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A Manual of Chemistry

Inorganic and Organic

For the Use of Students of Medicine

Arthur P. Luff, M.D., B.Sc. (Lond). M.R.C.P.


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MANUAL OF CHEMISTRY.

A MANUAL
OF
CHEMISTRY

Inorganic and Organic

WITH

AN INTRODUCTION TO THE STUDY OF CHEMISTRY.

BY

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A BELLE SAUVAGE

PREFACE.

This book is intended as a guide to the study of chemical science for the use of students of medicine. Now that Chemistry, and especially Organic Chemistry, has become so vast a science, the student of medicine is, on the one hand, apt to find himself out of his depth in attempting the perusal of the larger handbooks on the subject; and, on the other hand, with many of the smaller works, excellent in their way, he is hampered by omission of matter essential to the successful after-study and practice of medicine. This book has therefore been written to bring together in a concise form those portions of chemical science that directly or indirectly bear on the study and practice of medicine.

To gauge correctly the wants of the student of medicine, and to appreciate rightly the position that must be assigned to the study of Chemistry amongst his multifarious work, can, in my opinion, be best done by one who has himself been through the courses of study and work required for qualifying in medicine. I have therefore undertaken the task of writing this book in the hope that it may supply a long-felt want, and that it may assist the student in acquiring a sound knowledge of the fundamental principles of Chemistry.

A. P. L.

47, Weymouth Street, W.

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MANUAL OF CHEMISTRY.

Part I.

INTRODUCTION TO THE STUDY OF CHEMISTRY.

CHAPTER I.

Matter—Solids—Liquids—Gases—Latent Heat—Mixtures and Chemical Compounds—Chemical Attraction—Heat produced by Chemical Action.

Matter.—In order to commence the study of Chemistry clearly and definitely, it is absolutely necessary that the student should understand what matter is, the different forms in which it exists, and the laws which cause the existence of these different forms of matter.

The three forms of matter.—Matter is that which is evident to the senses, and it exists in three forms: viz. the *solid*, *liquid*, and *gaseous*. Any one of these forms of matter can be converted into either of the other two; thus, by melting *solid* ice it becomes *liquid* water, and by boiling the liquid water *gaseous* steam is produced. The particles of all bodies are under the influence of two forces: one a **force of attraction** (otherwise known as **cohesion**) and the other a **force of repulsion** (which, as will be presently explained, is identical with **latent heat**);

and according to the distribution of these forces of attraction and repulsion the different forms of matter result. If one of the forces is in excess of the other, one of the two extreme forms of matter (the solid or the gaseous) results; if the two forces are equally balanced, then the intermediate form of matter (the liquid) is the result.

Thus in all **solids** the force of attraction of the particles for one another is greater than the force of repulsion. The peculiarity of the solid form of matter is that the relative positions of its particles cannot be changed without the expenditure of more or less force; solids therefore tend to retain whatever form they may happen to possess.

In **liquids** the forces of attraction and repulsion of the particles are equally balanced. The distinctive peculiarity of the liquid state is that the particles readily glide over one another, and assume the shape of the vessel containing the liquid.

In **gases** the force of repulsion exercised by the particles is considerably greater than the force of attraction. The distinctive character of the gaseous state is that the particles are continually undergoing a struggle to occupy a larger space. It will now be easy for the student to understand why a gas can be compressed by additional pressure and expanded by partial removal of pressure: the compression of a gas being brought about by the mechanical force employed overcoming the repulsive force of its particles; and the expansion of a gas being caused by the repulsive force of the particles for one another coming into play, when the pressure is removed.

It must not be supposed that the particles of any one of these forms of matter are in absolute contact with one another, although such is a common opinion with regard to solids and liquids. That solids are in reality porous, that the particles are not absolutely close together, is proved by hammering or powerfully pressing them, when they will be found to occupy a smaller bulk than they did previous to being submitted to pressure; and again is proved by what is technically called the "sweating" of iron in the Bramah hydraulic press, where water under powerful pressure actually is forced through the pores of a stout iron cylinder, although to the eye the iron appears perfectly compact and homogeneous. That liquids are porous is best proved by mixing certain liquids together, when a contraction in bulk takes place. If spirit and water be mixed together, a diminution in volume occurs, the particles getting closer together than they formerly were, due to a molecular combination of the spirit with the water; thus, in making the proof spirit of the British Pharmacopœia, 100 fluid ounces of rectified spirit are mixed with 60 fluid ounces of water, yet only 156 fluid ounces of proof spirit result, a contraction of about $2\frac{1}{2}$ per cent. having taken place.

The student having now become acquainted with the different forms of matter, the next thing for him to understand is how and under what conditions any one form of matter is capable of being converted into another. Heat is the agent necessary for the transformation of one form of matter into another, and it is the addition or abstraction of heat that brings about the change of state in any form of matter. If a piece of roll sulphur (representing the solid form of matter) be heated in a test-tube or flask, it will first melt to a syrupy fluid (representing the liquid form of matter), and this on further heating will boil away, forming a heavy vapour of a reddish-brown colour (representing the gaseous form of matter); heat is therefore the agent that has converted the solid into a liquid, and the liquid into a gas or vapour. Now, if part of the heat be abstracted from the sulphur vapour, this will condense to a syrupy fluid ; and this fluid on further cooling (that is, on further abstraction of heat) will solidify to a mass of solid sulphur. From these simple experiments the following general law can be deduced :—

Either the addition or abstraction of heat is necessary for the conversion of any one form of matter into another form.

Latent heat.—The heat which is stored up in liquids and gases, and which prevents their change of state, is called *latent heat.* Latent or hidden heat is that heat which cannot be detected by the thermometer, which is doing other work than that of making itself sensible to the thermometer: viz. preventing the change of state of the body in which it is stored up. Thus, on applying heat to the piece of roll sulphur, a quantity of the heat is rendered latent and converted into energy, which keeps the sulphur in the liquid form ; on the further application of heat to the melted sulphur until it boils, more heat is rendered latent, in order to convert the liquid sulphur into the gaseous or vaporous form. To condense the sulphur vapour to a liquid, part of the latent heat must be abstracted by bringing the vapour into contact with some cool substance, which withdraws some of the latent heat by transforming it into sensible heat; the sulphur vapour, having now lost the force or energy which kept it in the gaseous form, condenses to a liquid ; if the latent heat of this liquid be in its turn abstracted by further cooling, the melted sulphur will solidify.

The subject of *latent heat* will be rendered more intelligible by quoting an example : the conversion of ice into water will be taken. If one pound of ice at 0° C. be mixed with one pound of water at 79° C., two pounds of water at 0° C. will be the result. In this case the heat which had raised one pound of water through 79° C. has disappeared, but it is not lost; it has converted the pound of ice into a pound of water, and in doing so the heat has been rendered latent by the melting ice; it has not raised the temperature of the ice, but has changed it from the solid to the liquid state; if the water be frozen, this latent heat would be transformed into, and given forth in the form of, sensible heat.

Mixtures and chemical compounds.—Before treating of the force known as chemical attraction, or chemical affinity, as it is sometimes termed, it will be well for the student to clearly understand the difference between a mixture of substances and a chemical compound. **A mixture** possesses all the properties of its ingredients, and these ingredients can be mixed in any proportions. **A chemical compound** possesses entirely different properties to those of its ingredients, and the proportion of each of its constituents is fixed and invariable. A very good example, illustrative of these two definitions, is furnished by a mixture of iron and sulphur, and by sulphide of iron, a chemical compound of iron and sulphur. If iron filings and powdered sulphur be rubbed together, it will be found that the mixture possesses all the properties of its constituents unaltered; for with a magnet the iron filings can be picked out and the sulphur left; or, by treating the mixture with a liquid called bisulphide of carbon, the sulphur can be dissolved out and the iron filings left; on evaporating the bisulphide of carbon solution, the sulphur will be left. But if the iron filings and sulphur be heated in a crucible, chemical combination takes place, and a black mass of sulphide of iron is formed, which chemical compound possesses entirely different properties to those of its constituents. A magnet is now incapable of abstracting the iron from it; bisulphide of carbon will not dissolve out the sulphur from it; on treating it with dilute sulphuric acid, a gas, called sulphuretted hydrogen, possessing an offensive odour, is evolved; neither iron nor sulphur possesses the property alone of evolving this gas when treated with dilute sulphuric acid. As may be readily comprehended, a mixture of iron filings and sulphur could be made with any proportions of the constituents, whereas the chemical compound sulphide of iron requires the constituents to be present in the fixed proportions of 56 parts by weight of iron to 32 parts by weight of sulphur. (The student will shortly learn that these are the atomic or combining weights of iron and sulphur.) If different proportions to these are used, then a mixture of sulphide of iron with excess of either iron or sulphur will be the result, accordingly as excess of iron or sulphur has been used.

Characters of chemical attraction.—It is necessary that the student should pay great attention to the peculiar characters by which the force of chemical attraction may be recognised, for it is by means of this force that the comparatively few elementary bodies arrange themselves into the numberless compounds of which the animal, vegetable, and mineral kingdoms are composed.

Chemical attraction is an extremely powerful force, which acts only on the smallest particles of matter, and between inappreciable distances. An example of the last mentioned fact is obtained by powdering and rubbing together in a mortar tartaric acid and carbonate of soda; no change whatever occurs, for it is impossible by such means to bring the two substances into sufficiently close contact to react on one another; but if water be now added to the mixture in the mortar, the two substances will dissolve, and in the dissolved state will come sufficiently close to one another to react, chemical action being manifested by the effervescence that takes place, due to the tartaric acid acting on the carbonate of soda, forming tartrate of soda, and liberating carbonic acid gas.

Chemical attraction exists between the particles of dissimilar kinds of matter, and the result of chemical combination is an entire change of properties in the compound produced. For instance: a piece of iron shows no desire to chemically unite with another piece of iron; but if the iron be heated with a dissimilar substance, as sulphur, chemical combination then takes place, and a new body—sulphide of iron—is formed, which possesses entirely different properties to those of its constituents, as has been previously explained.

A most important phenomenon, which is always the result of chemical combination, is the production of heat. It must be carefully borne in mind that *whenever chemical combination takes place heat is produced;* by remembering this, the student will be able to comprehend and explain many phenomena that will come under his notice, both while studying chemistry and while engaged in the duties of every-day life. The following are a few examples of heat produced by chemical action :—

If a piece of the metal potassium be thrown upon water, the potassium decomposes the water, forming hydrate of potassium, and evolving part of the hydrogen of the water; the heat produced by this chemical action is sufficient to set fire to the escaping hydrogen, which burns with a violet-coloured flame (the colour being due to a trace of potassium volatilised by the heat). If a small piece of dry phosphorus be placed on a fragment of iodine, the two substances will immediately commence to combine and form iodide of phosphorus, and the heat, produced by this chemical combination, ignites that portion of the phosphorus which has not already united with the iodine. The lime-light affords another good illustration of heat produced by chemical action; to produce the light, the oxy-hydrogen flame is made to impinge on a piece of lime; the oxygen and hydrogen in combining chemically with each other produce an intense heat, and this raises the particles of the lime, upon which the flame impinges, to a white heat; the particles of lime, glowing at this white heat, emit the dazzling light.

Another, and a still more common, example of heat produced by chemical action is that derived from the burning of coals in our fire-grates; in this case the constituents of the coal combine chemically with the oxygen of the air, the heat resulting from this chemical action causes the coals to glow, and inflames the gases escaping from the burning coal. In fact, in most cases where heat is obtained artificially, it is the result of chemical action.

One last important example of heat produced by chemical action is that of animal heat, or the heat which maintains the temperature of the living body; the oxygen of the air that we inhale is absorbed by the blood circulating through the lungs, and is then conveyed in the blood to the various tissues of the body, where the carbon and hydrogen of the tissues become oxidised, or burnt, by this oxygen to carbonic acid gas and water respectively, and it is the heat produced by this chemical action—by this oxidation—which serves to maintain the temperature of the animal body.

Having now given a general idea of the main facts and laws connected with the different forms of matter, the study of Chemistry proper will be proceeded with. In the first place, the most important principles connected with it will be brought under the notice of the student.

CHAPTER II.

Elements — Metals — Non-metals — Symbols — Atomic Theory — Atoms — Molecules — Atomic Weights — Laws of Chemical Combination—Quantivalence or Atomicity—Change or Variation of Quantivalence.

ELEMENTS AND COMPOUNDS.

Chemistry is the science that enables us to resolve complex forms of matter into simpler or elementary forms, and to construct compound forms of matter from the simpler or elementary forms. The resolution of complex bodies into simpler or elementary bodies is called **analysis** (ἀνά, up; λύσις, separation); and the construction of compounds from simpler bodies is called **synthesis** (σύν, together; θέσις, placing).

The numberless compounds met with in the animal, vegetable, and mineral kingdoms can all be resolved or split up by analysis, or otherwise, into about seventy simpler forms of matter, which are called the *elements;* of these seventy elements, only about forty are of medical interest. An **element** is a body (it may be a solid, a liquid, or a gas) that hitherto has resisted all attempts to decompose it into any simpler forms of matter; for example, silver and oxygen are two of the elements, and all attempts have, up to the present time, been incapable of decomposing them into simpler bodies. A **compound** is a body composed of two or more elements, and is therefore capable of being split up into them; for example, oxide of silver is a compound, for it is possible, by simply heating it, to resolve it into the two elements silver and oxygen, the former being left as finely-divided metal, and the latter escaping as a gas.

The following is a list of the elements, arranged alphabetically; classified lists of the more important elements as they are to be learnt and remembered by the student will be given shortly.

LIST OF THE ELEMENTS.

Aluminium
Antimony
Arsenicum
Barium
Beryllium
Bismuth
Boron *
Bromine *
Cadmium
Cæsium
Calcium
Carbon *
Cerium
Chlorine *
Chromium
Cobalt
Copper
Didymium
Erbium
Fluorine *
Gallium
Germanium
Gold
Hydrogen *
Indium
Iodine *
Iridium
Iron
Lanthanum
Lead
Lithium
Magnesium
Manganese
Mercury
Molybdenum
Nickel
Niobium
Nitrogen *
Osmium
Oxygen *
Palladium
Phosphorus *
Platinum
Potassium
Rhodium
Rubidium
Ruthenium
Scandium
Selenium *
Silicon *
Silver
Sodium
Strontium
Sulphur *
Tantalum
Tellurium *
Terbium
Thallium
Thorium
Tin
Titanium
Tungsten
Uranium
Vanadium
Ytterbium
Yttrium
Zinc
Zirconium

The elements are divided into two classes: viz. metals and non-metals. Fourteen non-metallic elements exist; they are distinguished in the above list by having asterisks attached to their names.

Metals and non-metals.—In much about the same way that all living things are divided into two great kingdoms, the animal and the vegetable, so the elements are divided into two classes, metals and non-metals; and just as no single character will distinguish every member of the animal kingdom from every member of the vegetable kingdom, so no single character is sufficient to distinguish all the metals from all the non-metals; for the two classes of elements gradually merge into and blend with one another, and only the far-separated members of the two classes possess any well-marked distinguishing characters. A few of the best-marked characters, and those that may be most readily recognised, are the following:—

Metals possess, or can be made to possess by polishing or by powerful compression, a peculiar greyish lustre, known as *metallic lustre*—a property that is well known to everyone. It is true that metals in a fine state of division, such as the reduced iron of the British Pharmacopœia, do not possess this lustre, but if by powerful pressure or hammering they are compressed into a mass, and this mass be polished, the metallic lustre is then developed. There are two of the common metals that do not possess the peculiar greyish lustre common to the other metals, but which are coloured: viz. **copper,** which is of a reddish colour, and **gold,** which is of a yellow colour. Non-metals are destitute of the peculiar lustre known as metallic lustre; it is impossible to develop a mirror-like surface on a stick of phosphorus or on a piece of sulphur; the only non-metallic element that possesses anything like a metallic lustre is *iodine*, which is too well known by its odour to be confounded with a metal. Metals are also good conductors of both heat and electricity, whereas non-metals are extremely bad conductors of these two forces.

Physical conditions of the elements.—Of all the elements, four only are gases: viz. *hydrogen*, *oxygen*, *nitrogen*, and *chlorine* (fluorine may possibly be a gaseous element, but as it has never been isolated in a state of purity, it cannot with fairness be included in the list of elementary gases). Two of the elements, *mercury* and *bromine*, are liquid at ordinary temperatures; the remaining elements are solids. The physical condition of any element can, however, be altered: for instance, the four elementary gases can be liquefied by subjecting them to powerful pressure and extreme cold; the feat of condensing hydrogen, oxygen, and nitrogen to liquids was accomplished in the latter part of 1877 by Cailletet and Pictet, these gases having up to that time resisted all attempts to liquefy them. The two liquid elements, mercury and bromine, can in their turn have their physical condition altered; thus, on boiling them they become converted into vapours or gases, and by exposing them to sufficiently low degrees of cold, they freeze, or assume the solid state (for instance, mercury frequently freezes in Arctic regions). Most of the solid elements undergo an alteration of state on the application of heat: for instance, the metals when heated melt or liquefy, and on the further application of an intense heat volatilise or form vapours.

SYMBOLS.

A **symbol** is a shorthand method of representing an element. The symbol of an element consists of one or two letters, derived generally from the Latin name of the element (the symbols for potassium and sodium are derived from Arabic words). When the symbol is composed of one letter only, that letter is the first one that occurs in the name (*e.g.* the symbol for hydrogen is H, for oxygen O, for nitrogen N, for carbon C); when the symbol is composed of two letters, the first letter is the first one in the name and the second is some characteristic letter in the same name (*e.g.* the symbol for chlorine is Cl, for magnesium Mg, for platinum Pt). In most cases the Latin names are the same as the English, but in a few cases they are not, and these exceptions must be well learnt in order to remember the symbols derived from them. The following is a list of those elements whose Latin names differ from their English ones; the symbols derived from these Latin names are given in the third column.

English Names.	Latin Names.	Symbols.
Antimony	Stibium...	Sb
Copper	Cuprum...	Cu
Gold	Aurum	Au
Iron	Ferrum	Fe
Lead	Plumbum	Pb
Mercury	Hydrargyrum	Hg
Potassium	Kalium (Arabic name) .	K
Silver...	Argentum	Ag
Sodium	Natrium (Arabic name)	Na
Tin	Stannum	Sn

The following is a list of the more common elements, with their respective symbols and atomic weights; an explanation of these atomic weights will shortly be given, but previous to reading that explanation it will be advisable for the student to commit to memory the atomic weights of the elements given in the list. The order in which the elements are arranged in this table is in that of their atomic weights, commencing with hydrogen, which possesses the lowest. This order greatly assists the memory, as after studying the list the student is enabled to picture mentally in what part of the list any particular element occurs, and so a clue is gained as to its atomic weight.

Elements.	Symbols.	Atomic Weights.
Hydrogen*	H*	1
Lithium	Li	7
Boron*	B*	11
Carbon*	C*	12

Elements.	Symbols.	Atomic Weights.
Nitrogen*	N*	14
Oxygen*	O*	16
Sodium	Na	23
Magnesium	Mg	24
Aluminium	Al	27·5
Phosphorus*	P*	31
Sulphur*	S*	32
Chlorine*	Cl*	35·5
Potassium	K	39
Calcium	Ca	40
Manganese	Mn	55
Iron	Fe	56
Copper	Cu	63·5
Zinc	Zn	65
Arsenicum	As	75
Bromine*	Br*	80
Silver	Ag	108
Tin	Sn	118
Antimony	Sb	120
Iodine*	I*	127
Barium	Ba	137
Mercury	Hg	200
Lead	Pb	207
Bismuth	Bi	210

The elements to which asterisks are attached are the non-metallic elements.

THE ATOMIC THEORY.

The student having now become acquainted with the differences existing between elements and compounds, the next subject to be considered is the prevailing theory with regard to the constitution of matter.

It is a familiar fact that most solid substances can, by mechanical means, be reduced to an extremely fine powder, but the particles of the finest powder when viewed under the microscope are seen in the form of little masses : that is, they are still capable of further division. Now, the questions that for ages have been before the minds of philosophers and chemists are—whether matter is really infinitely divisible, or whether there is a point at which the divisibility of matter ceases. The latter idea is the prevalent one, and for the exposition and adaptation of it to the laws of chemical combination, we are indebted to Dalton. The atomic theory, which is known as "Dalton's atomic hypothesis," regards matter as being composed of indivisible particles, called **atoms** (the term *atom* is derived from the Greek word *ἄτομος*, indivisible). It is impossible by any means, mechanical or otherwise, so to subdivide any body as to split it up into its constituent atoms, nor is it possible for anyone to mentally picture an atom, since it is inconsistent for the mind to conceive of anything that is incapable of further division, as the mind always invests mental images with boundaries. By assigning to each element a weight corresponding to its combining weight, Dalton was enabled to throw great light on, and produce satisfactory reasons for, all the observed numerical laws of chemical combination (which will shortly come under our consideration).

To understand fully the matter that follows, the definitions of the two words **atom** and **molecule** must be carefully remembered. An **atom** is the smallest proportion by weight in which an element enters into, or is expelled from, a chemical compound; the smallest weight of hydrogen so entering or leaving a chemical compound being taken as unity. More briefly, an **atom** may be defined as the smallest quantity of an *element* that is capable of existing, and it is indivisible. A **molecule** (the word *molecule* means a small mass) is the smallest quantity of a body, elementary or compound, that is capable of existing in the free state.

In the case of three elements, a molecule consists of one atom only: viz. mercury (Hg), zinc (Zn), and cadmium (Cd); the molecules of all the other elements contain two or more atoms. Thus, the molecule of oxygen contains two atoms, and is represented as O_2; the molecule of potassium contains two atoms, and is represented as K_2; the molecule of lead contains two atoms, and is represented as Pb_2; in fact, the only elementary bodies containing more than two atoms in the molecule are phosphorus and arsenicum, the molecules of which each contain four atoms; the molecule of phosphorus is therefore represented as P_4, and that of arsenicum as As_4. Ozone, which is a modified or condensed form of oxygen, contains three atoms in the molecule, and is represented as O_3.

Compounds are formed by the union of the atoms of different elements, and the smallest possible quantity of any compound—that is, the molecule of any compound—must contain at least two different atoms. As an example of a compound, the molecule of which only contains two elementary atoms, common salt (chloride of sodium) may be taken. This compound possesses an atom of sodium and an atom of chlorine in the molecule, which is therefore represented as NaCl. The number of atoms in the molecule of a compound is unlimited, some molecules containing a very large number, as the student will notice as he proceeds with the study of Chemistry.

ATOMIC WEIGHTS.

Every element has its own atom peculiar in properties and weight. The atomic weights of the elements have a *double significance*—(i) as representing their relative weights; (ii) as representing their combining weights; in fact, the relative weights of atoms are expressed by their combining weights.

(i) **Consideration of the atomic weights of the elements as their relative weights.**—It must not be supposed that the atomic weights of the elements represent any actual weights ; the weights are only comparative or relative to one another. For example, if equal volumes of hydrogen and oxygen be taken at the same temperature and under the same atmospheric pressure, it will be found that the bulk of oxygen is sixteen times as heavy as the equal bulk of hydrogen. Now, hydrogen being the lightest element, it is convenient to take it as the unit of the scale, because its combining weight is smaller than that of any other element ; but this is merely a matter of convenience. Taking, therefore, the atomic weight of hydrogen as 1, the relative or atomic weight of oxygen will be 16 ; nitrogen is fourteen times heavier than hydrogen, and therefore its atomic or relative weight is 14. One important point must be considered here and may have been noticed by the student: and that is, that in deducing the atomic weights of hydrogen and oxygen from the relative weights of equal bulks of the gases, it is apparently assumed that a volume of hydrogen gas contains just as many molecules as an equal volume of oxygen, when the two gases are measured at the same temperature and under the same atmospheric pressure; for if the equal volumes of the two gases did not contain an equal number of units, then the units of the two gases could not possess the relative weights that the equal bulks of gases bear to one another. This important point is something more than an assumption, for it admits of experimental proof ; it has been investigated by Avogadro and Ampère, and the following hypothesis bears their names.

Avogadro and Ampère's hypothesis. — *Equal volumes of different gases, at equal pressures and temperatures, contain equal numbers of molecules.*

As proof of this hypothesis, there is the fact that all gases are equally affected in volume by variations of pressure and temperature, physical agencies such as heat and pressure not affecting the nature of molecules, but only their distance from one another. Thus the heat that is necessary to cause half a pint of oxygen to expand to one pint also causes half a pint of hydrogen to expand to just one pint; and the pressure that is necessary to compress a pint of oxygen to half a pint will also compress a pint of hydrogen to half a pint. Now it is not conceivable that the two gases could behave in such a similar manner, unless they contained equal numbers of molecules in equal bulks.

(ii) **Consideration of the atomic weights of the elements as their combining weights.**—The most important fact to be remembered by the student in connection with the atomic weights of the elements is, that they represent the proportions in which the elements unite with one another to form compounds, or the proportions in which they displace one another in compounds. Thus in the case of chloride of sodium (common salt), 23 parts by weight of sodium unite with 35·5 parts by weight of chlorine, and the two elements will only unite together in these proportions. If 35·5 grains of chlorine be brought in contact with 23 grains of sodium, the two will combine and form 58·5 grains of chloride of sodium; but if more chlorine, say 50 grains, be brought in contact with 23 grains of sodium, then the 23 grains of sodium will only unite with 35·5 grains of chlorine, and 14·5 grains of chlorine (the remainder of the 50 grains) will be left in the free state. In like manner, if 35·5 grains of chlorine be brought in contact with more than 23 grains of sodium, then the 35·5 grains of chlorine will only be capable of uniting with 23 grains of sodium, and the remainder of the sodium will be left unattacked. (N.B.—It must not be supposed that all compounds can, like chloride of sodium, be made by bringing the elements of which they are composed simply into contact with one another; practically only a few compounds are capable of being prepared in such a manner.)

It will presently be shown that two elements are capable of uniting in different proportions to form different compounds, but the student will then notice that the varying proportions in which two elements unite with one another are always expressed by simple multiples of their atomic weights.

THE LAWS OF CHEMICAL COMBINATION.

The following are the three laws that regulate the combination of elements to form compounds:

1st law. The same chemical compound always contains the same elements, united in the same proportions.—This law declares that a chemical compound always possesses an unvarying composition. For instance, from whatever part of the globe chloride of sodium (common salt) be obtained, or by whatever method it may be manufactured, it will always be found on analysis to contain 23 parts by weight of sodium, to 35·5 parts by weight of chlorine, and these proportions will never vary in the compound. Again, if pure water be obtained from any source, and analysed, it will be found to contain 2 parts by weight of hydrogen to 16 parts by weight of oxygen, and in all samples of water these proportions are invariable.

This law, although a very simple one, is an extremely important one, for it confers on Chemistry the dignity of an exact science.

2nd law. When two elements unite together, in different proportions, to form

different compounds, they do so in simple multiples of each other.—Thus, let A and B represent two elements, the following arrangements then show how these two elements might combine in different proportions to form different compounds :

$A + B$, $A + 2B$, $A + 3B$, $A + 4B$, etc.
Or, $2A + B$, $2A + 3B$, $2A + 5B$, $2A + 7B$, etc.
Or, $A + B$, $A + 3B$, $A + 5B$, etc.

It will be noticed that the varying combining proportions of A and B are indicated by the simple multiples 1, 2, 3, 4, etc., no halving or quartering of an elementary atom ever taking place.

The student will meet with numerous examples of this law as he proceeds with the study of Chemistry ; for the present, it will be sufficient to bring before his notice a few illustrations of it in order to complete its explanation. Carbon forms with oxygen two compounds, the one containing the least oxygen is called carbonic oxide (CO), and the one containing most oxygen is called carbonic acid gas (CO_2) ; carbonic oxide contains by weight 12 parts of carbon to 16 of oxygen, and carbonic acid gas contains 12 parts of carbon to 32, or 16 × 2, of oxygen ; in this case the simple multiples 1 and 2 represent the different proportions in which the two elements carbon and oxygen unite with one another.

A few examples of different compounds belonging to some of the members of the graphic representations previously given, may assist the student in understanding this law.

EXAMPLES.

$2A+B$ ... N_2O ... Nitrous oxide
$2A+3B$... N_2O_3... Nitrous anhydride
$2A+5B$... N_2O_5... Nitric anhydride

Three of the compounds of nitrogen and oxygen.

$A+2B$ ...	SO_2 ...	Sulphurous anhydride	The two compounds of sulphur and oxygen.
$A+3B$ ...	SO_3 ...	Sulphuric anhydride	

$A+3B$ ...	PCl_3...	Phosphorus trichloride	The two compounds of phosphorus and chlorine.
$A+5B$ ...	PCl_5...	Phosphorus pentachloride	

This second law of chemical combination is an extremely important one, as it adds great weight to the idea of the existence of atoms; for, since an atom is supposed to be indivisible, it is easy to understand why, in cases where several compounds of the same elements exist, the increase is always in some simple multiple of the combining weight, in other words, there is no halving nor quartering of atoms; in fact, the theory of the existence of atoms is perfectly in harmony with the law of multiple proportions that has just been explained.

3rd law. The proportions in which any two elements unite with a third are the same proportions in which they unite with each other, or simple multiples of those proportions.—For example, 39 parts of potassium unite with 35·5 parts of chlorine to form chloride of potassium, and 39 parts of potassium unite with 127 parts of iodine to form iodide of potassium; therefore 35·5 parts of chlorine would unite with 127 parts of iodine to form a compound of iodine with chlorine (chloride of iodine). In this case, the proportions in which the two elements chlorine and iodine unite with the third element potassium are the same proportions in which they unite with each other.

CLASSIFICATION OF THE COMMONER ELEMENTS ACCORDING TO THEIR QUANTIVALENCES.

Univalents or Monads.	Bivalents or Dyads.	Trivalents or Triads.	Quadrivalents or Tetrads.	Quinquivalents or Pentads.	Sexivalents or Hexads.
Hydrogen ...H	Oxygen......O	Boron.........B	Carbon C	Nitrogen .. N	Sulphur ......S
Chlorine......Cl	Barium ......Ba	Gold ....Au	Silicon ......Si	Phosphorus P	Chromium...Cr
Bromine......Br	Calcium ...Ca	Bismuth ...Bi	Iron ....Fe	Arsenicum...As	Manganese Mn
Iodine.........I	Strontium...Sr	*Nitrogen** ...N	Aluminium Al	Antimony ...Sb	
Fluorine......F	Magnesium Mg	*Phosphorus**P	Tin............Sn		
Potassium ...K	Zinc ....Zn	*Arsenicum** As	Platinum ...Pt		
Sodium ......Na	Copper ......Cu	*Antimony** Sb	*Sulphur** ...S		
Lithium Li	Lead ....Pb		*Chromium** Cr		
Silver ....Ag	Mercury ...Hg		*Manganese** Mn		
*Nitrogen** ...N	Cadmium ...Cd				
	*Sulphur** ...S				
	*Chromium** Cr				
	*Manganese**Mn				
	*Carbon** ...C				
	*Iron** ......Fe				
	(in ferrous salts).				
	*Tin** ....Sn				
	(in stannous salts).				

* *See* page 26.

QUANTIVALENCE OR ATOMICITY.

By the quantivalence or atomicity of an element is meant its atom-fixing power: that is, the equivalent or saturating value possessed by the atom of an element, represented by the number of atoms of hydrogen to which it is equivalent. Any dyad or bivalent element possesses twice the atom-fixing power of a monad or univalent element; one atom of the dyad oxygen is therefore capable of combining with or saturating two atoms of the monad hydrogen. *Example.*—Water (H_2O) consists of two atoms of H united with one atom of O.

A triad or trivalent element possesses three times the atom-fixing power of a monad element, so that one atom of a triad will combine with and saturate three atoms of a monad. *Example.*—Chloride of bismuth ($BiCl_3$) consists of one atom of the triad element bismuth united with three atoms of the monad element chlorine.

The combination of a dyad with a triad does not at first seem so easy, but bearing in mind that a triad possesses an atom-fixing power represented by three, as compared with a dyad, which possesses an atom-fixing power represented by two, evidently, then, two atoms of a triad will unite with and satisfy three atoms of a dyad, for they will then both possess an equal atom-fixing power, represented by six; just as two threepenny pieces would be equal in value to three twopenny pieces. *Example.*—Oxide of bismuth (Bi_2O_3) consists of two atoms of the triad bismuth united with three atoms of the dyad oxygen.

One atom of a tetrad or quadrivalent element will combine with and saturate four atoms of a univalent element, or two atoms of a dyad or bivalent element. *Examples.*—Perchloride of platinum ($PtCl_4$) consists of one atom of the tetrad platinum united with four atoms of the monad chlorine. Carbonic acid gas (CO_2) consists of one atom of the tetrad carbon united with two atoms of the dyad oxygen.

One atom of a pentad or quinquivalent element is capable of uniting with and saturating five atoms of a monad or univalent element. *Example.*—Pentachloride of phosphorus (PCl_5) consists of one atom of the pentad phosphorus united with five atoms of the monad chlorine. When a pentad unites with a dyad, two atoms of the pentad will satisfy and saturate five atoms of the dyad, for two atoms of a pentad will possess an equal atom-fixing power to five atoms of a dyad, since they will then both possess an equal atom-fixing power, represented by ten, just as two fivepenny pieces would be equal in value to five twopenny pieces. *Example.*—Phosphoric anhydride (P_2O_5) consists of two atoms of the pentad phosphorus united with five atoms of the dyad oxygen.

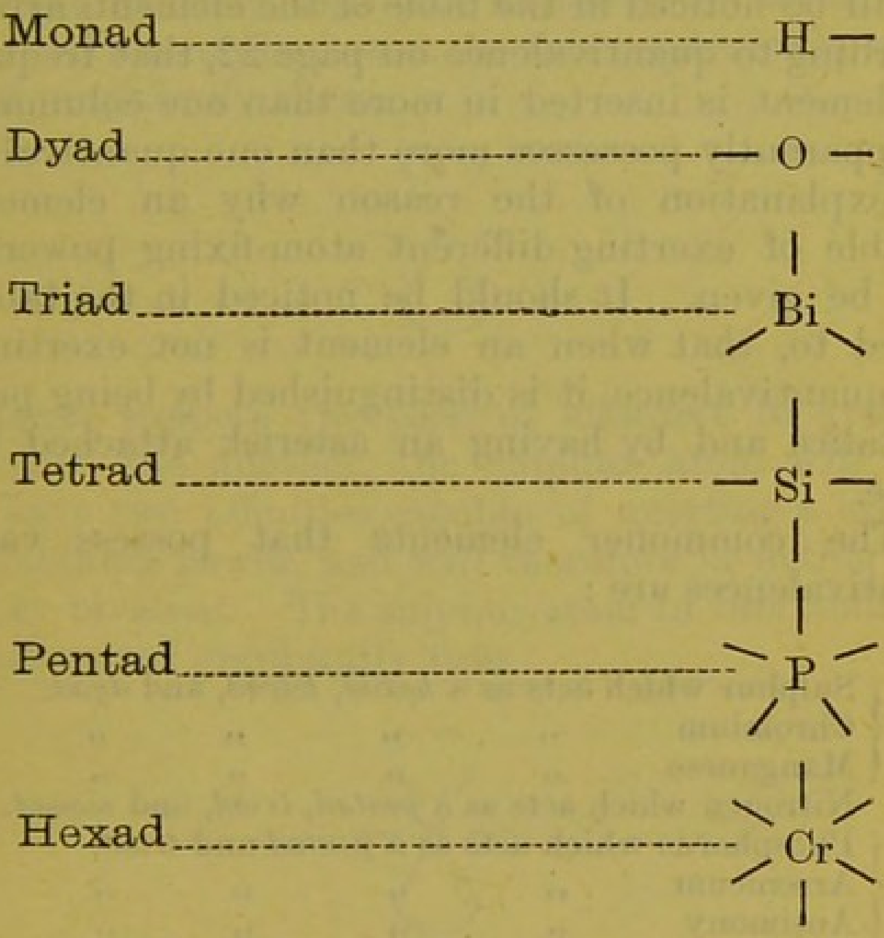
Lastly, a hexad or sexivalent element is one that possesses six times the atom-fixing power of a monad or univalent element, or three times the atom-fixing power of a dyad, and so on. *Examples.*—Fluoride of chromium (CrF_6) consists of one atom of the hexad chromium united with six atoms of the monad fluorine. Chromic anhydride (CrO_3) consists of one atom of the hexad chromium united with three atoms of the dyad oxygen.

The quantivalence or atomicity of an element is represented by small dashes or by Roman numerals placed over its symbol, thus:

Monad or univalent	H^{i}
Dyad or bivalent	O^{i}
Triad or trivalent	Bi^{i}
Tetrad or quadrivalent	S
Pentad or quinquivalent	P^{v}
Hexad or sexivalent	Cr^{v}

Graphic Representation of the Quantivalence or Atomicity of the Elements.

The quantivalence of an element may be represented graphically by fixing to its symbol *arms* corresponding in number to the degree of its atom-fixing power. A monad is represented as possessing one arm, a dyad as possessing two arms, a triad as possessing three arms, and so on ; thus :



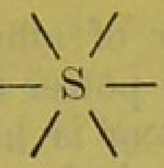
It is scarcely necessary to caution the student against supposing that elements actually have arms projecting from them ; all that we know is that such an element as oxygen possesses twice the atom-fixing power of hydrogen, and the graphic symbols serve the purpose of showing how one atom of oxygen is capable of uniting with two atoms of hydrogen ; they represent in a manner that at once appeals to the mind of the student how different elements are capable of exerting different atom-fixing powers. These hypothetical arms are generally spoken of and written of as "bonds," but the term "bond" is open to some objection, and the better and less objectionable term "affinity" will therefore be used in this book. Thus, a monad possesses one affinity, a dyad two affinities, a triad three affinities, and so on.

Change or variation of quantivalence.— It will be noticed in the table of the elements arranged according to quantivalence on page 22, that frequently an element is inserted in more than one column, that is, apparently possesses more than one quantivalence; an explanation of the reason why an element is capable of exerting different atom-fixing powers will now be given. It should be noticed in the table referred to, that when an element is not exerting its full quantivalence, it is distinguished by being printed in italics and by having an asterisk attached to its name.

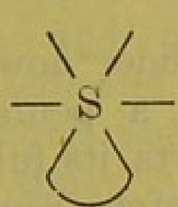
The commoner elements that possess varying quantivalences are:

Sulphur which acts as a *hexad*, *tetrad*, and *dyad*.
Chromium ,, ,, ,, ,,
Manganese ,, ,, ,, ,,
Nitrogen which acts as a *pentad*, *triad*, and *monad*.
Phosphorus which acts as a *pentad* and *triad*.
Arsenicum ,, ,, ,, ,,
Antimony ,, ,, ,, ,,
Carbon which acts as a *tetrad* and *dyad*.
Iron ,, ,, ,, ,,
Tin ,, ,, ,, ,,

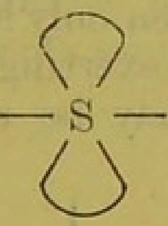
As an example of the first group, the members of which can act as hexads, tetrads, or dyads, we will take sulphur. The sulphur atom as a hexad is represented graphically as possessing six affinities, thus:



Now, supposing two of the six affinities cease to exert their atom-fixing power, which can be imagined by supposing a pair of affinities to grasp one another and so neutralise their fixing powers, the sulphur atom will then only be exerting an atom-fixing power represented by four, and will therefore be acting as a tetrad. The sulphur atom in this condition is represented graphically thus:



Again, suppose two pairs of affinities to grasp or neutralise one another, the sulphur atom will then only have two affinities capable of exerting a uniting or combining power, and will therefore be acting as a dyad or bivalent. The sulphur atom in this condition is represented graphically thus:

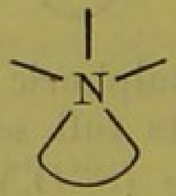


For instance, in sulphuric anhydride ($S^{vi}O^{ii}_3$) the sulphur is exerting its full *sexivalent* atomicity; in sulphurous anhydride ($S^{iv}O^{ii}_2$) the sulphur is only exerting *quadrivalent* atomicity; in sulphuretted hydrogen ($H^{i}_2S^{ii}$) the sulphur is only exerting *bivalent* atomicity.

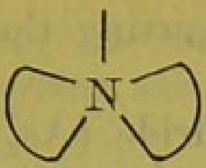
When two affinities neutralise one another, the act is spoken of as a pair of affinities becoming latent; that is, the combining power is not destroyed, but is simply rendered latent or is hidden for the time, for it is possible, by chemical means, to compel these pairs of latent affinities to unloose themselves and to exert their full atom-fixing power. Thus, as the student will learn later, it is possible to compel the S in H_2S, in which it is acting as a dyad, to unloose a pair of its latent affinities and act as a tetrad, and, in like manner, sulphur exerting the atomicity of a tetrad can be made to exert its full atom-fixing power as a hexad, by the opening of its last pair of latent affinities.

We will now consider how it is that nitrogen is capable of acting as a pentad, triad, and monad. Nitrogen when it exerts its full atom-fixing powers is a pentad, and is therefore represented graphically as possessing five affinities, thus:

If a pair of these affinities become latent, the nitrogen atoms will then only have three affinities left free, and will then be exerting the power of a triad; in this condition it may be represented graphically thus:

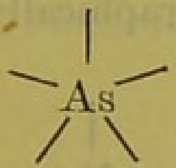


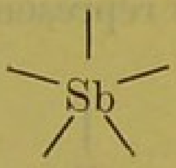
If now another pair of affinities become latent, the nitrogen atom will then only have one affinity left free, and will then exert only the power of a monad, thus:



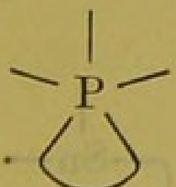
For instance, in nitric anhydride ($N_2^{v}O_5^{ii}$) the nitrogen is exerting *quinquivalent* atomicity ; in nitrous anhydride ($N_2^{iii}O_3^{ii}$) the nitrogen is only exerting *trivalent* atomicity ; in nitrous oxide or laughing gas ($N_2^{i}O^{ii}$) the nitrogen is only exerting univalent atomicity.

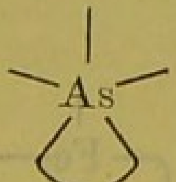
The remarks just used in dealing with nitrogen as a pentad and a triad apply to the three elements phosphorus, arsenicum, and antimony, which are capable of acting as pentads and triads. The atoms of these three elements when they act as pentads are represented graphically thus :

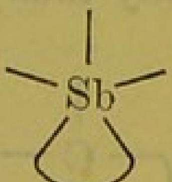




When acting as triads, or only exerting trivalent atomicity, a pair of affinities become latent, and the atoms of the three elements would then be represented graphically thus :





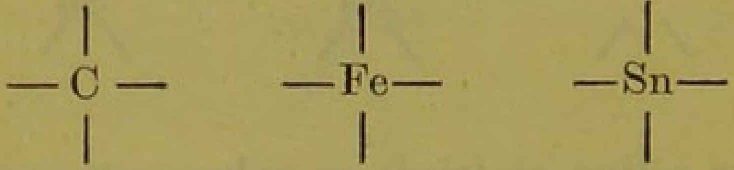


For instance, in phosphoric anhydride ($P_2^{v}O_5^{ii}$) the phosphorus is exerting its full power as a *pentad* or *quinquivalent ;* in phosphorous anhydride ($P_2^{iii}O_3^{ii}$) the phosphorus is only exerting the power of a *triad* or *trivalent.*

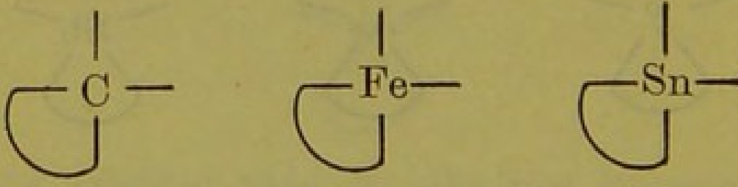
In arsenic anhydride ($As^{v}_2O^{ii}_5$) the arsenicum is exerting its full power as a *pentad* or *quinquivalent;* in arsenious anhydride ($As^{iii}_2O^{ii}_3$) the arsenicum is only exerting the power of a *triad* or *trivalent.*

In pentachloride of antimony ($Sb^{v}Cl^{i}_5$) the antimony is exerting its full power as a *pentad* or *quinquivalent;* in the trichloride of antimony ($Sb^{iii}Cl^{i}_3$) the antimony is only exerting the power of a *triad* or *trivalent.*

We will now briefly consider the cases of the three elements carbon, iron, and tin, the last in the list on page 26 of elements possessing varying quantivalences. These three elements are capable of exerting both quadrivalent and bivalent atomicities; the atoms of the three elements when acting as tetrads or quadrivalents are represented graphically thus:



When only acting as dyads or only exerting bivalent atomicity, a pair of affinities become latent, and the atoms of the three elements are then represented graphically thus:



For instance, in carbonic acid gas ($C^{iv}O^{ii}_2$) the carbon is exerting its full atom-fixing power as a *tetrad* or *quadrivalent;* in carbonic oxide ($C^{ii}O^{ii}$) the carbon is only exerting the power of a *dyad* or *bivalent.*

In ferric chloride ($Fe_2^{iv}Cl_6^{i}$) the iron is exerting its full power as a *tetrad* or *quadrivalent.* (N. B.—The student will very likely imagine on inspection of this formula that the iron is only acting as a triad or trivalent, since two atoms of iron are satisfied by six univalent chlorine atoms; the structure of this *apparently* abnormal molecule will be explained when we come to deal with formulæ in Chapter IV. In ferrous chloride ($Fe^{ii}Cl_2^{i}$) the iron is only exerting part of its atom-fixing power, namely, that of a *dyad* or *bivalent.*

In stannic chloride ($Sn^{iv}Cl_4^{i}$) the tin is exerting its full atom-fixing power as a *tetrad* or *quadrivalent;* in stannous chloride ($Sn^{ii}Cl_2^{i}$) the tin is only exerting the power of a *dyad* or *bivalent.*

CHAPTER III.

Acidulous Radicals—Elementary Radicals—Compound Radicals—Quantivalences of Acidulous Radicals—Acids—Bases—Salts.

ACIDULOUS RADICALS.

THE term **radical** signifies an unsaturated body, a body that requires something to combine with it and saturate it before it is capable of existing. Acidulous radicals may be divided into two groups, **elementary** and **compound radicals.** An **elementary radical** consists of an element in an unsaturated condition—for example, chlorine is the acidulous radical found in all chlorides; an elementary radical always consists of one atom of the element. A molecule of chlorine is represented by the formula Cl_2, and is capable of existing in the free state, for the affinities of the two chlorine atoms are capable of uniting with and saturating each other—

$$\mathrm{Cl—Cl}$$

Graphic representation of chlorine as a molecule.

The radical chlorine is represented by the symbol Cl, and is incapable of existing in the free state, for it is unsaturated; that is, the affinity is unoccupied, thus:

$$\mathrm{Cl—}$$

Graphic representation of chlorine as a radical.

