation of oxygen from water. How is oxygen commonly prepared for experimental purposes? What products are formed when phosphorus, carbon, sulphur, zinc and iron, respectively, are burnt in oxygen?

47. How is the solution of oxygen in water affected by change of temperature? What important functions does dissolved oxygen perform?

48. Describe the preparation of ozone. How can ozone be detected?

49. Why do we say that ozone is an allotropic modification of oxygen?

50. Define the terms "Allotropism" and "Isomerism," and give examples.

51. How can ozone be converted into oxygen? Describe the experimental proofs that the density of ozone is 24 on the hydrogen scale.

52. Into what classes can "oxides" be divided? Illustrate your answer by examples. What is a "hydroxide"?

53. Point out how the nature of the oxides of an element is used in the classification of elements into metals and non-metals.

54. What is a "salt"? Point out the difference between "normal," "acid" and "basic" salts, giving examples.

55. How would you define the term "combustion"? Describe an experiment to show that the terms "combustible" and "supporter of combustion" are purely relative.

56. What is "slow combustion"? Give examples.

57. A cubic inch of wood in burning gives out x units of heat. How much heat would be evolved if it had been allowed to slowly decay? Give a short description of the process taking place during respiration.

58. Give examples of cases in which natural oxidation (*i.e.*, slow combustion) gives rise to sufficient heat to induce rapid combustion.

59. A piece of freshly heated platinum foil when held in a stream of mixed coal gas and air becomes red hot, and continues to glow all the time it is held in the mixture. Explain fully the action which is taking place.

60. Certain compounds contain oxygen so loosely held in combination that they will give it up to any easily oxidisable bodies. What are such compounds called, and what is their use in explosives?

61. Summarise the conditions which tend to induce spontaneous combustion in large coal cargoes.

62. Show how you could prove that the proportions in which oxygen and hydrogen exist in water are by weight as 8 to 1.

63. Describe fully the synthetical method by which the composition of water by volume has been determined.

64. A pound of water at 80° C. is mixed with 1lb. of ice at 0° C. What will be the temperature of the two pounds of water formed?

65. Define the terms "latent heat," "thermal unit" and "boiling point." Upon what does the boiling point of a liquid depend? Illustrate your answer by the description of experiments.

66. How can the boiling point of water be raised above 100° C.?

67. On what conditions does the rate of solubility of a gas in water depend? A pint of water will dissolve a pint of carbon dioxide gas at 15° C. and 760 m.m. pressure; what volume of gas will be dissolved if the pressure be increased to 1,140 m.m.?

68. Why does a solid dissolve more quickly if the solvent be constantly agitated?

69. Explain the freezing of water by the rapid solution of ammonium nitrate. What is meant by "water of crystallisation" and "water of hydration"?

70. What is the purest form of natural water? What classes of impurities are found in rain, spring and river water respectively?

71. To what is hardness in water due? What is meant by the terms "a degree of hardness," "temporary hardness," and "permanent hardness"? Describe and explain Clarke's process for softening water.

72. Why is shallow well water especially liable to organic contamination?

73. Give two rough methods by which stream water charged with vegetable impurities may be rendered fairly fit for drinking. Why are rough tests of the fitness of a water for drinking purposes as a rule misleading?

74. On what grounds have the older forms of filtering material been generally condemned?

75. How is boiler deposit formed? What constituent of boiler deposit tends to render the scale hard? How does the composition of the deposit in land boilers differ from the deposit in marine boilers?

76. Explain the action of sodium carbonate as an "anti-incrustator." Sal-ammoniac is sometimes used for the prevention of incrustation in steam boilers; what is its action, and why would it be of no use for boilers using sea water?

77. Why should tallow and other animal and vegetable fats and oils not be employed as anti-incrustators? What kind of oil might be used for this purpose with advantage?

78. Explain why magnesium is found as magnesium hydroxide in boiler deposits. How does the decomposition of magnesium chloride in steam boilers affect the corrosion of boiler-plates?

79. How can hydrogen dioxide be prepared? Give an equation for its formation.

80. Hydrogen dioxide is brought in contact with (*a*) litmus solution, (*b*) silver oxide, (*c*) finely powdered platinum, (*d*) black oxide of manganese, respectively. What happens in each case?

81. By what tests can hydrogen dioxide be detected in solution?

82. How is marsh gas formed in Nature?

83. What weight of carbon will be contained in 23·32 litres of methane?

84. Explain the terms "fire damp" and "choke damp." On what principle is the safety lamp constructed?

85. In what proportions do marsh gas and air form the most explosive mixture?

86. How does ethylene or olefiant gas differ from methane or marsh gas? Describe an experiment which proves the presence of carbon in ethylene.

87. How can methane and ethylene be prepared? Illustrate your answer by equations.

88. Give a brief description of the manufacture of coal gas and point out the use of the "hydraulic main," "atmospheric condensers," "scrubbers," and "purifiers."

89. What are the "secondary products" of the manufacture of coal gas, and how are some of them utilised? Why must coal gas be purified from sulphur compounds?

90. Describe the structure of a candle flame. Why is the flame of a Bunsen burner non-luminous?

91. What do you understand by an "oxidising" and "reducing" flame, respectively?

92. Describe the preparation of carbon dioxide, and illustrate your method by an equation.

93. By what tests would you distinguish carbon dioxide from other gases? Give the characteristic properties of carbon dioxide and describe experiments to illustrate them.

94. How is carbon dioxide formed in Nature? What volume of carbon dioxide is formed by the combustion of 12 grams of carbon in oxygen? 16 litres of oxygen are converted into carbon dioxide, what volume will the gas occupy?

95. Describe and explain the preparation of carbon monoxide. Under what conditions is this gas formed during combustion?

96. How can you distinguish carbon monoxide from carbon dioxide and from hydrogen respectively?

97. Ten cubic feet of carbon dioxide are passed over red hot charcoal. What volume of carbon monoxide will be produced?

98. Explain the action taking place in a clear coke fire.

99. What is the composition of wood, and upon what does its value as fuel depend?

100. What advantages are gained by carbonising wood before using it as fuel? Describe the preparation of wood charcoal. What effect has the temperature and rate of burning upon the yield obtained from the charcoal heap? Why do we say that all our fuels are of vegetable origin?

101. What advantages are gained by converting coal into coke for metallurgical purposes?

102. How does "oven coke" differ from "gas coke"? What are the relative values of coke and coal as fuel?

103. Discuss the advantages to be derived from the use of "liquid fuel" in marine boilers.

104. Why would crude petroleum, as obtained from the wells, be unfit for use on board ship?

105. Into what two classes may the liquid fuels be divided?

106. Describe a method by which "heavy tar oil" may be burnt for heating or illuminating purposes.

107. Give an outline of the principal systems which have been employed for burning oil fuel.

108. How do coal gas, water gas, and generator gas differ in composition?

109. What is the *Calorie* and *British Thermal Unit?* In what relation do they stand to each other?

110. Calculate the thermal value of marsh gas on the assumption that it contains 75 per cent. carbon and 25 per cent. hydrogen. Why does the value so obtained differ from the value given by experiment? Give a formula for the calculation of the evaporative power of a fuel containing carbon, oxygen, and hydrogen.

111. Why does the calculated evaporative value of a fuel approach more nearly the actual value in the case of coke than with coal?

112. Describe the Mahler bomb calorimeter as used to determine the heat of combustion of various substances.

113. How does "calorific intensity" differ from "thermal value"?

114. Describe two methods for the isolation of atmospheric nitrogen.

115. 100 c.c. of *pure* nitrogen are required. Describe how you would prepare it, and give the quantity of material you would have to use.

116. How can nitrogen be distinguished from carbon dioxide?

117. What is the result of warming together a mixture of lime and sal-ammoniac?

118. A mixture of air and ammonia gas is given. How could you roughly determine the volume of ammonia present?

119. What is the composition of the fumes formed when ammonia gas comes in contact with hydrochloric acid gas? Why do we call the compounds formed by neutralising acids with ammonia, ammonium salts?

120. Describe the preparation and properties of nitrogen monoxide. Why is it often called "laughing gas"?

121. Why is nitrogen monoxide called an "endothermic" compound? How has its composition been determined?

122. Describe the preparation and physical properties of nitrogen dioxide. How can nitrogen dioxide be used as a test to distinguish between oxygen and nitrogen monoxide?