It can therefore be comprehended that the radical chlorine requires something to combine with its free affinity and saturate it.

A **compound radical** is composed of a group of elements that do not completely saturate one another, and which, therefore, require to be saturated by some other body or bodies in order to be capable of existing. By the quantivalence of a radical is meant its degree of unsaturation; thus, a univalent radical would require one atom of a univalent element to combine with and saturate it; a bivalent radical would require two atoms of a univalent element to saturate it; a trivalent radical would require three atoms of a univalent element, and so on.

We will now take a few examples, and show by graphic representations that it is the degree of unsaturation of a radical (simple or compound) that determines its quantivalence or atom-fixing power.

I. As examples of univalent acidulous radicals, we will select the radicals of

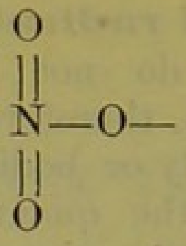
(*a*) Chlorides	... ...	Cl^{i}
(*b*) Nitrates	... ...	NO_3^{i}
(*c*) Nitrites	... ...	NO_2^{i}
(*d*) Cyanides	... ...	CN^{i}

(*a*) The radical of chlorides (Cl) is the atom of the element chlorine, which being a univalent element has, therefore, a combining power represented by one.

$$Cl—$$

Graphic representation of the radical of chlorides.

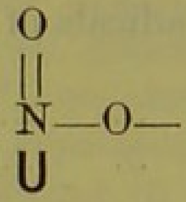
(*b*) The radical of nitrates ($N^{v}O_3^{ii}$) consists of three bivalent oxygen atoms united with one quinquivalent nitrogen atom; the five affinities of the nitrogen atom would therefore be capable of combining with five out of the six affinities of the three oxygen atoms, leaving one affinity unsaturated, and therefore constituting the radical a univalent one.



$$\begin{array}{l}\mathrm{O}\\ \|\\ \mathrm{N{-}O{-}}\\ \|\\ \mathrm{O}\end{array}$$

Graphic representation of the radical of nitrates.

(*c*) In the radical of nitrites ($N^{iii}O_2^{ii}$) the nitrogen is only exerting trivalent atomicity (a pair of its affinities being latent), and is united with two bivalent oxygen atoms; the three free affinities of the nitrogen atom will therefore saturate three out of the four affinities of the two oxygen atoms, leaving one affinity unsaturated, and therefore constituting the radical a univalent one.



$$\begin{array}{l}\mathrm{O}\\ \|\\ \mathrm{N{-}O{-}}\\ \mathrm{U}\end{array}$$

Graphic representation of the radical of nitrites.

(*d*) In the radical of cyanides ($C^{iv}N^{v}$) an atom of the quadrivalent element carbon is united with an atom of the quinquivalent element nitrogen; the four affinities of the carbon atom will therefore combine with four out of the five affinities of the nitrogen atom, leaving one affinity unsaturated, and so constituting the radical a univalent one.

$$\mathrm{C{\equiv}N{-}}$$

Graphic representation of the radical of cyanides.

2. As examples of bivalent acidulous radicals we will take the radicals of

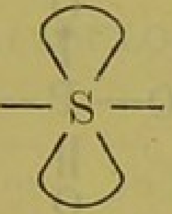
(*a*) Oxides	O^{ii}
(*b*) Sulphides	S^{ii}
(*c*) Sulphates	SO_4^{ii}

(*a*) The radical of oxides (O^{ii}) is the atom of the element oxygen, which, being a bivalent element, has a combining power represented by two.

—O—

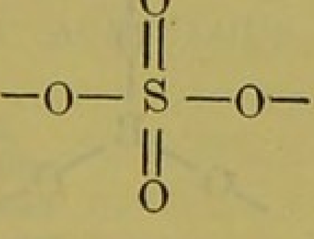
Graphic representation of the radical of oxides.

(*b*) In all sulphides the sulphur (S^{ii}), as a radical, is only exerting bivalent atomicity, two pairs of affinities of the sexivalent sulphur atom being latent.



Graphic representation of the radical of sulphides.

(*c*) In the radical of sulphates (SO_4^{ii}), one atom of sulphur which is exerting its full sexivalent atomicity is united with four atoms of the bivalent oxygen; the six affinities of the sulphur atom will satisfy or combine with six out of the eight affinities of the four oxygen atoms, leaving two affinities unsaturated, and therefore constituting the radical a bivalent one.



$$\begin{array}{c} O \\ \| \\ -O-S-O- \\ \| \\ O \end{array}$$

Graphic representation of the radical of sulphates.

Name.	Formula.
Radical of Chromates	CrO_4
,, Carbonates...	CO_3
,, Oxalates	C_2O_4
,, Tartrates	$C_4H_4O_6$

TRIVALENT ACIDULOUS RADICALS.

Name.	Formula.
Radical of Borates	BO_3
,, Arsenites	AsO_3
,, Arseniates	AsO_4
,, Phosphates	PO_4
,, Citrates	$C_6H_5O_7$

QUADRIVALENT ACIDULOUS RADICALS.

Name.	Formula.
Radical of Silicates	SiO_4
,, Ferrocyanides	FeC_6N_6 or $FeCy_6$

SEXIVALENT ACIDULOUS RADICALS.

Name.	Formula.
Radical of Ferricyanides	$Fe_2C_{12}N_{12}$ or Fe_2Cy_{12}

The formulæ of these acid radicals and their quantivalences, together with the symbols of the elements and their atomicities (*see* list on page 22), must be thoroughly committed to memory; the student will then be able easily to construct a formula, and, knowing how to construct formulæ, the representation of chemical reactions by means of equations is but another step forward. Before dealing with the construction of formulæ and equations, it will be as well, at this stage of the work, to introduce to the notice of the student three most important classes of bodies, viz. **acids, bases,** and **salts.**

Acids are bodies that always contain hydrogen, which hydrogen is capable of being partially or entirely displaced by a metal, to form a salt; in fact, the combination of any one of the acidulous radicals with its equivalent quantity of hydrogen, forms an acid. Acids that contain one atom of displaceable hydrogen are called *monobasic*; those containing two atoms of displaceable hydrogen, *dibasic*; those containing three atoms of displaceable hydrogen, *tribasic*; and so on. Thus nitric acid ($H^{i}NO_{3}^{i}$), which is composed of the univalent nitric radical united with one atom of hydrogen, is an example of a *monobasic acid*; sulphuric acid ($H_{2}^{i}SO_{4}^{ii}$), which is composed of the bivalent sulphuric radical united with two atoms of hydrogen, is an example of a *dibasic acid*; phosphoric acid ($H_{3}^{i}PO_{4}^{iii}$), which is composed of the trivalent phosphoric radical united with three atoms of hydrogen, is an example of a *tribasic acid*. It should be carefully remembered that when the term "acid" is applied to a body destitute of hydrogen, the term is erroneously employed; for example, the so-called "arsenious acid" (As_2O_3) of the British Pharmacopœia cannot be an acid, for it contains no hydrogen; it is the anhydride of arsenious acid, an *anhydride* being derived from an acid by the abstraction of the elements of water. Two distinguishing characters possessed by most acids are a sour taste and the property of changing the colour of blue litmus paper to red.

Bases are bodies that are capable of combining with acids, and, by so doing, destroying their peculiar properties. Bases generally possess a caustic or alkaline taste, and have the property of changing the colour of red litmus paper to blue. Bases may be divided into three classes:

(i) **Oxides,** of which lime, or oxide of calcium (CaO), and magnesia, or oxide of magnesium (MgO), may be mentioned as examples.

(ii) **Hydrates,** of which caustic potash, or hydrate of potassium (KHO), and slaked lime, or

Name.	Formula.
Radical of Chromates	CrO_4
,, Carbonates	CO_3
,, Oxalates	C_2O_4
,, Tartrates	$C_4H_4O_6$

TRIVALENT ACIDULOUS RADICALS.

Name.	Formula.
Radical of Borates	BO_3
,, Arsenites	AsO_3
,, Arseniates	AsO_4
,, Phosphates	PO_4
,, Citrates	$C_6H_5O_7$

QUADRIVALENT ACIDULOUS RADICALS.

Name.	Formula.
Radical of Silicates	SiO_4
,, Ferrocyanides	FeC_6N_6 or $FeCy_6$

SEXIVALENT ACIDULOUS RADICALS.

Name.	Formula.
Radical of Ferricyanides	$Fe_2C_{12}N_{12}$ or Fe_2Cy_{12}

The formulæ of these acid radicals and their quantivalences, together with the symbols of the elements and their atomicities (*see* list on page 22), must be thoroughly committed to memory; the student will then be able easily to construct a formula, and, knowing how to construct formulæ, the representation of chemical reactions by means of equations is but another step forward. Before dealing with the construction of formulæ and equations, it will be as well, at this stage of the work, to introduce to the notice of the student three most important classes of bodies, viz. **acids, bases,** and **salts.**

Acids are bodies that always contain hydrogen, which hydrogen is capable of being partially or entirely displaced by a metal, to form a salt; in fact, the combination of any one of the acidulous radicals with its equivalent quantity of hydrogen, forms an acid. Acids that contain one atom of displaceable hydrogen are called *monobasic;* those containing two atoms of displaceable hydrogen, *dibasic;* those containing three atoms of displaceable hydrogen, *tribasic;* and so on. Thus nitric acid ($H^{i}NO^{i}_{3}$), which is composed of the univalent nitric radical united with one atom of hydrogen, is an example of a *monobasic acid;* sulphuric acid ($H^{i}_{2}SO^{ii}_{4}$), which is composed of the bivalent sulphuric radical united with two atoms of hydrogen, is an example of a *dibasic acid;* phosphoric acid ($H^{i}_{3}PO^{iii}_{4}$), which is composed of the trivalent phosphoric radical united with three atoms of hydrogen, is an example of a *tribasic acid.* It should be carefully remembered that when the term "acid" is applied to a body destitute of hydrogen, the term is erroneously employed; for example, the so-called "arsenious acid" (As_2O_3) of the British Pharmacopœia cannot be an acid, for it contains no hydrogen; it is the anhydride of arsenious acid, an *anhydride* being derived from an acid by the abstraction of the elements of water. Two distinguishing characters possessed by most acids are a sour taste and the property of changing the colour of blue litmus paper to red.

Bases are bodies that are capable of combining with acids, and, by so doing, destroying their peculiar properties. Bases generally possess a caustic or alkaline taste, and have the property of changing the colour of red litmus paper to blue. Bases may be divided into three classes:

(i) **Oxides,** of which lime, or oxide of calcium (CaO), and magnesia, or oxide of magnesium (MgO), may be mentioned as examples.

(ii) **Hydrates,** of which caustic potash, or hydrate of potassium (KHO), and slaked lime, or hydrate of calcium (Ca2HO), may be mentioned as examples.

(iii) A small class of bodies, of which the best known member, ammonia gas (NH_3), may be mentioned as a typical example.

Salts are the compounds resulting from the action of a base on an acid; an *acid salt* is obtained by the partial neutralisation of an acid by a base, so that its properties are partly those of an acid and partly those of a salt; some examples of acid salts will shortly be given.

CHAPTER IV.

Formulæ—Construction of Formulæ—Formulæ of the Elements—Apparently Abnormal Formulæ—Molecular Weights—Specific Gravities of Gases and Vapours—Empirical, Molecular, and Constitutional Formulæ—Uses of Terminations.

FORMULÆ.

A **formula** is a representation of the composition of a body by means of symbols, which may be regarded as chemical shorthand; it consists of a grouping of the symbols of the elements composing the body, with numbers attached to these symbols indicating the proportions in which the elements occur in the body; when no number is attached to the symbol of an element, the number one is understood. We will now show, by a few examples, how to construct the formulæ of acids and salts.

An **acid** is simply a compound of an acidulous radical with hydrogen. Hydrogen being a univalent element, a univalent acidulous radical will unite with, and be saturated by, one atom of hydrogen; thus:

H^iCl^i is the formula of hydrochloric acid.
$H^iNO_3^i$,, ,, nitric acid.
$H^iC_2H_3O_2^i$,, ,, acetic acid.

A bivalent acidulous radical will require two atoms of the univalent hydrogen to saturate it; thus:

$H_2^iSO_4^{ii}$ is the formula of sulphuric acid.
$H_2^iC_2O_4^{ii}$,, ,, oxalic acid.
$H_2^iC_4H_4O_6^{ii}$,, tartaric acid.

A trivalent acidulous radical will, in its turn, require three atoms of hydrogen to saturate it and form an acid; thus:

$H^{i}_{3}BO^{iii}_{3}$ is the formula of boracic acid.
$H^{i}_{3}PO^{iii}_{4}$,, ,, phosphoric acid.
$H^{i}_{3}C_{6}H_{5}O^{iii}_{7}$,, ,, citric acid.

A quadrivalent acidulous radical will require four atoms of hydrogen to saturate it and form an acid; thus:

$H^{i}_{4}SiO^{iv}_{4}$ is the formula of silicic acid.
$H^{i}_{4}FeC_{6}N^{iv}_{6}$,, ,, hydroferrocyanic acid.

The student can therefore construct the formula of any acid by remembering the formula and quantivalence of the acidulous radical of that acid, and then uniting the radical with its equivalent number of hydrogen atoms.

The construction of the formulæ of **salts** is as easy as that of acids, though some of them may appear, at first, more complex. We will first consider the formulæ of salts containing univalent acidulous radicals.

Chloride of sodium is formed by the union of the univalent element sodium with the univalent radical chlorine, its formula is therefore

$$Na^{i}Cl^{i}.$$

In the case of chloride of barium, two equivalents of the univalent radical chlorine will be required to satisfy the bivalent metal barium; the formula is therefore:

$$Ba^{ii}Cl^{i}_{2}.$$

Nitrate of bismuth will require three equivalents of the univalent nitric radical to satisfy one equivalent of the trivalent metal bismuth, its formula is therefore :

$$Bi^{iii}(NO_3)^{i}_3.$$

Chloride of platinum will require four equivalents of the univalent radical chlorine to satisfy one equivalent of the quadrivalent element platinum, its formula is therefore :

$$Pt^{iv}Cl^{i}_4.$$

We will next take a few examples of the formulæ of salts containing bivalent acidulous radicals.

Sulphate of potassium is composed of the univalent metal potassium united with the bivalent sulphuric radical ; two equivalents of the former will therefore be required to satisfy one of the latter, so that the formula is :

$$K^{i}_2SO^{ii}_4.$$

Carbonate of calcium consists of the bivalent metal calcium united with the bivalent carbonic radical ; one equivalent of each will therefore satisfy one another, so that the formula is :

$$Ca^{ii}CO^{ii}_3.$$

Oxide of bismuth consists of the trivalent metal bismuth united with the bivalent element oxygen. Now, two atoms of the trivalent element bismuth will combine with and be saturated by three atoms of the bivalent element oxygen, for the two atoms of a trivalent element and three of a bivalent one will both have an equal atom-fixing power represented by six; the formula of oxide of bismuth is therefore:

$$\mathrm{Bi_2^{iii}O_3^{ii}}.$$

Oxide of silicon is composed of the quadrivalent silicon united with the bivalent oxygen; one atom of the silicon will therefore combine with two atoms of oxygen, so that the formula is:

$$\mathrm{Si^{iv}O_2^{ii}}.$$

Phosphorus pentoxide or phosphoric anhydride is composed of the quinquivalent phosphorus united with the bivalent oxygen. Now, for a quinquivalent and a bivalent to balance one another, two atoms of the former must be united with five of the latter, for they will then both have an equal atom-fixing power represented by ten; the formula is therefore:

$$\mathrm{P_2^{v}O_5^{ii}}.$$

We will now practise the construction of the formulæ of salts containing trivalent acidulous radicals.

The formula of citrate of potassium requires the union of the univalent element potassium with the trivalent citric radical; three atoms of the former will satisfy one equivalent of the latter; the formula is therefore:

$$\mathrm{K_3^{i}C_6H_5O_7^{iii}}.$$

The formula of phosphate of calcium requires the union of the bivalent metal calcium with the trivalent phosphoric radical. Now, three equivalents of the bivalent calcium will satisfy two equivalents of the trivalent phosphoric radical, for they will then both possess an atom-fixing power represented by six; the formula is therefore:

$$\mathrm{Ca}_3^{\mathrm{ii}}(\mathrm{PO}_4)_2^{\mathrm{iii}}.$$

Citrate of bismuth being composed of the trivalent metal bismuth united with the trivalent citric radical, an equivalent of each will form a saturated compound; the formula is therefore:

$$\mathrm{Bi}^{\mathrm{iii}}\mathrm{C}_6\mathrm{H}_5\mathrm{O}_7^{\mathrm{iii}}.$$

We will lastly give two examples of the formulæ of salts containing quadrivalent acidulous radicals.

The formula of ferrocyanide of potassium requires the union of the univalent metal potassium with the quadrivalent radical of ferrocyanides. Evidently, four equivalents of the former will satisfy one of the latter; the formula is therefore:

$$\mathrm{K}_4^{\mathrm{i}}\mathrm{FeCy}_6^{\mathrm{iv}}.$$

Silicate of calcium is composed of the bivalent metal calcium united with the quadrivalent silicic radical; two equivalents of the former will therefore satisfy one of the latter; the formula is therefore:

$$\mathrm{Ca}_2^{\mathrm{ii}}\mathrm{SiO}_4^{\mathrm{iv}}.$$

The student will find it good practice to write out the formulæ of the following salts, and have the results looked over by a teacher or some other competent person :—

Iodide of potassium.
Bromide of magnesium.
Acetate of copper.
Chlorate of calcium.
Hydrate of bismuth.
Cyanide of lead.
Tartrate of silver.
Carbonate of sodium.
Oxalate of calcium.
Sulphide of bismuth.
Sulphite of zinc.
Oxalate of bismuth.
Borate of sodium.
Phosphate of lead.
Citrate of magnesium.
Silicate of potassium.
Ferrocyanide of zinc.
Ferricyanide of lead.

FORMULÆ OF THE ELEMENTS.

The formulæ of the elements can easily be remembered, as, with six exceptions, elements contain two atoms in the molecule ; thus the formula of hydrogen is H_2, this may be represented graphically thus :

$$\mathrm{H}-\mathrm{H},$$

showing the affinity of the one hydrogen atom uniting with the affinity of the other hydrogen atom, and so producing a saturated body or molecule.

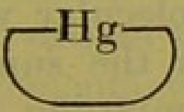
The formula of oxygen is O_2, which may be represented graphically by placing the two affinities of the one oxygen atom as uniting with and saturating the two affinities of the other oxygen atom, thus :

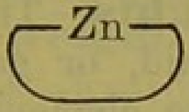
$$\mathrm{O}=\mathrm{O}.$$

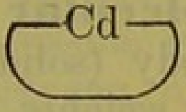
The six exceptions to the rule of the molecule of an element containing two atoms are mercury, zinc, and cadmium (which only contain one atom in the molecule), phosphorus and arsenicum (which contain four atoms in the molecule), and a modified or condensed form of oxygen known as ozone (which contains three atoms in the molecule).

The formula of Mercury is therefore Hg.
" " Zinc " Zn.
" " Cadmium " Cd.
" " Phosphorus " P_4.
" " Arsenicum " As_4.
" " Ozone " O_3.

In the cases of mercury, zinc, and cadmium, the student will no doubt wonder how an atom can exist in the free state as a molecule, that is, as a fully saturated body; these three elements are dyads, and it is therefore quite conceivable that the atom of a dyad element might exist singly in the free state, its two affinities satisfying each other; this may be represented graphically thus:





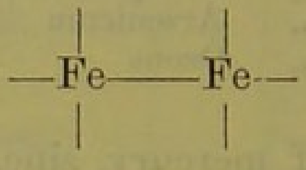


APPARENTLY ABNORMAL FORMULÆ.

Before proceeding to the study of the writing of equations, it will be as well to remove an obstacle from the student's path by explaining the constitution of those few bodies, the formulæ of which are apparently abnormal, and which at first sight seem to disagree with the remarks just made on the construction of formulæ.

To give an illustration of what is meant, we will take as an example *ferric chloride* (perchloride of iron). Iron, as it exists in ferric salts, will be found classed among the quadrivalent elements or tetrads (page 22). Now, the formula of ferric chloride is Fe_2Cl_6, in which the iron is apparently only acting as a triad.

The theoretical explanation of this formula is that an affinity of the one iron atom is joined to an affinity of the other iron atom, so that only six affinities of the two atoms are left free to combine with the chlorine. The condition of the two iron atoms in ferric chloride may be represented graphically thus :



$$-\overset{|}{\underset{|}{\mathrm{Fe}}}-\!\!-\overset{|}{\underset{|}{\mathrm{Fe}}}-$$

Now, since the correctness of this explanation entirely depends on a knowledge of the fact that the formula of ferric chloride is Fe_2Cl_6 and not $FeCl_3$, it is necessary to explain how such knowledge is obtained ; but before doing so, a brief description of the relation of molecular weights to the specific gravities of gases and vapours must be given, in order to render the matter that follows intelligible.

Molecular weights.—The molecular weight of any body (solid, liquid, or gas) is the sum of the atomic weights of the elements composing its molecule. Thus, the molecular weight of oxygen is 32.

$$O_2 = 16 \times 2 = 32.$$

The molecular weight of hydrochloric acid is 36·5.

$$\begin{aligned} \mathrm{H} &= 1 \\ \mathrm{Cl} &= \underline{35{\cdot}5} \\ &\ 36{\cdot}5 \end{aligned}$$

The molecular weight of nitric acid is 63.

$$\begin{aligned} \mathrm{H} \qquad\qquad &= 1 \\ \mathrm{N} \qquad\qquad &= 14 \\ \mathrm{O}_3 = 16 \times 3 &= \underline{48} \\ &\ 63 \end{aligned}$$

The molecular weight of sulphate of potassium is 174.

$$\begin{array}{l}K_2 = 39 \times 2 = 78 \\ S \qquad\qquad\quad = 32 \\ O_4 = 16 \times 4 = \underline{64} \\ \qquad\qquad\qquad\;\; 174\end{array}$$

Specific gravities of gases.—The specific gravity of a gas is its weight as compared with the weight of an equal volume of hydrogen at the same temperature and under the same atmospheric pressure; hydrogen being taken as the standard, and having its specific gravity represented as unity. The molecular weight of hydrogen being 2 ($H_2 = 1 \times 2 = 2$), and its specific gravity 1, it is evident that the specific gravity of hydrogen is half its molecular weight; and this applies to all other gases, both simple and compound, viz. **the specific gravity of any gas is half its molecular weight.** The specific gravities of the elementary gases—hydrogen, oxygen, nitrogen, and chlorine—will be the same as their atomic weights; for, since they all contain two atoms in the molecule, their molecular weights are the double of their atomic weights. The specific gravity of any compound gas can be calculated by finding its molecular weight and then halving it; thus, the specific gravity of carbonic acid gas (CO_2) is 22, of sulphuretted hydrogen (H_2S) 17, of ammonia gas (NH_3) 8·5.

Carbonic acid gas.

$$\begin{array}{l}C \qquad\qquad\quad = 12 \\ O_2 = 16 \times 2 = \underline{32} \\ \qquad\qquad\; 2\,)\,\underline{44} \text{ molecular weight.} \\ \qquad\qquad\quad\;\; 22 \text{ specific gravity.}\end{array}$$

Sulphuretted hydrogen.

$$\begin{array}{lrl}
H_2 = 1 \times 2 = & 2 & \\
S \qquad\qquad = & \underline{32} & \\
2\,) & \underline{34} & \text{molecular weight.} \\
 & 17 & \text{specific gravity.}
\end{array}$$

Ammonia gas.

$$\begin{array}{lrl}
N \qquad\qquad = & 14 & \\
H_3 = 1 \times 3 = & \underline{3} & \\
2\,) & \underline{17} & \text{molecular weight.} \\
 & 8{\cdot}5 & \text{specific gravity.}
\end{array}$$

From what has just been stated, it is evident that the molecular weight of a gas can be easily determined by experimentally taking the specific gravity of the gas, and then doubling that specific gravity.

Now, ferric chloride on the application of heat becomes a vapour, and vapours are nothing more than gases, and therefore are subject to the laws that govern gases. Now, if the specific gravity of the vapour of ferric chloride be taken and be then doubled, the molecular weight of ferric chloride is obtained, and it is then found to correspond with the molecular weight given by the formula Fe_2Cl_6, and not with that given by the formula $FeCl_3$: for example, the specific gravity of ferric chloride vapour is 162·5: this, when doubled, gives 325, which is the molecular weight given by the formula Fe_2Cl_6.

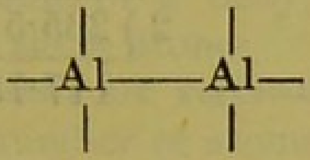
$$\begin{array}{lrl}
Fe_2 = 56 \times 2 \quad = & 112 & \\
Cl_6 = 35{\cdot}5 \times 6 = & \underline{213} & \\
2\,) & \underline{325} & \text{molecular weight.} \\
 & 162{\cdot}5 & \text{sp. gr. of vapour.}
\end{array}$$

If the formula of ferric chloride were $FeCl_3$, then the specific gravity of its vapour would only be 81·25.

$$\begin{array}{lr} Fe & = 56 \\ Cl_3 = 35{\cdot}5 \times 3 & = \underline{106{\cdot}5} \\ & 2\,\overline{)\,162{\cdot}5} \\ & \overline{81{\cdot}25} \end{array}$$

The student must therefore remember to represent all ferric compounds as containing at least two atoms of iron in the molecule.

It is for a similar reason that aluminium compounds contain two atoms of aluminium linked together in a molecule, and therefore aluminium apparently acts as a triad, although it is in reality a tetrad. The constitution of the two atoms of aluminium in chloride of aluminium (Al_2Cl_6) may be represented thus:



Another class of compounds that must be mentioned here, that possess apparently abnormal formulæ, are the mercurous salts, or lower salts of mercury. In some works on chemistry, mercury is stated to be a dyad in mercuric salts, and a monad in mercurous salts: for example, the formula of mercuric chloride is $HgCl_2$, and that of mercurous chloride is represented (in such books) as $HgCl$. Now it is impossible to conceive a dyad atom acting as a monad, for one affinity cannot render itself latent; but if the formulæ of mercurous salts are represented as containing two atoms of mercury in the molecule, the explanation as to why mercury in those salts apparently acts as a monad is then rendered easy. Thus, if the formula of mercurous chloride be written Hg_2Cl_2 (the double of HgCl), the constitution of the two mercury atoms may then be represented graphically thus:

$$-Hg-Hg-$$

Where each mercury atom possesses only one free affinity, the other affinities being employed in linking the two atoms together, the mercury in this condition is called a pseudo-monad (false monad); it is only apparently a monad, for in reality mercury is always a dyad. The reason why some chemists represent the formula of mercurous chloride as HgCl instead of Hg_2Cl_2, is on account of the specific gravity of its vapour being 117·75, which is half the weight given by the formula HgCl:

$$\begin{array}{l} Hg = 200 \\ Cl = 35{\cdot}5 \\ \hline 2\,)\,235{\cdot}5 \\ \hline 117{\cdot}75 \end{array}$$

This apparently crushing fact is, however, quite compatible with what is doubtless the correct formula of mercurous chloride: viz. Hg_2Cl_2, for when converted into vapour, mercurous chloride no doubt dissociates into equal volumes of mercuric chloride and mercury vapours: that is, Hg_2Cl_2 splits up into $HgCl_2$ and Hg, and the mean of the specific gravities of these two substances in the state of vapour is 117·75; thus:

$$\begin{array}{l} Hg \qquad\qquad\quad = 200 \\ Cl_2 = 35{\cdot}5 \times 2 = 71 \\ \hline \qquad\qquad 2\,)\,271 \\ \hline \qquad\qquad\quad 135{\cdot}5 \left\{ \begin{array}{l} \text{specific gravity of} \\ HgCl_2 \text{ vapour.} \end{array} \right. \end{array}$$

Hg = 200
2) 200
100 specific gravity of Hg vapour.

135·5 specific gravity of $HgCl_2$ vapour.
100 ,, ,, Hg ,,
2) 235·5
117·75 { mean of the specific gravities of the vapours of $HgCl_2$ and Hg.

EMPIRICAL, MOLECULAR, AND CONSTITUTIONAL FORMULÆ.

An empirical formula is the simplest possible expression of the composition of a body: that is, it simply represents the elements composing a body, and their relative proportions to one another.

A molecular formula indicates the number of atoms in the molecule of a body, but does not show the arrangement of those atoms.

A constitutional or rational formula indicates not only the number of atoms in the molecule of a body, but also the way in which those atoms are arranged: that is, it exhibits the constitution or architecture of the body.

The empirical and molecular formulæ of many bodies are identical, but in order to illustrate the meanings of the three definitions just given, we will take as an example acetic acid, which possesses distinct empirical, molecular, and constitutional formulæ.

The **empirical** formula of acetic acid is

$$CH_2O,$$

which simply represents that acetic acid is composed of the three elements carbon, hydrogen, and oxygen, and that to every atom of carbon there are two atoms of hydrogen and one of oxygen.

The **molecular** formula of acetic acid is

$$C_2H_4O_2,$$

which indicates the number of atoms in the molecule, and in this case is the double of the empirical formula.

The **constitutional** or **rational** formula of acetic acid is

$$HC_2H_3O_2,$$

which indicates that one atom of hydrogen has a different arrangement to the other three hydrogen atoms, and that these three hydrogen atoms are grouped together with the carbon and oxygen atoms, forming the *acetic radical* $C_2H_3O_2$.

USES OF TERMINATIONS.

In order to apply the correct names to the various chemical compounds, the student must become acquainted with the different terminations used in speaking of the various acids, salts, etc. For instance, he will continually have to use the terms *chloride*, *iodide*, *sulphite*, *sulphate*, and will often come across acids and salts, to the names of which the terminations *-ous* and *-ic* are affixed, such as *sulphurous*, *nitrous*, *sulphuric*, and *nitric* acids, *ferrous*, *ferric*, *mercurous* and *mercuric* salts. We will now proceed to explain the uses of the different terminations.

Sometimes an element, in uniting with hydrogen and oxygen to form an acid, unites with different quantities of oxygen to form different acids; the termination *-ic* is then applied to the acid containing the most oxygen, and the termination *-ous* to that containing the smaller proportion of oxygen ; thus :

H_2SO_4	is sulphur*ic* acid.	H_2SO_3	is sulphur*ous* acid.
HNO_3	is nitr*ic* acid.	HNO_2	is nitr*ous* acid.
H_3AsO_4	is arsen*ic* acid.	H_3AsO_3	is arseni*ous* acid.
$HClO_3$	is chlor*ic* acid.	$HClO_2$	is chlor*ous* acid.

The termination *-ate* is applied to the salts of those acids that possess the termination *-ic*, and the termination *-ite* is applied to the salts of those acids that terminate in *-ous ;* thus :

K_2SO_4	is sulph*ate*	of potassium.	K_2SO_3	is sulph*ite*	of potassium.
KNO_3	is nitr*ate*		KNO_2	is nitr*ite*	
K_3AsO_4	is arseni*ate*		K_3AsO_3	is arsen*ite*	
$KClO_3$	is chlor*ate*		$KClO_2$	is chlor*ite*	

Occasionally, after the naming of a group of acids, an acid has been discovered containing a greater proportion of oxygen than the one to which the termination *-ic* was applied ; the prefix *per-* (abbreviation of *super*, *above*) is then attached to the name of the acid ending in *-ic*, to distinguish the new acid ; thus :

$HClO_4$ is *perchloric* acid,
$HClO_3$ being *chloric* acid.

On the other hand, an acid is sometimes discovered containing a smaller proportion of oxygen than the acid to which the termination *-ous* had been applied ; the prefix *hypo-* (signifying *under*) is then attached to the name of the acid ending in *-ous*, to distinguish the new acid ; thus :

$HClO_2$ being *chlorous* acid,
$HClO$ is *hypochlorous* acid.

When an acid contains an element for its acidulous radical, the prefix *hydro-* (abbreviation of *hydrogen*) is used; thus:

HCl is *hydro*chloric acid.
HF is *hydro*fluoric acid.
HBr is *hydro*bromic acid.
HI is *hydri*odic acid.

The termination *-ide* is used in connection with those salts that possess an element as their acidulous radical; thus:

$NaCl$ is chlor*ide* of sodium.
KI is iod*ide* of potassium.
FeS is sulph*ide* of iron.
HgO is ox*ide* of mercury.

As was mentioned in the article on the quantivalence of the elements, some elements are capable of exerting different combining powers; those compounds in which an element is exerting its full combining power are distinguished by having the termination *-ic* attached to their names, the termination *-ous* being attached to the names of those compounds in which the element is exerting part of its combining power only; thus:

$P^{v}_{2}O^{ii}_{5}$ is phosphor*ic* $As^{v}_{2}O^{ii}_{5}$ is arsen*ic* } anhydride.	$P^{iii}_{2}O^{ii}_{3}$ is phosphor*ous* $As^{iii}_{2}O^{ii}_{3}$ is arseni*ous* } anhydride.
$Fe^{iv}_{2}Cl^{i}_{6}$ is ferr*ic* chloride.	$Fe^{ii}Cl^{i}_{2}$ is ferrous chloride.
$Sn^{iv}Cl^{i}_{4}$ is stann*ic* chloride.	$Sn^{ii}Cl^{i}_{2}$ is stann*ous* chloride.

Sometimes the prefixes *per-*, and *proto-* or *sub-*, are respectively employed instead of the terminations *-ic* and *-ous;* thus, ferric chloride may be called *per*chloride of iron, and ferrous chloride the *proto*chloride or *sub*chloride of iron; stannic chloride may be called the *per*chloride of tin, and stannous chloride the *proto*chloride or *sub*chloride of tin.

CHAPTER V.

Chemical Equations — Classification of Chemical Equations — Methods of Writing Chemical Equations.

CHEMICAL EQUATIONS.

THE changes that occur when two or more substances act chemically upon one another are represented by placing on the left the formulæ of the substances as they exist *before* the change, connected with each other by the sign +, signifying, as in algebra, addition; on the right are formulated the substances as they exist *after* the change, connected together, as before, by the sign +, and connected with the left hand portion by the sign of equality =; such a collection of symbols is known as a **chemical equation.** A thorough knowledge of the representation of chemical reactions by means of equations is absolutely necessary, and careful attention should be given to this subject. An endeavour will be made now to simplify the matter by arranging it in a systematic and definite manner, commencing with reactions that are represented by simple equations, and then proceeding step by step to the representation of the more difficult and complex reactions.

A large number of chemical reactions come under one or more of the four following divisions, in each of which a typical equation constructed of letters represents the kind of action taking place:—

I. ANALYSIS (ἀνά, up; λύσις, separation):

$$AB = A + B.$$

II. SYNTHESIS (σύν, together ; θέσις, placing) :

$$A + B = AB.$$

III. SINGLE DECOMPOSITION :

$$AB + C = A + BC$$

or

$$AB + C = AC + B.$$

IV. DOUBLE DECOMPOSITION :

$$AB + CD = AC + BD$$

or

$$AB + CD = AD + BC.$$

We will now take several examples of equations that come under these four heads :—

I. ANALYSIS (typical equation $AB=A+B$).—Under this head will come those equations which represent the splitting up of a compound body into its elements, or into less complex bodies. Thus (*a*), when mercuric oxide is heated, it splits up into its elements mercury and oxygen :

$$HgO = Hg + O.$$

This equation is not as yet quite correct, for it represents an atom of oxygen as possessing independent existence, which is an impossibility. We must, therefore, represent two molecules of mercuric oxide in the equation, which will then produce a molecule of free oxygen (O_2) which is capable of existing in the free state, thus :

$$2HgO = 2Hg + O_2.$$

The number is placed before the Hg to represent two molecules of mercury, for mercury is one of the three elements (Hg, Zn, Cd) that contain only one atom in the molecule.

The student must remember to represent the existence of molecules in equations, and therefore equations will frequently have to be doubled, as in the case of the one just given. In order to refer to a few more equations that come in the first division (Analysis), we will take the three following examples:—

(*b*) Oxide of silver when heated splits up into silver and oxygen :

$$2Ag_2O = 2Ag_2 + O_2.$$

On the right hand part of this equation the small 2 at the base of the Ag represents two atoms or one molecule of silver, the large 2 multiplies the whole and therefore represents two molecules of silver.

(*c*) The following equation represents the decomposition of water into its elements, a decomposition that can be brought about by means of electricity :

$$2H_2O = 2H_2 + O_2.$$

In this equation two molecules of H_2O are taken, so that the liberation of a molecule of oxygen (O_2) may be represented.

(*d*) The next equation represents the manner in which chlorate of potassium ($KClO_3$) splits up, when heated, into chloride of potassium and oxygen :

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

The equation $KClO_3 = 2KCl + O_3$ would not be correct since it represents the formation of a molecule and a half of oxygen, and half a molecule is incapable of a free existence. The large number 2 placed before the $KClO_3$ multiplies everything after it as far as the sign $=$; the small 3 placed under the O is therefore multiplied by the large 2.

II. SYNTHESIS (typical equation $A+B=AB$).—Equations of this kind represent the combination together of elements to form compounds, and also the combination of simple compounds to form more complex compounds.

(*a*) The following equation represents the formation of water by the union of hydrogen and oxygen :

$$2H_2 + O_2 = 2H_2O.$$

The equation $H_2 + O = H_2O$ would not be correct, as O represents an atom of oxygen which cannot exist in the free state (it will not be necessary to explain again why, in similar equations to this, the double number is taken to prevent the representation of a free atom).

(*b*) The next equation represents the formation of sulphide of iron (FeS) by the union of iron and sulphur (which can be effected by means of heat) :

$$Fe_2 + S_2 = 2FeS.$$

(*c*) The following equation represents the formation of sulphur dioxide (SO_2) by the combustion of sulphur in oxygen :

$$S_2 + 2O_2 = 2SO_2.$$

III. SIMPLE DECOMPOSITION (typical equations $AB + C = A + BC$ and $AB + C = AC + B$).—The student will meet with numerous equations of this kind in the study of Chemistry. The following are a few examples:

(*a*) The action of zinc on hydrochloric acid (HCl), when chloride of zinc ($ZnCl_2$) is formed and hydrogen set free:

$$Zn + 2HCl = ZnCl_2 + H_2.$$

(*b*) The action of iron on dilute sulphuric acid (H_2SO_4), when sulphate of iron ($FeSO_4$) is formed and hydrogen set free:

$$Fe_2 + 2H_2SO_4 = 2FeSO_4 + 2H_2.$$

(*c*) The reduction of oxide of copper (CuO) to the metallic state by means of charcoal, a decomposition that is effected by heating the two together, when the carbon abstracts the oxygen, forming carbon dioxide (CO_2):

$$4CuO + C_2 = 2Cu_2 + 2CO_2.$$

In this equation it is necessary to take C_2 so as to represent a molecule of carbon, and since the two atoms of carbon require four atoms of oxygen to form $2CO_2$, four molecules of CuO must be taken to furnish the requisite amount of oxygen.

(*d*) The formation of reduced iron (finely-divided iron), which is obtained by passing hydrogen over heated ferric oxide (Fe_2O_3), when the hydrogen abstracts the oxygen, with the formation of water and free iron:

$$Fe_2O_3 + 3H_2 = Fe_2 + 3H_2O.$$

In this equation it is necessary to take $3H_2$ in order to furnish sufficient hydrogen to unite with the three atoms of oxygen contained in the Fe_2O_3.

IV. DOUBLE DECOMPOSITION (typical equations $AB + CD = AC + BD$ and $AB + CD = AD + BC$).—Equations of this class are the most general that the student will meet with, reactions of double decomposition being of most common occurrence. We will take several examples of such equations.

When an oxide of a metal dissolves in an acid, as a rule, double decomposition takes place, the metal of the oxide uniting with the acid radical of the acid to form a salt, and the oxygen of the oxide uniting in its turn with the hydrogen of the acid to form water; thus:

(*a*) Equation representing the action of hydrochloric acid (HCl) on oxide of zinc (ZnO):

$$ZnO + 2HCl = ZnCl_2 + H_2O.$$

(*b*) Equation representing the action of nitric acid (HNO_3) on oxide of copper (CuO):

$$CuO + 2HNO_3 = Cu(NO_3)_2 + H_2O.$$

(*c*) Equation representing the action of hydrochloric acid (HCl) on ferric oxide (Fe_2O_3):

$$Fe_2O_3 + 6HCl = Fe_2Cl_6 + 3H_2O.$$

In writing this equation the student would have to bear in mind that ferric chloride contains six atoms of chlorine in the molecule; he would then write down $6HCl$ to furnish the six atoms of chlorine, the six atoms of hydrogen being just sufficient to unite with the three atoms of oxygen of the Fe_2O_3 to form water.

When a hydrate of a metal dissolves in an acid double decomposition takes place, the metal of the hydrate uniting with the acid radical of the acid to form a salt, and the radical of the hydrate (HO) at the same time uniting with the hydrogen of the acid to form water; thus:

(*d*) Equation representing the action of hydrochloric acid on caustic potash (hydrate of potassium):

$$KHO + HCl = KCl + H_2O.$$

(*e*) Equation representing the action of sulphuric acid on slaked lime (hydrate of calcium):

$$Ca(HO)_2 + H_2SO_4 = CaSO_4 + 2H_2O.$$

When solutions of two soluble salts are mixed together and an insoluble salt (called the precipitate) is produced, the reaction is generally one of double decomposition; thus:

(*f*) Equation representing the precipitation of sulphate of barium ($BaSO_4$) by adding sulphuric acid (H_2SO_4) to solution of chloride of barium ($BaCl_2$):

$$BaCl_2 + H_2SO_4 = BaSO_4 + 2HCl.$$

(*g*) Equation representing the precipitation of carbonate of calcium ($CaCO_3$) by the addition of solution of carbonate of sodium (Na_2CO_3) to solution of chloride of calcium ($CaCl_2$):

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl.$$

(*h*) Equation representing the precipitation of mercuric iodide (HgI_2) by the addition of solution of iodide of potassium (KI) to solution of mercuric chloride ($HgCl_2$):

$$HgCl_2 + 2KI = HgI_2 + 2KCl.$$

Several equations are more complex than those that have been given as yet, the products of decomposition being frequently more numerous than two, and sometimes more than two substances taking part in a reaction. Nothing but actual practice can teach a student such reactions; but the writing of equations can be very much simplified by a classification, so far as that is practicable, which we will now give, together with some hints that may prove useful on the methods of writing equations.

(i) The number of atoms on the right hand side of an equation must correspond with those on the left hand side; this, indeed, is evident from the position of the sign of equality (=), for one side of an equation could not be equal to the other unless the number of atoms contained on the one side corresponded with those on the other. So that, after writing an equation, the student should always verify it, by seeing if the number of atoms are equal on each side.

(ii) Whenever a hydrate of a metal dissolves in an acid, a salt of the metal and water are produced.

EXAMPLES.

$$\underset{\substack{\text{Potassium}\\\text{hydrate.}}}{KHO} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{KCl} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\substack{\text{Potassium}\\\text{hydrate.}}}{2KHO} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{sulphate}}}{K_2SO_4} + \underset{\text{Water.}}{2H_2O}$$

$Ca(HO)_2$	+	$2HCl$	=	$CaCl_2$	+	$2H_2O$
Calcium hydrate.		Hydrochloric acid.		Calcium chloride.		Water.

$Zn(HO)_2$	+	H_2SO_4	=	$ZnSO_4$	+	$2H_2O$
Zinc hydrate.		Sulphuric acid.		Zinc sulphate.		Water.

$Fe_2(HO)_6$	+	$6HCl$	=	Fe_2Cl_6	+	$6H_2O$
Ferric hydrate.		Hydrochloric acid.		Ferric chloride.		Water.

$Cu(HO)_2$	+	$2HNO_3$	=	$Cu(NO_3)_2$	+	$2H_2O$
Copper hydrate.		Nitric acid.		Cupric nitrate.		Water.

When commencing to write an equation of this class, the formulæ of the hydrate, acid, and salt formed should first be written down, the formula of the salt will then indicate the number of molecules of hydrate and acid required: for instance, in the fifth equation the formula Fe_2Cl_6 shows that one molecule of $Fe_2(HO)_6$ will be required to furnish the Fe_2, and that $6HCl$ will be required to furnish the Cl_6; having found these numbers, the H of the acid and the HO of the hydrate will always be in the proportion to form H_2O.

(iii) When an oxide of a metal dissolves in an acid, as a rule, a salt of the metal and water are produced, *the only exceptions being the peroxides or higher oxides of the metals.*

EXAMPLES.

BaO	+	$2HCl$	=	$BaCl_2$	+	H_2O
Barium oxide.		Hydrochloric acid.		Barium chloride.		Water.

CaO	+	$2HCl$	=	$CaCl_2$	+	H_2O
Calcium oxide.		Hydrochloric acid.		Calcium chloride.		Water.

MgO	+	H_2SO_4	=	$MgSO_4$	+	H_2O
Magnesium oxide.		Sulphuric acid.		Magnesium sulphate.		Water.
Fe_2O_3	+	$6HCl$	=	Fe_2Cl_6	+	$3H_2O$
Ferric oxide.		Hydrochloric acid.		Ferric chloride.		Water.
Sb_2O_3	+	$6HCl$	=	$2SbCl_3$	+	$3H_2O$
Antimony oxide.		Hydrochloric acid.		Antimony chloride.		Water.
PbO	+	$2HNO_3$	=	$Pb(NO_3)_2$	+	H_2O
Lead oxide.		Nitric acid.		Lead nitrate.		Water.
CuO	+	$2HNO_3$	=	$Cu(NO_3)_2$	+	H_2O
Copper oxide.		Nitric acid.		Copper nitrate.		Water.

When commencing to write an equation of this kind, the formulæ of the oxide and the acid employed should be written down on the left hand side of the equation, and the formula of the salt produced should be written on the right hand side, the latter will then indicate the number of molecules of acid that must be taken: thus, in the last equation of the above group, the formula $Cu(NO_3)_2$ indicates that $2HNO_3$ must be taken to furnish the $(NO_3)_2$, the 2H of the acid and the O of the oxide will then be in the proportion to form water.

(iv) Whenever a carbonate of a metal dissolves in an acid, a salt of the metal, water, and carbon dioxide (carbonic acid gas) are produced, the latter being evolved with effervescence.

EXAMPLES.

K_2CO_3	+	$2HCl$	=	$2KCl$	+	CO_2	+	H_2O
Potassium carbonate.		Hydrochloric acid.		Potassium chloride.		Carbon dioxide.		Water.

Na_2CO_3	$+$	H_2SO_4	$=$	Na_2SO_4	$+$	CO_2	$+$	H_2O
Sodium carbonate.		Sulphuric acid.		Sodium sulphate.		Carbon dioxide.		Water.

$CaCO_3$	$+$	$2HNO_3$	$=$	$Ca(NO_3)_2$	$+$	CO_2	$+$	H_2O
Calcium carbonate.		Nitric acid.		Calcium nitrate.		Carbon dioxide.		Water.

It will be noticed in these equations that the radical of the carbonate CO_3 splits up into CO_2 and O, the former escaping and the latter uniting with the H_2 of the acid to form water.

(v) When a metal dissolves in *hydrochloric acid*, a chloride of the metal is always formed, and hydrogen evolved.

EXAMPLES.

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

Fe_2	$+$	$4HCl$	$=$	$2FeCl_2$	$+$	$2H_2$
Iron.		Hydrochloric acid.		Ferrous chloride.		Hydrogen.

(vi) When a metal dissolves in *dilute sulphuric acid*, a sulphate of the metal is always formed and hydrogen evolved.

EXAMPLES.

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

Fe_2	$+$	$2H_2SO_4$	$=$	$2FeSO_4$	$+$	$2H_2$
Iron.		Sulphuric acid.		Ferrous sulphate.		Hydrogen.

(vii) When a metal dissolves in *strong sulphuric acid*, a sulphate of the metal is formed and sulphur dioxide (SO_2) evolved; the only common metals whose sulphates are made by the action of strong sulphuric acid on them are copper, mercury, and silver.

EXAMPLES.

Cu_2	$+ 4H_2SO_4 =$	$2CuSO_4 +$	$2SO_2 +$	$4H_2O$
Copper.	Sulphuric acid.	Copper sulphate.	Sulphur dioxide.	Water.
Hg	$+ 2H_2SO_4 =$	$HgSO_4 +$	$SO_2 +$	$2H_2O$
Mercury.	Sulphuric acid.	Mercuric sulphate.	Sulphur dioxide.	Water.
Ag_2	$+ 2H_2SO_4 =$	$Ag_2SO_4 +$	$SO_2 +$	$2H_2O$
Silver.	Sulphuric acid.	Silver sulphate.	Sulphur dioxide.	Water.

It will be noticed in each of these equations that *twice as much acid* is taken as is required to furnish SO_4 for the sulphate, the extra SO_4 splitting up into SO_2 and O_2, the former escaping and the latter uniting with the hydrogen of the acid to form water.

(viii) The ordinary metals (with the exception of tin, antimony, arsenicum, and zinc) when acted upon with slightly diluted nitric acid, form metallic nitrates and evolve nitrogen dioxide (N_2O_2).

EXAMPLES.

Ag_6	$+ 8HNO_3 =$	$6AgNO_3 +$	$N_2O_2 +$	$4H_2O$
Silver.	Nitric acid.	Silver nitrate.	Nitrogen dioxide.	Water.
Cu_3	$+ 8HNO_3 =$	$3Cu(NO_3)_2 +$	$N_2O_2 +$	$4H_2O$
Copper.	Nitric acid.	Copper nitrate.	Nitrogen dioxide.	Water.
Pb_3	$+ 8HNO_3 =$	$3Pb(NO_3)_2 +$	$N_2O_2 +$	$4H_2O$
Lead.	Nitric acid.	Lead nitrate.	Nitrogen dioxide.	Water.

$$\underset{\text{Mercury.}}{Hg_3} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\substack{\text{Mercuric}\\\text{nitrate.}}}{3Hg(NO_3)_2} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

$$\underset{\text{Bismuth.}}{Bi_2} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\substack{\text{Bismuth}\\\text{nitrate.}}}{2Bi(NO_3)_3} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

It will be noticed in all these equations, that *eight molecules of nitric acid* ($8HNO_3$) are taken; a sufficient number of atoms of the metal are then worked into the equation to unite with *six* out of the eight equivalents of the nitric radical present in the eight molecules of nitric acid, the remaining two equivalents of the nitric radical ($2NO_3$) then split up into N_2O_2 and O_4, the former escaping and the latter uniting with the hydrogen of the nitric acid to form water.

Part II.

THE NON-METALLIC ELEMENTS AND THEIR PRINCIPAL COMPOUNDS.

CHAPTER I.

HYDROGEN.

Hydrogen—Modes of Preparation—Preparation of Hydrogen from Water—Properties of Hydrogen—Combustion—Graham's Law of Diffusion—Test for Hydrogen.

HYDROGEN.

Symbol, H ; *formula*, H_2 ; *monad* ; *atomic weight*, 1 ; *molecular weight*, 2.

HYDROGEN exists in nature principally in combination with oxygen in the form of water, and it owes the derivation of its name (from ὕδωρ, water ; γεννάω, I produce) to the fact that when united with oxygen in certain proportions, it produces water.

Modes of preparation.—(i) Hydrogen is most conveniently prepared by the action of diluted sulphuric acid on the metal zinc. Pieces of granulated zinc are placed in a generating flask, to which is adapted a cork provided with a bent delivery-tube and a long funnel ; sufficient water is then poured into the flask to cover the zinc, and on pouring strong sulphuric acid down the funnel, hydrogen is evolved with brisk effervescence, and may be collected over water (Fig. 1), after sufficient time has been allowed to elapse for the escape of the air contained in the flask.

$$\begin{array}{ccccccc} Zn & + & H_2SO_4 & = & ZnSO_4 & + & H_2 \\ \text{Zinc.} & & \text{Sulphuric acid.} & & \text{Zinc sulphate.} & & \text{Hydrogen.} \end{array}$$

(ii) In a similar manner hydrogen may be prepared by the action of diluted sulphuric acid on the metal iron.

$$\begin{array}{ccccccc} Fe_2 & + & 2H_2SO_4 & = & 2FeSO_4 & + & 2H_2 \\ \text{Iron.} & & \text{Sulphuric acid.} & & \text{Ferrous sulphate.} & & \text{Hydrogen.} \end{array}$$

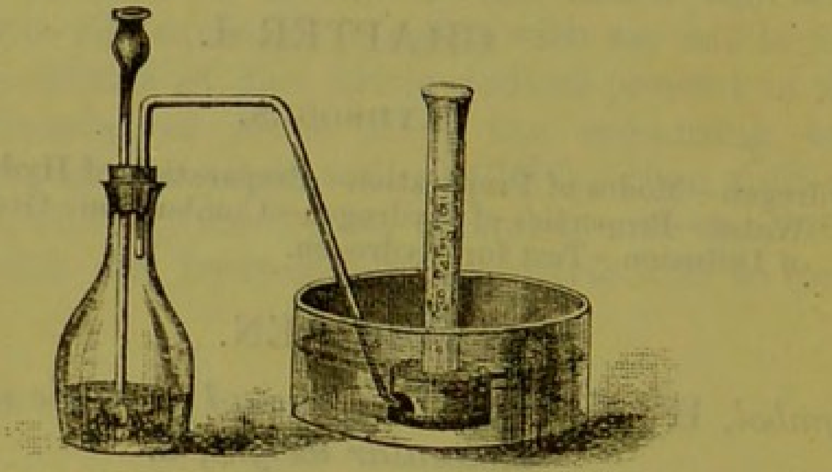


Fig. 1.—Preparation of Hydrogen from Zinc and Sulphuric Acid.

(iii) Hydrogen may also be obtained by the action of hydrochloric acid on the metal zinc, or on the metal iron.

$$\begin{array}{ccccccc} Zn & + & 2HCl & = & ZnCl_2 & + & H_2 \\ \text{Zinc.} & & \text{Hydrochloric acid.} & & \text{Zinc chloride.} & & \text{Hydrogen.} \end{array}$$

$$\begin{array}{ccccccc} Fe_2 & + & 4HCl & = & 2FeCl_2 & + & 2H_2 \\ \text{Iron.} & & \text{Hydrochloric acid.} & & \text{Ferrous chloride.} & & \text{Hydrogen.} \end{array}$$

(iv) Hydrogen may be obtained from water (*a*) by the *electrolysis* of water (see *water*, page 82), (*b*) by abstracting the oxygen from water, by passing steam over red-hot iron turnings contained in a heated iron pipe; the iron unites with the oxygen of the steam to form the black magnetic oxide of iron (Fe_3O_4), and free hydrogen passes on. This constitutes Barff's process for coating articles made of iron with a thin coating of the magnetic oxide of iron, which forms an extremely hard surface, and effectually prevents any future rusting of the article.

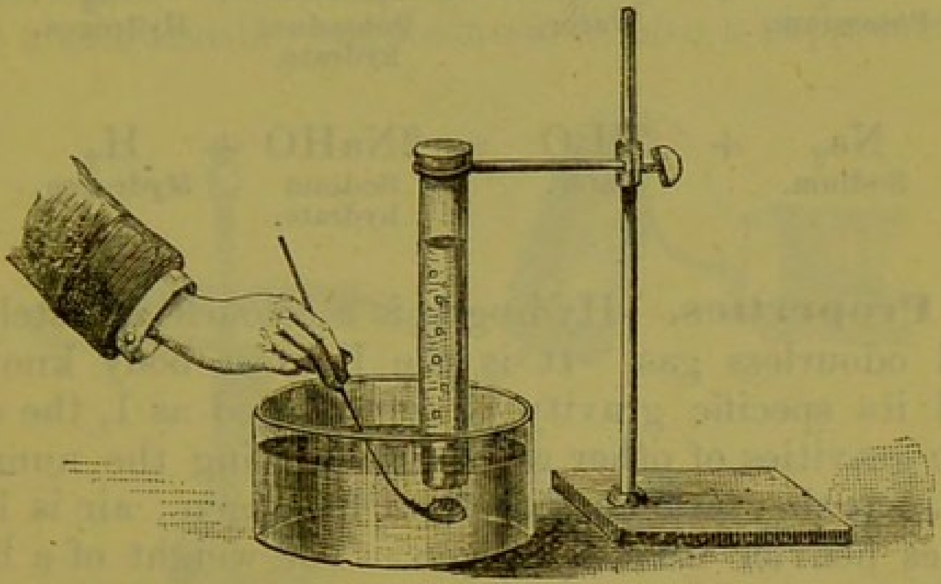


Fig. 2.—Preparation of Hydrogen from Potassium and Water.

$$\underset{\text{Iron.}}{Fe_3} + \underset{\text{Water.}}{4H_2O} = \underset{\substack{\text{Magnetic}\\\text{oxide of iron.}}}{Fe_3O_4} + \underset{\text{Hydrogen.}}{4H_2}$$

(*c*) By the action of either of the metals potassium or sodium on water at ordinary temperatures. Both these metals are lighter than water, and if either of them be thrown upon water, a violent action takes place, hydrogen being evolved. If the hydrogen is to be collected, it is necessary to wrap the piece of potassium or sodium in some wire gauze, which is then held beneath the water under an inverted jar full of water, within which the hydrogen will then collect (Fig. 2).

Both these metals only liberate one-half of the hydrogen of the water, uniting with the other half and with the oxygen to form respectively the hydrate of the metal, thus :

$$\underset{\text{Potassium.}}{K_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Potassium hydrate.}}{2KHO} + \underset{\text{Hydrogen.}}{H_2}$$

$$\underset{\text{Sodium.}}{Na_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Sodium hydrate.}}{2NaHO} + \underset{\text{Hydrogen.}}{H_2}$$

Properties.—Hydrogen is a colourless, tasteless, and odourless gas. It is the lightest body known, and its specific gravity is represented as 1, the specific gravities of other gases representing the number of times they are heavier than hydrogen ; air is 14·4 times heavier than hydrogen. The weight of a litre of hydrogen taken at 0° C. and 760 mm. barometric pressure is ·0896 gramme, and is known as the *crith* (from κριθή, a barleycorn) ; 1 gramme of hydrogen at 0° C. and 760 mm. barometric pressure occupies 11·2 litres (this latter fact will be found extremely useful in converting weights of various gases into volumes). Hydrogen is combustible, burning with an almost invisible flame if pure, and forming, by union with the oxygen of the air, water ; it is a non-supporter of combustion.

By the term combustion, as ordinarily employed, is meant union with the oxygen of the air, such union being accompanied by the production of heat and light, so that combustion may be defined as oxidation in which the chemical action is sufficiently great to be accompanied by the evident production of heat and light. It must, however, be clearly understood that the terms *combustible* and *supporter of combustion* are purely relative; thus, hydrogen is combustible in oxygen, and oxygen is a supporter of combustion; but if the atmosphere consisted of hydrogen, then oxygen would burn in it, and would then be the combustible body, the hydrogen then being the supporter of combustion. It therefore follows, according to the accepted meanings of these terms, that a combustible body cannot be also a supporter of combustion, nor conversely can a supporter of combustion be combustible.

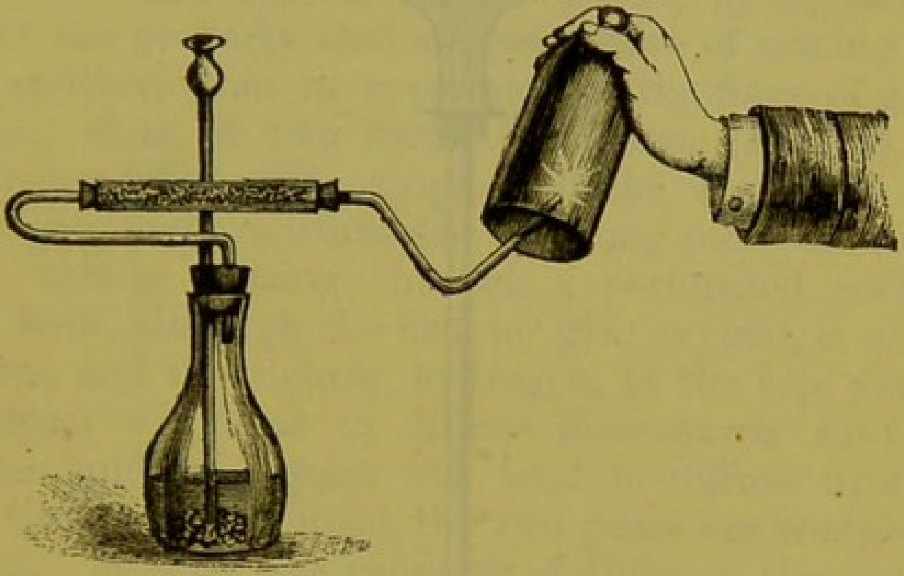


Fig. 3.—Formation of Water by the Combustion of Hydrogen.

The formation of water by the combustion of hydrogen can be demonstrated by allowing the jet of hydrogen to burn within a cool bell-jar, when the water condenses on the sides of the glass (Fig. 3).

The hydrogen flame is accompanied with the generation of intense heat, of which advantage is taken in the production of the lime-light. A jet of burning hydrogen (produced by the combustion of hydrogen with pure oxygen) is directed on to a piece of lime, the particles of which are raised to so high a temperature as to become incandescent, and glowing at a white heat they emit the dazzling light known as the lime-light. The reason why the ordinary hydrogen flame emits no light is, that there is present in it no solid matter that can be raised to a white heat and so emit light, for it is essential that for a flame to emit light there should be present in the flame some solid matter capable of being rendered incandescent; in the case of the lime-light the lime is the solid matter that is introduced into the flame, and is rendered incandescent by the intense heat generated by the burning hydrogen.

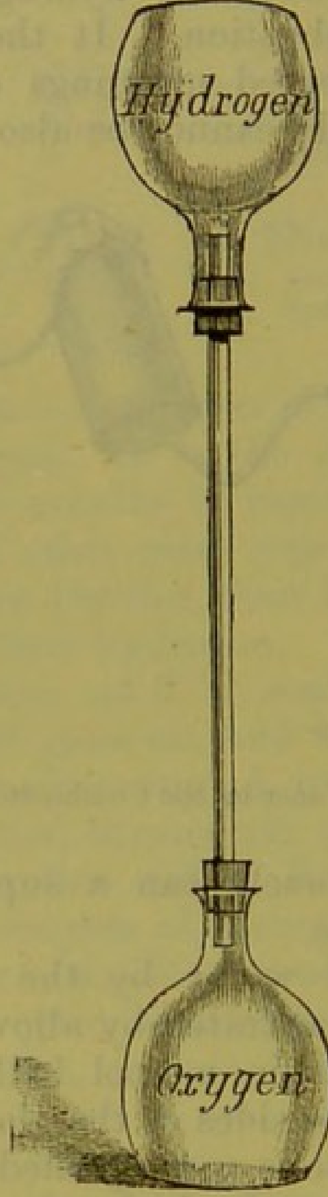


Fig. 4.—Apparatus for Diffusion of Gases.

When a light is applied to a mixture of hydrogen and oxygen, the union of the two gases is accompanied by an explosion; two volumes of hydrogen unite with one volume of oxygen, or two parts by weight of hydrogen with sixteen of oxygen, to form water.

Hydrogen is not appreciably soluble in water; it is not, in the ordinary sense of the term, a poisonous gas, although it is incapable of supporting life. It is the most diffusible of all the gases; by *diffusion* is meant the property that all gases have of mixing with one another, even in opposition to the force of gravitation; thus, if two flasks are taken (Fig. 4), the lower one filled with oxygen and the upper one with hydrogen, and are connected by a long piece of narrow glass tubing passing through a perforated cork in each flask, although the heavier gas, oxygen, is at the bottom, and the lighter, hydrogen, at the top, yet the hydrogen will tend to diffuse downwards into the oxygen, and the oxygen will tend to diffuse upwards into the hydrogen, until the two gases are completely mixed. It is by this property of diffusion that a small quantity of a bad-smelling gas escaping, say into the corner of a room, soon demonstrates by its odour that it has become mixed with the entire atmosphere of the room.

All gases do not diffuse at the same rate, lighter gases diffuse more quickly than heavier ones; the relation existing between the rate of diffusion of a gas and its specific gravity is formulated in what is known as **Graham's law of the diffusion of gases,** which is, *that gases diffuse inversely as the square roots of their specific gravities.* For instance, the specific gravity of hydrogen is 1 that of oxygen 16; the square root of the former is 1, of the latter 4; these numbers inverted give the rate of diffusion of hydrogen as four times that of oxygen.

Hydrogen is a reducing agent, by which is meant that, under certain conditions, it is capable of abstracting oxygen from a good many bodies containing that element; for instance, if hydrogen be passed over fragments of red-hot copper oxide, the oxygen is abstracted by the hydrogen to form water, the copper oxide being *reduced* to the metallic state; thus:

$$\underset{\text{Copper oxide.}}{2CuO} + \underset{\text{Hydrogen.}}{2H_2} = \underset{\text{Copper.}}{Cu_2} + \underset{\text{Water.}}{2H_2O}$$

Test.—The best test for hydrogen is its specific gravity, there being no substance lighter than it. The combined facts of its being odourless and burning with an almost invisible flame, would constitute a fairly trustworthy test.

CHAPTER II.

OXYGEN—OZONE.

Oxygen—Modes of Preparation—Preparation of Oxygen from Water—Electrolysis of Water—Preparation of Oxygen from Air—Properties of Oxygen—Test for Oxygen—Oxygen in Relation to Respiration—Ozone—Preparation—Tests for Ozone.

OXYGEN.

Symbol, O ; *formula*, O_2 ; *dyad* ; *atomic weight*, 16 ; *molecular weight*, 32.

OXYGEN is present to a very large extent in nature. In the compounds composing the solid crust of the earth it exists in considerable proportions, principally in chalk and limestone (calcium carbonate—$CaCO_3$, sand and flint (silica—SiO_2), and clay (aluminium silicate—$Al_4(SiO_4)_3$). It constitutes $\frac{8}{9}$ by weight of water, and $\frac{2}{9}$ by weight of air. Its name is derived from ὀξύς, acid, and γεννάω, I produce, since at one time it was believed to enter into the composition of all acids, a belief which for a long time has been known to be erroneous.

Modes of preparation.—(i) By heating mercuric oxide (red oxide of mercury) :

$$\underset{\text{Mercuric oxide.}}{2HgO} = \underset{\text{Mercury.}}{2Hg} + \underset{\text{Oxygen.}}{O_2}$$

This method, although by no means the best one for obtaining oxygen, is of interest from the fact that it was in this way that oxygen was first obtained and discovered by Priestley in 1774 ; mercury possesses the property, when heated to a temperature of 320° C.

with exposure to air, of slowly absorbing oxygen from the air, and forming mercuric oxide, which, when the temperature is raised a little higher, evolves its oxygen, the metal mercury being left. In 1775 it was obtained independently by Scheele, by heating strong sulphuric acid with black oxide of manganese:

$$\underset{\text{Manganese black oxide.}}{2MnO_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Manganese sulphate.}}{2MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}$$

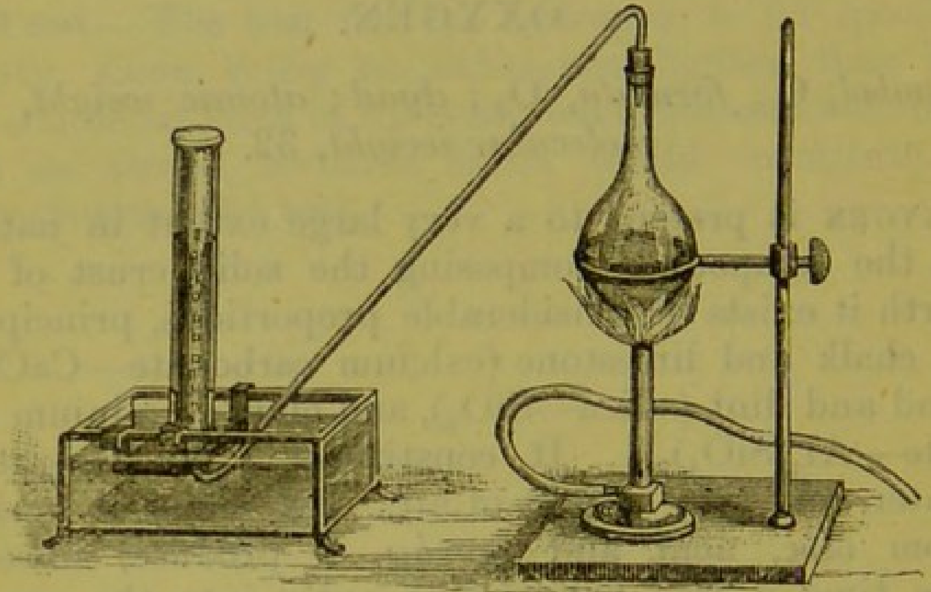


Fig. 5.—Preparation of Oxygen.

(ii) One of the best ways of obtaining oxygen, for experimental purposes, is by heating chlorate of potassium in a glass flask, to which is fitted a perforated cork and bent tube for conveying the gas to a pneumatic trough, where it can be collected over water (Fig. 5).

The whole of the oxygen of the chlorate of potassium is evolved, chloride of potassium being left:

$$\underset{\text{Potassium chlorate.}}{2KClO_3} = \underset{\text{Potassium chloride.}}{2KCl} + \underset{\text{Oxygen.}}{3O_2}$$

(iii) Oxygen may be obtained by strongly heating manganese dioxide (black oxide of manganese) in a gun-barrel closed at one end, and fitted at the other end with a perforated cork and tubing for carrying off the gas. The manganese dioxide only loses one-third of its oxygen, a lower oxide of manganese being left :

$$\underset{\text{Manganese dioxide.}}{3MnO_2} = \underset{\text{Trimanganic tetroxide.}}{Mn_3O_4} + \underset{\text{Oxygen.}}{O_2}$$

(iv) Oxygen is very readily obtained at a comparatively low temperature by heating a mixture of potassium chlorate and manganese dioxide; the oxygen is evolved from the chlorate of potassium only, but at a much lower temperature than would suffice if the chlorate were heated alone, possibly because the manganese dioxide (MnO_2) unites with the oxygen of the chlorate at a low temperature to form a higher oxide (MnO_3 possibly), which being extremely unstable, is immediately split up by the heat into manganese dioxide and oxygen.

(v) Oxygen may be obtained by heating powdered bichromate of potassium with strong sulphuric acid. (The student will learn later that this process is a convenient one for the oxidation of alcohols to their respective acids.)

$$\underset{\text{Potassium bichromate.}}{2K_2Cr_2O_7} + \underset{\text{Sulphuric acid.}}{8H_2SO_4} = \underset{\text{Chromium sulphate.}}{2Cr_2(SO_4)_3} + \underset{\text{Potassium sulphate.}}{2K_2SO_4} +$$

$$\underset{\text{Water.}}{8H_2O} + \underset{\text{Oxygen.}}{3O_2}$$

(vi) Oxygen may be obtained from water by two processes : (*a*) the electrolysis of water, and (*b*) decomposition of it by means of chlorine.

(*a*) *Electrolysis of water.*—This consists in decomposing water into its elements by means of a current of electricity. A glass vessel, A, (Fig. 6) is taken, into which project two platinum electrodes, which are connected through the bottom of the vessel with the wires B and C, which in their turn are connected respectively with the positive and negative poles of a battery. Some water acidulated with sulphuric acid (to render it a better conductor of electricity) is placed in A, and two glass tubes, D and E, are filled with this acidulated water, and then inverted over the platinum electrodes. On passing the current of electricity, the water is decomposed into its elements, the hydrogen being set free at the negative pole or electrode (C), and the oxygen at the positive pole or electrode (B), the hydrogen collecting in the tube placed over the negative electrode, and the oxygen in the tube over the positive electrode. The volume

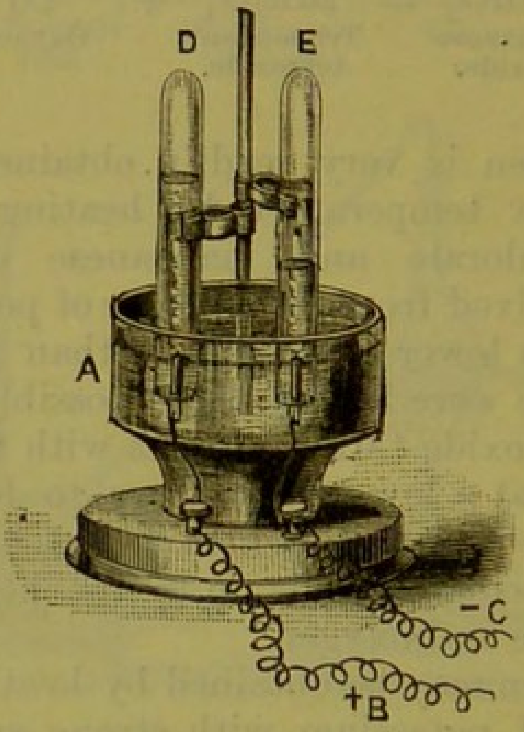


Fig. 6.—Electrolysis of Water.

of hydrogen evolved is double that of the oxygen, although if the volumes of the gases are very accurately compared, it will be found that the oxygen measures slightly less than one-half the volume of the hydrogen, this slight difference being due to the greater solubility of oxygen in water, as compared with hydrogen.

(*b*) *Decomposition of water by chlorine.*—If chlorine and steam be passed through a porcelain tube containing fragments of pumice-stone heated to bright redness, the chlorine unites with the hydrogen of the water, forming hydrochloric acid, and the oxygen is set free:

$$\underset{\text{Chlorine.}}{2Cl_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Oxygen.}}{O_2}$$

If the mixture of hydrochloric acid gas and oxygen be passed through a strong solution of caustic potash, the former is absorbed, potassium chloride being formed, and the oxygen is then obtained in the pure state.

(vii) Oxygen may be obtained from the atmosphere, in which it naturally occurs mixed with nitrogen in the proportions of 21 volumes of oxygen to 79 of nitrogen. As there is no method of absorbing the nitrogen from a limited amount of air, and so leaving the oxygen in the pure state, the method that must be resorted to, if it is desired to obtain pure oxygen from the air, is to roast some substance in contact with the air, which at one temperature will absorb or combine with the oxygen of the air, and at another temperature will give up in a pure state the oxygen so taken from the air. The two simplest processes for effecting this are (*a*) the mercury process, and (*b*) the baryta process.

(*a*) *The mercury process.*—This process has been described on page 79. It is of interest as being the process by which oxygen was first discovered.

(*b*) *The baryta process.*— This process depends upon the metal barium possessing two oxides, a lower one, baryta (BaO), and a higher one, barium dioxide (BaO_2). If baryta (BaO) be raised to a dull red heat, and air be passed over it, the oxygen of the air is absorbed, converting the baryta into barium dioxide (BaO_2):

$$\underset{\text{Baryta.}}{2BaO} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Barium}\\\text{dioxide.}}}{2BaO_2}$$

If now the barium dioxide be raised to a bright red heat, it is resolved into baryta and oxygen, and so the oxygen absorbed from the air is obtained in a pure state:

$$\underset{\substack{\text{Barium}\\\text{dioxide.}}}{2BaO_2} = \underset{\text{Baryta.}}{2BaO} + \underset{\text{Oxygen.}}{O_2}$$

This process is now employed on a manufacturing scale for obtaining pure oxygen.

Properties.—The specific gravity of oxygen is 16; it is a little heavier than air. It is colourless, tasteless, and odourless. Although non-combustible, it is a powerful supporter of combustion, substances burning in oxygen much more brilliantly than they do in air. For instance, phosphorus burns with a most intense light in oxygen, and even a steel-wire spiral tipped with a piece of burning tinder and placed in a jar of oxygen will burn brilliantly, producing a shower of oxide of iron sparks (Fig. 7).

Oxygen is soluble in water, 100 volumes of water dissolving about 3 volumes of oxygen, and it is by means of this dissolved oxygen that fishes' blood, circulating through the gills, becomes aërated. Oxygen is, of course, non-poisonous, being the life-sustaining principle of the air ; but if an animal be kept in pure oxygen it rapidly emaciates, on account of the increased waste of tissue substance generated by the absorption of pure oxygen into the blood, and this occurs although the animal may be plentifully supplied with food, which it greedily devours.

Fig. 7.—Combustion of Steel-wire in Oxygen.

Test.—The best test for oxygen is one depending upon its remarkable power of supporting combustion ; if a piece of wood which has been made incandescent or glowing at one extremity, be plunged into a jar of oxygen, it bursts into flame, and constitutes a sure test for oxygen.

Oxygen in relation to respiration.—The oxygen of the air taken into the lungs, during inspiration, dissolves in part in the moisture covering the walls of the pulmonary air-cells, and so passes, by a process of osmosis, through the walls of the blood-capillaries into the blood, where it unites with the hæmoglobin or colouring matter of the blood, to form a compound called oxyhæmoglobin. In this compound the oxygen is conveyed by the blood to all the tissues of the body, which abstract the oxygen from its loose union with the hæmoglobin, and undergo by means of it a process of combustion, and it is the heat resulting from these chemical changes that suffices to maintain the temperature of the human body. One of the necessary and chief products of the oxidation of the animal tissues is carbon dioxide, which is absorbed into the blood, the fluid portion of which, or *liquor sanguinis*, contains sodium carbonate in solution, which, with the carbon dioxide, forms bicarbonate of sodium :

$$\underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sodium}\\\text{bicarbonate.}}}{2NaHCO_3}$$

This is conveyed in the blood to the lungs, where, circulating through the capillaries in the walls of the air-cells, the bicarbonate of sodium becomes resolved into carbonate of sodium, the carbon dioxide which it had absorbed diffusing through the walls of the air-cells, and so passing away from the body in the expired air. There is thus a constant interchange of oxygen from the atmosphere, and of carbon dioxide from the blood, the air taken into the lungs losing four per cent. of oxygen and gaining in its place four per cent. of carbon dioxide. This carbon dioxide, which passes in the expired air out into the atmosphere, does not accumulate there, but is absorbed by the leaves of plants (through small openings called *stomata*) and brought into contact with the chlorophyll or green colouring-matter of the leaves, which possesses the important property of decomposing the carbon dioxide, the oxygen of which is returned to the air, and so the normal composition of the atmosphere is maintained at the same time the chlorophyll possesses the power forcing the carbon of the carbon dioxide into union with the elements of water, to eventually become converted into sugar, starch, and other organic substances.

These changes may be represented by the following equations. Carbon dioxide and water under the influence of chlorophyll reacting thus:

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Formic aldehyde.}}{CH_2O} + \underset{\text{Oxygen.}}{O_2}$$

producing formic aldehyde and oxygen. Six molecules of formic aldehyde, by becoming fused into one molecule, form grape sugar:

$$\underset{\text{Formic aldehyde.}}{6CH_2O} = \underset{\text{Grape sugar.}}{C_6H_{12}O_6}$$

The grape sugar is conveyed by the sap of the plant to the seeds, roots, and other parts, and being there deprived of the elements of water, starch is formed and deposited:

$$\underset{\text{Grape sugar.}}{C_6H_{12}O_6} - \underset{\text{Water.}}{H_2O} = \underset{\text{Starch.}}{C_6H_{10}O_5}$$

In this way the carbon excreted as carbon dioxide in the breath becomes again converted into an article of diet.

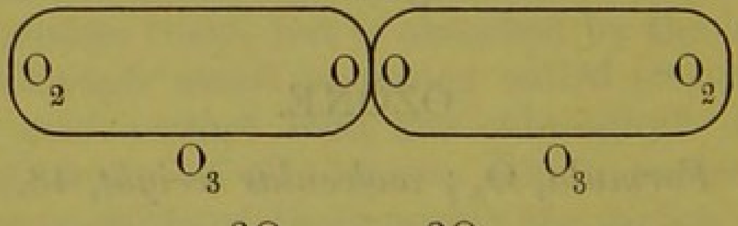
OZONE.

Formula, O_3; *molecular weight*, 48.

Ozone (from ὄζω, I smell) is an allotropic form of oxygen, three volumes being condensed into two. It occurs naturally in the atmosphere in very small quantities, being produced from the oxygen of the air either by electrical currents generated during a thunderstorm, or by the weak currents of frictional electricity generated by the friction of large masses of water (such as the sea) against the air, or possibly by the evaporation of water in presence of sunlight.

Modes of preparation.—Ozone is prepared by effecting the condensation of three volumes of oxygen into two, but by whatever process this may be effected, it is impossible to convert all the oxygen into ozone; in other words, ozone cannot be obtained in a pure state, but always contains admixed oxygen, a mixture containing about 20 per cent. of ozone to 80 per cent. of oxygen being about the strongest that has ever been made. This condensation of oxygen into ozone may be effected in the following ways.

(i) By the silent passage of electricity through damp oxygen or air; the peculiar odour noticed when a frictional electrical machine is being worked is due to the production of ozone by this process. The current of electricity no doubt possesses the property of splitting some of the oxygen molecules into their constituent atoms, which, being incapable of existing in the free state, immediately link themselves to adjacent oxygen molecules to produce ozone molecules. This may be represented as follows, where the production of two ozone molecules from three oxygen molecules is depicted :—



or $$\underset{\text{Oxygen.}}{3O_2} = \underset{\text{Ozone.}}{2O_3}.$$

(ii) Ozone may be prepared by exposing a stick of phosphorus to moist and warm oxygen or air. This is best effected by placing a stick of phosphorus at the bottom of a bottle containing sufficient water to cover partially the phosphorus, loosely plugging the mouth of the bottle, and placing it for half an hour near a fire. At the end of that time ozone will be found in the air of the bottle, if the proper tests are applied.

Properties.—The specific gravity of ozone is 24, and it is heavier than air; it is colourless, but possesses a peculiar odour which has been compared to that of diluted chlorine, or to phosphorus slowly oxidising. It is non-combustible, but is a supporter of combustion, and is slightly soluble in water. It is a powerful bleaching and oxidising agent, being capable of oxidising such metals as mercury and silver in the cold. It is an irritant to the eyes, nose, and bronchial tract, when present in the air in moderate quantities; and it is probable that the attacks of asthma to which some people are subject when at sea may be due to the amount of ozone in the sea air. In large quantities, ozone proves fatal to animals.

Tests.—The ordinary method for detecting ozone in the air depends upon the power that ozone possesses of liberating iodine from iodide of potassium, the free iodine being delicately detected by the blue colour that it gives with a solution of starch. A piece of filter paper is moistened with a mixed solution of iodide of potassium and starch, and is then suspended for some time in a current of the air to be tested, when, if ozone be present, it will assume a blue colour. The objections to the validity of this test are that other bodies besides ozone may be present in the air, which also possess the property of liberating iodine from iodide of potassium, and so giving a blue colour to the starch; these bodies are chlorine and nitrogen tetroxide. It will be seen from the following equations that when ozone liberates the iodine from iodide of potassium it first forms potassium oxide, which, with water, forms caustic potash, a body that is alkaline to test-paper; whereas chlorine and nitrogen tetroxide in liberating iodine from iodide of potassium form respectively chloride of potassium and nitrite of potassium, both of which are neutral to test-paper.

$$\underset{\substack{\text{Potassium}\\\text{iodide.}}}{6KI} + \underset{\text{Ozone.}}{O_3} = \underset{\substack{\text{Potassium}\\\text{oxide.}}}{3K_2O} + \underset{\text{Iodine.}}{3I_2}$$

then

$$\underset{\substack{\text{Potassium}\\\text{oxide.}}}{3K_2O} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Caustic potash}\\\text{(Potassium hydrate).}}}{6KHO}$$

$$\underset{\substack{\text{Potassium}\\\text{iodide.}}}{2KI} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{2KCl} + \underset{\text{Iodine.}}{I_2}$$

$$\underset{\substack{\text{Potassium}\\\text{iodide.}}}{2KI} + \underset{\substack{\text{Nitrogen}\\\text{tetroxide.}}}{N_2O_4} = \underset{\substack{\text{Potassium}\\\text{nitrite.}}}{2KNO_2} + \underset{\text{Iodine.}}{I_2}$$

So that the best test for ozone in the air will evidently depend, not on the liberation of iodine from iodide of potassium, since both chlorine and nitrogen tetroxide can effect this, but on ascertaining whether, with the liberation of the iodine, the solution of iodide of potassium becomes alkaline, since both chlorine and nitrogen tetroxide in liberating the iodine from iodide of potassium leave the solution neutral. The method of applying this modified and improved test for ozone in the air consists in exposing to the air in a shallow vessel for some hours, a solution of iodide of potassium coloured with red litmus, when, if ozone is present, the red colour changes to blue; whereas if chlorine or nitrogen tetroxide are present in the air, although they liberate the iodine from the iodide of potassium, yet the chloride of potassium and nitrite of potassium respectively formed, being neutral, are incapable of changing the colour of the red litmus.

CHAPTER III.

WATER—HYDROGEN DIOXIDE.

Water — Composition — Properties — Water of Crystallisation—Efflorescence—Deliquescence—Sources of Drinking Waters—Soft and Hard Waters—Temporary and Permanent Hardness—Mineral Waters—Hydrogen Dioxide—Modes of Preparation—Test for Hydrogen Dioxide.

WATER.

Formula, H_2O; *molecular weight*, 18.

Composition.—Water is composed of hydrogen and oxygen united in the proportion of two parts of hydrogen by weight to sixteen of oxygen, or, by volume, it is formed by the union of two volumes of hydrogen with one volume of oxygen. The composition of water may be proved in the following ways:

(i) *The analytical method.*—By electrolysis or the decomposition of water into its elements by means of a current of electricity (see page 82).

(ii) *The synthetical method.*—(*a*) By introducing a mixture of two parts by volume of hydrogen to one of oxygen into a eudiometer, and then exploding the mixture by means of an electric spark, when water will be formed. This may be effected in the Cavendish eudiometer (Fig. 8, A), which consists of a stout glass vessel, provided with a stop-cock at the lower part, and with two platinum wires fused through the glass at the upper part. The eudiometer is first exhausted of air by means of an air-pump, and is then filled with a mixture of two volumes of hydrogen to one volume of oxygen by connecting it with a bottle (B) containing the two gases in those proportions; the stop-cock is then closed and the eudiometer detached from B; the gases may then be exploded by means of an electric spark between the two platinum wires, the electricity being furnished by a charged Leyden jar (C). By the explosion of the hydrogen and oxygen

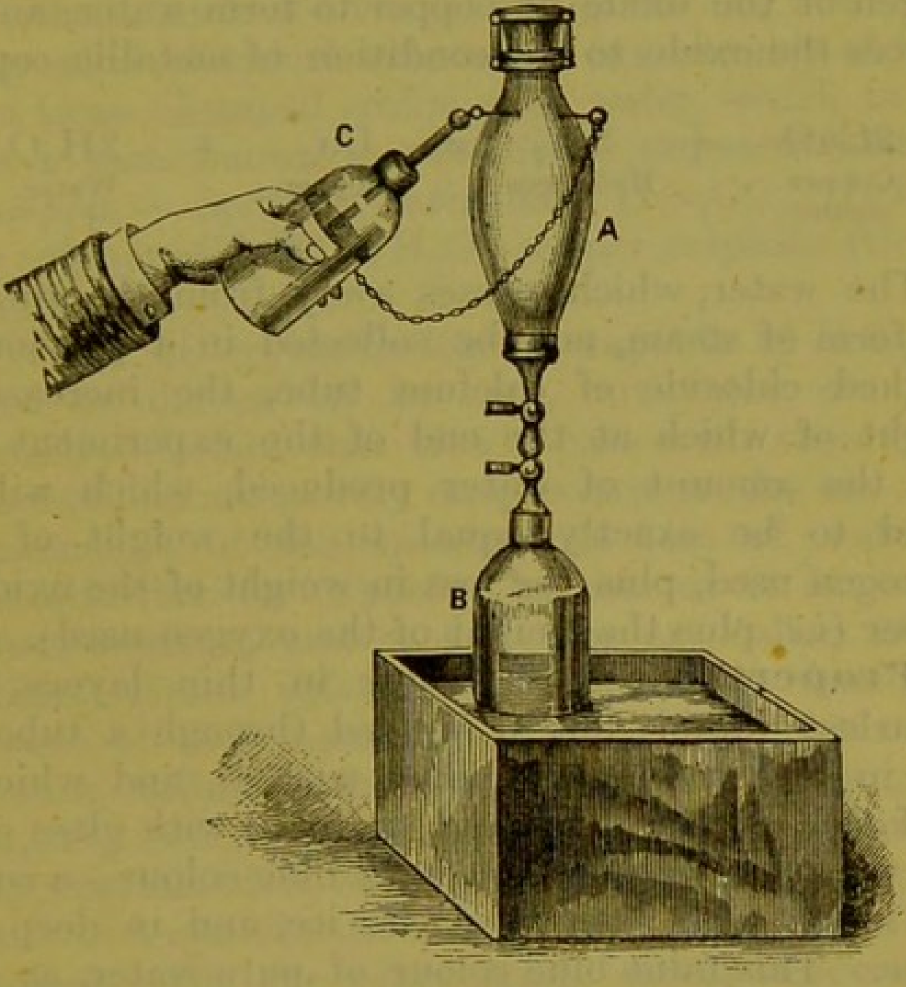


Fig. 8.—Formation of Water by the Explosion of Hydrogen and Oxygen in the Cavendish Eudiometer.

water will be formed, and will be deposited as a film upon the inner surface of the eudiometer, and the complete conversion of these two gases into water will be demonstrated by the fact that, on opening the stop-cock of the eudiometer under water, the interior of it will be immediately and completely filled by the water, on account of the vacuum left within the eudiometer by the union of the hydrogen and oxygen, and the condensation of the resulting water as a film on the inner surface of the vessel.

(*b*) The composition of water may also be proved by passing a known weight of hydrogen over a known weight of oxide of copper contained in a tube, and heated to redness. The hydrogen unites with the oxygen of the oxide of copper to form water, and so reduces the oxide to the condition of metallic copper.

$$\underset{\text{Copper oxide.}}{2CuO} + \underset{\text{Hydrogen.}}{2H_2} = \underset{\text{Copper.}}{Cu_2} + \underset{\text{Water.}}{2H_2O}$$

The water, which passes away from the tube in the form of steam, may be collected in a previously-weighed chloride of calcium tube, the increase in weight of which at the end of the experiment will give the amount of water produced, which will be found to be exactly equal to the weight of the hydrogen used, plus the loss in weight of the oxide of copper (*i.e.* plus the weight of the oxygen used).

Properties.—Pure water in thin layers is a colourless liquid, but if viewed through a tube six feet in length which is filled with it, and which is blackened at the sides and provided with glass ends, it is then seen to possess a faint blue colour—a colour that is also well seen in glacier ice, and in deep sea-water. This faint blue colour of pure water, as seen through a six-foot tube, is of some value in forming an opinion as to the purity of a drinking-water, since the presence of a very small amount of animal organic matter (sewage), or of vegetable organic matter (peat), will cause the blue colour of the water to be replaced by a yellow or brownish tint. Pure water is tasteless and odourless; its specific gravity is 1, that is, it is chosen as the standard with which the weights of equal volumes of all other liquids and solids are compared; it freezes at 0° C., and boils at 100° C., under the normal atmospheric pressure. A large number of solids and gases are capable of passing into the liquid state when placed in water, *i.e.* they are **soluble** in the water. Some liquids, such as alcohol and glycerine, are **miscible** with water in all proportions; others, such as chloroform and ether, only in small proportions; and others, such as olive oil and castor oil, not at all. Many solid chemical substances are capable of forming a loose chemical union with water, which in this form is then known as **water of crystallisation.** *Examples.* — Sodium carbonate (Na_2CO_3, $10H_2O$), zinc sulphate ($ZnSO_4$, $7H_2O$), copper sulphate ($CuSO_4$, $5H_2O$).

Water of crystallisation is capable of being expelled or driven off by heat, but there are some crystalline bodies that slowly part with their water of crystallisation merely on exposure to the air. This phenomenon of the spontaneous loss of water of crystallisation on exposure to the air is known as **efflorescence,** and such bodies are called **efflorescent** (from *efflorescens*, blossoming forth), on account of their assuming a powdery condition; for instance, sodium carbonate or ordinary washing soda (Na_2CO_3, $10H_2O$) is a good example of an efflorescent body, crystals of it, on exposure to the air, losing their water of crystallisation, and becoming opaque and powdery. On the other hand, **deliquescence** is the power possessed by certain solid substances of absorbing moisture from the air to such an extent as to become moist and finally liquid, from the solid dissolving in the absorbed water; such bodies are called **deliquescent** (from *deliquescens,* melting away), on account of the liquefaction that they undergo on exposure to the air; calcium chloride and potassium carbonate are two good examples of deliquescent substances, as they soon become liquid on exposure to the air.

Sources and varieties of water as used for drinking purposes.—Rain and snow are the natural sources from which drinking-waters are derived. Rain when it falls upon the surface of the earth is disposed of in three ways: (1) part of it is returned to the atmosphere by evaporation; (2) part of it flows according to the inclination of the surfaces, and so contributes to the formation of brooks, streams, and rivers; (3) part of it sinks or percolates into the soil until it reaches an impermeable stratum of hard rock or clay, and so forms the underground sources of water that are made available for the use of man either by coming to the surface as springs, or by being tapped by the sinking of wells or pumps.