123. What compound is formed when nitrogen trioxide is dissolved in ice-cold water?

124. Give an equation for the preparation of nitrogen tetroxide. What happens when this gas is dissolved in water?

125. How does nitrogen pentoxide differ from the other oxides of nitrogen?

126. How is nitric acid prepared? Explain your process by an equation. What are the characteristic properties of nitric acid? Why do we call it an oxidising agent?

127. What is the specific gravity of the strongest form of nitric acid? At what strength can you redistil it without decomposition?

128. How is nitric acid formed in Nature? Explain a process by which saltpetre can be artificially prepared. By what tests can a nitrate be recognised?

129. Describe experimental evidence to prove that the pressure exerted by the atmosphere is 15 lb. on the square inch.

130. How can the barometer be used as a measure of altitude? Explain fully the means by which Lavoisier demonstrated that the air contained oxygen and nitrogen.

131. What is the percentage of oxygen in air by volume and by weight?

132. Give a description of the eudiometric analysis of air. How is the composition of air by weight determined?

133. $3\frac{1}{2}$ million tons of oxygen are daily abstracted from the atmosphere and replaced by CO_2. Explain why it is that the composition of the air does not alter.

134. Into what classes may "local" impurities in air be divided? Give examples. What important actions depend upon the organic matter present in air?

135. Why is ozone rarely, if ever, found in the air of towns?

136. How is it that the carbon dioxide formed during combustion and respiration in cities does not accumulate there?

137. Why is it practically impossible to render a room air-tight? What important effect has this upon health?

138. Gases diffuse and intermingle at a rate which depends upon their density. Why should the air in a room diffuse out through the walls, etc., whilst fresh air diffuses in?

139. Describe an experiment to show that air which has once been breathed is unfit for respiration.

140. Discuss the effect of various illuminants on the air of a room. Why is good ventilation of especial importance on board a warship?

141. Describe experiments to prove that combustion may be so rapid as to produce explosion.

142. To what causes is explosion due? Define the term explosion.

143. Into what classes can explosives be divided? Give an example of each.

144. How is saltpetre found in Nature? Explain the probable method of formation of the Indian nitre beds.

145. Describe and fully explain the preparation of potassium nitrate from Chili saltpetre.

146. Describe the method employed in purifying "grough saltpetre" at Waltham Abbey.

147. Explain the chemical decomposition taking place when KNO_3 is heated (*a*) to a moderate temperature, (*b*) to a very high temperature.

148. Why does charcoal deflagrate when saltpetre is fused upon it?

149. Explain why a charcoal made at 320° C. is more inflammable than a specimen prepared at 560° C. Why is cocoa powder brown instead of black?

150. How is charcoal for gunpowder prepared?

151. Which form of sulphur is always employed in the manufacture of gunpowder? What objection can be urged against the use of "flowers of sulphur"?

152. Describe the manufacture of R.F.G. powder.

153. What are the chief points which must govern the selection of the powder for any particular class of gun? Why would the class of powder used in a fieldpiece be totally unsuited for a 6-inch gun?

154. How would you distinguish between the "black prism," "E.X.E.," and "S.B.C.," even if unable to see the colour?

155. What led to the introduction of prism powder? Discuss the properties of the powders which give high muzzle velocities with low pressure.

156. Briefly describe the methods used to determine the pressure and muzzle velocity given by powders.

157. What characteristic difference is found in the nitration products obtained from glycerin and benzene respectively?

158. Give the formula for cellulose, and with an equation show the change which it undergoes when acted upon by the strongest nitric acid.

159. Why is strong sulphuric acid used in the manufacture of gun-cotton? Give the proportions by weight and by volume of the mixed acids used for this purpose. What ought their respective specific gravities to be?

160. Give a short account of the manufacture of gun-cotton by the Abel and "displacement" processes. What advantages are gained by the latter?

161. Given a sample of gun-cotton, how would you test it for (*a*) free acid, (*b*) collodion cotton, (*c*) unconverted cotton?

162. Why is the presence of a large percentage of collodion cotton in gun-cotton to be avoided?

163. How should gun-cotton be fired to develop the maximum explosive force?

164. Explain why gun-cotton is not used as a propellant in large guns.

165. Why is gun-cotton one of the safest explosives?

166. From what source is glycerin obtained? Give its formula.

167. Describe the preparation of nitro-glycerin, and illustrate your method by an equation.

168. Why would the substitution of ammonium nitrate for potassium nitrate in gunpowder render it practically smokeless? What objection is there to the use of ammonium nitrate?

169. What methods have been employed to render gun-cotton sufficiently "tame" for use in small arm ammunition?

170. What conditions must a powder fulfil to be suitable for use in modern guns?

171. What are the chief causes of erosion? Trace the steps taken to overcome this trouble with Service powders.

172. Describe in detail the manufacture of cordite.

173. How is picric acid prepared? What are its advantages as a bursting charge in shells?

174. Contrast the conditions necessary in a blasting explosive with those necessary in a good propellant.

175. Why is dynamite a better and more convenient explosive for blasting purposes than nitro-glycerin?

176. Explain the theoretical grounds for considering blasting gelatine a more perfect explosive than gun-cotton. What is the composition of this explosive?

177. What is the principle of the "Sprengel explosives"?

178. Describe the preparation of mercuric fulminate, and write an equation illustrating its decomposition.

179. From what source is sulphur obtained? Describe the process by which it is refined.

180. Why is sulphur said to be "dimorphous" What is the crystalline form of native sulphur and how can it be artificially prepared?

181. Describe the preparation of prismatic and plastic sulphur. What changes do these forms undergo when kept? Describe the changes which sulphur undergoes between the temperatures of 0° C. and 1,000° C.

182. What compounds does sulphur form with hydrogen? Describe an experiment to show that sulphur and hydrogen will combine directly.

183. Give an equation for the preparation of sulphuretted hydrogen. What are the characteristic properties of the gas? How has its composition been determined?

184. A pint of oxygen is completely converted into sulphur dioxide by burning sulphur in it. What will be the volume of the resulting gas?

185. How would you prepare and collect pure sulphur dioxide? Explain fully the bleaching action of sulphur dioxide, and show how sulphur dioxide may be converted into sulphur trioxide.

186. Give a short description of the manufacture of sulphuric acid.

187. What part do the oxides of nitrogen play in the manufacture of sulphuric acid?

188. What is the specific gravity of "B. O. V." acid? How is "B. O. V." acid converted into oil of vitriol? What are the properties of sulphuric acid?

189. Describe some of the most characteristic properties of chlorine.

190. Describe two methods for the preparation of chlorine, and give equations in explanation of the actions which take place.

191. On what does the bleaching action of chlorine depend?

192. What is formed when bodies containing hydrogen are burnt in chlorine?

193. Under what conditions do chlorine and hydrogen unite to form hydrochloric acid? Describe the preparation and properties of hydrochloric acid gas. How can chlorides be detected in a solution?

194. What is the composition of bleaching powder and how is it prepared?

195. Explain fully the action which takes place when chlorine gas is passed into a cold dilute solution of potassium hydroxide. What change takes place when this solution is boiled? If chlorine is passed into a hot concentrated solution of potassium hydroxide, what reaction takes place?

196. Why is potassium chlorate called an "endothermic" compound? What bearing has this on its use as a source of oxygen?

197. By what tests could you distinguish a chlorate from a chloride?

198. What are the chief sources of iodine and bromine? Describe their preparation.

199. How has fluorine been isolated? What are the chief properties of hydrofluoric acid?

200. How is silicon obtained? Describe the preparation of silicic acid. What is glass? Mention some of the natural forms of silica.

201. What are the chief native compounds of phosphorus? How is phosphorus prepared? Explain your process by equations.

202. What are the characteristic properties of phosphorus, and how does amorphous phosphorus differ from the ordinary variety? How is amorphous phosphorus prepared from the ordinary variety?

203. How many oxides of phosphorus are there? How would you obtain metaphosphoric, pyrophosphoric and orthophosphoric acids respectively from phosphorus pentoxide?

204. Give an equation for the preparation of phosphuretted hydrogen. Why is it spontaneously inflammable in air? How could you deprive it of this property? What is "Holmes' light?"

205. What special properties distinguish the metals from the non-metals? What elements may be classed with either group?

206. Why are metals rarely found free in Nature, and with what other elements are they generally associated?

207. State the general methods used in metallurgical processes, and distinguish clearly between "reducing" and "oxidising" actions.

208. What is understood by the terms "ductility," "tenacity," "specific gravity," "conductivity for heat and electricity" of metals? Give a list for each in their relative order.

209. Give a brief outline of the Periodic Law and its application to the classification of elements.

210. Point out in what directions microscopic study has thrown light upon the nature and properties of metals and alloys.

211. Enumerate the principal iron ores from which the metal is obtained in large quantities.

212. What is a "flux" and for what purpose is it employed in metallurgical processes?

213. Give a full description of the production of pig iron in the blast furnace.

214. Trace the chemical changes proceeding in the blast furnace.

215. How do white and grey pig iron differ in composition and qualities? Under what circumstances does a furnace yield the one or the other?

216. What is the difference between ordinary cast iron and malleable cast iron? How are malleable castings prepared?

217. Outline the process by which pig iron is converted into "merchant bar" iron. What changes in composition of the metal are brought about?

218. Explain the terms "cold shortness" and "red shortness" as applied to iron.

219. In what relation does steel stand to cast iron and wrought iron? What is "blister steel" and "crucible steel"?

220. Describe in detail the production of an armour plate.

221. Contrast the differences in procedure and reactions taking place in the acid and basic Bessemer processes.

222. Under what circumstances would spiegeleisen and ferro-manganese respectively be used for re-carburising?

223. Give a brief outline of the acid "open hearth" process.

224. What difficulties are met with in the production of large sound steel ingots? Refer briefly to any methods which have been adopted to overcome these troubles.

225. Trace the important influences which carbon has on the cooling curve of iron.

226. What do you understand by the "critical point" in the cooling of steel? Trace the difference in structure between a "saturated" steel (*a*) quenched just above the critical point, (*b*) slowly cooled from below this point.

227. Summarise the effects of phosphorus, sulphur and silicon respectively on iron and steel.

228. Why is manganese of such great importance to the steel manufacturer?

229. Give a short account of the Welsh process of copper smelting.

230. Explain fully the chemical principles involved in the Welsh process.

231. How may copper be recovered from spent pyrites?

232. What are the physical properties of pure copper? Mention the most common impurities in the commercial metal, and state their effect upon it.

233. What chemical principles are involved in the "roasting and reaction" process for the production of lead?

234. What is "hard" lead? How is it softened?

235. Outline two processes which are employed for the recovery of small quantities of silver from commercial lead.

236. What class of waters are dangerous to store in lead cisterns?

237. How would you determine whether a sample of drinking water contained any lead?

238. What advantage has lead for use in the manufacture of rifle bullets?

239. Describe the manufacture of small shot.

240. Lead combines with oxygen in several proportions; give the formulæ and preparation of the principal compounds.

241. What is the difference between "white" and "red" lead? To what purposes are they put?

242. What preliminary treatment is necessary with most tin ores before reduction is possible?

243. Give a brief outline of the metallurgical processes to which the prepared tin ore is subjected for the production of the metal.

244. What is the action of the most common acids on tin?

245. Why is it essential that zinc blende shall undergo an oxidising roasting before the metal can be obtained from it?

246. Outline the Belgian process for the production of zinc.

247. Briefly describe the physical and chemical properties of zinc. What conditions are necessary for the successful rolling of the metal?

248. What is the source of the metal mercury? How is it obtained pure?

249. For what purposes is mercury used extensively?

250. Distinguish between the mercurous and mercuric compounds, and show how the one can be converted into the other.

251. Give the formulæ and chemical names for the following:—Corrosive sublimate, calomel, and vermilion.

252. Although aluminium occurs most abundantly in Nature, it has only recently been obtained on a commercial scale. Why is this?

253. Explain fully the production of aluminium in the electric furnace.

254. What properties give to aluminium a special value, and for what purposes is it finding employment?

255. What methods have been successfully employed in extracting gold?

256. What action has nascent chlorine on gold, and how would you proceed to dissolve up a gold ornament?

257. What is "Purple of Cassius"? What use has it in the manufacture of certain kinds of glass?

258. Why are gold and platinum classed with the noble metals?

259. What is meant by "parting" as applied to the metallurgy of gold? Outline three methods by which it is accomplished.

260. With what metal is silver generally found? Describe the cupellation process.

261. Silver does not directly combine with oxygen; to what cause is the tarnishing of silver due?

262. What is "lunar caustic"? What happens when a solution of common salt is added to silver nitrate?

263. What special properties have the salts of silver that render them useful in photographic processes?

264. In the solar spectrum, what rays are most chemically active?

265. What chemical change does silver chloride undergo when acted on by white light? Is this change always apparent to the eye?

266. What advantages has the dry plate process in photography?

267. By what means is the developed image on a plate made permanent?

268. What materials are used in the ferrotype and carbon processes?

269. What substances must not be fused in platinum crucibles, and why?

270. What special properties does the metal platinum possess, and to what uses are these put?

271. What action has nitric acid on antimony, bismuth and tin?

272. What are the sources of magnesium in Nature, and to what uses is the metal put?

273. Given the metal magnesium, how would you prepare the sulphate, oxide, carbonate, and nitrate?

274. Give the composition of dolomite, Epsom salts, magnesite and meerschaum.

275. Give the name and composition of the chief compounds of calcium found in Nature.

276. Which native compound of calcium is principally used for the formation of its salts, and why?

277. How is quicklime prepared, and how converted into slaked lime? How do impurities affect the result?

278 Carbon dioxide is bubbled through a solution of lime water; explain what happens, also state what further changes may take place.

279. Account for the hardness of some waters, and explain how it may sometimes be remedied.

280. What is plaster of Paris? How is it made, and what precautions must be taken in its preparation? What properties render it valuable for taking casts?

281. What compounds of barium and strontium are used in the Arts, and to what purpose?

282. What are the members of the alkali group of metals? In what properties do they resemble each other?

283 How can the metals potassium and sodium be obtained on a commercial basis?

284. Outline the modern electrolytic method of preparing caustic soda.

285. Describe the manufacture of commercial sodium carbonate by the "black ash" and "ammonia-soda" processes.

286. What happens when a platinum wire moistened with a solution containing calcium is heated in the non-luminous flame of a Bunsen burner? What differences are noted when solutions of barium or strontium salts are used?

287. Describe what is observed when a beam of white light is examined by means of a prism.

288. Describe the method of applying the spectroscope to the study of (1) solids, (2) gases. What conditions of the substances modify the effects observed?

289. Explain what is meant by the so-called Fraunhofer's lines.

290. How can the spectra of various metals be obtained, and what evidence is there for supposing that iron exists in the atmosphere of the sun?

291. A Bunsen flame coloured with sodium vapour gives two bright yellow lines. How can this experiment be altered to obtain a reversion of this phenomenon?

292. What do you understand by the terms "alloy" and "amalgam"?

293. Give illustrations of the advantages gained by alloying certain of the common metals.

294. What is meant by the "eutectic" alloy of a series?

295. Draw the freezing point curve for the copper silver alloys, and describe generally the three characteristic types of alloys in the series.

296. How is brass prepared? What material differences are there between standard brass and Muntz metal?

297. What would you consider an ideal composition for metal condenser tubes, and state your reasons?

298. Give a short account of the principal copper-tin alloys.

299. What are the advantages of manganese bronze for propellor blades?

300. To what special feature may the value of anti-friction metals be primarily ascribed?

301. Give the composition of the common lead-tin alloys. Which alloy is most suitable for plumbers' "wiped joints," and why?