Rain-water as it leaves the clouds is pure, but in its passage through the air it may absorb and collect many substances, such as oxygen, carbon dioxide, traces of ammonia, sulphur dioxide, nitrogen, tetroxide, chlorine, sodium chloride (if in the vicinity of the sea), particles of soot, and various fungoid and bacterial organisms. The rain-water percolating through, or flowing over, the soil may dissolve from it various substances, such as lime salts, magnesia salts, etc. Rain-water is a very soft water, and is therefore useful for washing purposes. A **soft water** is one in which soap can dissolve, and therefore readily form a lather without being precipitated; a **hard water,** on the other hand, is one in which soap, as fast as it dissolves, is precipitated by some substance or substances present in the water, and so the formation of a lather is rendered difficult. The hardness of a water may be temporary or permanent, or a combination of the two; **temporary hardness** is that which can be removed by boiling the water, and is due to the presence of the soluble bicarbonates of calcium and magnesium, which on boiling are converted into the insoluble carbonates of those metals, and these being deposited constitute the *fur* that accumulates in kettles and boilers. Temporary hardness is acquired by rain or stream water, containing carbon dioxide in solution, flowing over some form of calcium carbonate (chalk or limestone) or magnesium carbonate in the soil; such water containing carbon dioxide in solution is capable of forming a soluble bicarbonate with either of these carbonates, thus:

$$\underset{\text{Calcium carbonate.}}{\mathrm{CaCO_3}} + \underset{\text{Carbon dioxide.}}{\mathrm{CO_2}} + \underset{\text{Water.}}{\mathrm{H_2O}} = \underset{\text{Calcium bicarbonate.}}{\mathrm{Ca(HCO_3)_2}}$$

This soluble bicarbonate loses part of its carbon dioxide on boiling, and the insoluble calcium carbonate is once more formed and deposited, thus:

$$\underset{\text{Calcium bicarbonate.}}{\mathrm{Ca(HCO_3)_2}} = \underset{\text{Calcium carbonate.}}{\mathrm{CaCO_3}} + \underset{\text{Carbon dioxide.}}{\mathrm{CO_2}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

Permanent hardness is that which cannot be removed by boiling, and is generally due to the presence of calcium or magnesium sulphate, or, in the case of sea-water, to sodium chloride. The difficulty experienced with a hard water of obtaining a lather with ordinary soap (sodium oleate) is because that, as soon as some of the soap dissolves, it is converted into the insoluble calcium or magnesium oleate, whereas for obtaining a lather it is necessary that the soap should be in solution. The great waste of soap, consequent upon the use of hard waters, may be judged of by the fact that every grain of calcium carbonate or chalk held in solution in a water as the bicarbonate, is capable of wasting about eight grains of soap. In the case of sea-water, the hardness is due to the fact that ordinary soap (sodium oleate) is insoluble in a moderately strong solution of common salt (sodium chloride).

Mineral waters.—These are spring waters containing in solution some medicinal ingredient. In the following table the more important mineral waters are enumerated, with their sources and composition.

SOURCE.	COMPOSITION.
Vichy Carlsbad Ems Seltzer Malvern Apollinaris	Alkaline waters, containing sodium carbonate and bicarbonate; effervescence due to carbon dioxide.
Spa Tunbridge Some Cheltenham Waters	Chalybeate waters, containing ferrous carbonate held in solution by excess of carbon dioxide.
Harrogate Aix-la-Chapelle	Sulphuretted waters, containing free sulphuretted hydrogen.
Leamington Epsom	Aperient saline waters, containing magnesium sulphate.
Cheltenham Scarborough	Aperient saline waters, containing sodium sulphate and sodium chloride.
Bath Bristol Matlock	Calcareous waters, containing calcium bicarbonate and calcium sulphate.

HYDROGEN DIOXIDE.

Formula, H_2O_2; *molecular weight*, 34.

Water and hydrogen dioxide constitute the two oxides of hydrogen. Hydrogen dioxide is also known as peroxide of hydrogen, and as oxygenated water, the latter name being given to it on account of the facility with which it decomposes into water and oxygen.

Modes of preparation.—(i) Hydrogen dioxide may be obtained by the action of any acid on barium dioxide. Thus, if diluted hydrochloric acid be added to barium dioxide, double decomposition takes place, barium chloride and hydrogen dioxide being formed :

$$\underset{\substack{\text{Barium}\\\text{dioxide}}}{BaO_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Barium}\\\text{chloride.}}}{BaCl_2} + \underset{\substack{\text{Hydrogen}\\\text{dioxide.}}}{H_2O_2}$$

Hydrochloric acid, however, is not a convenient acid to use in the preparation of hydrogen dioxide, since this latter body is contaminated by the presence of the soluble barium chloride. It is therefore preferable to select an acid which will yield an insoluble barium salt, and so leave only the hydrogen dioxide in solution; carbonic acid answers these requirements admirably. If carbon dioxide be passed through water containing barium dioxide suspended in it, carbonate of barium is precipitated and a pure solution of hydrogen dioxide obtained :

$$\underset{\substack{\text{Barium}\\\text{dioxide.}}}{BaO_2} + \underset{\text{Water.}}{H_2O} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} = \underset{\substack{\text{Barium}\\\text{carbonate.}}}{BaCO_3} + \underset{\substack{\text{Hydrogen}\\\text{dioxide.}}}{H_2O_2}$$

(ii) Hydrogen dioxide is also obtained as one of the products of the atmospheric oxidation of several of the natural volatile oils in presence of moisture, such as the oils of turpentine, pine, eucalyptus, etc. The presence of this hydrogen dioxide in the atmosphere probably to some extent accounts for the hygienic and antiseptic properties that have for some time been attributed to the air of pine and eucalyptus forests.

Properties.—Hydrogen dioxide is a liquid, but is always obtained mixed with water, a 10 per cent.

solution being the usual strength of the commercial article. It is colourless and odourless, but possesses an astringent taste, and is miscible with water in all proportions. Its special property consists in the readiness with which it splits up into water and oxygen:

$$\underset{\text{Hydrogen dioxide.}}{2H_2O_2} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}$$

This decomposition may be brought about by boiling, or by bringing it in contact with bodies in want of oxygen, when the hydrogen dioxide readily parts with one-half of its oxygen; it is in this way that it acts as a disinfectant and deodoriser. Hydrogen dioxide is also a powerful bleaching agent by virtue of its power of rapidly oxidising colouring matters, and so bleaching them; its effect as a so-called hair-dye, in turning the hair yellow or white, is simply that of a bleaching agent.

Test.—Hydrogen dioxide possesses the property of liberating iodine from iodide of potassium, the liberated iodine turning starch solution blue; this is a property, however, possessed by other substances, but unlike all these other oxidising agents, hydrogen dioxide will liberate the iodine from iodide of potassium in presence of ferrous sulphate.

Another test for hydrogen dioxide is that when mixed with tincture of guaiacum and blood, a bluish-green colour is produced; advantage is taken of this reaction to detect the presence of blood in urine, a few drops of tincture of guaiacum being added to a small quantity of the urine in a test-tube, and then an ethereal solution of hydrogen dioxide (commonly known and sold as *ozonic ether*), when on shaking together the contents of the tube, a bluish-green colour will be developed if blood is present in the urine.

CHAPTER IV.

NITROGEN—THE ATMOSPHERE.

Nitrogen—Preparation and Properties of Nitrogen—Test for Nitrogen—Composition of the Atmosphere—Methods of determining the Composition of the Atmosphere—Proofs that the Atmosphere is a Mixture, and not a Compound, of Oxygen and Nitrogen—Aqueous Vapour in the Air—Carbon Dioxide in the Air—Ozone in the Air—Impurities in Air.

NITROGEN.

Symbol, N; *formula*, N_2; *pentad* (also capable of acting as a *triad* and *monad*, *see* page 28); *atomic weight*, 14; *molecular weight*, 28.

NITROGEN (meaning *generator of nitre*) owes its name to the fact that it is an essential constituent of nitre (nitrate of potash). Nitrogen is widely and extensively distributed in nature; it constitutes four-fifths of the bulk of the atmosphere, it is present in all natural nitrates, and forms an important constituent of the tissues and organs of all animals and plants; in animals it is present in albumin, fibrine, cartilage, casein, urea, etc.; in plants it is present in vegetable albumin and in all alkaloids.

Modes of preparation.—(i) Nitrogen may be obtained by removing the oxygen from a limited volume of air by any of the following processes:

(*a*) By burning phosphorus under a bell-jar standing over water; the phosphorus consumes all the oxygen of the air contained in the bell-jar, forming a white powder—phosphorus pentoxide (P_2O_5)—which dissolves in the water, forming phosphoric acid (H_3PO_4), and the space formerly occupied by the oxygen is filled by the water taking its place. The gas within the bell-jar now occupies four-fifths of the original volume of the air taken, and consists of pure nitrogen.

(*b*) By absorbing oxygen from a confined volume of air by means of a solution of pyrogallate of potassium.

(*c*) By passing air over red-hot copper turnings contained in a long porcelain tube, when the copper unites with the oxygen of the air to form copper oxide (CuO), and pure nitrogen passes on.

(*d*) By exploding in a eudiometer 42 volumes of hydrogen with 100 volumes of air (the latter containing just 21 volumes of oxygen), when the hydrogen and oxygen will unite to form water, which will condense on the sides of the eudiometer, and pure nitrogen will remain.

(ii) Nitrogen may be very readily obtained by boiling together solutions of potassium nitrite and ammonium chloride, when double decomposition between the two salts first takes place, resulting in the formation of ammonium nitrite and potassium chloride.

$$\underset{\substack{\text{Potassium}\\\text{nitrite.}}}{KNO_2} + \underset{\substack{\text{Ammonium}\\\text{chloride.}}}{NH_4Cl} = \underset{\substack{\text{Ammonium}\\\text{nitrite.}}}{NH_4NO_2} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{KCl}$$

The ammonium nitrite is then split up, by the heat of the boiling liquid, into nitrogen and water.

$$\underset{\substack{\text{Ammonium}\\\text{nitrite.}}}{NH_4NO_2} = \underset{\text{Nitrogen.}}{N_2} + \underset{\text{Water.}}{2H_2O}$$

(iii) Nitrogen may also be prepared by passing chlorine into solution of ammonia, when ammonium chloride is formed and nitrogen evolved.

$8NH_3$	+	$3Cl_2$	=	$6NH_4Cl$	+	N_2
Ammonia.		Chlorine.		Ammonium chloride.		Nitrogen.

This process for obtaining nitrogen is not a desirable one to employ, since, if the ammonia is not kept in excess, the chlorine would act upon the ammonium chloride, forming the terribly explosive chloride of nitrogen.

Properties.—The specific gravity of nitrogen is 14, and it is a little lighter than air. The properties of nitrogen are mainly negative; it is odourless, tasteless, colourless, not combustible, a non-supporter of combustion, and but slightly soluble in water; it is not poisonous, since the air contains about four-fifths of it by volume, but it is incapable of supporting life by itself. The main function of the nitrogen of the atmosphere is to dilute down the oxygen which would otherwise be too energetic in its action.

Test.—A lighted taper, if plunged into a jar of nitrogen, is immediately extinguished, and the gas itself does not ignite. The only other odourless, or comparatively odourless, gas that behaves in this way is carbon dioxide, and the two may be readily distinguished by carbon dioxide turning lime-water milky, whereas nitrogen has no effect upon lime-water. So that the combined facts of an odourless gas extinguishing a lighted taper, being non-combustible, and not turning lime-water turbid, will indicate that the gas is nitrogen.

THE ATMOSPHERE.

The atmosphere mainly consists of a mixture of oxygen and nitrogen in the following proportions:

	By volume.	By weight.
Oxygen	21	23
Nitrogen	79	77

Other bodies, however, are, or may be, present in the air in small quantities. In the following list are enumerated all the possible constituents of the atmosphere divided into three groups: 1, the principal constituents; 2, other useful constituents; and 3, impurities of the atmosphere.

Oxygen Nitrogen	Principal constituents of the atmosphere.
Water (in the form of aqueous vapour, clouds or mists) Carbon dioxide Ozone	Other useful constituents of the atmosphere.
Nitrogen tetroxide and nitric acid Sulphur dioxide and sulphurous and sulphuric acids Chlorine Sulphuretted hydrogen Carbon dioxide (in excess) Carbonic oxide Particles of soot Fungoid and bacterial organisms	Impurities that may be present in the atmosphere in small quantities.

In describing the chemistry of the atmosphere, it will be convenient to discuss separately the constituents of the air, in the order above given in the three divisions.

1. **The principal constituents of the atmosphere—oxygen and nitrogen.**—As previously stated, oxygen and nitrogen so nearly make up the entire bulk of the atmosphere that, in indicating the percentage composition of the air, it is customary to make the percentages of these two gases add up to 100, although actually a small fraction of the percentage composition should be reserved for the other constituents of the air.

Methods of determining the composition of the atmosphere. (*a*) *The eudiometric method.*

—By this method the amount of oxygen in the air is determined by observing the contraction that takes place after exploding a known volume of air in a eudiometer with excess of hydrogen; since two volumes of hydrogen unite with one volume of oxygen to form water, one-third of the contraction will be due to oxygen, and so the proportion of oxygen present in the known volume of air will be ascertained.

(*b*) *Pyrogallate of potassium method.*—This consists in exposing a measured volume of air, contained in a graduated tube standing over mercury, to the action of a strong solution of pyrogallate of potassium, which possesses the property of absorbing oxygen from the air; at the end of an hour the diminution in volume of the air is noted, and this represents the amount of oxygen contained in the measured volume of air originally taken.

(*c*) *The copper method.*—In this process a previously-weighed tube containing copper turnings is raised to a red-heat, and a known weight of air is then passed through it; the copper unites with the oxygen of the air, forming oxide of copper, and the nitrogen may be allowed to pass on into a glass globe provided with a stop-cock, which has been previously exhausted of air at the air-pump and then weighed; at the end of the experiment the increase in weight of the tube containing the copper turnings will give the amount of oxygen contained in the weighed quantity of air experimented with, while the increase in weight of the previously exhausted globe will give the amount of nitrogen.

(*d*) *The synthetical method.*—This consists in mixing together oxygen and nitrogen in the proportion of 21 volumes of oxygen to 79 volumes of nitrogen, when a mixture possessing all the properties of air will be obtained.

The atmosphere a mixture of oxygen and nitrogen, not a compound of those gases.—That the atmosphere is simply a mechanical mixture of oxygen and nitrogen, and not a chemical compound of those two gases, may be proved in various ways.

(*a*) *By the method of mixture.*—This consists, as just described, in mixing together 21 volumes of oxygen with 79 volumes of nitrogen, when no heat is evolved, as would occur if chemical union took place between the two gases, and yet the resulting mixture possesses all the physical and chemical properties of air.

(*b*) *By solution in water.*—Dissolved air is different in composition to ordinary air; if the air were a chemical compound of oxygen and nitrogen, then mere solution in water would be unable to alter its composition, whereas if it be a mixture of the two gases, then, on account of the greater solubility of oxygen in water as compared with nitrogen, the dissolved air should be richer in oxygen than ordinary air; this is actually the case.

If air be well agitated with water, and then the dissolved air expelled by boiling the water and collected in a tube, it will be found on making an analysis of this dissolved air that it contains more oxygen than ordinary air, as shown in the following table:—

	Composition by volume of	
	Ordinary air.	Dissolved air.
Oxygen	21	35
Nitrogen	79	65

(*c*) *By the diffusion experiment.*—If the air were a chemical compound of oxygen and nitrogen, then on submitting it to the process of diffusion it would diffuse unchanged in composition, since by diffusion alone it is impossible to separate the constituents of gaseous chemical compounds; but if it be a mechanical mixture of oxygen and nitrogen, then on submitting it to diffusion the relatively lighter gas nitrogen should diffuse at a greater rate than the heavier oxygen (*see* Graham's Law of Diffusion, page 77), and this is actually what does take place.

Fig. 9 represents the diffusion apparatus for proving that the atmosphere is a mechanical mixture of oxygen and nitrogen.

A is a porous tube, consisting of unglazed porcelain, passing through two perforated india-rubber corks, D and E; B is a stout glass tube fitting tightly over the corks D and E, and provided with an arm or outlet, C, by which it can be connected with an air-pump. By this means it is possible to produce a vacuum in B, and around that portion of the porous tube, A, lying between the corks D and E; if, now, air be passed through A it will tend to diffuse through the porous tube into the vacuum in B, and on examining this air which has diffused through into B it will be found to be much richer in nitrogen than ordinary air, owing to the lighter nitrogen having diffused through the pores of the tube A at a greater rate than the heavier oxygen; this separation by diffusion could only take place from a mechanical mixture of the two gases, and not from a chemical compound.

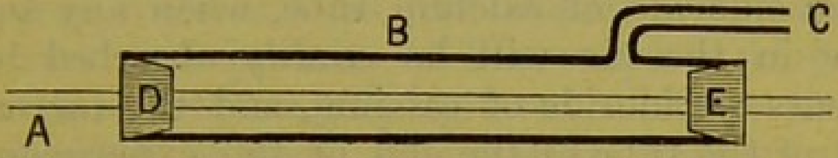


Fig. 9.—Diffusion Apparatus for proving Air to be a Mixture of Oxygen and Nitrogen.

2. **Useful constituents of the atmosphere other than oxygen and nitrogen.** (*a*) *Aqueous vapour.*—This is derived by evaporation from large masses of water, such as the sea,

lakes, rivers, etc. ; from the lungs of human beings and animals in exhaled air ; by evaporation from the skin ; and by evaporation from plants. This aqueous vapour of the air, by condensing to small particles of water, forms clouds and mists, and by further condensation to actual drops of water produces rain ; if when in the fine state of condensation it be frozen, snow is produced ; whereas if rain be frozen during its transit to the earth, hail is produced.

The detection of aqueous vapour and the estimation of its amount in the air are effected by passing a measured volume of the air through a previously-weighed chloride of calcium tube, when any aqueous vapour in the air will be readily absorbed by the fragments of chloride of calcium, and the increase in weight of the tube at the end of the experiment will indicate the amount of aqueous vapour in the volume of air employed.

(*b*) *Carbon dioxide.*—This gas, commonly known as carbonic acid gas, must be regarded as one of the useful constituents of the air on account of the extremely important part it takes in the main- allowed to accumulate in excessive quantities, it then tenance of vegetable life (*see* page 86), although if becomes an impurity of the atmosphere. It is derived from the respiration of human beings and animals, and from the combustion of fuel. The amount of carbon dioxide normally present in the air is very small, being 4 parts in 10,000 or ·04 per cent., and an amount slightly in excess of this in the air of inhabited rooms must be regarded as an impurity, not so much on account of the carbon dioxide itself, as because it is derived from the respiration of human beings, and in the air exhaled from the lungs, putrefiable organic matters are present that have a decidedly deleterious effect on the health of human beings breathing such air. When the carbon dioxide in the air of an inhabited room exceeds ·06 per cent., these putrefiable organic matters become noticeable by smell, rendering the air stuffy or foul, but since these organic matters are extremely difficult to estimate, the determination of the amount of carbon dioxide present becomes a useful gauge of the foulness of the air. To detect carbon dioxide in the air, all that is necessary is to expose some lime-water to the atmosphere, when the presence of carbon dioxide is indicated by the lime-water becoming turbid or milky, owing to the precipitation of carbonate of lime. To estimate the amount of carbon dioxide in the air, a half-gallon bottle is filled with the air to be examined, and a measured quantity of lime-water is poured into the bottle and thoroughly agitated with the air in it. The strength of the lime-water is previously determined by ascertaining how much of a standard solution of an acid is required to neutralise the same quantity of lime-water as that introduced into the half-gallon bottle. If now the measured quantity of lime-water that has been agitated with the half-gallon of air be filtered from the precipitated carbonate of lime, and its strength be determined by seeing the quantity of standard acid that is required to neutralise it, it will be found to be deficient in a certain amount of lime, which represents the quantity of lime precipitated by the carbon dioxide in the half-gallon of air, from which the amount of carbon dioxide present in the air can be easily calculated.

(*c*) *Ozone.*—This gas is present in minute quantities in country air and in the vicinity of the sea, but not, as a rule, in the atmosphere of towns. Its production in the air, and the means of detecting it, have been previously described (*see* pages 87, 90).

3. **Impurities that may be present in the atmosphere.** (*a*) *Nitrogen tetroxide and nitric acid.*—These are mainly derived from chemical works

and factories. Small quantities of nitrogen tetroxide may be formed by direct union of the nitrogen and oxygen of the air during a thunderstorm, the nitrogen tetroxide subsequently uniting with the moisture in the air to form nitrous and nitric acids.

$$\underset{\text{Nitrogen tetroxide}}{N_2O_4} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitrous acid.}}{HNO_2} + \underset{\text{Nitric acid.}}{HNO_3}$$

(*b*) *Sulphur dioxide and sulphurous and sulphuric acids.*—Derived from the combustion of sulphur in coal, and from chemical works and factories.

(*c*) *Chlorine.*—Derived from chemical works and factories.

(*d*) *Sulphuretted hydrogen.*—Derived from chemical works and gas works.

(*e*) *Carbon dioxide in excess.*—Derived from respiration and from combustion of fuel.

(*f*) *Carbonic oxide.*—Derived from combustion of fuel.

(*g*) *Particles of soot.*—Derived from fuel.

(*h*) *Fungoid and bacterial organisms.* — From various sources.

CHAPTER V.

OXIDES OF NITROGEN—NITRIC ACID.

Nitrogen Monoxide — Nitrogen Dioxide — Nitrogen Trioxide — Nitrogen Tetroxide—Nitrogen Pentoxide—Modes of Preparation and Properties of the Oxides of Nitrogen—Tests for the Oxides of Nitrogen—Nitrous Acid—Nitric Acid—Nitrates.

THE OXIDES OF NITROGEN.

There are five compounds of oxygen and nitrogen, viz. :

N_2O	Nitrogen monoxide, or nitrous oxide, or laughing gas.
N_2O_2	Nitrogen dioxide or nitric oxide.
N_2O_3	Nitrogen trioxide or nitrous anhydride.
N_2O_4	Nitrogen tetroxide or nitric peroxide.
N_2O_5	Nitrogen pentoxide or nitric anhydride.

Of these oxides, the first four mentioned are gases, the last is a white crystalline solid. The first two (N_2O and N_2O_2) are colourless gases, the second two (N_2O_3 and N_2O_4) are both of a reddish-brown colour.

The chemistry of the individual oxides of nitrogen will now be considered.

NITROGEN MONOXIDE.

Formula, N_2O ; *molecular weight*, 44.

Also known as *nitrous oxide* and *laughing gas*.

Mode of preparation.—Nitrous oxide is obtained by heating crystals of ammonium nitrate in a flask, and collecting the gas over warm water, as it is appreciably soluble in cold water (Fig. 10).

Properties.—The specific gravity of nitrous oxide is 22, and it is heavier than air; it is colourless and odourless, but has a slightly sweet taste; it is non-combustible, and is not a supporter of combustion (*see* below); it is fairly soluble in cold water, but considerably less so in hot. It is not a poisonous gas, although when inhaled in a pure state it produces insensibility, and is hence used for the painless performance of some minor operations. If the administration of it be continued for too long a time, death from asphyxia will result. The exaggerated name of "laughing gas" is due to the fact that if nitrous oxide be inhaled mixed with air, a feeling of exhilaration is produced. Nitrous oxide, when brought in contact with the air, remains unchanged.

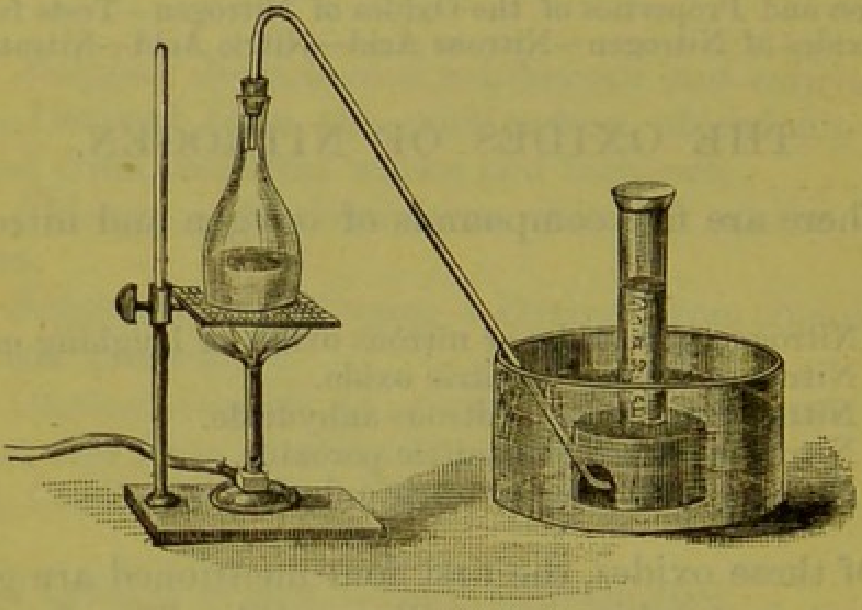


Fig. 10.—Preparation of Nitrogen Monoxide.

Test.—The fact that nitrous oxide is a colourless gas, and does not change colour on exposure to the air, is sufficient to distinguish it from the other oxides of nitrogen; and that it is an oxide of nitrogen can be demonstrated by the fact that a piece of sulphur feebly ignited is extinguished on being plunged into a jar of nitrous oxide, whereas, if the sulphur be more strongly heated and be burning vigorously, it will not only continue to burn, but will burn with increased vigour, on being plunged again into the gas. The fact that the feebly-ignited sulphur is extinguished when plunged into a jar of the gas is explained by nitrous oxide being a non-supporter of combustion; on the other hand, the reason for the more vigorously burning and hotter sulphur continuing to burn with even increased vigour when plunged into the same gas, is that the greater heat is capable of decomposing the nitrous oxide into its elements, and, in the free oxygen so produced, the combustion of the sulphur proceeds more vigorously than in air, since the proportion of oxygen to nitrogen is 1 to 2, whereas in air it is 1 to 4. It will now be understood that it is quite correct to describe nitrous oxide as a non-supporter of combustion, since it has to be decomposed into its elements for combustion to be possible, and it is then the free oxygen, and not the oxide of nitrogen, that is the supporter of combustion.

These remarks will also apply to the three following oxides of nitrogen.

NITROGEN DIOXIDE.

Formula, N_2O_2; *molecular weight*, 60.

Also known as *nitric oxide*.

Modes of preparation.—(i) Nitrogen dioxide is most readily obtained by pouring slightly diluted nitric acid (of sp. gr. 1·23) upon copper turnings, and collecting the gas over water (Fig. 11).

Of the nitric acid employed, only one-fourth furnishes the gas, the other three-fourths uniting with the copper to form copper nitrate, thus:

$$\underset{\text{Copper.}}{Cu_3} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Copper nitrate.}}{3Cu(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{N_2O_2} + \underset{\text{Water.}}{H_2O}$$

(ii) Nitrogen dioxide may also be prepared by the action of nitric acid, of the same strength as just mentioned, on any of the following metals: viz. iron, lead, mercury, silver, and bismuth.

Properties.—The specific gravity of nitrogen dioxide is 30, and it is heavier than air; it is a colourless gas, but on exposure to the air it becomes of a reddish-brown colour, due to its uniting with oxygen of the air to form either nitrogen trioxide or tetroxide. Thus, if it be brought in contact with a small quantity of air, nitrogen trioxide will be formed:

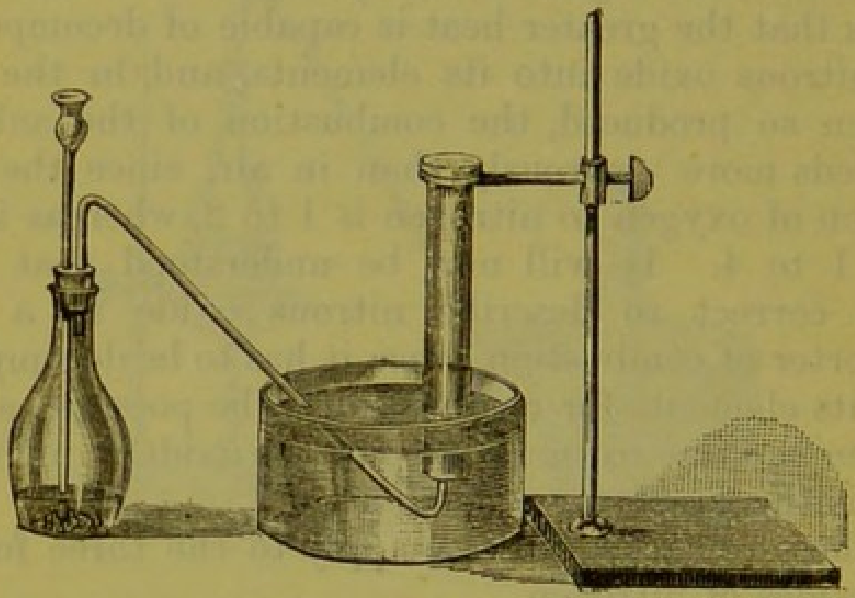


Fig. 11.—Preparation of Nitrogen Dioxide.

$$\underset{\text{Nitrogen dioxide.}}{2N_2O_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Nitrogen trioxide.}}{2N_2O_3}$$

If in contact with excess of air, then nitrogen tetroxide will be produced:

$$\underset{\text{Nitrogen dioxide.}}{N_2O_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Nitrogen tetroxide.}}{N_2O_4}$$

As regards the odour and taste of nitrogen dioxide nothing is definitely known, since it is impossible to either smell or taste it without its being brought into contact with air, in which case the smell and taste of either nitrogen trioxide or tetroxide would be observed. Nitrogen dioxide is non-combustible, and is not a supporter of combustion. (*See* remarks on page 113 concerning nitrogen monoxide.) It is practically insoluble in water, and it is a poisonous gas. If passed into a solution of ferrous sulphate ($FeSO_4$), the latter is blackened on account of the formation of a molecular compound ($FeSO_4$, N_2O_2), which is of a black colour ; advantage is taken of this property in the ordinary test for nitrates, in which ferrous sulphate and sulphuric acid are added as test-reagents.

Test.—Nitrogen dioxide is the only colourless gas that becomes of a reddish-brown colour on exposure to the air ; this is, therefore, a very simple and absolutely diagnostic test for the gas.

NITROGEN TRIOXIDE.

Formula, N_2O_3 ; *molecular weight*, 76.

Also known as *nitrous anhydride*.

Modes of preparation.—(i) Nitrogen trioxide is best prepared by the action of nitric acid, with moderate heat, on white arsenic (arsenious oxide), when the higher oxide of arsenic is produced, the nitrogen trioxide being evolved as a reddish-brown gas, thus :

$$\underset{\substack{\text{Arsenious}\\\text{oxide.}}}{As_2O_3} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} = \underset{\substack{\text{Arsenic}\\\text{oxide.}}}{As_2O_5} + \underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{N_2O_3} + \underset{\text{Water.}}{H_2O}$$

(ii) Nitrogen trioxide can be obtained, though not in a pure state, by the action of nitric acid, with heat, on starch.

(iii) Nitrogen trioxide may also be prepared by bringing nitrogen dioxide in contact with a limited amount of oxygen, or of air, thus:

$$\underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{2N_2O_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{2N_2O_3}$$

Properties.—The specific gravity of nitrogen trioxide is 38, and it is considerably heavier than air; it is a gas possessing a reddish-brown colour, a strong irritating odour, and an unpleasant acid taste. It is non-combustible, and as regards its being a supporter or non-supporter of combustion the remarks made on page 113 apply equally to this gas. When passed into water it readily dissolves, uniting with the water to form nitrous acid, thus:

$$\underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{N_2O_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Nitrous}\\\text{acid.}}}{2HNO_2}$$

Similarly, if passed into a solution of an alkali or of an alkaline carbonate, it will form a nitrite of the alkali metal, thus:

$$\underset{\substack{\text{Potassium}\\\text{hydrate.}}}{2KHO} + \underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{N_2O_3} = \underset{\substack{\text{Potassium}\\\text{nitrite.}}}{2KNO_2} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{N_2O_3} = \underset{\substack{\text{Sodium}\\\text{nitrite.}}}{2NaNO_2} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2}$$

Nitrogen trioxide is a poisonous gas, and when brought in contact with the air is converted into nitrogen tetroxide, although no change of colour takes place, since the two gases are of the same colour.

Test.—The characteristic reddish-brown colour indicates that the gas is either nitrogen trioxide or tetroxide, and these two gases are best distinguished by their different specific gravities, that of the former being 38, of the latter 46.

NITROGEN TETROXIDE.

Formula, N_2O_4; *molecular weight*, 92.

Also known as *nitric peroxide.*

Modes of preparation.—(i) The simplest way of obtaining nitrogen tetroxide, for experimental purposes, is by the action of strong nitric acid on the metal tin, when a violent action takes place with copious evolution of the gas and the production of a white powder, metastannic acid.

$$\underset{\text{Tin.}}{Sn_5} + \underset{\text{Nitric acid.}}{20HNO_3} = \underset{\substack{\text{Metastannic}\\\text{acid.}}}{H_{10}Sn_5O_{15}} + \underset{\substack{\text{Nitrogen}\\\text{tetroxide.}}}{10N_2O_4} + \underset{\text{Water.}}{5H_2O}$$

(ii) Nitrogen tetroxide may be obtained by mixing nitrogen dioxide with a sufficiency of oxygen, or of air.

$$\underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Nitrogen}\\\text{tetroxide.}}}{N_2O_4}$$

(iii) It may also be prepared by mixing nitrogen trioxide with oxygen or air.

$$\underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{2N_2O_3} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Nitrogen}\\\text{tetroxide.}}}{2N_2O_4}$$

Properties.—The specific gravity of nitrogen tetroxide is 46, and it is therefore considerably heavier than air. It possesses a similar reddish-brown colour to that of nitrogen trioxide, a strong irritating odour, and an unpleasant acid taste. It is non-combustible, and the remarks made on page 113, as to nitrogen monoxide being a supporter or non-supporter of combustion, apply to this gas. It dissolves readily in water, producing a mixture of nitrous and nitric acids.

N_2O_4	$+$	H_2O	$=$	HNO_2	$+$	HNO_3
Nitrogen tetroxide.		Water.		Nitrous acid.		Nitric acid.

Similarly, if passed into a solution of an alkali or of an alkaline carbonate, it will form a mixture of a nitrite and a nitrate of the alkali metal, thus :

$2KHO$	$+$	N_2O_4	$=$	KNO_2	$+$	KNO_3	$+$	H_2O
Potassium hydrate.		Nitrogen tetroxide.		Potassium nitrite.		Potassium nitrate.		Water.

Na_2CO_3	$+$	N_2O_4	$=$	$NaNO_2$	$+$	$NaNO_3$	$+$	CO_2
Sodium carbonate.		Nitrogen tetroxide.		Sodium nitrite.		Sodium nitrate.		Carbon dioxide.

Nitrogen tetroxide is a poisonous gas ; it is not changed when brought in contact with the air.

Test.—As previously stated, this gas and nitrogen trioxide are the only two gases possessing a characteristic reddish-brown colour, and they may be distinguished from one another by their different specific gravities.

NITROGEN PENTOXIDE.

Formula, N_2O_5 ; *molecular weight*, 108.

Also known as *nitric anhydride.*

Mode of preparation.—Nitrogen pentoxide, or nitric anhydride, is prepared by passing a stream of chlorine gas over solid nitrate of silver contained in a glass tube and gently heated, when the chlorine unites with the silver to form silver chloride, and the vapour of nitric anhydride and oxygen are evolved, the nitric anhydride condensing as a white crystalline solid in the cool part of the tube, and the oxygen escaping.

$$\underset{\text{Silver nitrate.}}{4AgNO_3} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Silver chloride.}}{4AgCl} + \underset{\text{Nitrogen pentoxide.}}{2N_2O_5} + \underset{\text{Oxygen.}}{O_2}$$

If too much heat is employed, the nitric anhydride is decomposed with violent explosive force.

Properties. — Nitrogen pentoxide, or nitric anhydride, is the only solid oxide of nitrogen ; it is a white crystalline substance. When placed in water it forms nitric acid.

$$\underset{\text{Nitrogen pentoxide.}}{N_2O_5} + \underset{\text{Water.}}{H_2O} = \underset{\text{Nitric acid.}}{2HNO_3}$$

Some of the more important physical properties of the oxides of nitrogen may be tabulated thus :

Gases	N_2O	Colourless, and not changing colour on exposure to the air.
	N_2O_2	Colourless, but changing to a reddish-brown colour on exposure to the air.
	N_2O_3 N_2O_4	Both of a reddish-brown colour.
Solid,	N_2O_5.	

Tabular view of the action of the oxides of nitrogen on water :

$$\text{No action}\begin{cases} N_2O \\ N_2O_2 \end{cases}$$

$$\text{Act on water}\begin{cases} N_2O_3 & \text{Forms nitrous acid.} \\ N_2O_4 & \text{Forms nitrous and nitric acids.} \\ N_2O_5 & \text{Forms nitric acid.} \end{cases}$$

NITRIC ACID.

Formula, HNO_3; *molecular weight*, 63.

Mode of preparation.—Nitric acid is prepared by the distillation of sulphuric acid with any nitrate. One of the natural nitrates, potassium nitrate or sodium nitrate, is employed, and according to the amount of sulphuric acid used, an acid sulphate or a neutral sulphate of the alkali metal will be left behind in the retort. Thus if the sulphuric acid be in excess, an acid sulphate is formed:

$$\underset{\substack{\text{Potassium}\\\text{nitrate.}}}{KNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{acid sulphate.}}}{KHSO_4} + \underset{\text{Nitric acid.}}{HNO_3}$$

If the nitrate be in excess, a neutral sulphate is formed:

$$\underset{\substack{\text{Potassium}\\\text{nitrate.}}}{2KNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4} + \underset{\text{Nitric acid.}}{2HNO_3}$$

Properties.—Nitric acid, if pure, is a colourless liquid, fuming on exposure to the air, and possessing an irritating smell. Commercial nitric acid consists of 70 per cent. of nitric acid, the remaining 30 per cent. being water, and it is of specific gravity 1·42. Pure nitric acid is of specific gravity 1·52, and is a very unstable body. *Aquafortis* is an old name for nitric acid, given to it on account of its property of acting on most of the metals; the only common metals not acted on by nitric acid are gold and platinum. A mixture of three parts of nitric acid to four parts of hydrochloric acid is known as *aqua regia*, on account of its property of dissolving gold, the "king of metals." A commercial article known as *yellow* or *fuming nitric acid*, which contains dissolved nitrogen tetroxide, is made by distilling potassium nitrate and strong sulphuric acid in the proportions to form the neutral potassium sulphate, and using a higher temperature than is employed in the manufacture of the ordinary acid. Nitric acid corrodes and stains the skin and articles of clothing, producing a yellow stain, the colour of which is not removed but intensified by the application of solution of ammonia. Strong nitric acid is a powerful corrosive and irritant poison.

Tests.—Nitric acid, whether in the free state or in the form of a nitrate, may be detected by the following tests:—(i) To a solution of a nitrate contained in a test-tube add two or three crystals of ferrous sulphate, shake for a few seconds, and then pour some strong sulphuric acid down the side of the tube, so that it may collect as a layer at the bottom of the tube; a black or dark brown colour will then appear at the junction of the two liquids, due to the liberated nitrogen dioxide forming a black compound with the ferrous sulphate. This test, when carefully conducted, is a delicate test for a nitrate.

(ii) To a solution of a nitrate add some copper turnings, apply a gentle heat, and then carefully add strong sulphuric acid, until a free liberation of gas occurs; this gas, which is nitrogen dioxide, will become of a reddish-brown colour as it mixes with the air in the test-tube.

NITRATES.

Nitrates occurring in nature are produced by the oxidation of organic nitrogenous bodies, the resulting nitric acid becoming neutralised by contact with salts of the alkali or alkaline earth metals. In many, if not in all cases, this oxidation of the nitrogen of organic nitrogenous bodies to nitric acid, is brought about by the influence of a ferment called the "nitrifying ferment," which may exist in the soil or in water. The nitre or saltpetre (KNO_3) formed in the surface soil of various parts of India is produced by the oxidation of organic nitrogenous bodies (especially the excreta of animals and human beings), under the influence of the nitrifying ferment and the tropical heat, in a soil rich in potassium salts.

The small quantities of nitrates (nitrates of calcium and magnesium) that may be present in well-waters or river-waters that have been contaminated with sewage are similarly produced by oxidation of the nitrogenous matters of the sewage, under the influence of the ferment, to nitric acid, and subsequent neutralisation of this acid by the carbonate of calcium or magnesium in the water.

A description of the various nitrates and nitrites will be given with their respective metals.

CHAPTER VI.

AMMONIA—AMMONIUM SALTS.

Ammonia—Preparation and Properties of Ammonia—Tests for Ammonia—Ammonium—Sources of Ammonium Salts—Ammonium Chloride—Ammonium Carbonate—Ammonium Nitrate—Ammonium Bromide—Ammonium Sulphide—Ammonium Acetate—Ammonium Citrate—Ammonium Oxalate—Ammonium Benzoate—Tests for Ammonium Salts.

AMMONIA.

Formula, NH_3; *molecular weight*, 17.

Modes of preparation.—(i) Ammonia gas is best prepared by heating a mixture of dry ammonium chloride and quicklime (CaO) or slaked lime ($Ca(HO)_2$):

$$\underset{\text{Ammonium chloride.}}{2NH_4Cl} + \underset{\text{Quicklime.}}{CaO} = \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Water,}}{H_2O}$$

or, $$\underset{\text{Ammonium chloride.}}{2NH_4Cl} + \underset{\text{Slaked lime.}}{Ca(HO)_2} = \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Water.}}{2H_2O}$$

The ammonia gas cannot be collected over water, on account of its extreme solubility, but may be collected over mercury, or by upward displacement (*see* Fig. 12), on account of its being lighter than air.

(ii) Ammonia may also be prepared by heating ammonium chloride, or any other ammonium salt, with caustic potash or caustic soda:

$$\underset{\text{Ammonium chloride.}}{NH_4Cl} + \underset{\text{Caustic potash.}}{KHO} = \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Potassium chloride.}}{KCl} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\text{Ammonium chloride.}}{NH_4Cl} + \underset{\text{Caustic soda.}}{NaHO} = \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Sodium chloride.}}{NaCl} + \underset{\text{Water.}}{H_2O}$$

(iii) Ammonia is obtained by the action of dilute nitric acid on the metal zinc :

$$\underset{\text{Zinc.}}{4Zn} + \underset{\text{Nitric acid.}}{9HNO_3} = \underset{\text{Zinc nitrate.}}{4Zn(NO_3)_2} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{3H_2O}$$

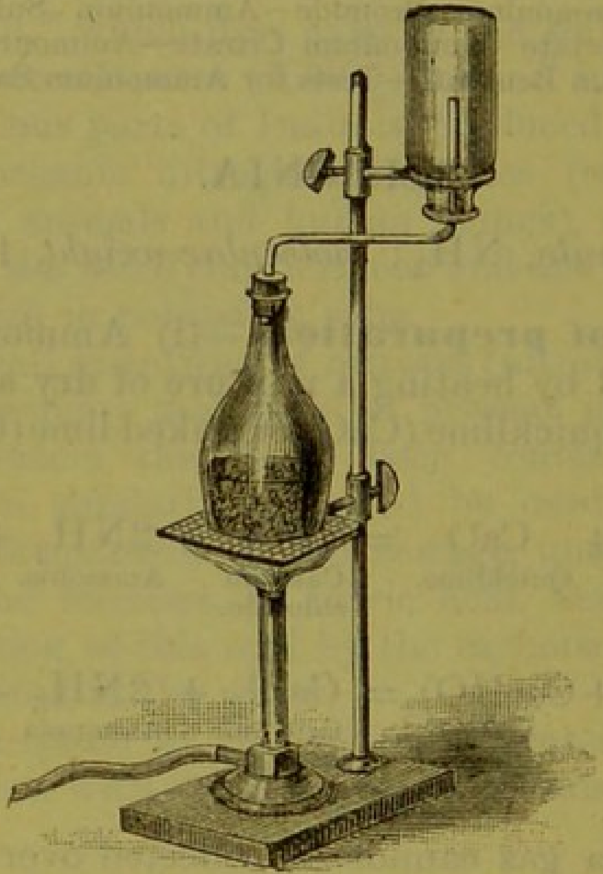


Fig. 12.—Preparation and Collection of Ammonia Gas.

The ammonia is not evolved in this case, but unites with some of the nitric acid to form ammonium nitrate, from which, however, it may be set free by heating with a caustic alkali.

(iv) Ammonia is also obtained by the action of dry heat without contact of air (destructive distillation), on various organic nitrogenous substances of both animal and vegetable origin. Thus, by the destructive distillation of the horns of animals, ammonia may be obtained; hence the derivation of the old name, "spirit of hartshorn," applied to solution of ammonia. Also during the destructive distillation of coals, a large proportion of the nitrogen unites with some of the hydrogen of the coal to form ammonia, which is ultimately found dissolved in the light "tar liquor" floating on the top of the condensed tar.

(v) Ammonia is also formed during the spontaneous decomposition of moist animal matter, and during the putrefaction of urine (*see* page 457).

(vi) By heating organic nitrogenous bodies with strong caustic alkalies, the nitrogen of the organic bodies is converted into ammonia. Advantage is taken of this fact in determining the proportion of nitrogen present in organic nitrogenous bodies, by ascertaining the amount of ammonia produced, when a weighed quantity of the organic body is heated with a caustic alkali.

Properties.—The specific gravity of ammonia is 8·5, and it is lighter than air; it is a colourless gas, with a characteristic strong pungent odour and alkaline taste; it is feebly combustible, not catching fire in air, but in oxygen it burns with a pale yellowish or greenish-yellow flame; it is not a supporter of combustion. It is the most soluble of all the gases in water; 1 volume of water dissolving over 800 volumes of the gas at ordinary temperatures. It is very easily liquefied by pressure, since at ordinary temperatures under a pressure of seven atmospheres it becomes liquid. It unites readily with acids, forming ammonium salts. If inhaled in large quantities and in the pure state, it is a poison, on account of its irritating action on the mucous membrane of the respiratory passages. Ammonia is composed of 1 volume of nitrogen united with 3 volumes of hydrogen, the 4 volumes being condensed, as a result of the union, to 2 volumes; therefore, if ammonia gas is decomposed into its elements its volume becomes doubled, thus:

$$\underset{\text{2 molecules.}}{2NH_3} = \underset{\text{1 molecule.}}{N_2} + \underset{\text{3 molecules.}}{3H_2}$$

From which it is seen that 2 molecules of ammonia gas produce 4 molecules of the mixture of nitrogen and hydrogen, and, since the molecules of all gases occupy the same bulk, therefore ammonia gas becomes doubled in bulk when it is resolved into its elements. This decomposition of ammonia gas into its elements can be effected at a high temperature, or by passing electric sparks for some time through the gas confined in a eudiometer over mercury (Fig. 13).