302. Give the approximate composition of any alloys used for special purposes.

303. What chemical changes are believed to take place during the rusting of iron when exposed to atmospheric influences?

304. Outline the causes which lead to "pitting" in boiler plates.

305. What are rust cones, and what causes lead to their formation?

306. Summarise the methods by which iron may be protected from corrosion.

307. Describe the processes for "galvanising" and "tinning" iron plates.

308. What essential difference is there in the protection afforded by zinc and that afforded by tin?

309. What precautions should always be taken in applying protective compositions to ships?

310. Criticise the use of poisons in anti-fouling compositions.

311. What objections can be urged against copper and its compounds in anti-fouling compositions?

312. What happens when white light falls on an opaque body, and on a transparent body?

313. Describe the process of manufacturing white lead. What advantages does zinc white have over white lead?

314. What chemical change takes place in the blackening of white lead?

315. Why are the black pigments so permanent?

316. What precautions must be taken when red oxide of iron is used for painting ironwork, and why is it necessary to have the substance pure?

317. What is red lead? To what special purposes is it put?

318. Give the composition of vermilion. Describe how it can be prepared from cinnabar and metallic mercury.

319. What advantages does cadmium yellow possess over yellow ochre?

320. Give a list of the green pigments containing copper. What other metal is generally associated with copper?

321. What is the source of indigo, and how is it used in processes of dyeing? What acid is used to dissolve indigo?

TABLE OF ELEMENTS.

Elements.	Symbol.	Atomic Weight.		Specific Heat.
		O = 16	H = 1	
Aluminium	Al	27·1	26·9	0·219
Antimony	Sb	120·2	119·3	0·049
Argon	A	39·9	39·6	—
Arsenic	As	75·0	74·4	0·083
Barium	Ba	137·4	136·4	—
Bismuth	Bi	208·5	206·9	0·030
Boron	B	11	10·9	0·254
Bromine	Br	79·96	79·36	—
Cadmium	Cd	112·4	111·6	0·054
Cæsium	Cs	132·9	131·9	0·048
Calcium	Ca	40·1	39·8	0·180
Carbon	C	12·00	11·91	variable
Cerium	Ce	140·25	139·2	0·044
Chlorine	Cl	35·45	35·18	—
Chromium	Cr	52·1	51·7	0·104
Cobalt	Co	59·0	58·56	0·103
Columbium	Cb	94	93·3	—
Copper	Cu	63·6	63·1	0·093
Erbium	Er	166	164·8	—
Fluorine	F	19	18·9	—
Gadolinium	Gd	156	155	—
Gallium	Ga	70	69·5	0·079
Germanium	Ge	72·5	71·9	0·074
Glucinum	Gl	9·1	9·03	—
Gold	Au	197·2	195·7	0·032
Helium	He	4	4	—
Hydrogen	H	1·008	1·000	—
Indium	In	115	113·1	—
Iodine	I	126·9	125·90	0·054
Iridium	Ir	193·0	191·5	0·032
Iron	Fe	55·9	55·5	0·112
Krypton	Kr	81·8	81·2	—
Lanthanum	La	138·9	137·9	0·045
Lead	Pb	206·9	205·35	0·031
Lithium	Li	7·03	6·98	0·940
Magnesium	Mg	24·36	24·18	0·245
Manganese	Mn	55·0	54·6	0·122
Mercury	Hg	200·0	198·5	0·033
Molybdenum	Mo	96·0	95·3	0·066

TABLE OF ELEMENTS—(*continued*).

Elements.	Symbol.	Atomic Weight.		Specific Heat.
		O = 16	H = 1	
Neodymium	Nd	143·6	142·5	—
Neon	Ne	20	19·9	—
Nickel	Ni	58·7	58·3	0·109
Nitrogen	N	14·04	13·93	—
Osmium	Os	191	189·6	0·031
Oxygen	O	16·00	15·88	—
Palladium	Pd	106·5	105·7	0·059
Phosphorus	P	31·0	30·77	0·202
Platinum	Pt	194·8	193·3	0·032
Potassium	K	39·15	38·86	0·166
Praseodymium	Pr	140·5	139·4	—
Radium	Rd	225	223·3	—
Rhodium	Rh	103·0	102·2	0·058
Rubidium	Rb	85·5	84·8	—
Ruthenium	Ru	101·7	100·9	0·061
Samarium	Sm	150·3	148·9	—
Scandium	Sc	44·1	43·8	—
Selenium	Se	79·2	78·6	0·084
Silicon	Si	28·4	28·2	0·165
Silver	Ag	107·93	107·12	0·056
Sodium	Na	23·05	22·88	0·293
Strontium	Sr	87·6	86·94	—
Sulphur	S	32·06	31·83	—
Tantalum	Ta	183	181·6	—
Tellurium	Te	127·6	126·6	0·048
Terbium	Tb	160	158·8	—
Thallium	Tl	204·1	202·6	0·032
Thorium	Th	232·5	230·8	0·027
Thulium	Tm	171	169·7	—
Tin	Sn	119·0	118·1	0·052
Titanium	Ti	48·1	47·7	0·112
Tungsten	W	184	182·6	0·034
Uranium	U	238·5	236·7	—
Vanadium	V	51·2	50·8	0·115
Xenon	Xe	128	127	—
Ytterbium	Yb	173·0	171·7	—
Yttrium	Yt	89·0	88·3	—
Zinc	Zn	65·4	64·9	0·093
Zirconium	Zr	90·6	89·9	0·066

Arrangement of the Elements in the Periodic System.

GROUP.

Series.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.			O
1							H 1				He 4
2	Li 7		B 11	C 12	N 14	O 16	F 19				Ne 20
3	Na 23	Mg 24·4	Al 27	Si 28·4	P 31	S 32	Cl 35·4				Ar 40
4	K 39	Ca 40	Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 58·7	
5	Cu 63·6	Zn 65·4	Ga 70	Ge 72·5	As 75	Se 79	Br 80				Kr 81·6
6	Rb 85·5	Sr 87·6	Yt 89	Zr 90·6		Mo 96		Ru 101·7	Rb 103	Pd 106	
7	Ag 108	Cd 112·4	In 115	Sn 119	Sb 120	Te 127	I 127				X 128
	Cs 133	Ba 137·4	La 139	Ce 140			Sa 150·3				
				Er 166							
10			Yb 173		Ta 183	W 184		Os 191	Ir 193	Pt 195	
11	Au 197	Hg 200	Tl 204	Pb 207	Bi 208·5						
12				Th 232·5		U 238·5					
Hydrogen or Halogen Compound	MX	MX_2	MX_3	MX_4	MX_3	MX_2	MX				
Highest Oxygen Compound	M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7	MO_3	MO_2	MO	

WEIGHTS AND MEASURES.

AVOIRDUPOIS WEIGHT.

Drachms.	oz.	lbs.	qrs.	cwts.	ton.	French Grammes.
1 =	·0625 =	·0039 =	·000139 =	·000035 =	·00000174 =	1·771846
16 =	1 =	·0625 =	·00223 =	·000558 =	·000028 =	28·34954
256 =	16 =	1 =	·0357 =	·00893 =	·000447 =	453·59
7,168 =	448 =	28 =	1 =	·25 =	·0125 =	12,700
28,672 =	1,792 =	112 =	40 =	1 =	·05 =	50,802
573,440 =	35,840 =	2,240 =	80 =	20 =	1 =	1,016,048

LONG MEASURE.

Ins.	feet.	yards.	fath.	poles.	furl.	mile.	French metres.
1 =	·083	·02778 =	·0139 =	·005 =	·000126 =	·0000158 =	·0254
12 =	1	·333 =	·1667 =	·0606 =	·00151 =	·0001894 =	·3048
36 =	3	1 =	·5 =	·182 =	·00454 =	·000568 =	·9144
72 =	6	2 =	1 =	·364 =	·0091 =	·001136 =	1·8287
198 =	16½	5½ =	2¾ =	1 =	·025 =	·003125 =	5·0291
7,920 =	660	220 =	110 =	40 =	1 =	·125 =	201·16
63,360 =	5,280	1,760 =	880 =	320 =	8 =	1 =	1 609·315

MEASURE OF CAPACITY.

Pints.	galls.	cubic ft.	litres.
1 =	·125 =	·02 =	·5676
8 =	1 =	·1604 =	4·541
16 =	2 =	·3208 =	9·082
64 =	8 =	1·283 =	36·32816
512 =	64 =	10·264 =	290·625
2,560 =	320 =	51·319 =	1,453·126
5,120 =	640 =	102·64 =	2,906·25

1 gallon = 277¼ cubic in. = 16 cubic ft. = 10 lbs. dist. water = 4·543458 litres.
cubic ft. × 6·2355 = gallons.
1 grain = ·064799 gram. 1 lb. avoir. = ·453593 kilogram.

USEFUL DATA.

1 lb. avoir. = 16 oz. = 7,000 grains = 453·59 grammes = 1·21527 lb. troy.
1 lb. troy = 12 ,, = 5,760 ,, = 373·242 ,, = 0·82285704 lb. avoir.
1 oz. avoir. = 437·5 grains = 28·35 grammes = 0·9114583 oz. troy.
1 cubic cent. = ·0610270734 cubic in. = ·282 fl. drms. = ·00176 pint = ·0352 fl. oz.
1 cubic ft. = 28315·3 c.c. = 6·2321 gallons = 28·3153 litres = 997·1364 fl. oz. = 49·8568 pints.
1 gallon = ·16046 cubic feet = 277·274 cubic in. = 4·54346 litres.
1 cubic in. = 16·386 c.c. = 4·616 fl. oz. = ·0164 litre = ·02885 pint.
1 litre. = ·035316 cubic ft. = ·220096 gallon = 61·0270 cubic in. = 1·761 pint.
1 fl. oz. = 28·396 c.c. = 1·7329 cubic in.
1 pint = 567·919 c.c. = ·020057 cubic ft. = 34·659 cubic in. = ·567920 litre.
1 gramme = ·002204 lb. = ·03527 oz. = 15·432348 grains.

Table for Converting Degrees of the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.
—90°	—130°	40°	104	170	338°
85	121	45	113	175	347
80	112	50	122	180	356
75	103	55	131	185	365
70	94	60	140	190	374
65	85	65	149	195	383
60	76	70	158	200	392
55	67	75	167	205	401
50	58	80	176	210	410
45	49	85	185	215	419
40	40	90	194	220	428
35	31	95	203	225	437
30	22	100	212	230	446
25	13	105	221	235	455
20	— 4	110	230	240	464
15	+ 5	115	239	245	473
10	14	120	248	250	482
— 5	23	125	257	255	491
0	32	130	266	260	500
+ 5	41	135	275	265	509
10	50	140	284	270	518
15	59	145	293	275	527
20	68	150	302	280	536
25	77	155	311	285	545
30	86	160	320	290	554
35	95	165	329	295	563

To convert °F to °C $\frac{(°F - 32) \times 5}{9} = °C.$

To convert °C to °F $\frac{°C \times 9}{5} + 32 = °F.$

Table of the corresponding Heights of the Barometer in Millimeters and English inches.

Millimeters.	=	English inches.	Millimeters.	=	English inches.	Millimeters.	=	English inches.
720	=	28·347	739	=	29·095	758	=	29·843
721	=	28·386	740	=	29·134	759	=	29·882
722	=	28·425	741	=	29·174	760	=	29·922
723	=	28·465	742	=	29·213	761	=	29·961
724	=	28·504	743	=	29·252	762	=	30·000
725	=	28·543	744	=	29·292	763	=	30·039
726	=	28·583	745	=	29·331	764	=	30·079
727	=	28·622	746	=	29·370	765	=	30·118
728	=	28·662	747	=	29·410	766	=	30·158
729	=	28·701	748	=	29·449	767	=	30·197
730	=	28·740	749	=	29·488	768	=	30·236
731	=	28·780	750	=	29·528	769	=	30·276
732	=	28·819	751	=	29·567	770	=	30·315
733	=	28·858	752	=	29·606	771	=	30·355
734	=	28·898	753	=	29·645	772	=	30·394
735	=	28·937	754	=	29·685	773	=	30·433
736	=	28·976	755	=	29·724	774	=	30·473
737	=	29·016	756	=	29·764	775	=	30·512
738	=	29·055	757	=	29·803			

Density of Sea Water on various Scales.

Density or specific gravity 1·025 at 0° C = $\frac{1}{32}$ salinometer = 10° densimeter.

" " 1·05 " = $\frac{2}{32}$ " = 20° "

" " 1·09 " = $\frac{3}{32}$ " = 30° "

" " 1·2 " = $\frac{7}{32}$ " = 70° "

Table of the Tension of Aqueous Vapour expressed in Inches of Mercury, at 32° F., *for each degree* F., *between* 0° *and* 100°.

Temp. °F.	Inches of Mercury.	Temp. °F.	Inches of Mercury.	Temp. °F.	Inches of Mercury.	Temp. °F.	Inches of Mercury.
0	0·0439	26	0·1395	51	0·3742	76	0·8964
1	0·0459	27	0·1457	52	0·3882	77	0·9266
2	0·0481	28	0·1522	53	0·4026	78	0·9577
3	0·0503	29	0·1589	54	0·4175	79	0·9898
4	0·0526	30	0·1660	55	0·4329	80	1·0227
5	0·0551	31	0·1733	56	0·4488	81	1·0566
6	0·0576	32	0·1810	57	0·4653	82	1·0915
7	0·0603	33	0·1883	58	0·4822	83	1·1274
8	0·0630	34	0·1959	59	0·4997	84	1·1643
9	0·0659	35	0·2038	60	0·5178	85	1·2023
10	0·0689	36	0·2119	61	0·5364	86	1·2413
11	0·0721	37	0·2204	62	0·5556	87	1·2815
12	0·0753	38	0·2291	63	0·5755	88	1·3228
13	0·0788	39	0·2381	64	0·5959	89	1·3652
14	0·0823	40	0·2475	65	0·6170	90	1·4088
15	0·0861	41	0·2571	66	0·6388	91	1·4537
16	0·0899	42	0·2672	67	0·6612	92	1·4998
17	0·0940	43	0·2775	68	0·6843	93	1·5471
18	0·0982	44	0·2882	69	0·7081	94	1·5958
19	0·1027	45	0·2993	70	0·7327	95	1·6457
20	0·1073	46	0·3108	71	0·7580	96	1·6971
21	0·1121	47	0·3226	72	0·7841	97	1·7498
22	0·1171	48	0·3349	73	0·8109	98	1·8039
23	0·1223	49	0·3476	74	0·8386	99	1·8595
24	0·1278	50	0·3607	75	0·8671	100	1·9170
25	0·1335						

Boiling Point and Latent Heat of Water under varying Pressures.

Pressure.	Boiling Point.	Latent Heat.
1 atmosphere	212° Fahr.	966 thermal units.
2 ,,	249° ,,	940 ,,
3 ,,	273° ,,	923 ,,
4 ,,	291° ,,	910 ,,
5 ,,	306° ,,	900 ,,
6 ,,	319° ,,	891 ,,

Table for Correction of Volumes of Gases for Temperature, giving the Divisor for the Formula.

$$V^1 = \frac{V + B}{760 \times (1 + \delta t)}$$

$\delta = 0{\cdot}003665$ = co-efficient of expansion for gases.

t	760 × (1 + δt)	Log [760 × (1 + δt)].	t	760 × (1 + δt)	Log [760 × (1 + δt)].	t	760 × (1 + δt)	Log [760 × (1 + δt)].
°C			°C			°C		
14·0	798·99	2·9025	18·0	810·13	2·9085	22·0	821·27	2·9144
2	799·55	8	2	810·69	8	2	821·88	7
4	800·10	2·9031	4	811·25	2·9091	4	822·39	2·9150
6	800·66	4	6	811·80	4	6	822·95	3
8	801·22	7	8	812·36	7	8	823·50	6
15·0	801·78	2·9040	19·0	812·92	2·9100	23·0	824·06	9
2	802·33	3	2	813·47	3	2	824·62	2·9162
4	802·89	6	4	814·03	6	4	825·17	5
6	803·45	9	6	814·59	9	6	825·73	8
8	804·00	2·9052	8	815·15	2·9112	8	826·29	2·9171
16·0	804·56	5	20·0	815·70	5	24·0	826·84	4
2	805·12	8	2	816·26	8	2	827·40	7
4	805·68	2·9061	4	816·82	29·121	4	827·96	2·9180
6	806·23	4	6	817·37	4	6	828·52	3
8	806·79	7	8	817·93	7	8	829·07	6
17·0	807·35	2·9070	21·0	818·49	2·9130	25·0	829·63	9
2	807·90	3	2	819·05	3	2	830·19	2·9191
4	808·46	6	4	819·60	6	4	830·74	4
6	809·02	9	6	820·16	9	6	831·30	7
8	809·58	2·9082	8	820·72	2·9141	8	831·86	2·2900

Table of Gaseous Volumes, Composition of Gases, Temperature, &c., for Modern Smokeless Explosives.