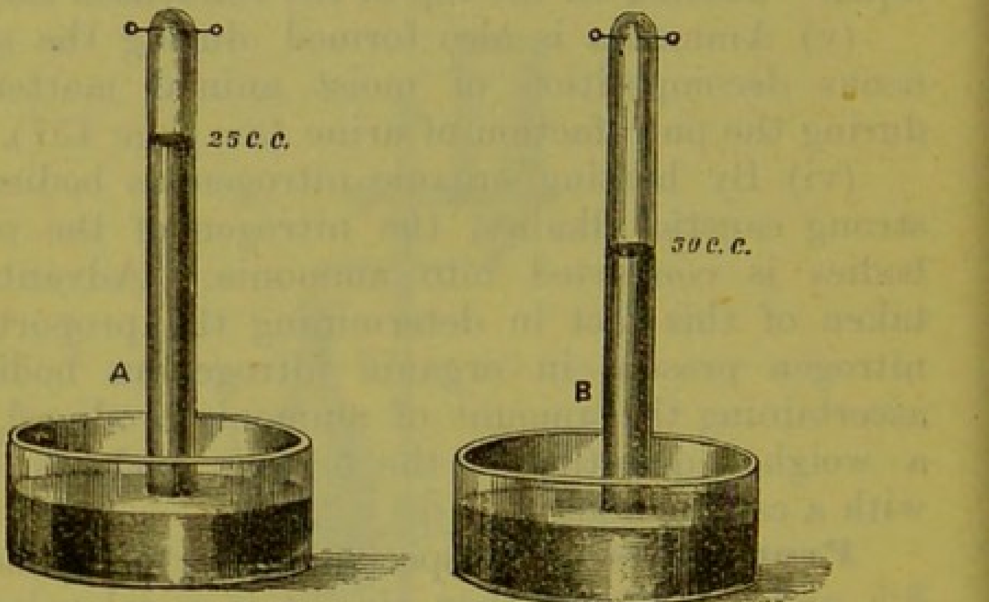


Fig. 13.—A, Ammonia gas before the passage of electric sparks; B, after passage of electric sparks for some time (volume doubled).

Tests.—(i) The odour of the gas constitutes a fairly delicate test.

(ii) Dense white fumes are produced on inserting a rod moistened with strong hydrochloric acid into a jar or tube of the gas.

(iii) Moistened red litmus paper is turned blue when brought in contact with the gas.

(iv) The most delicate test for small quantities of ammonia in solution, as in a drinking-water, is the "Nessler test"; this consists in adding to the water some Nessler reagent (*see* page 293), when a reddish-brown colour or precipitate is produced, according to the amount of ammonia present.

AMMONIUM AND ITS SALTS.

The radical ammonium (NH_4) has never been isolated, nor has the molecule $(NH_4)_2$. The latter, however, has been obtained in the form of an amalgam with mercury, by placing sodium amalgam in a strong solution of ammonium chloride, when the ammonium takes the place of the sodium, and a light, bulky amalgam with a metallic lustre is obtained.

$$\underset{\substack{\text{Sodium}\\\text{amalgam.}}}{HgNa_2} + \underset{\substack{\text{Ammonium}\\\text{chloride.}}}{2NH_4Cl} = \underset{\substack{\text{Ammonium}\\\text{amalgam.}}}{Hg(NH_4)_2} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl}$$

This ammonium amalgam is, however, very unstable, and in the course of a few minutes is resolved into free mercury, with escape of ammonia and hydrogen gases.

$$\underset{\substack{\text{Ammonium}\\\text{amalgam.}}}{Hg(NH_4)_2} = \underset{\text{Mercury.}}{Hg} + \underset{\text{Ammonia.}}{2NH_3} + \underset{\text{Hydrogen.}}{H_2}$$

Sources of the ammonium salts.—(i) The ammonium salts of commerce are principally prepared directly or indirectly from the *ammoniacal tar liquor* of the gasworks (*see* page 125); this contains, in solution, free ammonia, and on neutralisation with hydrochloric acid and subsequent concentration of the liquid by evaporation, crystals of ammonium chloride are obtained. (ii) The boracic acid of volcanic origin obtained in Tuscany (*see* page 174) is accompanied by ammonia salts, and on submitting the crude boracic acid to heat with carbonate of soda, a very pure carbonate of ammonium (the so-called volcanic carbonate of ammonium) volatilises and condenses. (iii) As mentioned on page 125, solution of ammonia (spirit of hartshorn) was formerly prepared by the destructive distillation of the horns of animals. (iv) The excreta of some animals, such as camels and serpents, contain large quantities of ammonium salts ; and by heating the excreta with sodium chloride (common salt), ammonium chloride volatilises and can be condensed in the solid form.

AMMONIUM SALTS.

Ammonium chloride (NH_4Cl). Also known as *sal ammoniac*. As previously described, this is obtained from the ammoniacal coal-tar liquor of the gasworks.

Ammonium carbonate ($N_4H_{16}C_3O_8$).—Prepared by heating a mixture of solid ammonium chloride and chalk (calcium carbonate), when the ammonium carbonate sublimes as a white solid. This, the commercial ammonium carbonate, is not the normal carbonate, but consists of a mixture of two molecules of the bicarbonate of ammonium (NH_4HCO_3) with one molecule of the carbamate of ammonium ($NH_4NH_2CO_2$), thus :

$$2NH_4HCO_3,\ NH_4NH_2CO_2 = N_4H_{16}C_3O_8.$$

By dissolving this commercial carbonate in water, the carbamate unites with the elements of water to form the normal carbonate, thus :

$$\underset{\substack{\text{Ammonium}\\\text{carbamate.}}}{NH_4NH_2CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Normal ammonium}\\\text{carbonate.}}}{(NH_4)_2CO_3}$$

Then, if some solution of ammonia be added to this solution, the bicarbonate is also converted into the normal carbonate, thus :

$$\underset{\substack{\text{Ammonium}\\\text{bicarbonate.}}}{2NH_4HCO_3} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\substack{\text{Normal ammonium}\\\text{carbonate.}}}{2(NH_4)_2CO_3}$$

So that to prepare a solution of the normal ammonium carbonate, such as is employed as a test-reagent, it is necessary to dissolve the commercial carbonate in water, and then to add some solution of ammonia.

Ammonium nitrate (NH_4NO_3).—Prepared by neutralising nitric acid with ammonium carbonate, or with solution of ammonia.

Ammonium bromide (NH_4Br).—Prepared by neutralising hydrobromic acid with ammonium carbonate, or with solution of ammonia.

Ammonium sulphide ($(NH_4)_2S$).—Prepared by saturating solution of ammonia with sulphuretted hydrogen gas.

$$\underset{\text{Ammonia.}}{2NH_3} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{H_2S} = \underset{\substack{\text{Ammonium}\\\text{sulphide.}}}{(NH_4)_2S}$$

Ammonium acetate ($NH_4C_2H_3O_2$), **Ammonium citrate** ($(NH_4)_3C_6H_5O_7$), **ammonium oxalate** ($(NH_4)_2C_2O_4$), and **ammonium benzoate** ($NH_4C_7H_5O_2$) are made by neutralising the respective acids with ammonium carbonate, or with solution of ammonia.

Tests for ammonium salts.

(i) If a solution of an ammonium salt be heated with caustic potash or caustic soda, ammonia gas will be evolved, which can be recognised by its odour, by its turning moistened red litmus paper blue, and by the white fumes produced when a glass rod moistened with strong hydrochloric acid is brought near it.

(ii) If to a solution of an ammonium salt some Nessler reagent be added, a reddish-brown colour or precipitate will be produced.

CHAPTER VII.

CHLORINE—OXIDES AND ACIDS OF CHLORINE.

Halogen Elements—Chlorine—Preparation and Properties of Chlorine—Tests for Chlorine—Hydrochloric Acid—Nitro-hydrochloric Acid—Chlorine Monoxide or Hypochlorous Anhydride—Chlorine Trioxide or Chlorous Anhydride—Chlorine Tetroxide or Chlorine Peroxide—Hypochlorous Acid—Chlorinated Bodies—Chlorous Acid—Chloric Acid—Perchloric Acid.

HALOGEN ELEMENTS.

THE halogen elements, viz. chlorine, bromine, iodine, and fluorine, are four elements that are closely allied to one another in their properties. With metals they all form compounds analogous to sea-salt, hence the derivation of the term halogen (from ἅλς, *sea-salt; γεννάω, I produce*). None of them occur free in nature. The haloid salts consist of two elements only, the haloid element and a metal; *e.g.* sodium chloride $NaCl$, potassium iodide KI, potassium bromide KBr, calcium fluoride CaF_2.

CHLORINE.

Symbol, Cl; *formula*, Cl_2; *monad; atomic weight*, 35·5; *molecular weight*, 71.

Chlorine occurs in nature combined with metals as chlorides, of which the commonest is sodium chloride, *sea-salt* or *rock-salt*. The name chlorine is derived from χλωρός, *green*, on account of the greenish-yellow colour of the gas.

Modes of preparation.—(i) Chlorine is most readily prepared by heating a mixture of strong hydrochloric acid and manganese dioxide (black oxide of manganese), and collecting the gas by downward displacement of air (Fig. 14).

The reaction takes place in two stages, the hydrochloric acid first forming manganese tetrachloride.

$$\underset{\substack{\text{Manganese}\\\text{dioxide.}}}{MnO_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{4HCl} = \underset{\substack{\text{Manganese}\\\text{tetrachloride.}}}{MnCl_4} + \underset{\text{Water.}}{2H_2O}$$

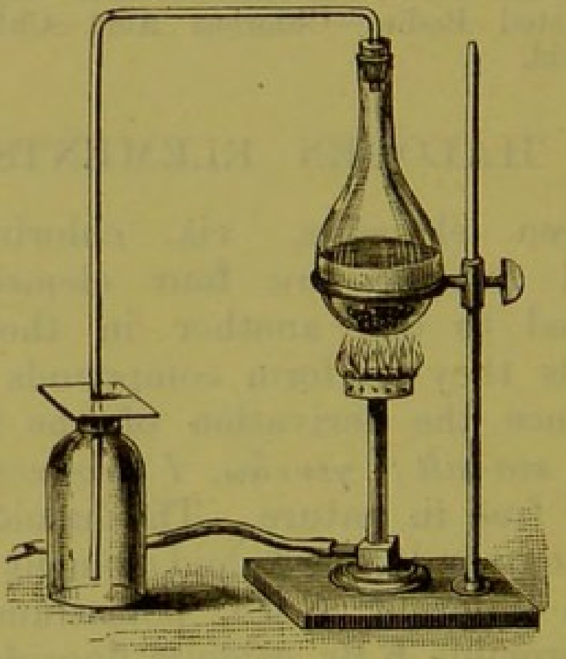


Fig. 14.—Preparation and Collection of Chlorine.

The manganese tetrachloride being then decomposed by the heat into the manganous chloride and chlorine.

$$\underset{\substack{\text{Manganese}\\\text{tetrachloride.}}}{MnCl_4} = \underset{\substack{\text{Manganous}\\\text{chloride.}}}{MnCl_2} + \underset{\text{Chloride.}}{Cl_2}$$

(ii) Chlorine may also be prepared by heating a mixture of common salt, manganese dioxide and sulphuric acid.

$$\underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl} + \underset{\substack{\text{Manganese}\\\text{dioxide.}}}{MnO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Manganese}\\\text{sulphate.}}}{MnSO_4} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + \underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Water.}}{2H_2O}$$

In a similar way, chlorine may be obtained by the action of manganese dioxide and sulphuric acid on any metallic chloride.

(iii) By passing a mixture of hydrochloric acid gas and air over red-hot bricks, chlorine is obtained; by this method the chlorine obtained is necessarily mixed with the nitrogen of the air, an admixture of but little importance when the chlorine is to be used for manufacturing purposes.

$$\underset{\substack{\text{Hydrochloric}\\\text{acid gas.}}}{4HCl} + \underset{\substack{\text{Oxygen}\\\text{of the air.}}}{O_2} = \underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{2Cl_2}$$

(iv) Deacon's process for the manufacture of chlorine consists in passing a mixture of hydrochloric acid gas and air over heated fragments of pumice stone saturated with cupric chloride. The cupric chloride is decomposed into cuprous chloride, evolving one-half of its chlorine.

$$\underset{\substack{\text{Cupric}\\\text{chloride.}}}{2CuCl_2} = \underset{\substack{\text{Cuprous}\\\text{chloride.}}}{Cu_2Cl_2} + \underset{\text{Chlorine.}}{Cl_2}$$

The cuprous chloride is then reconverted into cupric chloride by means of chlorine, which is liberated from the hydrochloric acid gas by the oxygen of the air.

$$\underset{\substack{\text{Cuprous}\\\text{chloride.}}}{2Cu_2Cl_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid gas.}}}{4HCl} + \underset{\substack{\text{Oxygen}\\\text{of the air.}}}{O_2} = \underset{\substack{\text{Cupric}\\\text{chloride.}}}{4CuCl_2} + \underset{\text{Water.}}{2H_2O}$$

The cupric chloride then again becomes reduced to cuprous chloride with evolution of half its oxygen, and so on.

(v) Chlorine may be obtained by the electrolysis of hydrochloric acid, using electrodes of gas-carbon; equal volumes of chlorine and hydrogen are evolved, the chlorine being set free at the positive pole, and the hydrogen at the negative pole.

Properties.—The specific gravity of chlorine is 35·5; it is a heavy gas, being $2\frac{1}{2}$ times heavier than air. It has a greenish-yellow colour, a very unpleasant suffocating odour, and a disagreeable taste. It is non-combustible, as chlorine will not combine directly with oxygen, but in an atmosphere of hydrogen chlorine will burn with a pale livid flame, producing hydrochloric acid; and conversely, hydrogen will burn in an atmosphere of chlorine. Chlorine is a supporter of combustion in a limited sense only; if a burning body contains hydrogen, then it will continue to burn in chlorine with a feeble flame, the chlorine uniting with the hydrogen to form hydrochloric acid, but not uniting with the carbon of the burning body. Thus, if a lighted candle be lowered into a jar of chlorine, the candle will continue to burn with a pale reddish flame, but all the carbon will be set free as a dense smoke. A piece of glowing charcoal will not burn in chlorine, since it contains no hydrogen. If a piece of paper saturated with oil of turpentine ($C_{10}H_{16}$) be thrown into a jar of chlorine, the turpentine catches fire from the heat produced by the rapid union of the chlorine with the hydrogen, but all the carbon is set free as dense smoke.

Chlorine is also a supporter of combustion as regards the following bodies. A piece of phosphorus catches fire when introduced into chlorine, forming the pentachloride of phosphorus (PCl_5). Chlorine will also combine with all metals, forming metallic chlorides; and if a metal in a fine state of division (such as powdered antimony) be thrown into a jar of chlorine it will ignite spontaneously, from the heat produced by the intensity of the union of the chlorine with the metal. Chlorine is soluble in water, 1 volume of water dissolving about $2\frac{1}{2}$ volumes of the gas; it cannot, therefore, be collected over water, nor over mercury, since it would combine with that metal.

When submitted to a pressure of six atmospheres, at ordinary temperatures, it is condensed to a yellow liquid. Chlorine is a poisonous gas, acting as a powerful irritant to the mucous membrane of the respiratory passages. Chlorine also possesses two very important properties as a bleaching and disinfecting agent; it bleaches all vegetable colours in presence of moisture, acting in two ways: partly by uniting with the hydrogen of the dye and replacing it by chlorine, and so forming a colourless substitution product; and partly by uniting with the hydrogen of the water and liberating oxygen, which in the nascent state oxidises and destroys the colouring matter. Chlorine does not bleach mineral colours. As a disinfecting agent, chlorine acts as a powerful germicide, but its unpleasant odour and irritating properties when inhaled prevent its general use as a disinfectant. Chlorine is also a deodoriser, acting by virtue of its affinity for hydrogen, by uniting with the hydrogen of bad-smelling gases and so decomposing them; for instance, if chlorine be brought in contact with sulphuretted hydrogen, hydrochloric acid is formed and sulphur precipitated.

$$\underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{2H_2S} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\substack{\text{Hydrochloric}\\\text{acid gas.}}}{4HCl} + \underset{\text{Sulphur.}}{S_2}$$

The two most marked chemical properties of chlorine are: (*a*) its property of combining with hydrogen; (*b*) its property of uniting with all metals. Several instances of both these properties have been given; one further illustration of the first-mentioned one may be given here. So great is the power of chlorine of uniting with hydrogen, that if chlorine water be simply exposed to direct sunlight it is decomposed, the chlorine uniting with the hydrogen of the water and setting free the oxygen.

$$\underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine}}{2Cl_2} = \underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Oxygen.}}{O_2}$$

Tests.—(i) The colour, the odour and the fact that a piece of moistened litmus paper (blue or red) is bleached by the gas, constitute very fair tests for chlorine.

(ii) The most delicate test for chlorine is based upon the fact of its liberating iodine from iodide of potassium, the liberated iodine in contact with starch forming a blue compound. If a piece of blotting-paper be dipped in a mixed solution of potassium iodide and starch paste, and then be brought in contact with chlorine, it is turned of a blue colour. (N.B.—This reaction is also produced by ozone, and by nitrogen trioxide and tetroxide, *see* pages 89, 90.)

HYDROCHLORIC ACID.

Formula, HCl; *molecular weight*, 36·5.

Also known as *muriatic acid* and *spirit of salts*. The latter name is applied to an impure form of the acid, which is of a yellowish colour from contamination with ferric chloride; it also generally contains arsenic as an impurity, derived from the impure sulphuric acid that is used in its manufacture.

Modes of preparation.—(i) Hydrochloric acid is most easily prepared by heating a mixture of sodium chloride (common salt) and sulphuric acid.

$2NaCl$	$+$	H_2SO_4	$=$	Na_2SO_4	$+$	$2HCl$
Sodium chloride.		Sulphuric acid.		Sodium sulphate.		Water.

The hydrochloric acid is given off as a gas, and after washing it through a small quantity of water, it is conveyed into water contained in a bottle kept cool by being surrounded with water (Fig. 15).

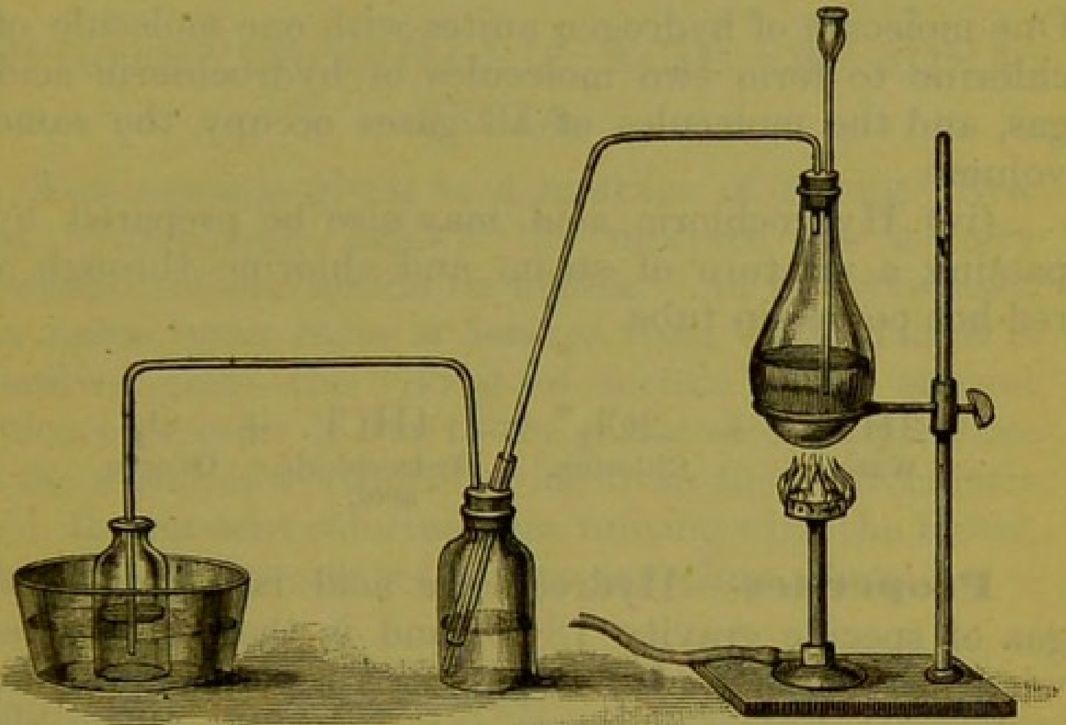


Fig. 15.—Preparation of Hydrochloric Acid.

It readily dissolves in the water, and this solution constitutes the hydrochloric acid of commerce.

(ii) In a similar manner, hydrochloric acid may be prepared by heating sulphuric acid with any metallic chloride.

(iii) Hydrochloric acid may be prepared by mixing together equal volumes of hydrogen and chlorine, and exposing the mixture of gases to diffused light, when they combine quietly; if the mixture be exposed to strong sunlight, or if a light be applied, the two gases unite suddenly with an explosion. The volume of hydrochloric acid gas formed is exactly equal to the volumes of the constituents; for

$$\underset{\text{1 molecule.}}{H_2} + \underset{\text{1 molecule.}}{Cl_2} = \underset{\text{2 molecules.}}{2HCl}$$

One molecule of hydrogen unites with one molecule of chlorine to form two molecules of hydrochloric acid gas, and the molecules of all gases occupy the same volume.

(iv) Hydrochloric acid may also be prepared by passing a mixture of steam and chlorine through a red-hot porcelain tube.

$$\underset{\text{Water.}}{2H_2O} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{4HCl} + \underset{\text{Oxygen}}{O_2}$$

Properties.—Hydrochloric acid is a colourless gas of specific gravity 18·25, and is therefore somewhat heavier than air; it possesses a pungent odour, and an intensely acid taste; it is neither combustible nor a supporter of combustion. It fumes when brought in contact with the air, owing to its dissolving in the moisture of the air, and forming a cloud of solution of hydrochloric acid. It is very soluble in water, 1 volume of water dissolving 454 volumes of the gas at ordinary temperatures; this solution of the gas in water constitutes the commercial *hydrochloric* or *muriatic acid.* The commercial acid is a fuming liquid of specific gravity 1·16, and containing 32 per cent. by weight of hydrochloric acid. It is decomposed by a current of electricity (using gas-carbon electrodes) into its elements, equal volumes of chlorine and hydrogen being evolved, the former from the positive pole and the latter from the negative pole.

Tests.—(i) *For the gas.*—It fumes when brought in contact with the air, and also produces a dense white cloud when brought in contact with ammonia gas; it turns blue litmus paper red.

(ii) *For the liquid.*—Nitrate of silver gives a white curdy precipitate, which is insoluble in strong nitric acid, but is soluble in solution of ammonia.

NITRO-HYDROCHLORIC ACID OR AQUA REGIA.

This name is given to a mixture of strong nitric and hydrochloric acids; the mixture has a very powerful solvent action on metals. As we have seen, the name *aqua regia* is derived from the fact that it dissolves gold—the "king of metals." Its solvent action on metals is due to the nitric acid, in presence of the metal, liberating chlorine from the hydrochloric acid, the nascent chlorine then uniting with the metal. This is best represented in two equations, thus:

$$\underset{\text{Nitric acid.}}{2HNO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} = \underset{\text{Water.}}{4H_2O} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Chlorine.}}{3Cl_2}$$

then

$$\underset{\text{Gold.}}{Au_2} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Gold chloride.}}{2AuCl_3}$$

COMPOUNDS OF CHLORINE AND OXYGEN.

Chlorine and oxygen do not unite directly; but indirectly they may be made to form the three following oxides of chlorine:

Cl_2O	Chlorine monoxide or hypochlorous anhydride.
Cl_2O_3	Chlorine trioxide or chlorous anhydride.
Cl_2O_4	Chlorine tetroxide or chlorine peroxide.

CHLORINE MONOXIDE OR HYPOCHLOROUS ANHYDRIDE.

Formula, Cl_2O; *molecular weight*, 87.

Mode of preparation.—By the action of chlorine gas on the yellow or precipitated mercuric oxide.

$$\underset{\text{Mercuric oxide.}}{2HgO} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\substack{\text{Mercuric}\\\text{oxychloride.}}}{Hg_2OCl_2} + \underset{\substack{\text{Chlorine}\\\text{monoxide.}}}{Cl_2O}$$

Properties.—Chlorine monoxide is a yellowish gas possessing an odour similar to that of chlorine, when heated it decomposes into its elements with explosive violence. It unites with water, forming hypochlorous acid.

$$\underset{\substack{\text{Hypochlorous}\\\text{anhydride.}}}{Cl_2O} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Hypochlorous}\\\text{acid.}}}{2HClO}$$

CHLORINE TRIOXIDE OR CHLOROUS ANHYDRIDE.

Formula, Cl_2O_3; *molecular weight*, 119.

Mode of preparation.—By gently warming a mixture of potassium chlorate, arsenious oxide (white arsenic), and nitric acid.

$$\underset{\substack{\text{Potassium}\\\text{chlorate.}}}{2KClO_3} + \underset{\substack{\text{Arsenious}\\\text{oxide.}}}{As_2O_3} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} = \underset{\substack{\text{Chlorine}\\\text{trioxide.}}}{Cl_2O_3} +$$

$$\underset{\substack{\text{Arsenic}\\\text{oxide.}}}{As_2O_5} + \underset{\substack{\text{Potassium}\\\text{nitrate.}}}{2KNO_3} + \underset{\text{Water.}}{H_2O}$$

Properties.—Chlorine trioxide is a yellow gas possessing an odour similar to that of chlorine, and decomposing into its elements when heated, the decomposition being accompanied by an explosion. With water it unites to form chlorous acid, but this acid is never obtained in a pure state.

$$\underset{\substack{\text{Chlorous}\\\text{anhydride.}}}{Cl_2O_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Chlorous}\\\text{acid.}}}{2HClO_2}$$

CHLORINE TETROXIDE OR CHLORINE PEROXIDE.

Formula, Cl_2O_4; *molecular weight*, 135.

Mode of preparation.—By very gently heating potassium chlorate with pure sulphuric acid.

Properties.—Chlorine tetroxide is a dark yellow gas, exploding with terrific violence when heated. Great care is required in its preparation.

OXYACIDS OF CHLORINE.

There are four oxyacids of chlorine, viz. :

$HClO$	Hypochlorous acid.
$HClO_2$	Chlorous ,,
$HClO_3$	Chloric ,,
$HClO_4$	Perchloric ,,

HYPOCHLOROUS ACID.

Formula, $HClO$.

Mode of preparation.—By the action of hypochlorous anhydride on water.

$$\underset{\substack{\text{Hypochlorous}\\\text{anhydride.}}}{Cl_2O} + \underset{\text{Water}}{H_2O} = \underset{\substack{\text{Hypochlorous}\\\text{acid.}}}{2HClO}$$

Properties and compounds.—Hypochlorous acid when mixed with hydrochloric acid suffers decomposition, chlorine being evolved.

$$\underset{\text{Hypochlorous acid.}}{HClO} + \underset{\text{Hydrochloric acid.}}{HCl} = \underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Water.}}{H_2O}$$

Hypochlorous acid enters into the composition of the **chlorinated bodies,** which consist of a mixture of a chloride and a hypochlorite. The following are the principal chlorinated bodies:—

$CaCl_2$, $Ca(ClO)_2$	Chlorinated	lime.
$NaCl$, $NaClO$	,,	soda.
KCl, $KClO$	,,	potash.

They are made by the action of chlorine gas on the caustic alkalies, or on the soluble alkaline carbonates. When acted on by acids they evolve their chlorine; when their solutions are boiled they split up into chlorates and chlorides.

Chlorinated lime.—This is prepared by passing chlorine into damp slaked lime.

$$\underset{\text{Slaked lime.}}{2Ca(HO)_2} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Chlorinated lime.}}{CaCl_2, Ca(ClO)_2} + \underset{\text{Water.}}{2H_2O}$$

Properties.—Chlorinated lime constitutes *bleaching powder*, or the disinfectant known as *chloride of lime.* When treated with an acid, such as sulphuric acid, hydrochloric and hypochlorous acids are first set free, and then immediately react on one another, producing free chlorine.

$$\underset{\text{Chlorinated lime.}}{CaCl_2, Ca(ClO)_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Calcium sulphate.}}{2CaSO_4} + \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Hypochlorous acid}}{2HClO}$$

then

$$\underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2HCl} + \underset{\substack{\text{Hypochlorous}\\ \text{acid.}}}{2HClO} = \underset{\text{Chlorine.}}{2Cl_2} + \underset{\text{Water.}}{2H_2O}$$

Chlorinated lime is acted on by the weakest acids, for even when exposed to the air, the carbon dioxide (carbonic acid gas) of the air sets free hypochlorous acid, which then decomposes with evolution of chlorine; it is in this way that *chloride of lime* acts as a disinfectant. Its bleaching powers also depend on the evolution of chlorine. If a solution of chlorinated lime be boiled, it yields chlorate and chloride of calcium.

$$\underset{\text{Chlorinated lime.}}{3(CaCl_2, Ca(ClO)_2)} = \underset{\substack{\text{Calcium}\\ \text{chlorate.}}}{Ca(ClO_3)_2} + \underset{\substack{\text{Calcium}\\ \text{chloride.}}}{5CaCl_2}$$

Chlorinated soda. — Prepared by passing chlorine into solution of caustic soda or solution of sodium carbonate.

$$\underset{\text{Caustic soda.}}{2NaHO} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Chlorinated soda.}}{NaCl, NaClO} + \underset{\text{Water.}}{H_2O}$$

or

$$\underset{\substack{\text{Sodium}\\ \text{carbonate.}}}{Na_2CO_3} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Chlorinated soda.}}{NaCl, NaClO} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2}$$

Properties.—The properties of chlorinated soda are similar to those of chlorinated lime. Acids liberate chlorine from it; boiling its solution converts it into chlorate and chloride of sodium.

Chlorinated potash. — Prepared by passing chlorine into solution of caustic potash, or into solution of potassium carbonate.

$$\underset{\substack{\text{Caustic}\\\text{potash.}}}{\mathrm{2KHO}} + \underset{\text{Chlorine.}}{\mathrm{Cl_2}} = \underset{\substack{\text{Chlorinated}\\\text{potash.}}}{\mathrm{KCl, KClO}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

or

$$\underset{\substack{\text{Potassium}\\\text{carbonate.}}}{\mathrm{K_2CO_3}} + \underset{\text{Chlorine.}}{\mathrm{Cl_2}} = \underset{\substack{\text{Chlorinated}\\\text{potash.}}}{\mathrm{KCl, KClO}} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{\mathrm{CO_2}}$$

Properties.—Similar to those of chlorinated lime. By boiling its solution, potassium chlorate and chloride are obtained; this constitutes the manufacturing process for the preparation of potassium chlorate.

$$\underset{\text{Chlorinated potash.}}{\mathrm{3(KCl, KClO)}} = \underset{\substack{\text{Potassium}\\\text{chlorate.}}}{\mathrm{KClO_3}} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{\mathrm{5KCl}}$$

CHLOROUS ACID.

Formula, $\mathrm{HClO_2}$.

Mode of preparation.—Obtained in an impure state by the action of chlorous anhydride on water.

$$\underset{\substack{\text{Chlorous}\\\text{anhydride.}}}{\mathrm{Cl_2O_3}} + \underset{\text{Water.}}{\mathrm{H_2O}} = \underset{\substack{\text{Chlorous}\\\text{acid.}}}{\mathrm{2HClO_2}}$$

CHLORIC ACID.

Formula, $\mathrm{HClO_3}$.

Mode of preparation.—Chloric acid is most readily prepared by adding sulphuric acid to a solution of barium chlorate, allowing the precipitated barium sulphate to subside, and then pouring off the clear liquid.

$$\underset{\substack{\text{Barium}\\\text{chlorate.}}}{\mathrm{Ba(ClO_3)_2}} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{\mathrm{H_2SO_4}} = \underset{\substack{\text{Chloric}\\\text{acid.}}}{\mathrm{2HClO_3}} + \underset{\substack{\text{Barium}\\\text{sulphate.}}}{\mathrm{BaSO_4}}$$

Properties.—Chloric acid is a most powerful oxidising agent. Its salts are the chlorates, of which the most important is potassium chlorate. No chlorates exist in nature, they therefore have to be made artificially, and, as previously mentioned, they are readily obtained by boiling solutions of the chlorinated bodies.

Potassium chlorate ($KClO_3$).—Prepared by boiling a solution of chlorinated potash (*see* page 144), or by passing chlorine into a heated solution of caustic potash, in which case the chlorinated potash is first formed, and is then immediately decomposed by the heat into potassium chlorate and chloride. On concentrating the solution by evaporation, and then allowing it to cool, the potassium chlorate crystallises out, leaving the more soluble potassium chloride in solution.

PERCHLORIC ACID.

Formula, $HClO_4$.

Mode of preparation.—If potassium chlorate be strongly heated it evolves all its oxygen, leaving potassium chloride; but if it be heated until it just melts, and then kept for a short time at that temperature, only one-third of the oxygen is evolved, and a mixture of potassium perchlorate and chloride is left.

$$\underset{\substack{\text{Potassium}\\\text{chlorate.}}}{2KClO_3} = \underset{\substack{\text{Potassium}\\\text{perchlorate.}}}{KClO_4} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{KCl} + \underset{\text{Oxygen.}}{O_2}$$

From this mixture the potassium chloride can be removed by virtue of its greater solubility in water, and the perchlorate obtained pure.

By heating potassium perchlorate with sulphuric acid, perchloric acid distils over.

$2KClO_4$	+	H_2SO_4	=	K_2SO_4	+	$2HClO_4$
Potassium Perchlorate.		Sulphuric acid.		Potassium sulphate.		Perchloric acid

Properties. — Perchloric acid is a colourless fuming liquid, and is a very powerful oxidising agent.

CHAPTER VIII.

BROMINE. IODINE. FLUORINE.

Bromine—Preparation and Properties of Bromine—Tests for Bromine—Hydrobromic Acid—Hypobromous Acid—Sodium Hypobromite—Iodine—Preparation and Properties of Iodine—Tests for Iodine—Hydriodic Acid—Iodic Acid—Chlorides of Iodine—Iodide of Nitrogen—Fluorine—Hydrofluoric Acid.

BROMINE.

Symbol, Br ; *formula*, Br_2 ; *monad ; atomic weight*, 80 ; *molecular weight*, 160.

BROMINE does not occur in nature in the free state, but in the form of metallic bromides. The bromides of sodium and magnesium are present in small quantities in many mineral springs, and in sea-water ; bromide of potassium is also present in the Stassfurt salts, which occur as deposits on a large scale in Northern Germany.

Mode of preparation.—Bromine may be prepared from the mother liquors of mineral spring waters, or from *bittern*, the mother liquor of concentrated sea-water (from which most of the chlorides have crystallised out), or from Stassfurt salts. The bromine is set free by distilling the mother liquors or the Stassfurt salts with sulphuric acid and manganese dioxide, using only sufficient of these two bodies to liberate the bromine, otherwise the chlorine would also be liberated from the chlorides that are always present, and would contaminate the bromine by forming with it a chloride of bromine. The liberation of the bromine, by the manganese dioxide and sulphuric acid, takes place in a similar manner to the liberation of chlorine by the same reagents.

$$\underset{\text{Sodium bromide.}}{2NaBr} + \underset{\text{Manganese dioxide.}}{MnO_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Bromine.}}{Br_2} + \underset{\text{Sodium sulphate.}}{Na_2SO_4} + \underset{\text{Manganese sulphate.}}{MnSO_4} + \underset{\text{Water.}}{2H_2O}$$

The bromine passes over as a heavy reddish-brown vapour, which is condensed to a liquid by means of a suitable condenser and cool receiver. The bromine so obtained generally contains small quantities of chlorine, present as chloride of bromine, from which it can be purified by redistilling with some potassium bromide, thus :

$$\underset{\text{Bromine chloride.}}{BrCl_3} + \underset{\text{Potassium bromide.}}{3KBr} = \underset{\text{Potassium chloride.}}{3KCl} + \underset{\text{Bromine.}}{2Br_2}$$

Properties.—Bromine is a heavy liquid (bromine and mercury are the only liquid elements, at ordinary temperatures) of a dark red-brown colour, and of specific gravity 3·18. It is very volatile, forming a reddish-brown vapour possessing a disagreeable odour, somewhat resembling that of chlorine, but much more intense; this vapour is poisonous, and is extremely irritating to the mucous membranes of the eye, nose, and respiratory passages; the name of the element is derived from *βρῶμος, a stink*, on account of its extremely disagreeable smell. It is soluble to a certain extent in water, bromine-water being of a reddish-brown colour. Its chemical affinities are weaker than those of chlorine, which can be demonstrated by adding a few drops of chlorine-water to a solution of potassium bromide, when the development of a reddish-brown colour in the solution indicates the liberation of the bromine, thus :

$2KBr$	+	Cl_2	=	$2KCl$	+	Br_2
Potassium bromide.		Chlorine.		Potassium chloride.		Bromine.

Tests.—In the pure state, bromine is readily recognised by its colour and smell; in the diluted state, such as in weak bromine-water, it may be recognised (*a*) by its colour becoming intensified by the addition of some decoction of starch; (*b*) by giving a white precipitate on the addition of an aqueous solution of carbolic acid.

HYDROBROMIC ACID OR HYDROGEN BROMIDE.

Formula, HBr; *molecular weight*, 81.

Hydrobromic acid, like hydrochloric acid, is a colourless gas, fuming when brought in contact with the air, and very soluble in water; its solution forming the commercial hydrobromic acid.

Modes of preparation.— (i) Hydrobromic acid is obtained by the action of tribromide of phosphorus on water, phosphorous and hydrobromic acids resulting, the latter passing over on the application of heat.

PBr_3	+	$3H_2O$	=	H_3PO_3	+	$3HBr$
Phosphorus tribromide.		Water.		Phosphorous acid.		Hydrobromic acid.

(ii) Hydrobromic acid is very easily prepared by shaking together strong solutions of potassium bromide and tartaric acid, the mixture is then allowed to stand for some time to enable the precipitated acid tartrate of potassium to subside, and the clear solution of hydrobromic acid can then be poured off from the precipitate.

$$\underset{\substack{\text{Potassium}\\\text{bromide.}}}{KBr} + \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} = \underset{\substack{\text{Hydrobromic}\\\text{acid.}}}{HBr} + \underset{\substack{\text{Potassium}\\\text{acid tartrate.}}}{KHC_4H_4O_6}$$

(iii) Hydrobromic acid is obtained by distilling potassium bromide with phosphoric acid, phosphate of potassium being formed, and hydrobromic acid passing over.

(iv) By passing sulphuretted hydrogen through bromine-water, hydrobromic acid is formed and sulphur precipitated.

$$\underset{\text{Bromine.}}{2Br_2} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{2H_2S} = \underset{\substack{\text{Hydrobromic}\\\text{acid.}}}{4HBr} + \underset{\text{Sulphur.}}{S_2}$$

(v) Hydrogen and bromine may be made to unite by heat.

$$\underset{\text{Hydrogen.}}{H_2} + \underset{\text{Bromine.}}{Br_2} = \underset{\substack{\text{Hydrobromic}\\\text{acid.}}}{2HBr}$$

Tests.—(i) On the addition of a few drops of chlorine-water to a solution of hydrobromic acid or a bromide, bromine is liberated, a yellowish-red colour being communicated to the solution; on the addition of some decoction of starch this colour is deepened to an orange-red.

(ii) On the addition of nitrate of silver to a solution of hydrobromic acid or a bromide, a yellowish-white precipitate is formed, insoluble in nitric acid, and but sparingly soluble in ammonia.

OXYACIDS OF BROMINE.

There are two of these acids, viz. :—

$HBrO$	Hypobromous acid.
$HBrO_3$	Bromic „

HYPOBROMOUS ACID.

Formula, $HBrO$.

Prepared by shaking bromine-water with the yellow precipitated mercuric oxide.

$$\underset{\substack{\text{Mercuric}\\\text{oxide.}}}{2HgO} + \underset{\text{Bromine.}}{2Br_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Mercuric}\\\text{oxybromide.}}}{Hg_2OBr_2} + \underset{\substack{\text{Hypobromous}\\\text{acid.}}}{2HBrO}$$

Sodium hypobromite ($NaBrO$) is employed in the estimation of urea in urine. It decomposes the urea, oxidising the carbon and hydrogen to carbon dioxide and water, and setting free the nitrogen, thus :

$$\begin{aligned}\underset{\text{Urea.}}{CH_4N_2O} + \underset{\substack{\text{Sodium}\\\text{hypobromite.}}}{3NaBrO} &= \underset{\substack{\text{Sodium}\\\text{bromide.}}}{3NaBr} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \\ &\quad \underset{\text{Water.}}{2H_2O} + \underset{\text{Nitrogen.}}{N_2}\end{aligned}$$

The nitrogen can then be collected and measured (the process is described fully on page 458).

BROMIC ACID.

Formula, $HBrO_3$.

Prepared by passing chlorine into bromine-water.

$$\underset{\text{Bromine.}}{Br_2} + \underset{\text{Water.}}{6H_2O} + \underset{\text{Chlorine.}}{5Cl_2} = \underset{\substack{\text{Bromic}\\\text{acid.}}}{2HBrO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{10HCl}$$

IODINE.

Symbol, I ; *formula*, I_2 ; *monad ; atomic weight*, 127 ; *molecular weight*, 254.

Iodine does not occur in nature in the free state. The iodides of sodium and magnesium are present in small quantities in certain mineral spring waters, and in still smaller quantities in sea-water. The amount of iodides (mainly sodium iodide) present in sea-water is so minute as to make it impracticable to extract the iodine from sea-water, but sea-weeds possess the property of absorbing the iodides into their tissues in considerable quantities, and it is from sea-weeds that iodine is extracted. The sea-weeds (Scottish and Irish sea-weeds being especially rich in iodine) are collected, dried, and burnt, when an ash named *kelp* is obtained, and it is from this kelp that iodine is prepared. The bulk of kelp, or sea-weed ash, consists of sodium carbonate, together with sodium chloride, sodium sulphate and sodium sulphide, and small quantities of sodium and magnesium iodides.

Mode of preparation of iodine from kelp.—(i) The kelp is treated with boiling water, and the solution poured off from insoluble matter ; (ii) to the solution sulphuric acid is added, when carbon dioxide and sulphuretted hydrogen gases are evolved, sulphur is thrown down, and after standing for twenty-four hours a large quantity of sodium sulphate crystallises out ; (iii) the mother liquor from the sodium sulphate crystals is then poured off, and contains in solution the iodides with some sodium chloride and free sulphuric acid ; to it manganese dioxide is added, and the mixture distilled at a temperature not exceeding 80° C., at which temperature the manganese dioxide and sulphuric acid liberate the iodine, but not the chlorine, or only in very small quantities.

$$\underset{\substack{\text{Sodium}\\\text{iodide.}}}{2NaI} + \underset{\substack{\text{Manganese}\\\text{dioxide.}}}{MnO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} +$$

$$\underset{\substack{\text{Manganese}\\\text{sulphate.}}}{MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Iodine.}}{I_2}$$

The iodine passes over in the form of a violet-coloured vapour, which is made to pass through a series of cooled glass condensers, on the sides of which it condenses as a dark-coloured solid. The iodine so prepared generally contains a small quantity of chlorine in the form of a chloride of iodine, from which it can be purified by resubliming it with some potassium iodide.

$$\underset{\substack{\text{Iodine}\\\text{chloride.}}}{ICl} + \underset{\substack{\text{Potassium}\\\text{iodide.}}}{KI} = \underset{\substack{\text{Potassium}\\\text{chloride.}}}{KCl} + \underset{\text{Iodine.}}{I_2}$$

Properties.—Iodine is a solid crystalline substance, possessing a dark grey colour, a metallic lustre, and a peculiar odour somewhat resembling that of diluted chlorine. When heated it volatilises, producing a violet-coloured vapour (hence its name, from ἰώδης, *violet-coloured*), which is very irritating to the mucous membrane of the eyes and nose. Iodine possesses a strong unpleasant taste, it stains the skin yellow, and is poisonous. It is slightly soluble in water, to which it imparts a yellowish-brown colour; it is much more soluble in a solution of iodide of potassium, in alcohol, ether, chloroform, and bisulphide of carbon.

Tests.—(i) A solution of free iodine gives with a cold decoction of starch a deep blue colour.

(ii) If with an aqueous solution of iodine some chloroform or bisulphide of carbon be well agitated, and the mixture allowed to stand, the chloroform or bisulphide of carbon will settle to the bottom of the tube, carrying the iodine in solution, a pink or purple colour being imparted to the chloroform or bisulphide of carbon by the dissolved iodine.

HYDRIODIC ACID OR HYDROGEN IODIDE.

Formula, HI; *molecular weight*, 128.

Hydriodic acid, like hydrochloric and hydrobromic acids, is a colourless gas, fuming when brought in contact with the air, and very soluble in water, its solution forming the ordinary hydriodic acid.

Hydriodic acid can be prepared by union of its elements, but only with great difficulty. By distilling potassium iodide with strong sulphuric acid, hydriodic acid is obtained, but in a very impure state, on account of a quantity of iodine being set free at the same time by the sulphuric acid. The following are therefore the best methods of preparing hydriodic acid.

Modes of preparation.—(i) By the action of phosphorus tri-iodide on water, when phosphorous and hydriodic acids are obtained, the latter passing over on the application of heat.

$$\underset{\text{Phosphorus tri-iodide.}}{PI_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphorous acid.}}{H_3PO_3} + \underset{\text{Hydriodic acid.}}{3HI}$$

(ii) By shaking together strong solutions of potassium iodide and tartaric acid, allowing the mixture to stand for some time to allow the precipitated acid tartrate of potassium to subside, and then pouring off the solution of hydriodic acid.

$$\underset{\text{Potassium iodide.}}{KI} + \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} = \underset{\text{Hydriodic acid.}}{HI} + \underset{\text{Potassium acid tartrate.}}{KHC_4H_4O_6}$$

(iii) By distilling potassium iodide with phosphoric acid, when phosphate of potassium is formed, and the hydriodic acid passes over.

(iv) By passing sulphuretted hydrogen through iodine-water, or through water in which iodine is suspended, when the hydrogen of the sulphuretted hydrogen unites with the iodine to form hydriodic acid, and sulphur is precipitated.

$$\underset{\text{Iodine.}}{2I_2} + \underset{\text{Sulphuretted hydrogen.}}{2H_2S} = \underset{\text{Hydriodic acid.}}{4HI} + \underset{\text{Sulphur.}}{S_2}$$

Properties.—Both chlorine and bromine have stronger affinities for hydrogen and for the metals than iodine has, therefore both chlorine and bromine possess the property of liberating iodine from hydriodic acid or from an iodide, thus:

$$\underset{\text{Hydriodic acid.}}{2HI} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Hydrochloric acid.}}{2HCl} + \underset{\text{Iodine.}}{I_2}$$

$$\underset{\text{Hydriodic acid.}}{2HI} + \underset{\text{Bromine.}}{Br_2} = \underset{\text{Hydrobromic acid.}}{2HBr} + \underset{\text{Iodine.}}{I_2}$$

Hydriodic acid on exposure to light becomes coloured from liberation of iodine.

Tests.—(i) On the addition of a few drops of chlorine-water to a solution of hydriodic acid or of an iodide, a yellowish-brown colour is produced, due to the liberation of iodine; if some decoction of starch be added to this, a deep blue colour will be produced.

(ii) On the addition of nitrate of silver to a solution of hydriodic acid or of an iodide, a yellowish precipitate is formed, insoluble in nitric acid, and but sparingly soluble in ammonia.

IODIC ACID.

Formula, HIO_3.

Iodic acid is a white crystalline substance, and is prepared (i) by the action of strong nitric acid on iodine, (ii) by passing chlorine into iodine-water.

$$\underset{\text{Iodine.}}{I_2} + \underset{\text{Water.}}{6H_2O} + \underset{\text{Chlorine.}}{5Cl_2} = \underset{\text{Iodic acid.}}{2HIO_3} + \underset{\text{Hydrochloric acid.}}{10HCl}$$

CHLORIDES OF IODINE.

There are two compounds of iodine and chlorine, viz. ICl, a liquid, and ICl_3, a solid. They are both obtained by direct union of the elements.

IODIDE OF NITROGEN.

Formula, NI_3.

This is obtained by mixing a strong alcoholic solution of iodine (such as tincture of iodine) with an aqueous solution of ammonia, thus :

$$\underset{\text{Ammonia}}{4NH_3} + \underset{\text{Iodine.}}{3I_2} = \underset{\text{Nitrogen iodide.}}{NI_3} + \underset{\text{Ammonium iodide.}}{3NH_4I}$$

Properties. — Iodide of nitrogen is a dark-coloured powder, which when dried explodes violently with the slightest touch, decomposing into its elements. The importance to medical men of bearing in mind its existence lies in the fact that free iodine and ammonia are incompatibles, and should not therefore be prescribed together in a liniment.

FLUORINE.

Symbol, F; *formula*, F_2; *monad; atomic weight*, 19; *molecular weight*, 38.

Fluorine occurs in nature as *fluor-spar* or calcium fluoride (CaF_2), and as *cryolite*, a double fluoride of aluminium and sodium (Al_2F_6, 6NaF) found in Greenland. The fluorides of calcium and sodium are also present in minute quantities in the blood, bones, and teeth of human beings and animals.

Fluorine has not been isolated, not on account of any difficulty in liberating the element from its compounds, but on account of its powerful affinity, when liberated, for all bodies except oxygen. Thus, it cannot be prepared in glass vessels on account of its immediately attacking the silica of the glass, and with all metals it immediately unites. An attempt has been made to prepare it by decomposing fluoride of silver (AgF) with chlorine, in a vessel made of fluor-spar (CaF_2), a body already fully saturated with fluorine, and in this way a heavy yellow gas was obtained; but it probably was a compound of fluorine and chlorine.

HYDROFLUORIC ACID OR HYDROGEN FLUORIDE.

Formula, HF.

Also known as *fluoric acid.* Like hydrochloric, hydrobromic, and hydriodic acids, hydrofluoric acid is a colourless gas, fuming on contact with the air, and very soluble in water; its solution constituting the commercial hydrofluoric or fluoric acid.

Mode of preparation.—Hydrofluoric acid is obtained by the action of strong sulphuric acid on powdered fluor-spar, thus :

$$\underset{\substack{\text{Calcium}\\\text{fluoride.}}}{CaF_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Hydrofluoric}\\\text{acid.}}}{2HF} + \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4}$$

It has to be prepared in leaden or platinum vessels, as it readily attacks glass ; on conducting the gas into water, the commercial solution of hydrofluoric acid is obtained.

Properties.—The most important property of this acid is its power of etching glass, which is due to its attacking the silica of glass, forming with it a gaseous silicon fluoride, thus :

$$\underset{\text{Silica.}}{SiO_2} + \underset{\substack{\text{Hydrofluoric}\\\text{acid.}}}{4HF} = \underset{\substack{\text{Silicon}\\\text{fluoride.}}}{SiF_4} + \underset{\text{Water.}}{2H_2O}$$

If a design is to be etched on glass, the surface of the glass is first covered with wax, and some of the wax is then scraped away in the shape of the desired design ; the surface is then exposed for a few minutes either to the fumes of hydrofluoric acid (evolved from fluor-spar and sulphuric acid), or the solution of hydrofluoric acid is poured over the surface; on washing the surface with a stream of water, and then scraping or melting off the wax, the design will be found to be etched on the glass. On account of its power of attacking glass, the solution of hydrofluoric acid is kept in bottles made of gutta-percha, provided with a stopper of the same material.

Test.—The test for hydrofluoric acid is to expose to it a piece of waxed glass, on which some simple design has been scratched, when the design will be found to be etched on the glass.

CHAPTER IX.

CARBON. SILICON. BORON.

Carbon—Allotropic forms of Carbon—Properties of Carbon—Carbon Monoxide—Preparation and Properties of Carbon Monoxide—Carbon Dioxide—Preparation and Properties of Carbon Dioxides—Carbon Oxychloride—Carbon Bisulphide—Silicon, Silica, Silicates, Glass, Porcelain, and Earthenware—Boron—Boric Acid—Metaboric Acid—Borax.

CARBON.

Symbol, C; *formula*, C_2; *tetrad; atomic weight*, 12; *molecular weight*, 24.

Carbon occurs in nature in the free state in the diamond, graphite, plumbago, coal, etc. In the combined state it enters into the composition of an immense number of bodies, for the number of carbon compounds (both natural and artificial) far exceeds those of any other element; it occurs in all organic substances, whether of animal or vegetable origin, and in all carbonates, such as marble, limestone, chalk, magnesite, etc.

Carbon exists in three allotropic forms, of which two are crystalline, viz. *diamond* and *graphite*, and one amorphous, viz. *charcoal* in its different forms. The term *allotropic* (from ἄλλος, *another*; τρόπος, *condition*) is applied to substances that are similar in composition and constitution, but that differ in their properties.

The allotropic forms of carbon.—(1) *Diamond.*—This is the rarest form of free carbon, and occurs in nature in octohedral crystals belonging to the regular system; it consists of nearly pure carbon, but when a diamond is burnt in oxygen, a minute amount of ash is left, consisting of silica, alumina, and sometimes oxide of iron. It is the hardest body known, and is on that account employed for cutting glass ; its lustre is due to its high power of refracting light.

(2) *Graphite*, *plumbago*, or *blacklead.*—This is the second crystalline form of carbon, and crystallises in six-sided plates. It is a dark-grey crystalline substance, soft and greasy to the touch, and when drawn across paper leaves a mark. It is employed in blacklead pencils, in plumbago crucibles (made of plumbago mixed with clay), for blacking iron grates, and as a dry lubricant for machinery.

(3) *Amorphous carbon.*—This occurs in various forms.

(*a*) *Wood charcoal* is prepared by heating or charring wood out of contact with air. This form of amorphous carbon is used in the manufacture of gunpowder. It is extremely porous, possessing the power of absorbing gases, and hence is used as a deodoriser.

(*b*) *Animal charcoal* is obtained by roasting bones out of contact with air. This form of amorphous carbon is sold commercially under the names of *bone-black*, *animal-black*, and *ivory-black ;* it contains the inorganic constituents of the bones, viz. phosphate and carbonate of lime, from which, however, it may be freed by digesting with hydrochloric acid, which dissolves these lime salts, so that on filtering, and washing the charcoal with water, it is obtained pure. Animal charcoal possesses in a very high degree the power of absorbing colouring matters, and hence is very useful as a decolourising agent. In the preparation of several of the alkaloids, the colouring matter is removed by boiling the alkaloidal solution with animal charcoal.

(*c*) Amorphous carbon is the chief constituent of *coal.* Coal has been produced by the slow decay of vegetable matter out of contact with air, possibly combined with elevation of temperature and considerable pressure. Coal contains a fair proportion of hydrogen, and when deprived of this hydrogen by strongly heating out of contact with air, *coke* is produced, so that coke may be regarded as coal deprived of its hydrogen.

(*d*) *Peat*, another form of fuel, but inferior to coal, contains a quantity of amorphous carbon; it is produced in marshy localities by the gradual decay of grasses, mosses, etc.

(*e*) *Tinder* is another variety of amorphous carbon.

(*f*) *Soot* and *lampblack* are two varieties of amorphous carbon in a fine state of division.

Properties of carbon.—In all three of its forms carbon is infusible at all temperatures, but it volatilises at the high temperature of the electric arc. It is insoluble in all ordinary solvents, but molten iron at the temperature of the blast-furnace dissolves from 4 to 5 per cent. of carbon; as the iron cools part of the carbon crystallises out as small crystals of graphite, and part remains in union with the iron as carbide of iron (*see* page 261). Carbon when heated to redness has a powerful affinity for oxygen, either in the free state as in air, or in the combined state; it is therefore largely employed as a reducing agent in depriving several of the metallic oxides of their oxygen, and so reducing them to the metallic state. If carbon be burnt in a free supply of air it produces carbon dioxide (CO_2), but if burnt in a limited supply of air it produces mainly carbon monoxide (CO).

Carbon produces with hydrogen a large number of compounds known as hydrocarbons, some of which will be described later, but only one such compound is obtained by direct union of carbon and hydrogen, viz. *acetylene* (C_2H_2), and then only at the extremely high temperature of the electric arc; if the electric arc is produced between carbon poles in an atmosphere of hydrogen, then the two elements unite to form acetylene, thus:

$$\underset{\text{Carbon.}}{C_2} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Acetylene.}}{C_2H_2}$$

Test.—Any form of carbon (including the diamond) when burnt in oxygen produces carbon dioxide, which can be recognised by its turning lime-water turbid.

CARBON MONOXIDE.

Formula, CO; *molecular weight*, 28.

Also known as *carbonic oxide*.

Modes of preparation.—(i) By passing carbon dioxide through a tube containing pieces of red-hot charcoal.

$$\underset{\substack{\text{Carbon}\\\text{dioxide.}}}{2CO_2} + \underset{\text{Carbon.}}{C_2} = \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{4CO}$$

The blue flames seen at the top of a well-drawing clear fire consist of burning carbon monoxide, which has been produced by the carbon dioxide, formed at the lower part of the fire, having to pass over the red-hot coal on its upward way to the chimney.

(ii) Carbon monoxide is very easily prepared by heating potassium ferrocyanide with strong sulphuric acid.

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{K_4Fe(CN)_6} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{6H_2SO_4} + \underset{\text{Water.}}{6H_2O} = \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{2K_2SO_4} +$$

$$\underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{FeSO_4} + \underset{\substack{\text{Ammonium}\\\text{sulphate.}}}{3(NH_4)_2SO_4} + \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{6CO}$$

(iii) Carbon monoxide is also readily prepared by heating formic acid ($HCHO_2$) or sodium formate ($NaCHO_2$) with strong sulphuric acid. The action of the sulphuric acid is simply to abstract water from the formic acid, when carbon monoxide is evolved, thus:

$$\underset{\text{Formic acid.}}{HCHO_2} = \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon monoxide.}}{CO}$$

(iv) If oxalic acid ($H_2C_2O_4$) be heated, either alone or with sulphuric acid, it decomposes into water and the two oxides of carbon, thus:

$$\underset{\text{Oxalic acid}}{H_2C_2O_4} = \underset{\text{Water.}}{H_2O} + \underset{\text{Carbon monoxide.}}{CO} + \underset{\text{Carbon dioxide.}}{CO_2}$$

By passing the two gases through a strong solution of caustic potash, the carbon dioxide is absorbed (forming potassium carbonate), and the carbon monoxide can then be collected in the pure state.

(v) When charcoal or carbonaceous substances are burnt with an insufficient supply of air, carbon monoxide is formed.

Properties.—The specific gravity of carbon monoxide is 14, and it is slightly lighter than air; it is a colourless, odourless, and tasteless gas; it is combustible, burning with a pale blue flame, and forming carbon dioxide; it is a non-supporter of combustion; it is insoluble in water, and therefore may be collected over it. It is a poisonous gas, as it possesses the property of displacing the oxygen from its union with the hæmoglobin of the blood, forming a compound with the hæmoglobin that acts as a narcotic poison; inhaling the fumes of burning charcoal, placed in the centre of a closed and non-ventilated room (a not uncommon method of committing suicide in

France), causes death from carbonic oxide poisoning. Carbon monoxide in contact with caustic potash at a high temperature forms potassium formate, thus :

$$\underset{\text{Caustic potash}}{KHO} + \underset{\text{Carbon monoxide.}}{CO} = \underset{\text{Potassium formate.}}{KCHO_2}$$

Test.—Carbon monoxide gives no precipitate with lime-water, but on applying a light it burns with a pale blue flame, and the resulting gas (carbon dioxide) then produces a precipitate with lime-water.

CARBON DIOXIDE.

Formula, CO_2; *molecular weight*, 44.

Also known as *carbonic anhydride*, *carbonic acid gas*, and *choke-damp*. It is always formed when carbon in any form, or any compound of carbon, is burnt with a free supply of air. It is one of the gases evolved from volcanoes, and in certain instances from fissures in the earth, as in the Grotto del Cane near Naples, and in the poison valley of Java.

Modes of preparation.—(i) It is most easily prepared by the action of hydrochloric acid on calcium carbonate in the form of marble or chalk.

$$\underset{\text{Calcium carbonate.}}{CaCO_3} + \underset{\text{Hydrochloric acid.}}{2HCl} = \underset{\text{Calcium chloride.}}{CaCl_2} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

It may be collected in the pneumatic trough over water, or, since it is heavier than air, it can be collected by downward displacement of air (Fig. 16).

Sulphuric acid may be substituted for hydrochloric acid, but in this case the insoluble calcium sulphate forms a coating over the marble or chalk, and is apt to stop the evolution of the gas.

$$\begin{array}{ccccccccc} CaCO_3 & + & H_2SO_4 & = & CaSO_4 & + & CO_2 & + & H_2O \\ \text{Calcium} & & \text{Sulphuric} & & \text{Calcium} & & \text{Carbon} & & \text{Water.} \\ \text{carbonate.} & & \text{acid.} & & \text{sulphate.} & & \text{dioxide.} & & \end{array}$$

(ii) Carbon dioxide is evolved by heating chalk or limestone, as in the preparation of lime in the limekilns.

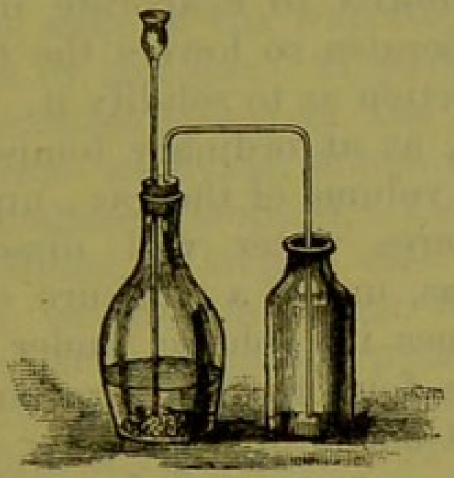


Fig. 16.—Preparation and Collection of Carbon Dioxide.

$$\begin{array}{ccccc} CaCO_3 & = & CaO & + & CO_2 \\ \text{Calcium} & & \text{Lime.} & & \text{Carbon} \\ \text{carbonate.} & & & & \text{dioxide.} \end{array}$$

(iii) Carbon dioxide is also evolved by heating a bicarbonate, such as sodium or potassium bicarbonate.

$$\begin{array}{ccccccc} 2NaHCO_3 & = & Na_2CO_3 & + & CO_2 & + & H_2O \\ \text{Sodium} & & \text{Sodium} & & \text{Carbon} & & \text{Water.} \\ \text{bicarbonate.} & & \text{carbonate.} & & \text{dioxide.} & & \end{array}$$

(iv) By burning carbon monoxide in oxygen or in air, carbon dioxide is produced.

$$\begin{array}{ccccc} 2CO & + & O_2 & = & 2CO_2 \\ \text{Carbon} & & \text{Oxygen.} & & \text{Carbon} \\ \text{monoxide.} & & & & \text{dioxide.} \end{array}$$

Properties.—The specific gravity of carbon dioxide is 22, and it is heavier than air; it is a colourless gas, possessing a peculiar faint pungent odour in quantity, and a faint acid taste; it is not combustible, neither is it a supporter of combustion, a lighted taper being immediately extinguished when lowered into the gas. It can be liquefied by high pressure, and if the liquid is allowed to evaporate in the air, the portion that evaporates so lowers the temperature of the remaining portion as to solidify it. It is slightly soluble in water, as at ordinary temperatures water dissolves its own volume of the gas; under a pressure of two atmospheres water will dissolve twice its volume of the gas, under a pressure of three atmospheres three times its volume, under a pressure of four atmospheres four times its volume, and so on. So that if a pint bottle of soda-water that has been charged under a pressure of four atmospheres be opened, three pints of the gas will escape with effervescence, one pint remaining in solution, since there is still the ordinary pressure of the atmosphere upon the water. The solution of carbon dioxide in water faintly reddens blue litmus paper, the liquid probably containing true carbonic acid (H_2CO_3), thus:

$$\underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Carbonic acid.}}{H_2CO_3}$$

It is for this reason that carbon dioxide is also called carbonic anhydride (the anhydride of carbonic acid) and carbonic acid gas. Carbon dioxide is not a poison if swallowed into the stomach, as in the form of effervescent waters and drinks it is taken in considerable quantities, but if inhaled in quantity it produces death from suffocation, not that it unites with the hæmoglobin of the blood, but because it dilutes down and takes the place of the necessary oxygen of the air. After explosions in coal-mines, it is the carbon dioxide or choke-damp, produced by the explosion of the marsh gas or fire-damp with the air, that causes in so many cases the suffocation of the miners. Since carbon dioxide is evolved, as previously mentioned, from limekilns, it is not an uncommon occurrence for tramps and others sleeping close to a limekiln for the sake of the warmth, to die in their sleep, suffocated by this gas. If pure carbon dioxide is inhaled, it produces spasm of the glottis and consequent death from asphyxia, unless the inhalation of the gas is immediately stopped. Carbon dioxide, as previously explained, is largely used in the so-called aërated waters, to give to them their effervescent character and their pleasant sharp taste.

Carbon dioxide if passed into a solution of an alkali, forms first a carbonate, and then afterwards converts the carbonate into a bicarbonate. Thus, with caustic potash it first forms potassium carbonate.

$$\underset{\substack{\text{Caustic}\\ \text{potash.}}}{2KHO} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} = \underset{\substack{\text{Potassium}\\ \text{carbonate.}}}{K_2CO_3} + \underset{\text{Water.}}{H_2O}$$

By its further action it converts the carbonate into the bicarbonate.

$$\underset{\substack{\text{Potassium}\\ \text{carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Potassium}\\ \text{bicarbonate.}}}{2KHCO_3}$$

Carbon dioxide passed into lime-water (solution of calcium hydrate) first renders it turbid by precipitating calcium carbonate.

$$\underset{\substack{\text{Calcium}\\ \text{hydrate.}}}{Ca(HO)_2} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} = \underset{\substack{\text{Calcium}\\ \text{carbonate}}}{CaCO_3} + \underset{\text{Water.}}{H_2O}$$

By its further action it converts the insoluble calcium carbonate into the soluble bicarbonate, and so renders the liquid clear again.

$$\underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Calcium}\\\text{bicarbonate.}}}{Ca(HCO_3)_2}$$

Test.—Carbon dioxide turns lime-water turbid or milky when shaken up with it.

CARBON OXYCHLORIDE.

Formula, $COCl_2$.

Also known as *carbonyl chloride* and *phosgene gas* (so named on account of its being produced by the action of light).

This body may be regarded either as carbon monoxide united with chlorine, or as carbon dioxide from which one atom of oxygen has been displaced by two atoms of chlorine.

Mode of preparation.—It is produced with an explosion when equal volumes of carbon monoxide and chlorine are exposed to direct sunlight, thus:

$$\underset{\substack{\text{Carbon}\\\text{monoxide.}}}{CO} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Carbon}\\\text{oxychloride.}}}{COCl_2}$$

When the two gases unite, the volume of the mixed gases diminishes to one-half.

$$CO + Cl_2 = COCl_2$$

$$\begin{array}{lclcl} & \text{1 molecule} & + & \text{1 molecule} & = \text{1 molecule} \\ \therefore & \text{1 volume} & + & \text{1 volume} & = \text{1 volume.} \end{array}$$

CARBON BISULPHIDE OR DISULPHIDE.

Formula, CS_2.

This body may be regarded as carbon dioxide in which the oxygen has been displaced by sulphur, and just as carbon dioxide is produced by burning carbon in oxygen, so carbon bisulphide is produced by burning carbon in sulphur vapour.

Mode of preparation.—By passing the vapour of sulphur over red-hot charcoal, and then conveying the vapour of the bisulphide of carbon through a spiral tube kept cool by immersion in water, by which means the bisulphide of carbon condenses to a liquid.

Properties.—Bisulphide of carbon is a colourless, mobile, very volatile liquid. When first prepared it possesses a very disagreeable odour, from which it can be to a great extent purified by shaking with mercury and corrosive sublimate, and afterwards distilling it. It is heavier than water, and after agitation with water it sinks to the bottom, leaving a very small quantity dissolved in the water. It is a very inflammable liquid, and its vapour is also very inflammable, forming carbon dioxide and sulphur dioxide when burnt.

$$\underset{\substack{\text{Carbon}\\ \text{bisulphide.}}}{CS_2} + \underset{\text{Oxygen}}{3O_2} = \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} + \underset{\substack{\text{Sulphur}\\ \text{dioxide.}}}{2SO_2}$$

Carbon bisulphide is used for many technical purposes, as it is a remarkable solvent of many bodies, possessing the property of dissolving sulphur, phosphorus, fats, resins, and indiarubber. It is used to impregnate indiarubber with sulphur in the manufacture of vulcanised rubber, and also to extract fat from wool, and oils from oily seeds.

With certain of the metallic sulphides carbon disulphide will unite, forming sulphocarbonates, which may be regarded as carbonates in which the oxygen has been displaced by sulphur, thus with potassium sulphide it forms potassium sulphocarbonate.

$$\underset{\text{Potassium sulphide.}}{K_2S} + \underset{\text{Carbon disulphide.}}{CS_2} = \underset{\text{Potassium sulphocarbonate.}}{K_2CS_3}$$

SILICON.

Symbol, Si; *formula*, Si_2; *tetrad; atomic weight*, 28; *molecular weight*, 56.

Silicon is widely and abundantly distributed in nature, but not in the free state. The oxide of silicon (silica) occurs both free and in combination with bases as the various natural silicates, the greater part of the solid crust of the earth being composed of silicates and silica.

Preparation of silicon.—The element silicon may be obtained by heating the double fluoride of potassium and silicon ($2KF, SiF_4$) with the metal potassium, which abstracts the fluorine from its combination with the silicon, setting free that element. Prepared in this way, silicon is obtained as a dark brown amorphous powder. It may, however, be obtained in the crystalline condition by heating for some time the same ingredients, viz. the double fluoride of potassium and silicon, and the metal potassium, with the metal zinc; on cooling, an ingot of zinc is obtained with crystals of silicon embedded in it; by treating this with hydrochloric acid, the zinc is dissolved, leaving prismatic crystals of the element silicon.

SILICA.

Formula, SiO_2.

Also known as *oxide of silicon* and *silicic anhydride.*

Silica occurs in the free state in nature as *rock crystal*, *quartz*, *flint*, *sand*, *sandstone*, *agate*, *opal*, *jasper*, and *amethyst.* The so-called *infusorial earth*, or the inorganic remains of certain infusoria, consists essentially of amorphous silica. Silica is also present in the stems of certain grasses, cereals, and rushes, and in the feathers of many birds.

SILICIC ACID.

There are two varieties of silicic acid, a tetrabasic acid (H_4SiO_4) which enters into the composition of the natural silicates, and a dibasic acid (H_2SiO_3) which contains a molecule of water less than the tetrabasic one, and enters into the composition of the artificial silicates contained in the different varieties of glass.

Natural silicates.—*Clay*, or aluminium silicate ($Al_4(SiO_4)_3$), is the most widely distributed of the natural silicates; the colour of common or brown clay is due to iron contained in it. Clay in its purest form occurs as *kaolin* or *china-clay*, and is produced from a felspar, a double silicate of aluminium and potassium, by the action of the carbon dioxide of the air, which unites with the potassium to form potassium carbonate, which is washed away, leaving the silicate of aluminium in a white state.

Felspar is a double silicate of aluminium and potassium or sodium. Felspar enters into the composition of granite.

Meerschaum is a silicate of magnesium combined with silica.

French chalk is silicate of magnesium.

Asbestos is a fibrous silicate of calcium and magnesium.

Pumice-stone, a substance of volcanic origin, is a porous silicate of aluminium and the alkali or alkaline-earth metals.

Glass.—The different varieties of glass consist of metallic compounds of the dibasic acid (H_2SiO_3).

Crown glass, common window glass, bottle glass, or *soda glass* is made by fusing together chalk ($CaCO_3$), sodium carbonate (Na_2CO_3), and sand (SiO_2). It consists of the calcium and sodium silicates; the green colour of common bottle glass is due to iron derived from the sand, and existing in the glass as ferrous silicate; the colour can be removed by adding to the melted glass a small quantity of manganese dioxide, which oxidises the green ferrous silicate to the colourless ferric silicate.

Hard glass or *potash glass* contains potassium in the place of sodium, and is made by fusing together chalk, potassium carbonate, and sand. It consists of the calcium and potassium silicates, and requires a much higher temperature to melt it than does soda glass; it is therefore useful in the manufacture of hard glass-tubing, and of chemical apparatus required to stand a high temperature.

Flint glass or *crystal glass* is a potash glass containing lead in the place of calcium, and is made by fusing together potassium carbonate (K_2CO_3), litharge or lead oxide (PbO), and sand (SiO_2). It consists of potassium and lead silicates, and is distinguished by its lustre and refractive power, hence it is valuable for optical purposes.

Soluble glass is either sodium or potassium silicate, generally the former. If it is the sodium silicate, it is prepared by fusing together sodium carbonate and sand. It is a thick syrupy liquid, miscible with, or soluble in, water; if painted over a surface, such as a wall, it is decomposed by the carbon dioxide of the air, a film of silica being left as a hard protective surface on the wall.

Coloured glasses are made by the addition of different metallic oxides to glass while in a molten condition. Blue glass is made by adding oxide of cobalt; red glass by adding cuprous oxide.

Porcelain and earthenware.—Porcelain and earthenware articles consist of clay that has been moulded into the required shapes, then baked hard, and afterwards covered with some substance that fuses at a high temperature, and forms a glaze, so preventing the passage of liquids through what would otherwise be a porous medium. The glaze used for the finer kinds of porcelain is generally produced by dipping the unglazed article into water containing powdered felspar suspended in it; on draining the article the water sinks into the porous substance, leaving a film of felspar over its surface, and on strongly heating the article in a furnace this film of felspar melts and forms the glaze. Common earthenware, which is of a reddish-brown colour, is frequently glazed with litharge (oxide of lead), which forms an easily fusible lead silicate on the application of heat, this lead silicate constituting the glaze; if acid articles of food, such as vinegar, lemon-juice, lime-juice, etc., be kept in such vessels, the lead may be dissolved by the acid, and so the glaze may become a source of lead poisoning. Another common glaze is *salt glaze;* common salt (sodium chloride) is thrown into the furnace containing the strongly-heated articles, the sodium chloride volatilises and decomposes at the heated surfaces of the clay articles, forming a deposit of fused aluminium and sodium silicates over them.

BORON.

Symbol, B ; *formula*, B_2 ; *triad ; atomic weight*, 11 ; *molecular weight*, 22.

Boron does not occur in nature in the free state, but is found as free boric acid, and also in the form of various natural borates.

Preparation of boron.—Amorphous boron is obtained by heating boron trioxide (B_2O_3) with the metal sodium. Crystalline boron is prepared by dissolving the amorphous variety in molten aluminium ; on cooling, the boron crystallises in the mass of the aluminium, from which the crystals may be obtained by dissolving the aluminium in hydrochloric acid.

BORIC OR BORACIC ACID.

Formula, H_3BO_3.

Boracic acid is found in the jets of steam known as *suffioni* or *fumaroli*, issuing from fissures in the earth in the volcanic districts of Tuscany ; these jets of steam condense and form small lagoons, by the concentration of the water of which boracic acid is obtained. Since this volcanic boracic acid is always accompanied by salts of ammonia, it is possible that it is produced deep down in the earth by the contact of boron nitride with steam, as these two bodies are known to decompose one another as follows :

$$\underset{\text{Boron nitride.}}{BN} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Boracic acid.}}{H_3BO_3} + \underset{\text{Ammonia.}}{NH_3}$$

Boracic acid may also be prepared by mixing together a concentrated hot solution of borax with sulphuric or hydrochloric acids; on cooling, the boracic acid crystallises out.

Properties.—Boracic acid is a white solid, crystallising in small flaky crystals, very soluble in hot, and moderately soluble in cold, water. It possesses antiseptic properties, and is used as an antiseptic lotion and as a preservative.

Tests.—(i) If boracic acid be mixed with some alcohol, and a light applied to the mixture, the boracic acid communicates a green colour to the flame of the burning alcohol.

(ii) Boracic acid turns yellow turmeric paper brown, in this way acting on turmeric in a similar manner to alkalies. It is the only acid that turns turmeric brown.

METABORIC OR METABORACIC ACID.

Formula, HBO_2.

This acid is obtained by gently heating boracic acid, when each molecule of the acid loses a molecule of water, thus:

$$\underset{\text{Boracic acid.}}{H_3BO_3} = \underset{\text{Metaboracic acid.}}{HBO_2} + \underset{\text{Water.}}{H_2O}$$

If further heat be applied, all the water is driven off and boracic anhydride or boron trioxide (B_2O_3) is left, thus:

$$\underset{\text{Metaboracic acid.}}{2HBO_2} = \underset{\text{Boracic anhydride.}}{B_2O_3} + \underset{\text{Water.}}{H_2O}$$

The only interest attaching to metaboracic acid is that it is the acid that enters into the composition of borax, which is a compound of metaboracic acid, and not of boracic acid.

BORAX.

Formula, $2NaBO_2, B_2O_3, 10H_2O$.

This is a crystalline compound of sodium metaborate and boracic anhydride. Native borax occurs as *tincal*, found in Persia and elsewhere; of late, borax has been found in large quantities in California.

Preparation of borax.—If the crude volcanic boracic acid be heated with sodium carbonate, ammonium carbonate volatilises (*see* page 128), and borax remains.

Tests.—(i) If sulphuric acid be added to borax (to set free boracic acid), and the mixture stirred with alcohol, and a light applied, a green-coloured flame will be obtained.

(ii) If to a solution of borax, hydrochloric acid be added (to set free boracic acid), and a piece of turmeric paper be dipped in the mixture, then on carefully drying the turmeric paper over a Bunsen flame, the yellow colour will be changed to brown.

CHAPTER X.

PHOSPHORUS. COMPOUNDS OF PHOSPHORUS.

Phosphorus—Ordinary or Yellow Phosphorus—Red or Amorphous Phosphorus—Phosphorus Trioxide—Phosphorus Pentoxide—Phosphoric Acid—Pyrophosphoric Acid—Metaphosphoric Acid—Phosphorous Acid—Hypophosphorous Acid—Gaseous Phosphoretted Hydrogen—Liquid Phosphoretted Hydrogen—Compounds of Phosphorus and Chlorine—Compounds of Phosphorus and Bromine—Compounds of Phosphorus and Iodine.

PHOSPHORUS.

Symbol, P; *formula*, P_4; *pentad; atomic weight*, 31; *molecular weight*, 124.

PHOSPHORUS and arsenicum are the only two elements that contain four atoms in the molecule; the molecular weight of phosphorus is therefore four times the atomic weight.

Phosphorus (from φῶς, *light*; φέρειν, *to bear*) derives its name from its property of shining, or being luminous, in the dark; it occurs in nature principally as calcium phosphate in the minerals *apatite* and *phosphorite*, and in soils in small quantities; from soils plants possess the power of abstracting the calcium phosphate, and of storing it in their tissues partly in the form of a soluble calcium phosphate, and partly in the form of complex organic bodies containing phosphorus; animals by using plants as foods convey phosphorus into their systems, and the calcium phosphate becoming deposited in bones constitutes the principal inorganic and hardening constituent of bones, whilst phosphorus in the form of complex organic bodies forms an essential constituent of the brain, nervous, and other tissues; in our food more phosphorus is taken than the system requires, the excess being got rid of mainly by excretion as phosphates, principally in the urine, partly in the fæces, and so being returned to the soil. Phosphorus was first prepared from the calcium phosphate obtained from concentrated urine; later, the discovery was made that bones also contain calcium phosphate, and it is from this source that phosphorus is now prepared.

There are two allotropic forms of phosphorus, the *ordinary* or *yellow*, and the *red* or *amorphous*, which differ remarkably from one another in their properties.

ORDINARY OR YELLOW PHOSPHORUS.

This is prepared from bones in the following manner:—(i) The bones are calcined to obtain bone-ash, an impure calcium phosphate; (ii) the bone-ash is digested with sulphuric acid to yield the soluble acid phosphate of calcium, or calcium superphosphate.

$$\underset{\text{Calcium phosphate.}}{Ca_3(PO_4)_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Calcium acid phosphate.}}{CaH_4(PO_4)_2} + \underset{\text{Calcium sulphate.}}{2CaSO_4}$$

(iii) The solution of the acid phosphate of calcium is filtered from the insoluble calcium sulphate, evaporated to dryness and heated, to convert it into calcium metaphosphate.

$$\underset{\text{Calcium acid phosphate.}}{CaH_4(PO_4)_2} = \underset{\text{Calcium metaphosphate.}}{Ca(PO_3)_2} + \underset{\text{Water.}}{2H_2O}$$

(iv) The calcium metaphosphate is then mixed with charcoal, and the mixture is strongly heated in a retort, when phosphorus distils over and is received under water.

$$\underset{\substack{\text{Calcium}\\\text{metaphospbate.}}}{3Ca(PO_3)_2} + \underset{\text{Charcoal.}}{5C_2} = \underset{\text{Phosphorus.}}{P_4} + \underset{\substack{\text{Calcium}\\\text{phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{10CO}$$

(v) The phosphorus so obtained is coloured from impurities, and is purified either by redistillation or by pressing it when melted under water through leather; the purified phosphorus is then cast into sticks, and is kept under cold water.

Properties.—Phosphorus is a colourless transparent solid when first prepared, somewhat resembling white wax in appearance and consistency, but it gradually becomes brittle and yellowish in colour by keeping. It melts at 44° C. (110° F.), ignites at a slightly higher temperature, boils at 290° C., and out of contact with air may be distilled unchanged; it is luminous in the dark and, if exposed to the air at ordinary temperatures, it gives off, without igniting, white fumes of phosphorus trioxide or phosphorous anhydride (P_2O_3); when burnt, it forms a white powder, the phosphorus pentoxide or phosphoric anhydride (P_2O_5). If phosphorus be held in the hands for a short time, it is very apt to catch fire, and it is therefore kept under water. It is slightly soluble in ether and in the fixed oils, and is very soluble in carbon bisulphide; if its solution in this body be poured on a sheet of paper or on the floor, the carbon bisulphide rapidly evaporates, and the phosphorus is left in so fine a state of division that it ignites spontaneously in a very short time. Phosphorus is very poisonous, and is a common constituent of the *rat-pastes*, sold for destroying rats, which consist of yellow phosphorus, fat, sugar, flour, and prussian blue; most cases of phosphorus poisoning are due to the swallowing of rat-paste.

RED OR AMORPHOUS PHOSPHORUS.

This is prepared by heating ordinary phosphorus in an atmosphere of carbon dioxide or of hydrogen to 240° C. for some time. It is also very slowly formed by the exposure of a stick of phosphorus kept under water to light, when, after some time, a red coating of amorphous phosphorus forms on the stick.

If amorphous phosphorus be heated (while in an atmosphere of carbon dioxide or of hydrogen) to 260° C., it changes back to the ordinary phosphorus, the reconversion being attended with an explosion; great care is therefore required in its preparation that the temperature shall not be raised much above 240° C.

Properties.—This allotropic form of phosphorus is a red-brown amorphous powder; it does not fume in the air, nor is it luminous in the dark; it does not melt at 250° C., and catches fire only at 260° C., when it becomes reconverted into ordinary phosphorus; there is therefore no necessity for keeping it under water; it is insoluble in carbon bisulphide, and all liquids; it is odourless and non-poisonous.

Use of phosphorus in lucifer matches.—Both varieties of phosphorus are used in the manufacture of lucifer matches. Common matches are tipped with a mixture containing ordinary phosphorus, and ignite when rubbed on any rough surface, the friction producing sufficient heat to set the phosphorus on fire. *Safety matches* have no phosphorus on their tips, but are tipped with a mixture of potassium chlorate, red lead, and black sulphide of antimony, the phosphorus being on the side of the box in the form of amorphous phosphorus, stuck on with common glue; when a safety match is rubbed against this, the portion of amorphous phosphorus rubbed by the match is by the heat of friction changed to the ordinary phosphorus, which, adherering to the tip of the match, causes it to catch fire.

The following table contrasts the different properties of the two allotropic forms of phosphorus :—

Ordinary Phosphorus.	**Amorphous Phosphorus.**
Form.—In sticks.	In powder.
Colour.—Colourless, or yellow.	Red-brown.
Odour.—Peculiar.	None.
Luminosity. — Luminous in dark.	Not luminous.
Inflammability. — Ignites at 45° C., and is apt to ignite when handled.	Ignites at 260° C., and may be handled with impunity.
Exposure to air.—White fumes evolved.	No fumes evolved.
Solubility.—Soluble in carbon bisulphide, and slightly so in ether and the fixed oils.	Insoluble in all liquids.
Physiological action. — Very poisonous.	Not poisonous.

COMPOUNDS OF PHOSPHORUS AND OXYGEN.

There are two oxides of phosphorus, viz. phosphorus trioxide or phosphorous anhydride (P_2O_3), and phosphorus pentoxide or phosphoric anhydride (P_2O_5).

PHOSPHORUS TRIOXIDE.

Formula, P_2O_3.

This oxide is obtained in the form of white fumes, either by exposing a stick of phosphorus to the air, or by burning phosphorus in a very limited supply of air.

PHOSPHORUS PENTOXIDE.

Formula, P_2O_5.

This oxide is obtained as a white powder by burning phosphorus in oxygen, or in a free supply of air. At a high temperature it can be volatilised; it has a very powerful attraction for moisture, being one of the most hygroscopic substances known. It is the anhydride of phosphoric acid, and if dissolved in hot water it forms phosphoric acid at once; if dissolved in cold water it forms at first metaphosphoric acid.

The metaphosphoric acid then gradually unites with more water to form ordinary phosphoric acid.

$$\underset{\substack{\text{Phosphoric}\\ \text{anhydride.}}}{P_2O_5} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Metaphosphoric}\\ \text{acid.}}}{2HPO_3}$$

The metaphosphoric acid then gradually unites with more water to form ordinary phosphoric acid.

$$\underset{\substack{\text{Metaphosphoric}\\ \text{acid.}}}{HPO_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Phosphoric.}\\ \text{acid.}}}{H_3PO_4}$$

ACIDS OF PHOSPHORUS.

There are three acids of phosphorus, viz.:

H_3PO_4	Phosphoric acid.
H_3PO_3 or H_2PHO_3	Phosphorous acid.
H_3PO_2 or HPH_2O_2	Hypophosphorous acid.

Of phosphoric acid there are two derivatives, viz. pyrophosphoric acid ($H_4P_2O_7$) and metaphosphoric acid (HPO_3), which consist of phosphoric acid deprived of different amounts of water; these, however are not separate acids of phosphorus, but are derivatives or varieties of phosphoric acid, in connection with which they will be described.

PHOSPHORIC OR ORTHO-PHOSPHORIC ACID.

Formula, H_3PO_4.

This is the ordinary or common phosphoric acid, and is called ortho-phosphoric acid (*ὀρθός*, *straight*) in order to distinguish it from its two derivatives.

Modes of preparation.—(i) By dissolving phosphoric anhydride in hot water.

$$\underset{\text{Phosphoric anhydride.}}{P_2O_5} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphoric acid.}}{2H_3PO_4}$$

(ii) The phosphoric acid used in medicine is obtained by boiling together for some time phosphorus, nitric acid, and water; the phosphorus is oxidised by the nitric acid to phosphoric anhydride, and this with the boiling water forms phosphoric acid.

$$\underset{\text{Phosphorus.}}{3P_4} + \underset{\text{Nitric acid.}}{20HNO_3} + \underset{\text{Water.}}{8H_2O} = \underset{\text{Phosphoric acid.}}{12H_3PO_4} + \underset{\text{Nitrogen dioxide.}}{10N_2O_2}$$

(iii) Phosphoric acid may be obtained by the action of phosphorus pentachloride on water, the hydrochloric acid being driven off by subsequent evaporation.

$$\underset{\text{Phosphorus pentachloride.}}{PCl_5} + \underset{\text{Water.}}{4H_2O} = \underset{\text{Phosphoric acid.}}{H_3PO_4} + \underset{\text{Hydrochloric acid.}}{5HCl}$$

Properties.—Phosphoric acid is one of the strongest inorganic acids, as it even expels sulphuric acid from its compounds. It forms three sodium salts, viz. Na_3PO_4, Na_2HPO_4, and NaH_2PO_4; the last-mentioned salt is acid to test-paper, and to its presence in human urine the acidity of normal urine is due.

Tests.—(i) Phosphoric acid when neutralised with ammonia gives a canary-yellow precipitate of silver phosphate with solution of silver nitrate; this precipitate is readily dissolved, both by solution of ammonia and by nitric acid.

(ii) If to phosphoric acid excess of ammonia be added, and then solutions of ammonium chloride and magnesium sulphate, a white crystalline precipitate will form on shaking the mixture; this precipitate is the magnesium ammonium phosphate ($MgNH_4PO_4$).

PYROPHOSPHORIC ACID.

Formula, $H_4P_2O_7$.

This derivative of phosphoric acid is obtained by heating that acid a little above 200° ; two molecules of phosphoric acid lose one molecule of water, forming pyrophosphoric acid.

$$\underset{\text{Phosphoric acid.}}{2H_3PO_4} - \underset{\text{Water.}}{H_2O} = \underset{\text{Pyrophosphoric acid.}}{H_4P_2O_7}$$

It may also be obtained in the form of its sodium salt by heating ordinary sodium phosphate, thus :

$$\underset{\text{Sodium phosphate.}}{2Na_2HPO_4} = \underset{\text{Sodium pyrophosphate.}}{Na_4P_2O_7} + \underset{\text{Water}}{H_2O}$$

Tests.—(i) When neutralised with ammonia, pyrophosphoric acid gives a white precipitate with silver nitrate, thus distinguishing it from phosphoric acid, which gives a yellow precipitate.

(ii) Pyrophosphoric acid does not coagulate albumen, thus distinguishing it from metaphosphoric acid. (*See* below.)

METAPHOSPHORIC ACID.

Formula, HPO_3.

This last derivative or variety of phosphoric acid is obtained by heating that acid to redness; one molecule of phosphoric acid loses one molecule of water, forming metaphosphoric acid, thus:

$$\underset{\text{Phosphoric acid.}}{H_3PO_4} - \underset{\text{Water.}}{H_2O} = \underset{\text{Metaphosphoric acid.}}{HPO_3}$$

Metaphosphoric acid is obtained as a vitreous mass, and hence is known as *glacial phosphoric acid*; it dissolves in water, and its solution changes slowly at ordinary temperatures, but rapidly with heat, into ordinary phosphoric acid.

Tests.—(i) When neutralised with ammonia, metaphosphoric acid gives a white precipitate with silver nitrate, thus distinguishing it from ordinary phosphoric acid, which gives a yellow precipitate.

(ii) If some unboiled white of egg be shaken with metaphosphoric acid, the albumen is coagulated; this test distinguishes metaphosphoric acid from pyrophosphoric acid, which does not possess the power of coagulating albumen.

PHOSPHOROUS ACID.

Formula, H_3PO_3 or H_2PHO_3.

This acid contains in the molecule one atom of oxygen less than phosphoric acid, but it is not a tribasic acid like phosphoric acid, since only two-thirds of its hydrogen can be displaced by metals; its constitutional formula is therefore H_2PHO_3.

Modes of preparation.—(i) By passing the fumes of phosphorous anhydride, obtained by exposing sticks of phosphorus to the air, into water.

$$\underset{\text{Phosphorous anhydride.}}{P_2O_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphorous acid.}}{2H_3PO_3}$$

(ii) By the action of phosphorus trichloride on water, the hydrochloric acid being driven off by subsequent evaporation.

$$\underset{\text{Phosphorus trichloride.}}{PCl_3} + \underset{\text{Water.}}{3H_2O} = \underset{\text{Phosphorous acid.}}{H_3PO_3} + \underset{\text{Hydrochloric acid.}}{3HCl}$$

Properties.—Phosphorous acid has a very strong attraction for oxygen, and if exposed to the air forms phosphoric acid; on account of its affinity for oxygen it is a powerful reducing agent.

HYPOPHOSPHOROUS ACID.

Formula, H_3PO_2 or HPH_2O_2.

This acid contains one atom of oxygen less in the molecule than phosphorous acid; it is a monobasic acid, and its constitutional formula is therefore

HPH_2O_2. It may be prepared by decomposing its barium salt (barium hypophosphite) with sulphuric acid, and filtering from the insoluble barium sulphate.

$$\underset{\substack{\text{Barium}\\\text{hypophosphite.}}}{Ba(PH_2O_2)_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Hypophosphorous}\\\text{acid.}}}{2HPH_2O_2} + \underset{\substack{\text{Barium}\\\text{sulphate.}}}{BaSO_4}$$

Preparation of the hypophosphites.—The sodium, potassium, calcium, and barium hypophosphites are prepared by boiling respectively the alkaline hydrate of the metal with phosphorus and water; in each case gaseous phosphoretted hydrogen is evolved. The two hypophosphites most employed in medicine are the sodium and calcium salts, the preparation of which is shown in the following equations:

$$\underset{\substack{\text{Sodium}\\\text{hydrate.}}}{3NaHO} + \underset{\text{Phosphorus.}}{P_4} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Sodium}\\\text{hypophosphite.}}}{3NaPH_2O_2} + \underset{\substack{\text{Phosphoretted}\\\text{hydrogen.}}}{PH_3}$$

$$\underset{\substack{\text{Calcium}\\\text{hydrate.}}}{3Ca(HO)_2} + \underset{\text{Phosphorus.}}{2P_4} + \underset{\text{Water.}}{6H_2O} = \underset{\substack{\text{Calcium}\\\text{hypophosphite.}}}{3Ca(PH_2O_2)_2} + \underset{\substack{\text{Phosphoretted}\\\text{hydrogen.}}}{2PH_3}$$

COMPOUNDS OF PHOSPHORUS AND HYDROGEN.

There are two compounds of these elements, a gas (PH_3) and a liquid (P_2H_4).

GASEOUS PHOSPHORETTED HYDROGEN OR PHOSPHINE.

Formula, PH_3.