Name of Explosive.	Calories per gram.	Gases evolved in c.c. per gram, calculated at 0°C and 760 m.m.			Percentage Composition of Permanent Gases.					Co-efficient of potential energy.	Density of loading.	Pressure, tons.
		Permanent.	Water vapour.	Total volume.	CO_2.	CO.	H.	CH_4.	N.			
Nitroglycerin	1652	464	257	741	63·0	(yields	4·0 of	oxygen)	33·0	1224	·017	—
Nitrocellulose (13·3 N.)	1061	673	203	876	22·3	45·4	14·9	0·5	16·9	929	·017	—
,, (strand)	1068	689	163	852	29·1	32·9	20·1	0·75	17·5	910	—	3
,, (pellet)	1037	725	162	887	25·7	39·3	18·7	—	16·2	919	—	3
Nitrocellulose powders—												
R. R. Rottweil, German	896	815	178	993	17·9	43·45	24·4	0·6	13·6	890	·05	3·3
,, ,,	931	759	163	922	25·1	36·55	20·2	4·7	13·4	859	·22	16·5
,, ,,	1037	681	135	816	35·0	27·8	12·6	11·1	13·4	846	·45	40·5
Troisdorf, German	943	700	195	895	18·7	47·9	17·4	0·8	15·2	844	·017	—
Walsrode	1014	669	206	875	21·3	48·2	10·1	0·4	14·8	887	·008	—
Nitrocellulose with metallic nitrates—												
B. N., French	833	738	168	906	13·2	53·1	19·4	0·7	13·6	755	·017	—
,,	1003	616	206	822	28·1	32·4	21·9	0·8	16·8	824	—	6
E. C., English	800	420	154	574	22·9	40·6	15·5	0·5	20·5	459	·017	—
,,	762	718	158	876	11·9	52·1	23·9	0·5	11·6	667	·008	—
Schultze	786	576	160	736	15·5	46·7	23·0	0·8	14·0	578	·008	—
Imperial Schultze	742	763	152	915	8·9	52·7	27·0	1·0	10·4	679	·008	—
Amberite	745	635	156	791	12·0	50·0	25·5	0·4	12·1	589	·008	—
Cannonite	845	725	146	871	14·6	49·9	22·2	0·6	12·7	736	·008	—

Nitrocellulose with organic nitro-compounds—												
S. S.	799	584	150	734	18·2	45·4	20·0	0·7	15·7	586	·017	—
,,	755	695	131	816	11·8	51·3	23·7	0·8	12·4	616	·008	—
Rifleite, English	864	766	159	925	14·2	50·1	20·5	0·3	14·9	799	·017	—
Shot gun rifleite	896	705	169	874	19·0	45·3	21·5	0·8	13·4	783	·008	—
Kynoch's smokeless	807	600	126	726	14·8	49·5	18·8	0·7	16·2	586	·008	—
Nitrocellulose with nitroglycerin—												
Cordite, nitroglycerin, 60%	1280	627	236	863	26·7	39·8	12·8	0·5	20·2	1105	·017	—
,, insol. nitrocellulose, 35%												
,, nitroglycerin, 58%	1253	647	235	882	24·9	40·3	14·8	0·7	19·8	1105	·017	—
,, insol. nitrocellulose, 37%												
,, ,, ,,	1272	678	200	878	27·1	34·3	17·5	0·3	20·7	1117	·05	3
,, ,, ,,	1242	692	179	871	31·7	28·9	18·9	1·6	18·8	1082	·25	21
,, ,, ,,	1360	624	175	799	41·9	19·1	12·1	7·05	19·85	1086	·5	53
,, ,, ,, (size ·255)	1284	692	194	886	27·0	34·2	26·9	trace	12·0	1137	—	10
Ballistite, nitroglycerin, 50%, English	1349	568	249	817	36·5	32·5	8·4	0·2	22·4	1102	·017	—
,, sol. nitrocell., 50%												
,, ,, German	1291	591	231	822	33·1	35·4	10·1	0·5	20·9	1061	·017	—
,, ,, Italian	1317	581	245	826	35·9	32·6	9·0	0·3	22·2	1088	·017	—
,, ,,	1365	610	197	807	37·3	27·8	19·1	trace	15·8	—	—	6
,, nitroglycerin, 50%	1410	550	247	797	41·8	27·5	6·0	—	24·7	1124	·017	—
,, insol. nitrocell., 50%												
,, sporting	1286	591	234	825	32·2	37·1	10·1	0·4	20·2	1061	·008	—
Cordite M. D., nitroglycerin, 30%	1031	726	215	941	16·3	50·4	19·7	—	13·6	970	·008	—
,, insol. nitrocell., 65%												
,, ,,	1036	782	173	955	18·15	42·6	23·15	0·35	15·75	989	·05	2·7
,, ,,	1041	745	143	888	26·75	33·65	19·8	4·65	15·15	924	·25	21
,, ,,	1190	676	134	810	36·6	24·8	11·9	10·7	16·0	964	·45	43
Experimental—												
Nitroglycerin. 20%	1159	637	227	864	26·6	40·8	12·0	0·1	20·5	1001	·017	—
Insol. nitrocell., 80%												
Nitroglycerin, 20%	1062	675	226	901	21·7	45·4	15·7	0·1	17·1	957	·017	—
Sol. nitrocell., 80%												

Note.—Where pressure in tons is given, the figures are from Sir Andrew Noble's experiments. In other cases, from the work of M'Nab and Ristori.

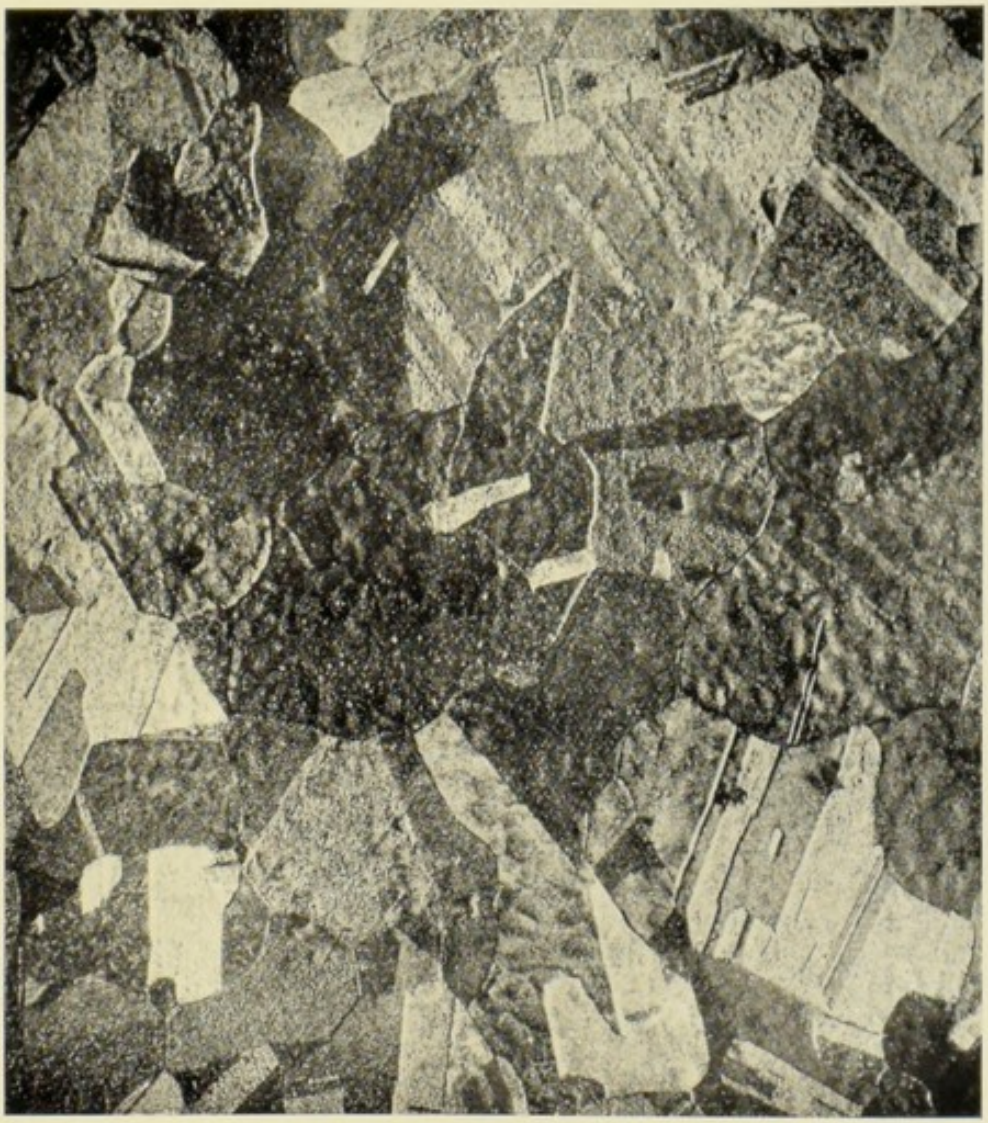


PLATE II.