Modes of preparation.—(i) As described above, this compound is produced when phosphorus is boiled with an alkali and water; the gas that is evolved is not, however, quite pure, since on coming in contact with the air it ignites spontaneously, whereas pure gaseous phosphoretted hydrogen is not spontaneously inflammable; its spontaneous inflammability, when prepared by the action of phosphorus on an alkali, is due to its being contaminated with a small quantity of the vapour of the liquid phosphoretted hydrogen, which is spontaneously inflammable.

(ii) The pure gas is obtained by strongly heating phosphorous acid, which decomposes under the influence of heat into phosphoric acid and phosphoretted hydrogen.

$$\underset{\substack{\text{Phosphorous}\\\text{acid.}}}{4H_3PO_3} = \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{3H_3PO_4} + \underset{\substack{\text{Phosphoretted}\\\text{hydrogen.}}}{PH_3}$$

Properties. — The specific gravity of phosphoretted hydrogen is 17, and it is somewhat heavier than air; it is a colourless gas, with a very unpleasant garlic-like odour, nearly insoluble in water, and igniting when a light is applied to it, forming by its combustion phosphorus pentoxide and water.

Liquid Phosphoretted Hydrogen.

Formula, P_2H_4.

Preparation.—This body is obtained by the action of calcium phosphide on water.

$$\underset{\substack{\text{Calcium}\\\text{phosphide.}}}{Ca_2P_2} + \underset{\text{Water.}}{4H_2O} = \underset{\substack{\text{Phosphoretted}\\\text{hydrogen (liquid).}}}{P_2H_4} + \underset{\substack{\text{Calcium}\\\text{hydrate.}}}{2Ca(HO)_2}$$

Properties.—A liquid possessing a very unpleasant odour, and catching fire spontaneously on exposure to the air; it is very unstable, especially if exposed to sunlight, decomposing into the gaseous phosphoretted hydrogen and free phosphorus.

$$\underset{\substack{\text{Phosphoretted}\\\text{hydrogen (liquid).}}}{6P_2H_4} = \underset{\substack{\text{Phosphoretted}\\\text{hydrogen (gaseous).}}}{8PH_3} + \underset{\text{Phosphorus.}}{P_4}$$

COMPOUNDS OF PHOSPHORUS AND CHLORINE.

There are two chlorides of phosphorus, a trichloride and a pentachloride.

Phosphorus Trichloride or Phosphorous Chloride.

Formula, PCl_3.

A colourless liquid, fuming in moist air, and produced by burning phosphorus in chlorine, keeping the phosphorus in excess. Phosphorus trichloride is decomposed by water, with formation of phosphorous and hydrochloric acids.

$$\underset{\substack{\text{Phosphorus}\\\text{trichloride.}}}{PCl_3} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Phosphorous}\\\text{acid.}}}{H_3PO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3HCl}$$

Chlorine converts phosphorus trichloride into the pentachloride.

Phosphorus Pentachloride or Phosphoric Chloride.

Formula, PCl_5.

A white crystalline body, volatilising and fuming in the air. It is produced (i) by the action of chlorine on the trichloride of phosphorus; (ii) by burning phosphorus in excess of chlorine; (iii) by passing chlorine into a solution of phosphorus in carbon bisulphide. Phosphorus pentachloride is decomposed by water, with formation of phosphoric and hydrochloric acids.

$$\begin{array}{ccccccc} PCl_5 & + & 4H_2O & = & H_3PO_4 & + & 5HCl \\ \text{Phosphorus} & & \text{Water.} & & \text{Phosphoric} & & \text{Hydrochloric} \\ \text{pentachloride.} & & & & \text{acid.} & & \text{acid.} \end{array}$$

If exposed to moist air, phosphorus pentachloride produces white fumes of phosphorus oxychloride.

$$\begin{array}{ccccccc} PCl_5 & + & H_2O & = & POCl_3 & + & 2HCl \\ \text{Phosphorus} & & \text{Water.} & & \text{Phosphorus} & & \text{Hydrochloric} \\ \text{pentachloride.} & & & & \text{oxychloride.} & & \text{acid.} \end{array}$$

COMPOUNDS OF PHOSPHORUS AND BROMINE.

There are two bromides of phosphorus, a tribromide (PBr_3), which is a liquid body, and a pentabromide (PBr_5), which is a solid body. They are both produced by direct combination of the two elements.

COMPOUNDS OF PHOSPHORUS AND IODINE.

There are two iodides of phosphorus, a di-iodide (P_2I_4), and a tri-iodide (PI_3). They are both solid bodies, and are produced by direct combination of the requisite quantities of the two elements. No penta-iodide of phosphorus is known.

CHAPTER XI.

SULPHUR. OXIDES, ACIDS, AND COMPOUNDS OF SULPHUR.

Sulphur—Allotropic forms of Sulphur—Properties of Sulphur—Sulphur Dioxide or Sulphurous Anhydride—Sulphur Trioxide or Sulphuric Anhydride—Sulphurous Acid—Sulphuric Acid—Nordhausen or Fuming Sulphuric Acid—Sulphuretted Hydrogen—Hydrogen Persulphide—Thiosulphuric Acid—Compounds of Sulphur and Chlorine.

SULPHUR.

Symbol, S; *formula*, S_2; *hexad*; *atomic weight*, 32; *molecular weight*, 64.

Sulphur, commonly known as *brimstone*, occurs in nature in considerable quantities, in both the free and combined states. In the free state it is found in the volcanic districts of Sicily, Italy, and Iceland, in the form of yellow crystals, or in the amorphous state embedded in blue clay. In the combined state it exists as the various native metallic sulphides (*e.g.* *iron pyrites* FeS_2, *blende* ZnS, *black antimony* Sb_2S_3, *copper sulphide* CuS, *galena* PbS, *cinnabar* HgS), and as native metallic sulphates (*e.g.* *gypsum* $CaSO_4, 2H_2O$, *Epsom salts* $MgSO_4, 7H_2O$, *heavy spar* $BaSO_4$). Sulphur is obtained from the clay, in which it occurs in volcanic districts, by a process of sublimation; on heating the mixture of sulphur and clay, the sulphur is converted into vapour, which is conducted into a large and cool brick chamber, in which it becomes cooled, and condenses to a yellow powder, *flowers of sulphur*.

There are three allotropic forms of sulphur, corresponding to the three allotropic forms of carbon, viz.

two crystalline forms (the octahedral and the prismatic) and an amorphous form.

The allotropic forms of sulphur. — (i) *Octahedral variety.*—This is obtained by dissolving powdered stick sulphur in carbon bisulphide, and allowing the solution to evaporate spontaneously, when octahedral crystals of sulphur are deposited.

(ii) *Prismatic variety.* — This may be obtained by heating sulphur in a crucible until it just melts, allowing it to cool until a crust forms on the surface, and then perforating the crust with an iron rod and pouring out the molten sulphur from underneath, when long prismatic crystals of sulphur will be found adhering to the sides of the crucible. If sulphur be just melted, and then poured into a mould to cool, it sets to a solid mass of small prismatic crystals, constituting the *stick* or *roll sulphur* of commerce ; also, if the vapour of sulphur be suddenly cooled, it condenses to a yellow powder consisting of minute prismatic crystals, constituting the *flowers of sulphur* of commerce.

(iii) *Amorphous variety.*—This may be produced in two forms, plastic sulphur and precipitated sulphur. *Plastic sulphur* is prepared by melting sulphur at a temperature a little above 200° C., and then pouring it into cold water, when it forms a plastic mass which can be drawn out like soft caoutchouc ; it does not, however, retain its plasticity for long, as it gradually becomes hard and brittle, owing to its conversion into the crystalline condition. *Precipitated sulphur* is obtained by boiling flowers of sulphur with calcium hydrate (slaked lime) and water, when the sulphur passes into solution as calcium pentasulphide (CaS_5) and calcium thiosulphate (CaS_2O_3), from which solution the sulphur may be precipitated in the amorphous form by hydrochloric acid, which unites with the calcium and so sets free the sulphur.

$$\underset{\text{Calcium hydrate}}{3Ca(HO)_2} + \underset{\text{Sulphur}}{6S_2} = \underset{\text{Calcium pentasulphide.}}{2CaS_5} + \underset{\text{Calcium thiosulphate}}{CaS_2O_3} + \underset{\text{Water.}}{3H_2O}$$

$$\underset{\text{Calcium pentasulphide.}}{2CaS_5} + \underset{\text{Calcium thiosulphate.}}{CaS_2O_3} + \underset{\text{Hydrochloric acid.}}{6HCl} = \underset{\text{Calcium chloride.}}{3CaCl_2} + \underset{\text{Sulphur.}}{6S_2} + \underset{\text{Water.}}{3H_2O}$$

This is the process for preparing the *precipitated sulphur* of the British Pharmacopœia; if sulphuric acid is used instead of hydrochloric acid, calcium sulphate will be produced instead of calcium chloride; but since the calcium sulphate is insoluble, it will be thrown down with the precipitated sulphur. This mixture of calcium sulphate and sulphur used to be known as *milk of sulphur*, formerly an official preparation in the Pharmacopœia, but its use has been discontinued on account of the large quantity of insoluble sulphate present in it.

Properties.—Sulphur is a solid, possessing a pale yellow colour, odourless, tasteless, and insoluble in water; it burns with a pale blue flame, producing sulphur dioxide or sulphurous anhydride, a gas having a very pungent odour. At 115° C. sulphur melts to a clear mobile liquid, which, if allowed to cool, resolidifies to the ordinary yellow sulphur (the prismatic variety); if more strongly heated it undergoes a peculiar change, for, instead of becoming more mobile, it becomes more viscid, and darker in colour, so that at 200° C. it is a dark brown liquid, and so viscid that the vessel containing it may be inverted without the sulphur flowing out; if heated above 200° C., and up to 400° C., it gradually becomes mobile again, and boils at 448° C. Sulphur unites directly with oxygen, chlorine, phosphorus, carbon, and most of the metals. Sulphur is soluble in carbon disulphide.

Test.—Its yellow colour, combined with its burning with a pale blue flame, and producing the pungent smelling gas sulphur dioxide, renders the recognition of sulphur very easy.

COMPOUNDS OF SULPHUR AND OXYGEN.

There are two oxides of sulphur, viz. a gaseous oxide, sulphur dioxide or sulphurous anhydride (SO_2), and a solid oxide, sulphur trioxide or sulphuric anhydride (SO_3).

SULPHUR DIOXIDE OR SULPHUROUS ANHYDRIDE.

This compound is contained in the gases of volcanoes.

Modes of preparation. — (i) By the combustion of sulphur in air or oxygen.

$$\underset{\text{Sulphur.}}{S_2} + \underset{\text{Oxygen.}}{2O_2} = \underset{\text{Sulphur dioxide.}}{2SO_2}$$

(ii) By roasting iron pyrites in air.

$$\underset{\text{Iron pyrites.}}{4FeS_2} + \underset{\text{Oxygen.}}{11O_2} = \underset{\text{Ferric oxide.}}{2Fe_2O_3} + \underset{\text{Sulphur dioxide.}}{8SO_2}$$

(iii) For experimental purposes sulphur dioxide is most readily prepared by the action of strong sulphuric acid with heat on the metal copper.

$$\underset{\text{Copper.}}{Cu_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{4H_2SO_4} = \underset{\substack{\text{Copper}\\\text{sulphate.}}}{2CuSO_4} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2SO_2} + \underset{\text{Water.}}{4H_2O}$$

(iv) Sulphur dioxide can be cheaply prepared by the action of strong sulphuric acid with heat on charcoal; it is not, however, pure, as it is mixed with carbon dioxide, which is produced at the same time.

$$\underset{\substack{\text{Sulphuric}\\\text{acid.}}}{4H_2SO_4} + \underset{\text{Charcoal.}}{C_2} = \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{4SO_2} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{2CO_2} + \underset{\text{Water.}}{4H_2O}$$

Properties.—The specific gravity of sulphur dioxide is 32, and it is considerably heavier than air; it is a colourless gas, with a very pungent irritating odour, and an acid taste; it is neither combustible, nor is it a supporter of combustion; it is very poisonous, and is freely soluble in water, forming with the water sulphurous acid. If cooled by means of a freezing mixture it condenses to a liquid; the apparatus for liquefying it is shown in Fig. 17. A is a flask in which the sulphur dioxide is prepared by heating strong sulphuric acid with copper. The gas is then passed through a wash-bottle B, and then through a spiral tube surrounded by a freezing mixture C, the liquefied gas being then received in a flask D, which is also surrounded by a freezing mixture. Sulphur dioxide is a bleaching agent, and also a powerful antiseptic, on account of its germicidal properties; as an antiseptic it is employed in the thorough disinfection of rooms in which patients suffering from infectious fevers have been kept. To produce it, sulphur is burnt in an iron vessel with a little methylated spirit (to facilitate the combustion of the sulphur) in the room, the windows and the doors being closed; 1 to 1½ lb. of sulphur should be used to every 1,000 cubic feet of air-space in the room. If sulphur dioxide and sulphuretted hydrogen gases be mixed, a cloud of free sulphur is formed.

$$\underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Sulphuretted hydrogen.}}{4H_2S} = \underset{\text{Sulphur.}}{3S_2} + \underset{\text{Water.}}{4H_2O}$$

It is possible that much of the sulphur found free

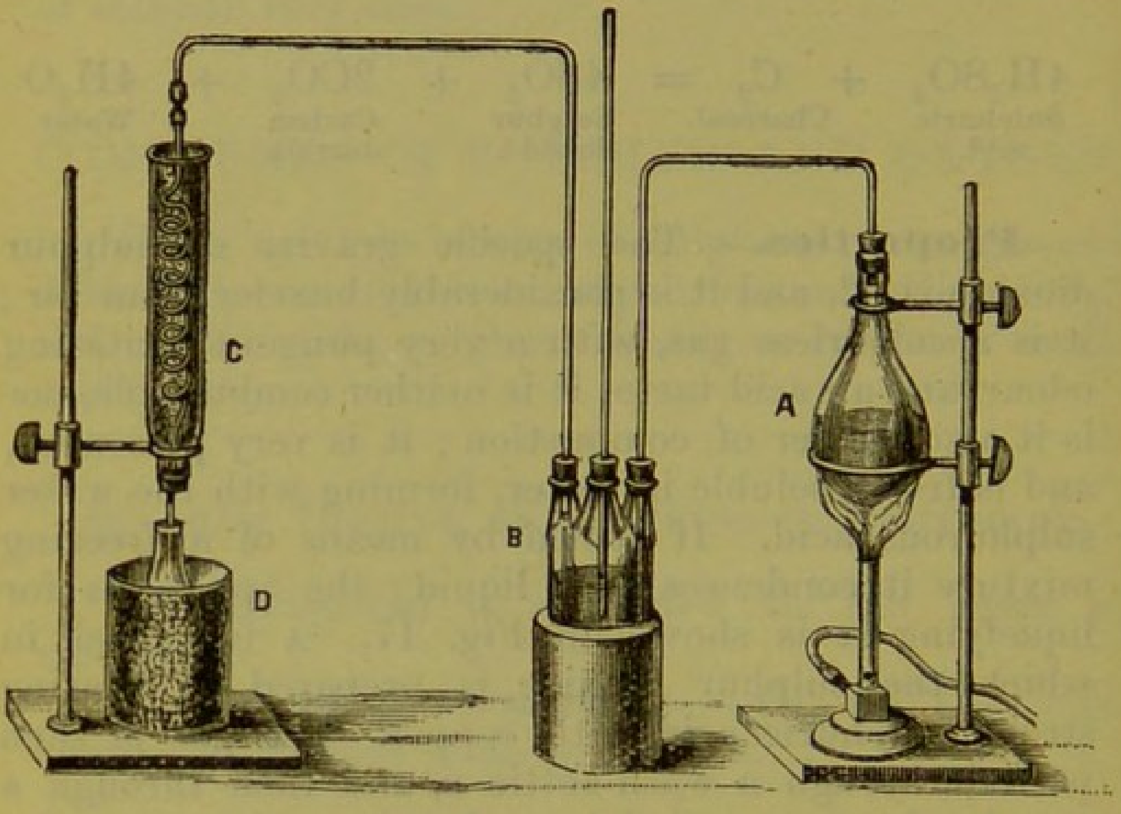


Fig. 17.—Preparation and Liquefaction of Sulphur Dioxide.

in nature in volcanic districts is produced in this manner.

Test.—The peculiar pungent and irritating odour would be sufficient to distinguish this gas.

SULPHUR TRIOXIDE OR SULPHURIC ANHYDRIDE.

Formula, SO_3.

Modes of preparation.—(i) By passing a mixture of sulphur dioxide and oxygen over heated and finely-divided platinum, when the two gases unite to form the higher oxide of sulphur.

$$\underset{\substack{\text{Sulphur}\\\text{dioxide}}}{2SO_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Sulphur}\\\text{trioxide.}}}{2SO_3}$$

(ii) By gently heating Nordhausen or fuming sulphuric acid, when sulphuric anhydride volatilises over and condenses.

$$\underset{\substack{\text{Nordhausen}\\\text{sulphuric acid.}}}{H_2SO_4, SO_3} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} + \underset{\substack{\text{Sulphur}\\\text{trioxide.}}}{SO_3}$$

(iii) By distilling sulphuric acid with phosphoric anhydride.

$$\underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} + \underset{\substack{\text{Phosphoric}\\\text{anhydride.}}}{P_2O_5} = \underset{\substack{\text{Phosphoric}\\\text{acid.}}}{2H_3PO_4} + \underset{\substack{\text{Sulphuric}\\\text{anhydride.}}}{3SO_3}$$

Properties.—Sulphur trioxide is a solid body, occurring in white silky needles. It dissolves with avidity in water, uniting with it to form sulphuric acid.

$$\underset{\substack{\text{Sulphuric}\\\text{anhydride.}}}{SO_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4}$$

SULPHUROUS ACID.

Formula, H_2SO_3.

Mode of preparation.—By passing sulphurous anhydride into water.

$$\underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphurous}\\\text{acid.}}}{H_2SO_3}$$

Properties.—Sulphurous acid possesses the characteristic pungent odour of sulphurous anhydride. If exposed to the air oxygen is absorbed, and the sulphurous acid is converted into sulphuric acid ($2H_2SO_3 + O_2 = 2H_2SO_4$). On account of this readiness to combine with oxygen, sulphurous acid is a powerful reducing agent. Nascent hydrogen can, however, reduce sulphurous acid, depriving it of all its oxygen, and setting free sulphuretted hydrogen ($H_2SO_3 + 3H_2 = H_2S + 3H_2O$). If sulphurous acid be neutralised with an alkaline hydrate or carbonate, a sulphite is produced; sulphites are more easily prepared by the union of sulphurous anhydride with the strong bases; thus, if sulphurous anhydride be passed into solutions of caustic potash or caustic soda, sulphites of the metals are produced, thus:

$$\underset{\substack{\text{Caustic}\\\text{soda.}}}{2NaHO} + \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{SO_2} = \underset{\substack{\text{Sodium}\\\text{sulphite.}}}{Na_2SO_3} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\substack{\text{Caustic}\\\text{potash.}}}{2KHO} + \underset{\substack{\text{Sulphurous}\\\text{anhydride.}}}{SO_2} = \underset{\substack{\text{Potassium}\\\text{sulphite.}}}{K_2SO_3} + \underset{\text{Water.}}{H_2O}$$

Tests.—(i) If to a solution of a sulphite some hydrochloric acid be added, sulphurous acid is set free, and this can be readily detected on warming by the evolution of the pungent-smelling sulphur dioxide.

(ii) If to sulphurous acid or a solution of a sulphite some zinc and hydrochloric acid are added, the nascent hydrogen will reduce the sulphurous acid to sulphuretted hydrogen (*see* above), which can readily be detected by its odour, and by its blackening a piece of filter-paper moistened with a solution of lead acetate.

SULPHURIC ACID.

Formula, H_2SO_4.

Modes of preparation.—Sulphuric acid is obtained by the oxidation of sulphurous acid. This may be effected, though very slowly, by exposing sulphurous acid to the air. Sulphuric acid is now manufactured on an enormous scale, the process consisting in oxidising sulphurous acid to sulphuric acid in large leaden chambers, the oxidation being effected in the first place by means of nitric acid, and afterwards by means of nitrogen tetroxide produced from the nitric acid and oxygen of the air. The leaden chambers, which are supported by means of wooden frameworks, are arranged in a series communicating

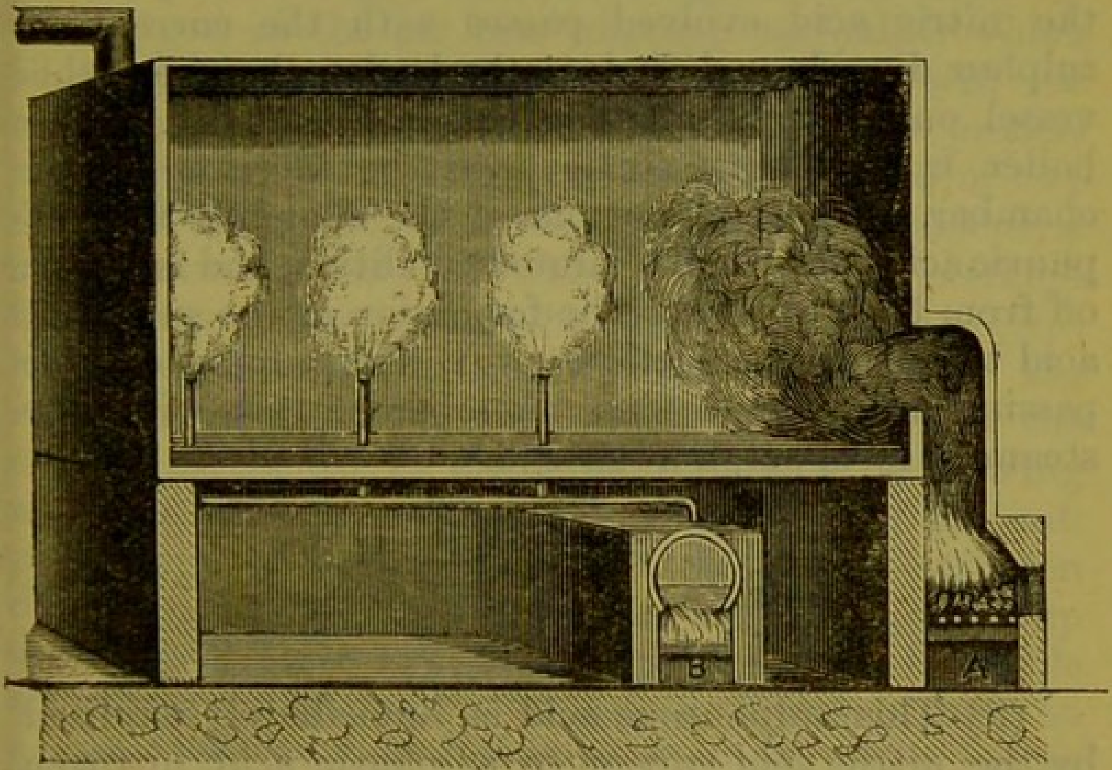


Fig. 18.—Sulphuric Acid Leaden Chamber.

with one another. Into the first one the flue of a furnace passes; the last one is connected with a tower. Fig. 18 represents the first of the leaden chambers. In the furnace A is burnt sulphur or iron pyrites (FeS_2), the resulting sulphur dioxide passing along with a current of air into the leaden chamber. At the commencement of the process, a vessel containing some sodium nitrate and sulphuric acid is placed within the furnace on one side, so that the vapour of the nitric acid evolved passes with the current of sulphur dioxide and air into the leaden chamber; this vessel only requires re-charging occasionally. The boiler B discharges steam into the interior of the chamber, and at the bottom of the chamber the sulphuric acid collects in a diluted condition, and is drawn off from time to time. The formation of the sulphuric acid takes place as follows:—(i) The sulphur dioxide passing into the leaden chamber unites with the steam to form sulphurous acid.

$$\underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{SO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sulphurous}\\\text{acid.}}}{H_2SO_3}$$

(ii) This sulphurous acid is immediately oxidised by the nitric acid vapour to sulphuric acid, nitrogen dioxide being evolved.

$$\underset{\substack{\text{Sulphurous}\\\text{acid.}}}{3H_2SO_3} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{H_2O}$$

(iii) The nitrogen dioxide then unites with the oxygen of the air that has passed into the chamber to form nitrogen tetroxide.

$$\underset{\substack{\text{Nitrogen}\\\text{dioxide}}}{N_2O_2} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Nitrogen}\\\text{tetroxide.}}}{N_2O_4}$$

(iv) This nitrogen tetroxide then oxidises more sulphurous acid to sulphuric acid, nitrogen dioxide being again formed.

$$\underset{\substack{\text{Sulphurous}\\\text{acid.}}}{2H_2SO_3} + \underset{\substack{\text{Nitrogen}\\\text{tetroxide.}}}{N_2O_4} = \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2}$$

(v) The nitrogen dioxide is again converted by the oxygen of the air into nitrogen tetroxide, which then oxidises more sulphurous acid. It will be noticed, therefore, that in this lead-chamber process the oxidation of the sulphurous acid is effected in two different ways: (*a*) by means of nitric acid vapour, a small quantity only of which has to be generated from time to time to start the work of oxidation; (*b*) by means of the nitrogen dioxide, produced by the reduction of the nitric acid, acting as a carrier of the oxygen of the air to the sulphurous acid, by forming nitrogen tetroxide, which, oxidising some of the sulphurous acid to sulphuric acid, reproduces nitrogen dioxide, which then carries on its work of picking up the oxygen of the air. This nitrogen dioxide is unable to continue this work for an indefinite period, on account of its being gradually swept away in the current that is passing through the leaden chambers; for since the air that passes into the chambers contains four-fifths of its bulk of nitrogen, this nitrogen must pass away to make room for the fresh gases and air streaming in. As with this escaping nitrogen a considerable quantity of nitrogen tetroxide must pass away, and as this latter gas would very seriously vitiate the atmosphere in the neighbourhood of the sulphuric acid works if allowed to pass into it, some provision has to be made for the absorption of this gas. To effect this, the gases as they escape from the last of the series of leaden chambers are made to pass up a tall tower, known as a Gay-Lussac's tower, in which strong sulphuric acid is kept slowly trickling down over pieces of coke; the nitrogen tetroxide is absorbed by the strong sulphuric acid, from which it can be liberated by dilution with water, and so can be conducted into the first of the leaden chambers, to start its work of oxidation over again. The sulphuric acid that collects at the bottom of the leaden chambers, and is drawn therefrom, is in a diluted condition, and is concentrated by evaporation at first in leaden vessels, and afterwards in glass or platinum vessels.

Properties.—Sulphuric acid, which is commonly known as *oil of vitriol*, is one of the strongest acids; the commercial acid is of specific gravity 1·843, and contains 98 per cent. of sulphuric acid, the remaining 2 per cent. being principally water; it is generally of a light brown colour, from the presence of traces of organic substances (produced mainly from dust). If strong sulphuric acid is mixed with water, the mixture becomes extremely hot, on account of the union of the acid with the water to form a molecular compound (H_2SO_4,H_2O). On account of its powerful attraction for water, strong sulphuric acid is employed for the purpose of drying those gases on which it has no chemical action. If sulphuric acid be allowed to drop on hot bricks, or pieces of heated pumice-stone, it is decomposed into water, sulphur dioxide, and oxygen ($2H_2SO_4 = 2H_2O + 2SO_2 + O_2$).

Commercial sulphuric acid is very apt to contain small quantities of lead, arsenic, and nitrogen tetroxide as impurities. The lead exists as the sulphate, and is derived from the leaden evaporating vessels in which the acid is concentrated. Although lead sulphate is soluble in strong sulphuric acid, it is not soluble in the dilute acid, and therefore comes down as a white precipitate on diluting the strong acid with water

Arsenic is derived from iron pyrites being used as the source of the sulphur dioxide ; arsenic may be detected in the sulphuric acid by diluting it with water, and passing a stream of sulphuretted hydrogen gas through it, when a yellow precipitate of sulphide of arsenic is produced, if that impurity is present, or it may be detected by Marsh's test (*see* page 319) ; sulphuric acid can be manufactured free from arsenic by employing Sicilian sulphur in the place of iron pyrites. Nitrogen tetroxide is derived from the atmosphere of the leaden chambers ; it can be detected by shaking the strong sulphuric acid with powdered ferrous sulphate, which will turn of a dark colour if any nitrogen tetroxide be present. Sulphuric acid can be freed from this impurity by boiling with a few crystals of ammonium sulphate, when ammonium nitrite is formed, and immediately decomposed by the heat into nitrogen and water ($NH_4NO_2 = N_2 + 2H_2O$).

Test.—Sulphuric acid, or a soluble sulphate, gives with solution of barium nitrate or chloride a white precipitate, which is insoluble in strong hydrochloric acid, or, in fact, in any acid.

NORDHAUSEN OR FUMING SULPHURIC ACID.

This is a commercial form of strong sulphuric acid containing sulphuric anhydride in solution, the fumes which it gives off on exposure to the air being caused by the liberation of this sulphuric anhydride. Its composition is sometimes indicated by the formula H_2SO_4, SO_3, but this is not correct, as it is not a definite chemical compound. It is obtained by first drying crystallised ferrous sulphate ($FeSO_4$, $7H_2O$), which loses six-sevenths of its water, having then the formula $FeSO_4$, H_2O, and then strongly heating this dried ferrous sulphate in clay or earthenware retorts, when the fuming sulphuric acid distils over, ferric oxide (Fe_2O_3) being left in the retort.

SULPHURETTED HYDROGEN.

Formula, H_2S.

This gas is analogous to water in its composition: the one being an oxide of hydrogen (H_2O), the other a sulphide of hydrogen (H_2S).

Modes of preparation.—(i) This gas is generally prepared for laboratory purposes by the action of sulphuric acid on sulphide of iron.

$$\underset{\substack{\text{Ferrous}\\\text{sulphide.}}}{FeS} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{FeSO_4} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{H_2S}$$

Small lumps of sulphide of iron are placed in a gas-generating bottle provided with a long funnel (Fig. 19), and are covered with water; strong sulphuric acid is then poured down the funnel till a brisk evolution of the gas occurs; it is then allowed to pass through some water in a wash-bottle, and thence into whatever solution it is required to be passed into.

(ii) It may also be prepared by the action of hydrochloric acid on the native sulphide of antimony.

$$\underset{\substack{\text{Antimony}\\\text{sulphide.}}}{Sb_2S_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} = \underset{\substack{\text{Antimony}\\\text{chloride.}}}{2SbCl_3} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3H_2S}$$

(iii) Pure sulphuretted hydrogen, such as should be employed in toxicological inquiries, may be obtained by the action of hydrochloric acid on calcium sulphide.

CaS	+	$2HCl$	=	$CaCl_2$	+	H_2S
Calcium sulphide		Hydrochloric acid		Calcium chloride.		Sulphuretted hydrogen.

The calcium sulphide is employed in the form of small cubes, which are prepared by mixing powdered calcium sulphide with sufficient anhydrous calcium sulphate and water to form a thick paste, which is spread out on a plate, cut into cubes, and dried.

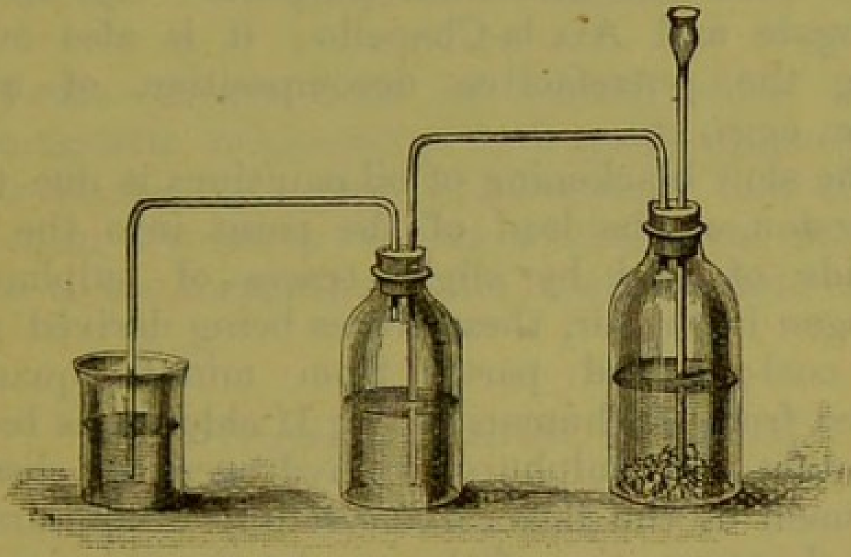


Fig. 19.—Preparation of Sulphuretted Hydrogen.

(iv) Sulphuretted hydrogen can be obtained in small quantities by direct union of its elements, as when hydrogen is passed over heated sulphur.

Properties.—The specific gravity of sulphuretted hydrogen is 17, and it is somewhat heavier than air; it is a combustible gas, burning with a pale blue flame, and producing sulphur dioxide and water; it is not a supporter of combustion. Sulphuretted hydrogen is a colourless gas, but possesses a peculiar and very disagreeable odour, similar to that of rotten eggs, and an unpleasant taste. Water at ordinary temperatures dissolves about three times its volume of the gas; but if the solution is kept in a bottle half full of air, the sulphuretted hydrogen is gradually decomposed by the oxygen of the air, sulphur becoming deposited ($2H_2S + O_2 = 2H_2O + S_2$). Sulphuretted hydrogen is a poisonous gas; it can be liquefied by pressure. In a high state of dilution, sulphuretted hydrogen is contained in some mineral waters used for medicinal purposes: *e.g.* those of Harrogate and Aix-la-Chapelle; it is also evolved during the putrefactive decomposition of animal matter, eggs, etc.

The slow blackening of oil-paintings is due to the conversion of the lead of the paint into the black sulphide of lead by slight traces of sulphuretted hydrogen in the air, these traces being derived partly from coal-gas and partly from minute quantities evolved from the human body. If chlorine is brought in contact with sulphuretted hydrogen the disagreeable smell of the latter immediately disappears, due to the decomposition of the gas by the chlorine, with liberation of sulphur ($2H_2S + 2Cl_2 = 4HCl + S_2$). As most of the metallic sulphides are insoluble in water, therefore sulphuretted hydrogen precipitates many of the metals from solutions of their salts, and hence is of great use in the separation of many of the metals for analytical purposes. The following equations show the action of sulphuretted hydrogen on some of the metallic salts:

$HgCl_2$	$+$	H_2S	$=$	HgS	$+$	$2HCl$
Mercuric chloride.		Sulphuretted hydrogen.		Mercuric sulphide.		Hydrochloric acid.

$CuSO_4$	$+$	H_2S	$=$	CuS	$+$	H_2SO_4
Copper sulphate.		Sulphuretted hydrogen.		Copper sulphide.		Sulphuric acid.

$$\underset{\substack{\text{Lead}\\\text{acetate.}}}{Pb(C_2H_3O_2)_2} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{H_2S} = \underset{\substack{\text{Lead}\\\text{sulphide.}}}{PbS} + \underset{\substack{\text{Acetic}\\\text{acid.}}}{2HC_2H_3O_2}$$

$$\underset{\substack{\text{Bismuth}\\\text{nitrate.}}}{2Bi(NO_3)_3} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3H_2S} = \underset{\substack{\text{Bismuth}\\\text{sulphide.}}}{Bi_2S_3} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{6HNO_3}$$

$$\underset{\substack{\text{Arsenious}\\\text{acid.}}}{2H_3AsO_3} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3H_2S} = \underset{\substack{\text{Arsenious}\\\text{sulphide.}}}{As_2S_3} + \underset{\text{Water.}}{6H_2O}$$

Test.—Apart from its odour, which is very characteristic, sulphuretted hydrogen may be detected by its blackening a piece of filter-paper that has been dipped in a solution of lead acetate; the darkening is due to the formation of the black sulphide of lead.

HYDROGEN PERSULPHIDE.

Formula, H_2S_2.

This body is analogous to hydrogen peroxide (H_2O_2) in its composition. It may be obtained by pouring a solution of potassium pentasulphide (K_2S_5) into strong hydrochloric acid, when, in addition to the liberation of sulphuretted hydrogen and sulphur, a heavy oily liquid sinks to the bottom, which is the persulphide of hydrogen in a somewhat impure condition. It is a very unstable body, readily decomposing into sulphuretted hydrogen and sulphur.

THIOSULPHURIC ACID.

Formula, $H_2S_2O_3$.

This acid is not known in the free state, but only in its salts, of which the only important one is sodium thiosulphate ($Na_2S_2O_3$), commercially known as *hyposulphite of soda.*

Preparation of sodium thiosulphate.—(i) By warming together for some time a solution of sodium sulphite and powdered sulphur.

$$\underset{\substack{\text{Sodium}\\\text{sulphite.}}}{2Na_2SO_3} + \underset{\text{Sulphur.}}{S_2} = \underset{\substack{\text{Sodium}\\\text{thiosulphate.}}}{2Na_2S_2O_3}$$

(ii) If crude calcium sulphide (the alkali-waste obtained in the manufacture of sodium carbonate) is exposed to the air, it is partly converted into calcium thiosulphate (CaS_2O_3), which by treatment with sodium carbonate yields the soluble sodium thiosulphate and the insoluble calcium carbonate.

$$\underset{\substack{\text{Calcium}\\\text{thiosulphate.}}}{CaS_2O_3} + \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} = \underset{\substack{\text{Sodium}\\\text{thiosulphate.}}}{Na_2S_2O_3} + \underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3}$$

Properties.—Sodium thiosulphate is so named because it is regarded as sodium sulphate (Na_2SO_4) from which one atom of oxygen is withdrawn and an atom of sulphur (*θεῖον*, sulphur) substituted for it. It is largely employed (under the commercial name of hyposulphite of soda) in photography, on account of the property that it possesses of dissolving the bromide, iodide, and chloride of silver, provided these compounds have not been changed by the action of light; a sensitive photographic plate is covered with a thin layer of one or more of these silver compounds, which becomes decomposed on those parts only on which the light has fallen; to make the picture permanent, the silver salt that remains unchanged is removed by immersing the plate in a solution of hyposulphite of soda.

Test.—If to a solution of sodium thiosulphate some hydrochloric acid be added, the smell of sulphur dioxide is evolved, and sulphur is precipitated after the solution has stood for a short time. This reaction is due to the liberation of thiosulphuric acid, which, being extremely unstable, is quickly decomposed into sulphurous acid and sulphur, the former evolving sulphur dioxide, which is known by its odour.

$$\underset{\substack{\text{Sodium}\\\text{thiosulphate.}}}{Na_2S_2O_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Thiosulphuric}\\\text{acid.}}}{H_2S_2O_3} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl}$$

$$\underset{\substack{\text{Thiosulphuric}\\\text{acid.}}}{2H_2S_2O_3} = \underset{\substack{\text{Sulphurous}\\\text{aci}}}{2H_2SO_3} + \underset{\text{Sulphur.}}{S_2}$$

COMPOUNDS OF SULPHUR AND CHLORINE.

The three following chlorides of sulphur exist they are all prepared by direct union of sulphur and chlorine :

S_2Cl_2	Disulphur dichloride.
SCl_2	Sulphur dichloride.
SCl_4	Sulphur tetrachloride.

Part III.

THE METALLIC ELEMENTS AND THEIR PRINCIPAL COMPOUNDS.

CHAPTER I.

CLASSIFICATION OF THE METALS—POTASSIUM.

Classification of the Metals—Potassium—Natural Compounds of Potassium—Preparation and Properties of the Metal Potassium—Preparation of the Potassium Salts—Tests for Potassium.

Classification of the metals.—The metals are most conveniently arranged in groups according to the properties of their oxides and sulphides. The following six groups include all the important metals. A description of the rarer metals, the salts of which are not employed in medicine nor for technical purposes, will be unnecessary in this book :

Group I. *Metals of the alkalies.*—Potassium, sodium, lithium. These metals form oxides, which with water produce soluble hydrates, possessing a powerfully alkaline reaction.

Group II. *Metals of the alkaline earths.*—Calcium, barium, magnesium, strontium. These metals yield oxides, which are slightly soluble in water, producing hydrates of a faintly alkaline reaction.

Group III. *Metals of the earths.*—Aluminium and some of the rarer metals. These metals yield oxides completely insoluble in water.

Group IV.—Iron, manganese, chromium, zinc, cobalt, nickel. These metals yield sulphides insoluble in water, but mostly soluble in dilute acids; they are therefore precipitated by ammonium sulphide, but not by sulphuretted hydrogen passed through acid solutions of their salts.

Group V.—Copper, mercury, lead, arsenicum, antimony, bismuth, tin. These metals yield sulphides insoluble in water and in dilute acids; they are therefore precipitated when sulphuretted hydrogen is passed through acid solutions of their salts.

Group VI. *Noble metals.*—Gold, platinum, silver. These metals do not oxidise when exposed to the air at any temperature.

In the description of the metals which will now be given, the following order of treatment will be adopted with each metal:—(i) A description of the compounds of the metal occurring in nature. (ii) The preparation of the metal from one or more of its natural compounds, together with the physical and chemical properties of the metal. (iii) The preparation of all the important salts of the metal, together with their principal properties. (iv) The analytical tests for the metal.

POTASSIUM.

Symbol, K; *formula*, K_2; *monad; atomic weight*, 39; *molecular weight*, 78.

Natural compounds of potassium.—(i) *Potash felspar* (a double silicate of aluminium and potassium) in granite rocks is the original source of the potassium salts. Plants possess the property of separating and assimilating the potash from rocks and soils, storing it up in their tissues in the form of potassium salts of organic acids (tartrate, citrate, malate, etc.). On burning the wood of plants these organic salts are converted by the heat into the carbonate of potassium, which in a somewhat impure condition constitutes *wood-ash* or *pearl-ash*, from which the carbonate of potassium is extracted by water. (ii) *Saltpetre* or *nitre* is native nitrate of potassium (*see* page 122). (iii) *Carnallite* is a double chloride of potassium and magnesium found in Stassfurt, in Germany. (iv) *Argol* is the crude acid tartrate of potassium, or cream of tartar ($KHC_4H_4O_6$), found as a deposit in wine casks. Acid tartrate of potassium is originally present in solution in the juice of the grape; and whilst this undergoes fermentation in the preparation of wines, the grape sugar becomes converted into alcohol, the latter throwing the acid tartrate of potassium out of solution (it being insoluble in alcohol). The acid tartrate, carrying down with it some of the colouring matter of the juice, constitutes the deposit known as *argol*.

Preparation of the metal potassium.—This metal is obtained by distilling potassium carbonate with charcoal.

$$\underset{\substack{\text{Potassium} \\ \text{carbonate.}}}{K_2CO_3} + \underset{\text{Charcoal.}}{C_2} = \underset{\text{Potassium.}}{K_2} + \underset{\substack{\text{Carbon} \\ \text{monoxide.}}}{3CO}$$

Properties of the metal.—Potassium is a metal of a silver-white colour and possesses a bright lustre when a piece of it is freshly cut, the cut surface rapidly tarnishing, however, on account of the action on it of the oxygen of the air, which forms a film of potassium oxide; on account of this strong affinity of potassium for oxygen, the metal has to be kept immersed in mineral naphtha, a liquid free from oxygen, otherwise, if potassium be kept exposed to the air, it is soon completely converted into potassium oxide (K_2O). Potassium is a metal that is lighter than water, and therefore floats when thrown on the surface of water; at the same time it energetically decomposes the water, forming potassium hydrate, and liberating one-half of the hydrogen. On account of the violent chemical action, sufficient heat is produced to ignite this escaping hydrogen, which, from the presence of a little potassium in it, burns with a lavender-coloured flame.

$$\begin{array}{ccccccc} K_2 & + & 2H_2O & = & 2KHO & + & H_2 \\ \text{Potassium.} & & \text{Water.} & & \text{Potassium} & & \text{Hydrogen.} \\ & & & & \text{hydrate.} & & \end{array}$$

On sulphuric and hydrochloric acids potassium acts with explosive violence, forming respectively potassium sulphate and chloride, and liberating the hydrogen.

Potassium Salts.

Potassium hydrate or **caustic potash** (KHO).—Prepared by boiling together potassium carbonate, slaked lime, and water, and filtering from the insoluble calcium carbonate produced.

$$\begin{array}{ccccccc} K_2CO_3 & + & Ca(HO)_2 & = & 2KHO & + & CaCO_3 \\ \text{Potassium} & & \text{Slaked} & & \text{Potassium} & & \text{Calcium} \\ \text{carbonate.} & & \text{lime.} & & \text{hydrate.} & & \text{carbonate.} \end{array}$$

Potassium bicarbonate ($KHCO_3$). — Prepared by passing a stream of carbon dioxide through a cold saturated solution of potassium carbonate.

$$\begin{array}{ccccccc} K_2CO_3 & + & CO_2 & + & H_2O & = & 2KHCO_3 \\ \text{Potassium} & & \text{Carbon} & & \text{Water.} & & \text{Potassium} \\ \text{carbonate.} & & \text{dioxide.} & & & & \text{bicarbonate.} \end{array}$$

The potassium bicarbonate being less soluble than the carbonate, crystallises out as it is formed. If boiling water be added to potassium bicarbonate, it is resolved into the carbonate, with evolution of carbon dioxide.

$$\underset{\substack{\text{Potassium}\\\text{bicarbonate.}}}{2KHCO_3} = \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

It should not, on this account, be dissolved in hot water.

Potassium acetate ($KC_2H_3O_2$).—Prepared by neutralising acetic acid with potassium carbonate.

$$\underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\substack{\text{Potassium}\\\text{acetate.}}}{2KC_2H_3O_2} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Potassium tartrate ($K_2C_4H_4O_6$).—Prepared by neutralising potassium acid tartrate (cream of tartar), dissolved in boiling water, with potassium carbonate.

$$\underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Potassium}\\\text{acid tartrate.}}}{2KHC_4H_4O_6} = \underset{\substack{\text{Potassium}\\\text{tartrate.}}}{2K_2C_4H_4O_6} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Potassium citrate ($K_3C_6H_5O_7$).—Prepared by neutralising a solution of citric acid with potassium carbonate.

$$\underset{\substack{\text{Potassium}\\\text{carbonate.}}}{3K_2CO_3} + \underset{\text{Citric acid.}}{2H_3C_6H_5O_7} = \underset{\substack{\text{Potassium}\\\text{citrate.}}}{2K_3C_6H_5O_7} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{3CO_2} + \underset{\text{Water.}}{3H_2O}$$

Potassium citrate is also prepared by the action of citric acid on potassium bicarbonate; the ordinary effervescing mixture, frequently administered to fever patients, is produced by mixing a dose of the mixture containing in solution 20 grains of potassium bicarbonate, with 16 grains of powdered citric acid, the dose being drunk during effervescence; by using these quantities, a slight excess of citric acid is employed over and above what is required to neutralise the potassium bicarbonate, and so an agreeable acidity is given to the mixture.