Silver (× 15).

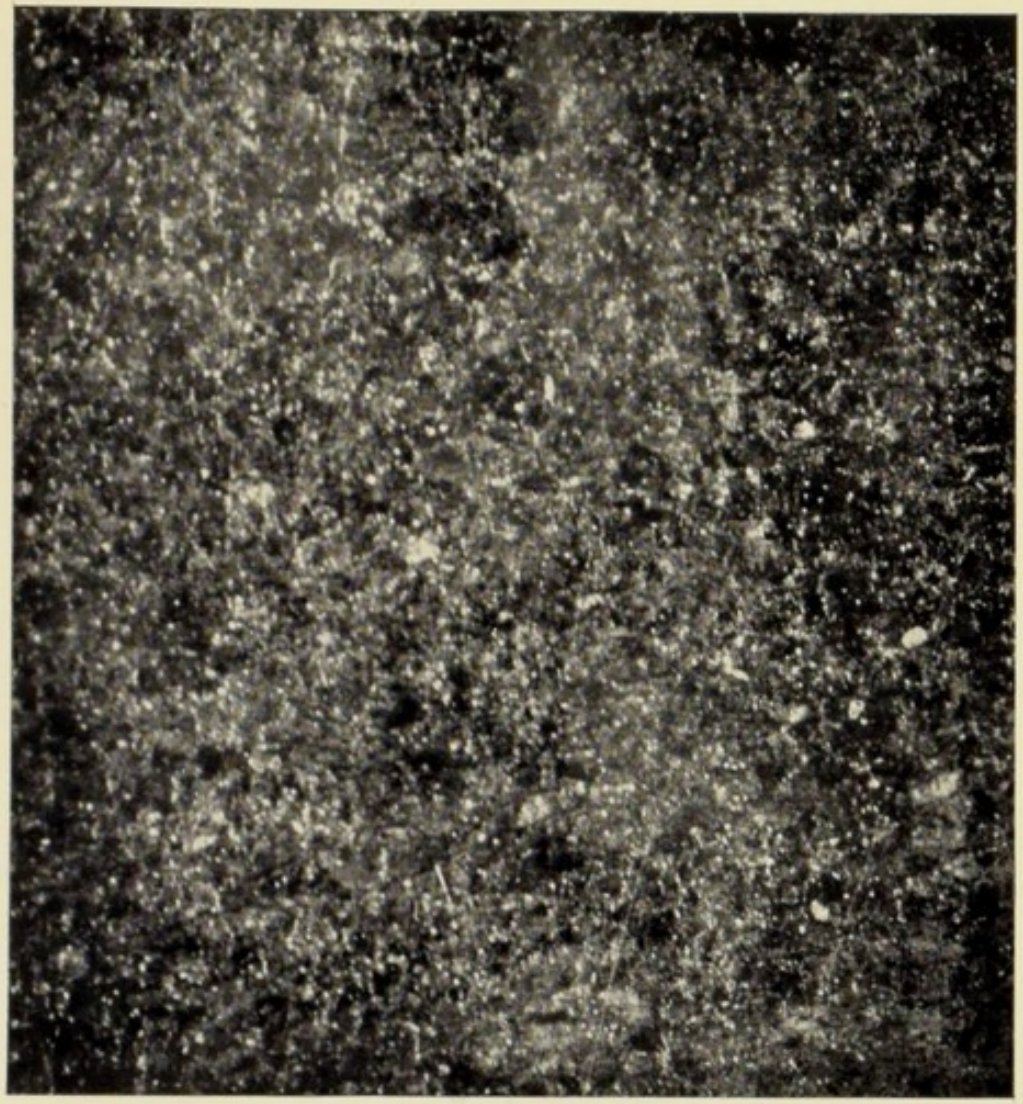


PLATE III.

HARD-ROLLED BRASS (×50).

PLATE IV.

ANNEALED BRASS (×50).

PLATE V.

ANNEALED BRASS (× 50).

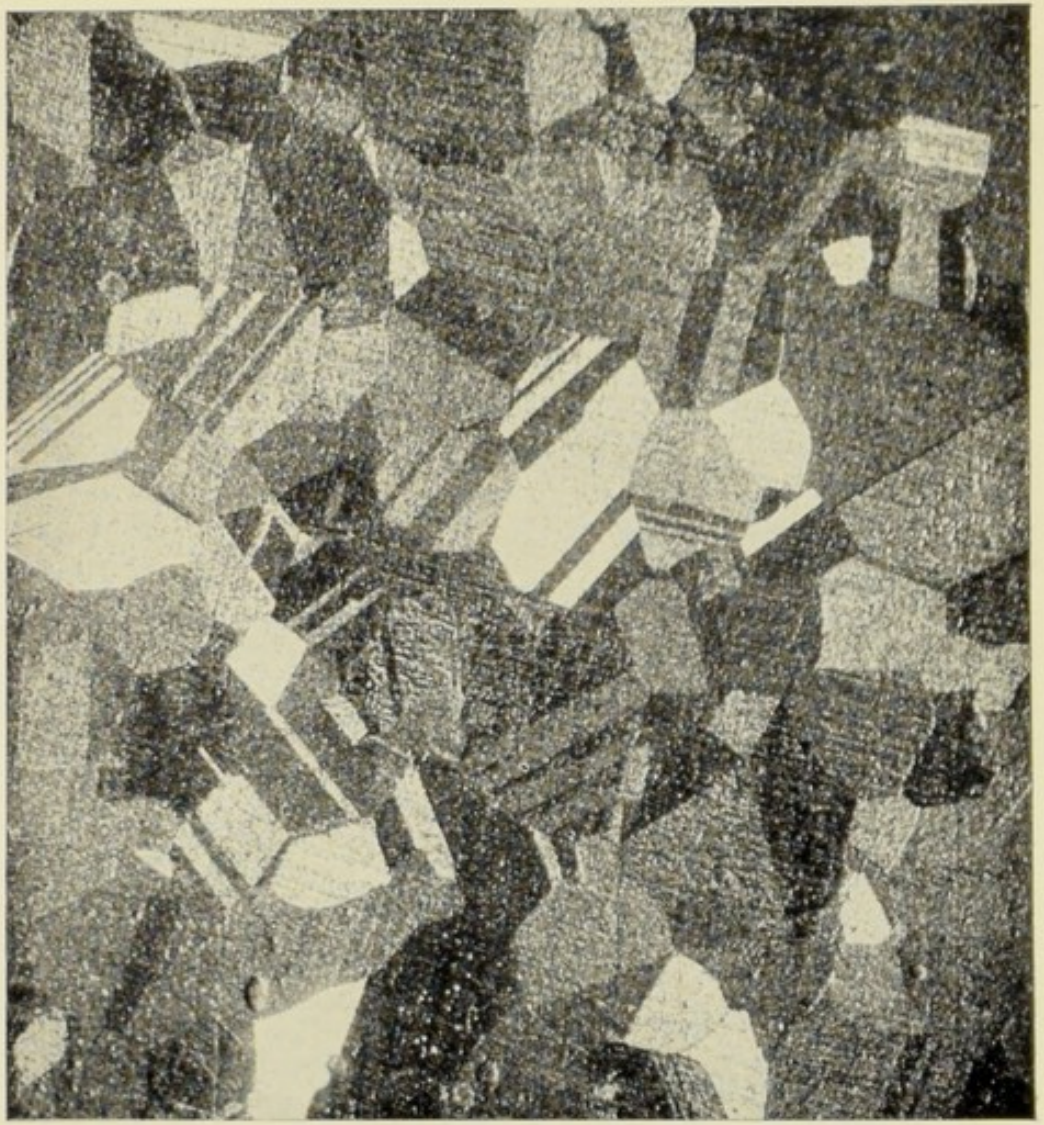
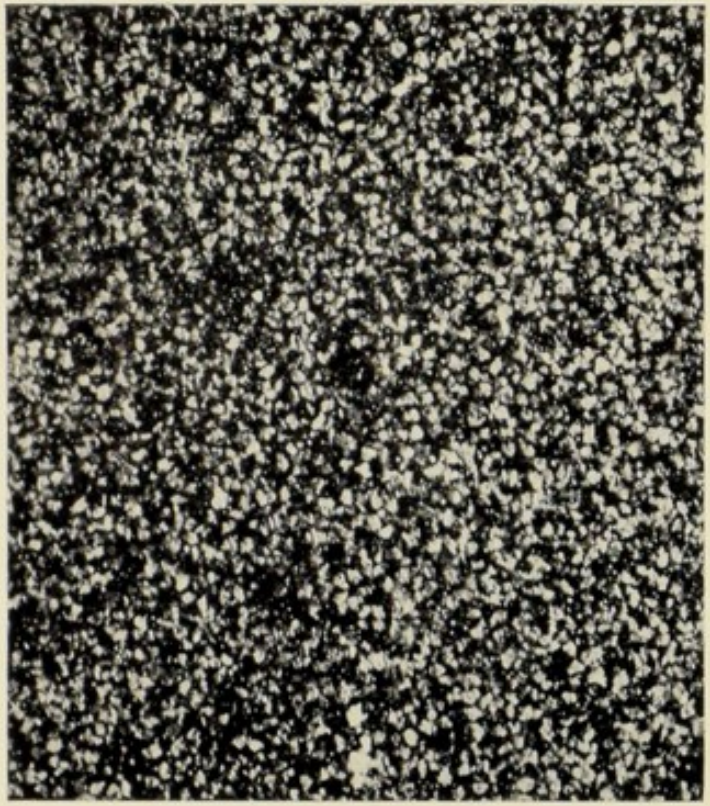


PLATE VI.

ANNEALED BRASS (× 50).



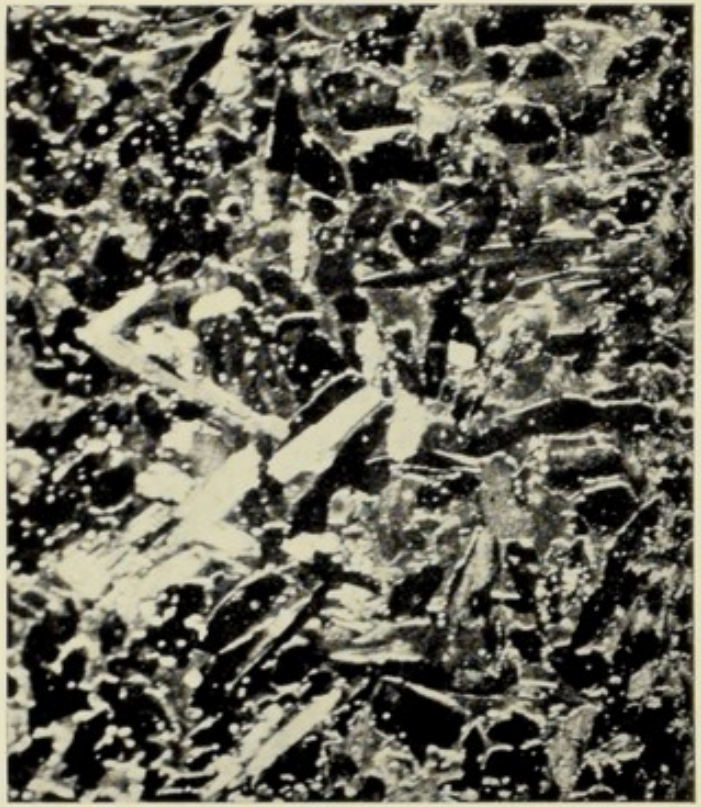


PLATE IX.

HARD ROLLED (×50). GUN METAL. ANNEALED (×50).

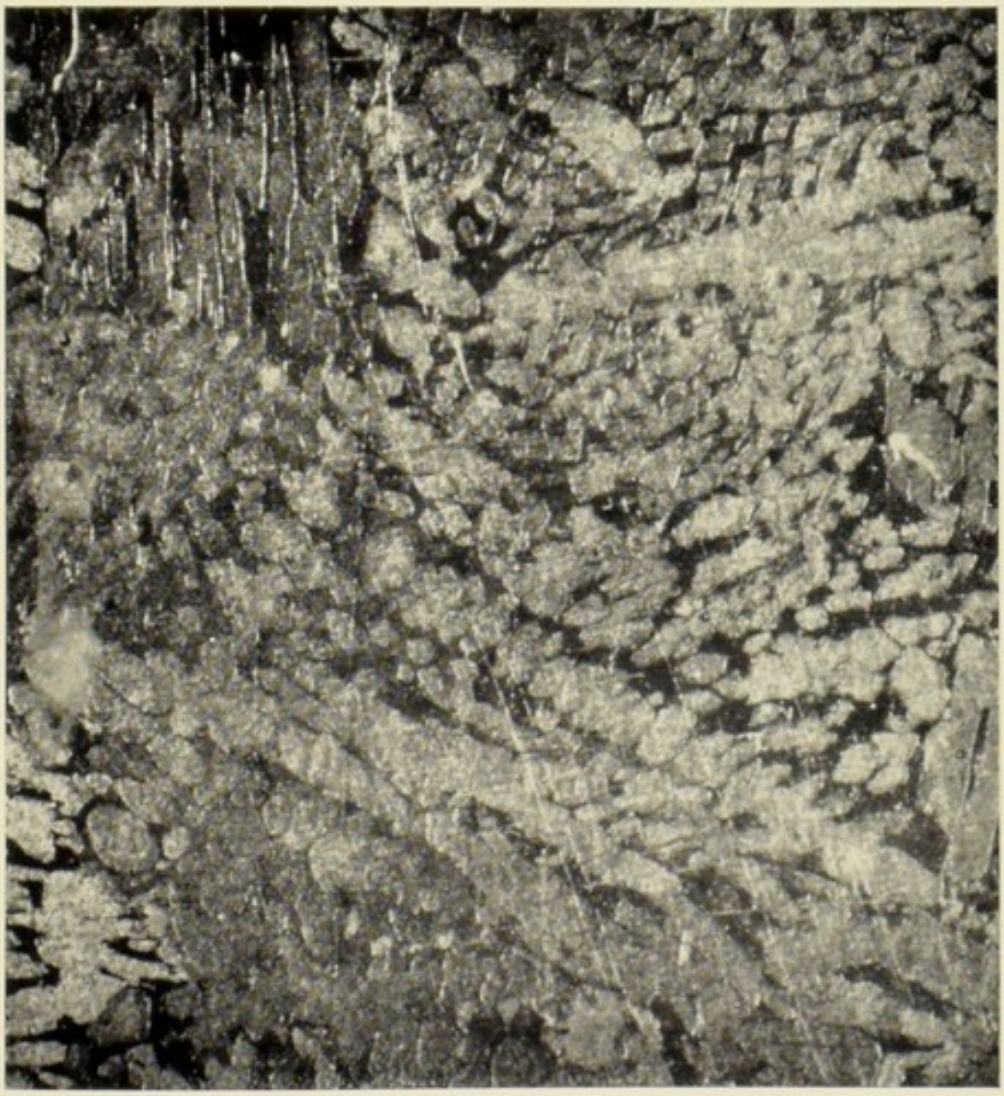


PLATE X.

ANNEALED MUNTZ METAL (×50).

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