Potassium sulphate (K_2SO_4).—Prepared by neutralising sulphuric acid with potassium carbonate.

$$\underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Also obtained as a bye-product in the preparation of nitric acid from potassium nitrate and sulphuric acid.

$$\underset{\substack{\text{Potassium}\\\text{nitrate.}}}{2KNO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3}$$

Potassium nitrate (KNO_3).—Found in nature as *nitre* or *saltpetre*. It may be prepared by neutralising nitric acid with potassium carbonate. This salt is largely employed in the manufacture of gunpowder, which is a mixture of charcoal, sulphur, and nitre;

when the gunpowder is fired, the oxygen of the nitre converts the charcoal into the two gaseous oxides of carbon, carbon monoxide and dioxide, the nitrogen of the nitre is set free, and the sulphur unites with the potassium of the nitre to form potassium sulphide, which, blown into the air in minute particles, constitutes the smoke. The explosive violence is due to the sudden expansion of the large volume of the heated gases produced.

Potassium nitrite (KNO_2).—If potassium nitrate be heated to redness for some time, it loses one-third of its oxygen, and potassium nitrite is formed.

Potassium chloride (KCl) occurs in nature as *carnallite;* it can be prepared by neutralising hydrochloric acid with potassium carbonate.

Potassium iodide (KI).—This important salt is prepared (i) by saturating a solution of caustic potash with iodine, by which means potassium iodide and iodate are obtained in solution.

$$\underset{\substack{\text{Potassium}\\\text{hydrate.}}}{6KHO} + \underset{\text{Iodine.}}{3I_2} = \underset{\substack{\text{Potassium}\\\text{iodide.}}}{5KI} + \underset{\substack{\text{Potassium}\\\text{iodate.}}}{KIO_3} + \underset{\text{Water.}}{3H_2O}$$

(ii) The solution is then evaporated to dryness, and the residue is mixed with charcoal and heated, so as to convert the iodate into iodide; the carbon abstracting the oxygen from the iodate, and so reducing it to the iodide.

$$\underset{\substack{\text{Potassium}\\\text{iodate.}}}{2KIO_3} + \underset{\text{Carbon.}}{3C_2} = \underset{\substack{\text{Potassium}\\\text{iodide.}}}{2KI} + \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{6CO}$$

(iii) The roasted mass on cooling is boiled with water, the solution of potassium iodide is filtered from excess of charcoal, and is then evaporated to a low bulk, and set aside to crystallise. It is very important that the iodate of potassium should be completely converted into iodide, as any acid possesses the property of liberating iodine from a mixture of the two salts; and since iodide of potassium is frequently administered in medicine in very large doses, if it contained iodate the hydrochloric acid of the gastric juice would liberate iodine from the two salts within the stomach, and so the iodine might be set free in poisonous quantities. The hydrochloric acid of the gastric juice would first liberate from the iodide and iodate hydriodic and iodic acids respectively.

$$\underset{\substack{\text{Potassium}\\\text{iodide.}}}{5KI} + \underset{\substack{\text{Potassium}\\\text{iodate.}}}{KIO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} = \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{5HI} +$$

$$\underset{\substack{\text{Iodic}\\\text{acid.}}}{HIO_3} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{6KCl}$$

These two acids would then by their action on one another produce free iodine and water.

$$\underset{\substack{\text{Hydriodic}\\\text{acid.}}}{5HI} + \underset{\substack{\text{Iodic}\\\text{acid.}}}{HIO_3} = \underset{\text{Iodine.}}{3I_2} + \underset{\text{Water.}}{3H_2O}$$

Potassium bromide (KBr).—This salt is prepared in a similar manner to the iodide, with the substitution of bromine for iodine. Solution of caustic potash is saturated with bromine, by which means potassium bromide and bromate are produced.

$$\underset{\substack{\text{Potassium}\\\text{hydrate.}}}{6KHO} + \underset{\text{Bromine.}}{3Br_2} = \underset{\substack{\text{Potassium}\\\text{bromide.}}}{5KBr} + \underset{\substack{\text{Potassium}\\\text{bromate.}}}{KBrO_3} +$$

$$\underset{\text{Water.}}{3H_2O}$$

The solution is then evaporated to dryness, and the residue is mixed with charcoal and heated, in order to reduce the bromate to bromide.

$2KBrO_3$	$+$	$3C_2$	$=$	$2KBr$	$+$	$6CO$
Potassium bromate.		Carbon.		Potassium bromide.		Carbon monoxide.

From the roasted mass the bromide is extracted in a similar way to that employed in the extraction of the iodide.

Potassium manganate (K_2MnO_4).—Prepared by fusing together in a crucible caustic potash, potassium chlorate and manganese dioxide, and extracting the mass with *cold* water, when a green-coloured solution of potassium manganate is obtained.

$6KHO$	$+$	$KClO_3$	$+$	$3MnO_2$	$=$	$3K_2MnO_4$	$+$	KCl	$+$	$3H_2O$
Potassium hydrate.		Potassium chlorate.		Manganese dioxide.		Potassium manganate.		Potassium chloride.		Water.

This solution of potassium manganate is used as a disinfectant under the name of *Condy's green fluid;* it acts partly as a germicide, and partly by the readiness with which it oxidises organic substances. It is not employed so much as the permanganate, which is a better and more powerful disinfectant.

Potassium permanganate ($KMnO_4$).—This salt is also known as the *red manganate of potash*, and as a disinfectant is largely used under the name of *Condy's red fluid.* It is obtained from the manganate by the abstraction of one-half of the potassium, which can be effected either by boiling the solution of the green manganate, or by passing a stream of carbon dioxide or of chlorine through it. In the first two cases one-half of the potassium is removed respectively as potassium hydrate and carbonate, some manganese dioxide being precipitated; in the last case one-half of the potassium is abstracted as potassium chloride.

$$\underset{\substack{\text{Potassium}\\\text{manganate.}}}{3K_2MnO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Potassium}\\\text{permanganate.}}}{2KMnO_4} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{4KHO} + \underset{\substack{\text{Manganese}\\\text{dioxide.}}}{MnO_2}$$

$$\underset{\substack{\text{Potassium}\\\text{manganate.}}}{3K_2MnO_4} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{2CO_2} = \underset{\substack{\text{Potassium}\\\text{permanganate.}}}{2KMnO_4} + \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{2K_2CO_3} + \underset{\substack{\text{Manganese}\\\text{dioxide.}}}{MnO_2}$$

$$\underset{\substack{\text{Potassium}\\\text{manganate.}}}{2K_2MnO_4} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Potassium}\\\text{permanganate.}}}{2KMnO_4} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{2KCl}$$

By evaporating the deep red solution to a low bulk and allowing it to cool, potassium permanganate separates in long, dark-red, almost black, needles, with somewhat of a metallic lustre. Potassium permanganate is one of the most powerful oxidising agents known, and is also a powerful disinfectant; as a disinfectant it acts in a similar manner to the manganate, partly by being a powerful germicide, and partly by the readiness with which it oxidises organic substances; when it is being so employed, the red solution loses its colour, a brown deposit of manganese dioxide being produced; the splitting up of potassium permanganate when employed as a disinfectant is shown in the following equation:—

$$\underset{\substack{\text{Potassium}\\ \text{permanganate.}}}{4KMnO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Manganese}\\ \text{dioxide.}}}{4MnO_2} + \underset{\substack{\text{Potassium}\\ \text{hydrate.}}}{4KHO} + \underset{\text{Oxygen.}}{3O_2}$$

On account of the staining that would result from the deposition of the manganese dioxide, a solution of potassium permanganate should never be employed in the disinfection of linen or of articles of clothing.

Sulphurated potash.—This preparation, which is a mixture of potassium pentasulphide (K_2S_5) and potassium sulphate (K_2SO_4), is obtained by fusing together potassium carbonate and sulphur. It is an unstable preparation and was formerly known as *liver of sulphur*.

Potassium chlorate. (*See* page 145.)

Potassium cyanide, cyanate, ferrocyanide, and ferricyanide.—These salts will be described in the Organic Chemistry Section (*see* pages 386, 388, 392, 394).

Tests for Potassium.

(i) If a potassium salt, or a solution of a potassium salt, be introduced on a loop of platinum wire into a Bunsen flame, a characteristic lavender tint will be imparted to the flame. If a sodium salt be also present, the yellow colour imparted by the sodium to the flame will entirely mask the lavender tint produced by the potassium salt; but if such a flame be viewed through a piece of dark-blue glass, the yellow sodium rays will be absorbed by the blue of the glass, while the lavender-coloured rays produced by the potassium salt will pass through the glass unchanged.

(ii) If a solution of a potassium salt contained in a watch-glass be acidulated with hydrochloric acid, and then a few drops of platinic chloride added, and the mixture well stirred with a glass rod, a yellow crystalline deposit of the double platinum and potassium chloride ($PtCl_4,2KCl$) will be formed. A similar reaction is also produced with ammonium salts.

(iii) If to a concentrated solution of a potassium salt a strong solution of tartaric acid be added, and the mixture then be well shaken or stirred, a white granular or crystalline precipitate of potassium acid tartrate ($KHC_4H_4O_6$) will be formed

CHAPTER II.

SODIUM—LITHIUM.

Sodium—Natural Compounds of Sodium—Preparation and Properties of the Metal Sodium—Preparation of the Sodium Salts—Leblanc process—Ammonia-Soda process—Test for Sodium—Lithium—Natural Compounds of Lithium—Preparation and Properties of the Metal Lithium—Preparation of the Lithium Salts—Test for Lithium.

SODIUM.

Symbol, Na ; *formula,* Na_2 ; *monad; atomic weight,* 23 ; *molecular weight,* 46.

Natural compounds of sodium.—(i) Sodium chloride is the principal sodium compound occurring in nature ; in the solid form it occurs as *common salt,* or *rock salt;* in solution it is present in large quantities in sea-water. (ii) Sodium nitrate, known as *cubic nitre* or *Chili saltpetre,* occurs in immense quantities in South America. (iii) Just as potassium salts are present in land plants, and leave the carbonate when the plants are burnt, so sodium salts are present in sea-weeds, and are left as sodium carbonate when sea-weeds are burnt (*see* page 152). (iv) *Cryolite* is a double aluminium and sodium fluoride ($Al_2F_6,6NaF$).

Preparation of the metal sodium.—This metal is prepared by a similar process to that employed in the preparation of potassium, viz. by distilling sodium carbonate with charcoal.

$$\underset{\substack{\text{Sodium}\\ \text{carbonate.}}}{Na_2CO_3} + \underset{\text{Carbon.}}{C_2} = \underset{\text{Sodium.}}{Na_2} + \underset{\substack{\text{Carbon}\\ \text{monoxide.}}}{3CO}$$

Properties of the metal.—Sodium very much resembles potassium in many of its properties. It is a metal of a silver-white colour and possesses a bright lustre when freshly cut, the cut surface rapidly tarnishing, however, on account of its uniting with the oxygen of the air to form a film of sodium oxide; it is on account of this powerful affinity of sodium for oxygen that the metal has to be kept immersed in mineral naphtha, a liquid free from oxygen; as otherwise, if kept exposed to the air, it would become completely converted into sodium oxide (Na_2O). Sodium is lighter than water, and therefore floats when thrown on it, at the same time decomposing the water energetically, forming sodium hydrate, and liberating one-half of the hydrogen of the water.

$$\underset{\text{Sodium.}}{Na_2} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Sodium hydrate.}}{2NaHO} + \underset{\text{Hydrogen.}}{H_2}$$

There is not as much heat generated by the action of sodium on water as by potassium on water, and therefore during the action of sodium on water the escaping hydrogen is not ignited; but if the movements of the sodium on the surface of the water be restrained, as, for instance, by throwing a piece of sodium on to wet blotting-paper, when it remains fixed in one spot, then the heat, being concentrated at this one spot, is sufficiently intense to ignite the escaping hydrogen. On sulphuric and hydrochloric acids sodium acts with explosive violence, forming respectively sodium sulphate and chloride, and liberating the hydrogen.

SODIUM SALTS.

Sodium carbonate (Na_2CO_3).—This salt, commonly known as *washing-soda*, is manufactured on an enormous scale from common salt (NaCl). There are two methods of manufacturing sodium carbonate on a large scale, one known as the *Leblanc process,* the other and more recent one as the *ammonia-soda process.*

Leblanc process.—In this process the sodium is furnished by common salt (NaCl), and the carbonic radical by chalk or limestone ($CaCO_3$). The roasting of these two substances together would be useless, since even if sodium carbonate and calcium chloride were found, yet they could not be separated from one another, for both being soluble in water they would, on the addition of water, react on one another, reproducing sodium chloride and calcium carbonate. The object of the process is therefore to finally obtain an insoluble calcium compound from which the sodium carbonate may be removed by solution in water. This is effected by the following steps :—

(i) The sodium chloride is converted into sodium sulphate by the action of strong sulphuric acid.

$$\underset{\substack{\text{Sodium}\\ \text{chloride.}}}{2NaCl} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\ \text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2HCl}$$

(ii) The sodium sulphate (*salt-cake*) is then mixed with small coal and crushed limestone, and the mixture thoroughly roasted in a furnace ; the sodium sulphate is first reduced by the carbon of the coal to sodium sulphide.

$$\underset{\substack{\text{Sodium}\\ \text{sulphate.}}}{Na_2SO_4} + \underset{\text{Carbon.}}{2C_2} = \underset{\substack{\text{Sodium}\\ \text{sulphide.}}}{Na_2S} + \underset{\substack{\text{Carbon}\\ \text{monoxide.}}}{4CO}$$

Double decomposition then takes place between the sodium sulphide and the calcium carbonate (limestone), resulting in the formation of sodium carbonate and calcium sulphide.

$$\underset{\substack{\text{Sodium}\\\text{sulphide.}}}{Na_2S} + \underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3} = \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Calcium}\\\text{sulphide.}}}{CaS}$$

(iii) The roasted mass (*black-ash*) is then boiled with water in order to dissolve out the sodium carbonate, the calcium sulphide remaining insoluble; the latter is allowed to deposit; the solution of sodium carbonate is poured off and evaporated to dryness. The crude sodium carbonate so obtained is, however, impure, from the presence of caustic soda (sodium hydrate). This has been formed from (*a*) a portion of the limestone during the roasting becoming converted into lime (calcium oxide),—

$$\underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3} = \underset{\text{Lime.}}{CaO} + \underset{\substack{\text{Carbon}\\\text{dioxide;}}}{CO_2}$$

(*b*) this lime during the treatment with water becoming converted into slaked lime (calcium hydrate),—

$$\underset{\text{Lime.}}{CaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Slaked lime;}}{Ca(HO)_2}$$

(*c*) the slaked lime then decomposing a portion of the sodium carbonate with formation of caustic soda (sodium hydrate) and calcium carbonate,—

$$\underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Calcium}\\\text{hydrate.}}}{Ca(HO)_2} = \underset{\substack{\text{Sodium}\\\text{hydrate.}}}{2NaHO} + \underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3}$$

(iv) The crude sodium carbonate is mixed with sawdust, and the mixture is thoroughly roasted, in order to convert the caustic soda into the carbonate; this result is effected by the caustic soda and the sawdust first forming sodium oxalate ($Na_2C_2O_4$), which, under the influence of heat, is converted into sodium carbonate.

$$\underset{\substack{\text{Sodium}\\ \text{oxalate.}}}{Na_2C_2O_4} = \underset{\substack{\text{Sodium}\\ \text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Carbon}\\ \text{monoxide.}}}{CO}$$

(v) Finally the roasted mass is extracted with boiling water, the solution is strained and concentrated by evaporation, and on cooling, the sodium carbonate crystallises out.

Ammonia-soda process.—This consists in mixing together strong solutions of common salt and ammonium bicarbonate under a pressure of about two atmospheres, when double decomposition takes place with the formation of sodium bicarbonate and ammonium chloride.

$$\underset{\substack{\text{Sodium}\\ \text{chloride.}}}{NaCl} + \underset{\substack{\text{Ammonium}\\ \text{bicarbonate.}}}{NH_4HCO_3} = \underset{\substack{\text{Sodium}\\ \text{bicarbonate.}}}{NaHCO_3} + \underset{\substack{\text{Ammonium}\\ \text{chloride.}}}{NH_4Cl}$$

The sodium bicarbonate, after separating out, is converted into the sodium carbonate by heat.

$$\underset{\substack{\text{Sodium}\\ \text{bicarbonate.}}}{2NaHCO_3} = \underset{\substack{\text{Sodium}\\ \text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

The process is carried out in the following manner. A saturated solution of common salt is mixed with solution of ammonia, and the mixture is then saturated with carbon dioxide gas under a pressure of two atmospheres.

The carbon dioxide converts the ammonia into ammonium bicarbonate, which, with the sodium chloride, forms sodium bicarbonate, and this not being very soluble in water, separates out, is filtered off under pressure, and converted into the normal carbonate by heating. The carbon dioxide gas which is then given off, is again used to reconvert the ammonia which is recovered from the ammonium chloride into ammonium bicarbonate.

Sodium carbonate, commonly known as *washing-soda*, is largely used to soften water for washing purposes; the water is usually first boiled, by which means the temporary hardness is got rid of (*see* page 96), and some washing-soda is then added to get rid of the permanent hardness, which is mainly due to calcium and magnesium sulphates; these compounds are converted into the insoluble calcium and magnesium carbonates by the washing-soda.

Sodium bicarbonate ($NaHCO_3$) is prepared by passing a stream of carbon dioxide through a saturated solution of sodium carbonate, when the bicarbonate separates out, on account of its lesser solubility.

$$\underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{Sodium bicarbonate.}}{2NaHCO_3}$$

Sodium bicarbonate, when employed in medicine, should not be dissolved in hot water, as it is converted by the heat into sodium carbonate.

$$\underset{\text{Sodium bicarbonate.}}{2NaHCO_3} = \underset{\text{Sodium carbonate.}}{Na_2CO_3} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Sodium hydrate or **caustic soda** (NaHO) is prepared by boiling together sodium carbonate, slaked lime, and water, and filtering from the insoluble calcium carbonate produced.

$$\underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Calcium}\\\text{hydrate.}}}{Ca(HO)_2} = \underset{\substack{\text{Sodium}\\\text{hydrate.}}}{2NaHO} + \underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3}$$

Sodium sulphate (Na_2SO_4).—This salt, a saline purgative, is known as *Glauber's salt.* It is prepared either by neutralising sulphuric acid with sodium carbonate, or as a bye-product in the preparation of hydrochloric acid from common salt and sulphuric acid.

$$\underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + \underset{\text{Water.}}{H_2O} +$$

$$\underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2}$$

$$\underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl}$$

Sodium phosphate (Na_2HPO_4) is prepared by partially saturating phosphoric acid with caustic soda. This salt, although an acid phosphate in constitution, is yet alkaline to test-paper. Another sodium phosphate (NaH_2PO_4), which can be prepared by only one-third neutralising phosphoric acid with caustic soda, is acid to test-paper, and to it the acidity of urine is normally due.

Sodium ammonium hydrogen phosphate or **microcosmic salt** ($NaNH_4HPO_4$) is prepared by mixing boiling solutions of sodium phosphate and ammonium chloride.

$$\underset{\substack{\text{Sodium}\\\text{phosphate.}}}{Na_2HPO_4} + \underset{\substack{\text{Ammonium}\\\text{chloride.}}}{NH_4Cl} = \underset{\substack{\text{Microcosmic}\\\text{salt.}}}{NaNH_4HPO_4} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{NaCl}$$

It is used in blowpipe tests, as it yields, when heated, a transparent bead of sodium metaphosphate.

$$\underset{\substack{\text{Microcosmic}\\\text{salt.}}}{NaNH_4HPO_4} = \underset{\substack{\text{Sodium}\\\text{metaphosphate.}}}{NaPO_3} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Water.}}{H_2O}$$

Microcosmic salt occurs in stale urine, and owes its name to the fact that it was formerly obtained from the urine of man, who was called the *microcosmos*, or *little world.*

Sodium arseniate (Na_2HAsO_4) is prepared by fusing together arsenious oxide (white arsenic), sodium carbonate, and sodium nitrate, and dissolving the mass in water.

$$\underset{\substack{\text{Arsenious}\\\text{oxide.}}}{As_2O_3} + \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Sodium}\\\text{nitrate.}}}{2NaNO_3} =$$

$$\underset{\substack{\text{Sodium}\\\text{pyroarseniate.}}}{Na_4As_2O_7} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{N_2O_3}$$

$$\underset{\substack{\text{Sodium}\\\text{pyroarseniate.}}}{Na_4As_2O_7} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Sodium}\\\text{arseniate.}}}{2Na_2HAsO_4}$$

Sodium hypophosphite ($NaPH_2O_2$) is prepared either by boiling phosphorus with solution of caustic soda (*see* page 187), or by decomposing a solution of calcium hypophosphite with sodium carbonate, when calcium carbonate is precipitated and sodium hypophosphite remains in solution.

$$\underset{\substack{\text{Calcium}\\\text{hypophosphite.}}}{Ca(PH_2O_2)_2} + \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} = \underset{\substack{\text{Sodium}\\\text{hypophosphite.}}}{2NaPH_2O_2} + \underset{\substack{\text{Calcium}\\\text{carbonate.}}}{CaCO_3}$$

Sodium iodide (NaI) and **sodium bromide** ($NaBr$).—These salts are prepared in similar ways to the corresponding potassium salts, substituting caustic soda for caustic potash (*see* pages 216, 217).

Sodium acetate ($NaC_2H_3O_2$) is prepared by neutralising acetic acid with sodium carbonate.

$$\underset{\text{Acetic acid.}}{2HC_2H_3O_2} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Sodium acetate.}}{2NaC_2H_3O_2} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Sodium potassium tartrate ($KNaC_4H_4O_6$).—This salt, which is largely used as a saline purgative, is known as *Rochelle salt;* it is prepared by neutralising a hot solution of potassium acid tartrate (cream of tartar) with sodium carbonate.

$$\underset{\text{Potassium acid tartrate.}}{2KHC_4H_4O_6} + \underset{\text{Sodium carbonate.}}{Na_2CO_3} = \underset{\text{Sodium potassium tartrate.}}{2KNaC_4H_4O_6} + \underset{\text{Carbon dioxide.}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

This salt constitutes the main ingredient of a *Seidlitz powder*, the blue packet of which contains a mixture of Rochelle salt and sodium bicarbonate, whilst the white packet contains tartaric acid; the contents of the blue packet are first dissolved in water, and then the contents of the white packet added; the sodium bicarbonate is neutralised by the tartaric acid, with formation of sodium tartrate and copious effervescence of carbon dioxide gas.

$$\underset{\substack{\text{Sodium}\\\text{bicarbonate.}}}{2NaHCO_3} + \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} = \underset{\substack{\text{Sodium}\\\text{tartrate.}}}{Na_2C_4H_4O_6} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{2CO_2} + \underset{\text{Water.}}{2H_2O}$$

But as the white packet contains a slight excess of tartaric acid over and above what is required to neutralise the bicarbonate, this slight excess of acid will convert a small portion of the sodium tartrate into the acid tartrate, which will then give an agreeable acidity to the draught.

$$\underset{\substack{\text{Sodium}\\\text{tartrate.}}}{Na_2C_4H_4O_6} + \underset{\text{Tartaric acid.}}{H_2C_4H_4O_6} = \underset{\substack{\text{Sodium acid}\\\text{tartrate.}}}{2NaHC_4H_4O_6}$$

So that when the contents of the two packets constituting the "seidlitz powder" are mixed in water, three salts, all of them saline purgatives, are contained in the draught, viz. sodium potassium tartrate (Rochelle salt), sodium tartrate, and sodium acid tartrate.

Sodium citro-tartrate.—This effervescing preparation, known as the *effervescing citro-tartrate of soda*, is prepared by mixing together in the solid states, sodium bicarbonate, citric acid, tartaric acid, and sugar, and then carefully heating the mass until it becomes granular. When the granules are dissolved in water, effervescence takes place, with the production of sodium citro-tartrate.

Sodium hypochlorite. (*See* page 143.)

Sodium thiosulphate or **hyposulphite.** (*See* page 208.)

Sodium borate. (*See* page 176.)

Test for Sodium.

If a fragment of a sodium salt, or some solution of a sodium salt, be introduced on a loop of platinum wire into a Bunsen flame, an intense yellow colour will be communicated to the flame; this test will be rendered all the more trustworthy by observing the effect of the yellow-coloured sodium flame upon the skin of the hand when held near the flame, the skin then appearing of a ghastly livid colour.

LITHIUM.

Symbol, Li; *formula*, Li_2; *monad; atomic weight*, 7; *molecular weight*, 14.

Natural compounds of lithium.—Lithium occurs in the minerals *lepidolite* and *petalite*, and is also found in minute quantities in numerous mineral springs.

Preparation and properties of the metal lithium.—Lithium can be prepared by electrolysis of its fused chloride; the metal depositing on the negative pole and chlorine being liberated at the positive pole. Lithium is the lightest solid known; it is a silver-white metal, harder than potassium or sodium, but oxidising less easily than those metals; its cut surface, however, soon tarnishes from absorption of oxygen and formation of lithium oxide, and it is therefore kept immersed in mineral naphtha. Like potassium and sodium, it decomposes water when thrown upon it, with the formation of lithium hydrate and hydrogen, but the escaping hydrogen is not inflamed.

Lithium Salts.

Lithium carbonate (Li_2CO_3) is prepared from *lepidolite*, a double fluoride of potassium and lithium with silicate of aluminium, by decomposing it with sulphuric acid to form the three soluble sulphates of potassium, lithium, and aluminium, adding ammonia to precipitate the aluminium, filtering, evaporating to dryness, igniting the residue to expel ammonia salts, dissolving the potassium and lithium sulphates in a small quantity of water, and adding potassium carbonate to precipitate the carbonate of lithium.

Lithium bicarbonate ($LiHCO_3$) is prepared by suspending lithium carbonate in water, and passing carbon dioxide gas through, when the bicarbonate is formed and dissolves in the water.

$$\underset{\substack{\text{Lithium}\\ \text{carbonate.}}}{Li_2CO_3} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Lithium}\\ \text{bicarbonate.}}}{2LiHCO_3}$$

This is the salt that is present in lithia water (*Liquor lithiæ effervescens*), a preparation that is frequently prescribed for gouty persons, the object being to convert the slightly soluble sodium urate, which is deposited in the cartilages of joints and elsewhere in gouty subjects, into the more soluble lithium urate, and so secure the elimination from the system of the excess of uric acid.

Lithium citrate ($Li_3C_6H_5O_7$) is prepared by neutralising a solution of citric acid with lithium carbonate.

$$\begin{aligned}\underset{\substack{\text{Lithium}\\ \text{carbonate.}}}{3Li_2CO_3} + \underset{\text{Citric acid.}}{2H_3C_6H_5O_7} &= \underset{\text{Lithium citrate.}}{2Li_3C_6H_5O_7} + \\ &\quad \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{3CO_2} + \underset{\text{Water.}}{3H_2O}\end{aligned}$$

Test for Lithium.

Lithium salts impart a magnificent crimson colour to the Bunsen flame, when introduced into the flame on a loop of platinum wire; the colour is rendered more intense by previously moistening the wire with hydrochloric acid, so as to form lithium chloride.

CHAPTER III.

CALCIUM—BARIUM—MAGNESIUM—STRONTIUM.

Calcium—Natural Compounds of Calcium—Preparation of the Calcium Salts—Mortars and Cements—Tests for Calcium—Barium—Natural Compounds of Barium—Preparation of the Barium Salts—Tests for Barium—Magnesium—Natural Compounds of Magnesium—Preparation and Properties of the Metal Magnesium—Preparation of the Magnesium Salts—Test for Magnesium—Strontium.

CALCIUM.

Symbol, Ca ; *formula*, Ca_2 ; *dyad ; atomic weight*, 40 ; *molecular weight*, 80.

Natural compounds of calcium.—(i) The chief calcium compound found in nature is the carbonate, which occurs in a variety of forms ; in a pure crystalline form it occurs as *Iceland spar* and *calc spar;* in less pure forms it constitutes *marble*, *chalk*, *limestone*, *oolite*, and *coral*, the last being the remains of minute sea-animals ; the shells of mollusca and the egg-shells of birds consist mainly of calcium carbonate ; *stalactites* consist of a porous form of calcium carbonate, produced by the evaporation of hard water containing the calcium bicarbonate in solution ; they are found hanging from the roofs of limestone caves. (ii) Calcium sulphate occurs in nature as *alabaster*, used as an ornamental stone ; as *selenite*, which is found in transparent plates, and is used for optical purposes ; and as *gypsum*, a form of calcium sulphate containing water of crystallisation ($CaSO_4,2H_2O$). By heating gypsum for some time at 130° to 140° C.

the water of crystallisation is expelled, and commercial *plaster of Paris* is obtained; this, if mixed with sufficient water to form a paste, sets to a solid in a short time, due to the plaster of Paris ($CaSO_4$) uniting with the water to form gypsum ($CaSO_4, 2H_2O$), a body in which the water is in the solid state of crystallisation. Plaster of Paris is largely employed in this way as a cement, and by the surgeon to form a rigid casing for fractured limbs, etc. (iii) Calcium fluoride is native *fluor-spar*. (iv) Calcium phosphate is the principal constituent of the minerals *apatite* and *phosphorite*. (v) Calcium silicate is a constituent of many rocks.

Preparation and properties of the metal calcium.—This is a rare metal; it may be prepared by the electrolysis of fused calcium chloride, the calcium being deposited upon the negative pole. It is a metal of a pale yellow colour, oxidising in the air, and decomposing water with the formation of calcium hydrate and hydrogen, the liberated hydrogen, however, not being inflamed.

CALCIUM SALTS.

Calcium chloride ($CaCl_2$) is prepared by dissolving chalk or marble (calcium carbonate) in hydrochloric acid.

$$\underset{\substack{\text{Calcium}\\ \text{carbonate.}}}{CaCO_3} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{2HCl} = \underset{\substack{\text{Calcium}\\ \text{chloride.}}}{CaCl_2} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Solid calcium chloride is one of the most hygroscopic bodies known; if exposed to the air for a short time it becomes liquid, owing to its absorbing sufficient water from the air to dissolve in; on account of its hygroscopic properties it is frequently employed to dry gases.

Calcium carbonate ($CaCO_3$).—This compound, as previously mentioned, occurs native in several forms. As *precipitated carbonate of lime*, it is prepared by precipitating a solution of calcium chloride with a solution of sodium carbonate.

$$\underset{\substack{\text{Calcium}\\ \text{chloride.}}}{CaCl_2} + \underset{\substack{\text{Sodium}\\ \text{carbonate.}}}{Na_2CO_3} = \underset{\substack{\text{Calcium}\\ \text{carbonate.}}}{CaCO_3} + \underset{\substack{\text{Sodium}\\ \text{chloride.}}}{2NaCl}$$

Prepared chalk is merely washed chalk that has been worked into small conical lumps and then dried; if washed chalk be made into larger rolls it constitutes *whiting*.

Calcium oxide or **lime** (CaO) is prepared by roasting limestone (calcium carbonate) until all the carbon dioxide is expelled.

$$\underset{\substack{\text{Calcium}\\ \text{carbonate.}}}{CaCO_3} = \underset{\text{Lime.}}{CaO} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2}$$

The manufacture of lime, or quicklime as it is commonly called, is carried on in specially constructed furnaces called *lime-kilns*. Fig. 20 represents such a kiln, which is constructed of fire-bricks, and is filled with pieces of limestone (A). A fire is kept up at the side (B), and the lime is raked out from the bottom of the kiln (C) as it is produced, fresh limestone being introduced at the top to supply its place.

Calcium hydrate or **slaked lime** ($Ca(HO)_2$) is prepared by the addition of water to lumps of quicklime, when considerable heat is produced, due partly to the chemical action taking place between the quicklime and the water, and partly to the conversion of the latent heat of the water into sensible heat, as the water passes from the liquid state into the solid state in which it exists in calcium hydrate.

$$\underset{\text{Quicklime.}}{CaO} + \underset{\text{Water.}}{H_2O} = \underset{\text{Slaked lime.}}{Ca(HO)_2}$$

Lime-water (*Liquor calcis*, B. P.) is a saturated solution of slaked lime in water, each pint containing about 13 grains of calcium hydrate in solution; calcium hydrate is much more soluble in an aqueous solution of sugar, and such a solution is the *saccharated lime water* (*Liquor calcis saccharatus*, B. P.), which contains about 14 times as much slaked lime as ordinary lime-water. If lime-water be exposed to the air it soon diminishes in strength, owing to the absorption of carbon dioxide from the air, and consequent precipitation of calcium carbonate.

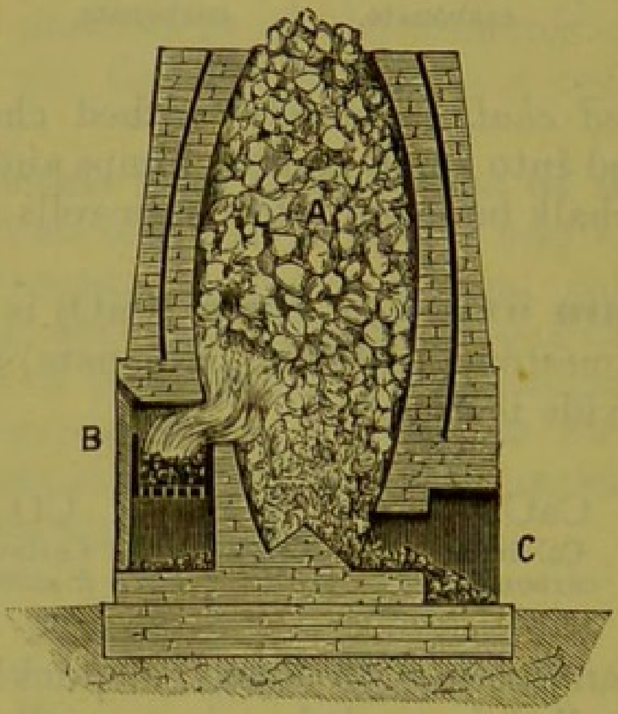


Fig. 20.—Section of Lime-Kiln.

Slaked lime is largely employed in the preparation of *mortar*, which consists of slaked lime, sand, and water mixed so as to form a paste. *Hydraulic mortars* or *cements* are preparations which, when mixed with water, solidify, and then continue to harden under water, until they assume a stone-like hardness; such are *Roman cement* and *Portland cement*, which are obtained by calcining a mixture of limestone and clay; on mixing the cement with water, compounds of lime and alumina and lime and silica are produced, which set to a hard mass impervious to water. The advantage of lining privies and cesspools with such a cement is obvious, as percolation of sewage matter into the soil and the consequent possible contamination of drinking-water are thereby prevented. *Concrete* consists of hydraulic cement mixed with gravel or crushed pebbles.

Calcium phosphate ($Ca_3(PO_4)_2$) is prepared by digesting bone-ash (impure calcium phosphate) in hydrochloric acid, by which means the insoluble calcium phosphate is converted into the soluble calcium superphosphate or acid phosphate and calcium chloride.

$$\underset{\substack{\text{Calcium}\\ \text{phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{4HCl} = \underset{\substack{\text{Calcium}\\ \text{acid phosphate.}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium}\\ \text{chloride.}}}{2CaCl_2}$$

This acid solution is then filtered from insoluble matter, and ammonia added to precipitate the pure calcium phosphate.

$$\underset{\substack{\text{Calcium}\\ \text{acid phosphate.}}}{CaH_4(PO_4)_2} + \underset{\substack{\text{Calcium}\\ \text{chloride.}}}{2CaCl_2} + \underset{\substack{\text{Ammonium}\\ \text{hydrate.}}}{4NH_4HO} =$$

$$\underset{\substack{\text{Calcium}\\ \text{phosphate.}}}{Ca_3(PO_4)_2} + \underset{\substack{\text{Ammonium}\\ \text{chloride.}}}{4NH_4Cl} + \underset{\text{Water.}}{4H_2O}$$

Calcium hypophosphite. (*See* page 187.)

Calcium sulphide (CaS) is prepared by heating lime in a stream of sulphuretted hydrogen gas,—

$$\underset{\substack{\text{Calcium}\\\text{oxide.}}}{CaO} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{H_2S} = \underset{\substack{\text{Calcium}\\\text{sulphide.}}}{CaS} + \underset{\text{Water ;}}{H_2O}$$

or by roasting a mixture of calcium sulphate and charcoal, the latter reducing the sulphate to sulphide,—

$$\underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4} + \underset{\text{Carbon.}}{2C_2} = \underset{\substack{\text{Calcium}\\\text{sulphide.}}}{CaS} + \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{4CO.}$$

If calcium sulphide be exposed to light, it is afterwards for some time phosphorescent in the dark. It is the chief constituent of *Balmain's luminous paint.* If treated with an acid, such as hydrochloric acid, sulphuretted hydrogen gas is evolved, and in this way is obtained in a very pure state, such as is required in toxicological investigations.

$$\underset{\substack{\text{Calcium}\\\text{sulphide.}}}{CaS} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Calcium}\\\text{chloride.}}}{CaCl_2} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{H_2S}$$

Chlorinated lime, or **bleaching powder** (*see* page 142).

Tests for Calcium.

(i) Ammonium oxalate gives, with a solution of a calcium salt, a white precipitate of calcium oxalate, which is insoluble in acetic acid, but soluble in hydrochloric acid.

(ii) If a calcium salt be introduced into the Bunsen flame, on a piece of platinum wire previously moistened with hydrochloric acid, a pale reddish colour is communicated to the flame, the colour, however, rapidly fading away.

BARIUM.

Symbol, Ba ; *formula*, Ba_2 ; *dyad ; atomic weight*, 137 ; *molecular weight*, 274.

The salts of barium have a high specific gravity ; hence the derivation of the name from *βαρὺς*, *heavy*.

Natural compounds of barium. — (i) *Witherite* is the native carbonate of barium. (ii) *Heavy spar* is the native sulphate of barium.

Preparation and properties of the metal barium.—Barium may be prepared in a similar manner to calcium, by electrolysis of the fused chloride. It is of a pale yellow colour, and possesses very similar properties to those of calcium.

BARIUM SALTS.

Barium nitrate ($Ba(NO_3)_2$) is prepared either by dissolving the carbonate in nitric acid, or by reducing the sulphate to sulphide by roasting with charcoal, and then dissolving the sulphide in nitric acid.

Barium chloride ($BaCl_2$) is prepared by similar processes to those for obtaining the nitrate, with the substitution of hydrochloric for nitric acid.

Barium oxide or **baryta** (BaO).—This oxide is most conveniently prepared by roasting the nitrate.

$$\underset{\text{Barium nitrate.}}{2Ba(NO_3)_2} = \underset{\text{Barium oxide.}}{2BaO} + \underset{\text{Nitrogen tetroxide.}}{2N_2O_4} + \underset{\text{Oxygen.}}{O_2}$$

When water is added to barium oxide, evolution of heat takes place, and *barium hydrate* or *slaked baryta* ($Ba(HO)_2$) is produced, the reaction being similar to that which occurs during the slaking of lime. Barium hydrate is much more soluble in water than calcium hydrate; its solution is known as *baryta water*, and, like lime-water, if exposed to the air it absorbs carbon dioxide, producing a white deposit of barium carbonate.

Barium dioxide, or **barium peroxide** (BaO_2).—This oxide is prepared by heating baryta to a dull red heat in a stream of air or oxygen.

$$\underset{\text{Baryta.}}{2BaO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Barium dioxide.}}{2BaO_2}$$

If the higher oxide be further heated it is converted into the lower oxide, with evolution of oxygen; in this way pure oxygen may be obtained from the air (*see* page 84). Barium dioxide is also employed in the preparation of hydrogen dioxide (*see* page 99).

Tests for Barium.

(i) Barium salts give, with dilute sulphuric acid, a white precipitate of barium sulphate, which is insoluble in either hydrochloric or nitric acids.

(ii) Solution of potassium chromate gives a yellow precipitate of barium chromate with barium salts; this precipitate is insoluble in acetic acid, but is soluble in either hydrochloric or nitric acids.

(iii) If a barium salt be introduced into the Bunsen flame, on a piece of platinum wire previously moistened with hydrochloric acid, a yellowish-green colour is communicated to the flame.

MAGNESIUM.

Symbol, Mg ; *formula*, Mg_2 ; *dyad; atomic weight*, 24 ; *molecular weight*, 48.

Natural compounds of magnesium.—(i) The carbonate occurs in nature in a fairly pure form as *magnesite* ($MgCO_3$), and as a double carbonate of magnesium and calcium in *dolomite* ($MgCO_3,CaCO_3$). (ii) Magnesium sulphate is found in certain mineral spring waters ; in Epsom spring waters, in England ; in Friedrichshall water, in Germany ; and in Hunyadi János water, in Hungary. (iii) Various compounds of magnesium and silica occur in nature ; *talc* is magnesium silicate ; *meerschaum* is magnesium silicate, combined with excess of silica ; *asbestos* is a double silicate of magnesium and calcium.

Preparation and properties of the metal magnesium.—Magnesium is prepared by heating in a crucible a mixture of magnesium chloride and the metal sodium, when the latter abstracts the chlorine, forming sodium chloride, and the metal magnesium sinks to the bottom of the crucible. Magnesium is made into ribbon or wire for burning purposes, in order to produce the powerful light known as the *magnesium light.* When burnt, it produces a white ash of magnesium oxide, or magnesia.

MAGNESIUM SALTS.

Magnesium sulphate ($MgSO_4$), commonly known as *Epsom salts,* on account of its natural occurrence in Epsom spring waters, is prepared by dissolving the native magnesium carbonate in diluted sulphuric acid, concentrating the liquor, and allowing the salt to crystallise out.

$$\underset{\substack{\text{Magnesium}\\\text{carbonate.}}}{MgCO_3} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Magnesium}\\\text{sulphate.}}}{MgSO_4} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Epsom salts resemble remarkably in their crystalline appearance the crystals of zinc sulphate, and also to a certain extent the crystals of oxalic acid, both of which poisonous materials have been mistaken for Epsom salts. From zinc sulphate, Epsom salts may be distinguished by its solution yielding no precipitate, either with ammonium sulphide, or with potassium ferrocyanide, whereas zinc sulphate yields a white precipitate with both reagents; from oxalic acid, Epsom salts may be distinguished by being neutral to test-paper, whereas the former is strongly acid.

Magnesium carbonate ($3MgCO_3, Mg(HO)_2$).—The normal magnesium carbonate ($MgCO_3$) occurs native in magnesite and dolomite; the carbonate that is used in medicine, and which is obtained by precipitation, is a basic carbonate, consisting of three molecules of the carbonate to one of the hydrate. It is prepared by mixing solutions of magnesium sulphate and sodium carbonate, when it is thrown down as a white precipitate.

$$\underset{\substack{\text{Magnesium}\\\text{sulphate.}}}{4MgSO_4} + \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{4Na_2CO_3} + \underset{\text{Water.}}{H_2O} =$$

$$\underset{\text{Magnesium carbonate.}}{3MgCO_3, Mg(HO)_2} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{4Na_2SO_4} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2}$$

There are two forms of magnesium carbonate employed in medicine, the *light carbonate* and the *heavy carbonate*. The former, which is a very fine and light precipitate, is prepared by mixing somewhat diluted and cold solutions of magnesium sulphate and sodium carbonate; the latter, which is a dense and more compact precipitate, is prepared by mixing strong and hot solutions of the same salts.

Magnesium bicarbonate ($Mg(HCO_3)_2$). — This soluble salt is contained in fluid magnesia (*Liquor magnesii carbonatis*, B. P.); it is prepared by passing a stream of carbon dioxide gas through water in which magnesium carbonate is suspended.

$$\underset{\substack{\text{Basic magnesium}\\ \text{carbonate.}}}{3MgCO_3, Mg(HO)_2} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{5CO_2} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Magnesium}\\ \text{bicarbonate.}}}{4Mg(HCO_3)_2}$$

If this solution be heated, carbon dioxide is evolved, and the magnesium carbonate is deposited.

Magnesium oxide or magnesia (MgO).— This is obtained by heating the basic magnesium carbonate.

$$\underset{\substack{\text{Basic magnesium}\\ \text{carbonate.}}}{3MgCO_3, Mg(HO)_2} = \underset{\substack{\text{Magnesium}\\ \text{oxide.}}}{4MgO} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{3CO_2} + \underset{\text{Water.}}{H_2O}$$

There are two varieties of the oxide, *light magnesia* and *heavy magnesia;* they are respectively prepared by the action of heat on the light and heavy carbonates. The old name for either of these preparations was "calcined magnesia."

Magnesium citrate ($Mg_3(C_6H_5O_7)_2$). — This salt is contained in the *Liquor magnesii citratis*, B. P., in which it is prepared by dissolving the basic carbonate in solution of citric acid. "Effervescing citrate of magnesia" is a granular preparation largely used as a mild saline purgative, and effervescing when mixed with water; it consists of sodium bicarbonate, citric and tartaric acids, magnesium carbonate or sulphate, and sugar.

Test for Magnesium.

The presence of magnesium can only be proved after the removal of the other alkaline earth metals, viz. calcium, barium, and strontium ; these metals are precipitated by ammonium carbonate in presence of ammonium chloride, whereas, under such conditions, magnesium is not precipitated, the ammonium chloride keeping the magnesium carbonate in solution. To test for magnesium, it is therefore necessary to add to the solution ammonium chloride and ammonium carbonate, and then to warm ; if calcium, barium, or strontium are present, they will be precipitated, and on filtering from the precipitate, the presence of magnesium in the filtrate can be demonstrated by the addition of solution of ammonia and of sodium phosphate, when a white granular or crystalline precipitate (ammonio-magnesium phosphate, $MgNH_4PO_4$) will be thrown down. Since the metals calcium, barium, and strontium all yield precipitates with sodium phosphate, the necessity for removing them before testing for magnesium is obvious.

STRONTIUM.

Symbol, Sr ; *formula*, Sr_2 ; *dyad ; atomic weight*, 87·5 ; *molecular weight*, 175.

Strontium occurs in nature as the carbonate *strontianite*, and as the sulphate *celestine.* The salts of strontium are not of any medical importance ; they are prepared by processes similar to those employed in the manufacture of the calcium and barium salts.

Test for Strontium.

Strontium salts when introduced into the Bunsen flame on a piece of platinum wire previously moistened with hydrochloric acid, communicate a beautiful crimson colour to the flame. They are on this account largely employed by firework manufacturers.

CHAPTER IV.

ALUMINIUM—ZINC.

Aluminium—Natural Compounds of Aluminium—Preparation and Properties of the Metal Aluminium—Alums—Preparation of the Aluminium Salts—Tests for Aluminium—Zinc—Natural Compounds of Zinc—Preparation and Properties of the Metal Zinc—Preparation of the Zinc Salts—Tests for Zinc.

ALUMINIUM.

Symbol, Al; *formula*, Al_2; *tetrad; atomic weight*, 27; *molecular weight*, 54.

Natural compounds of aluminium. — (i) Aluminium occurs largely in nature combined with silica; the different forms of *clay* consist of aluminium silicate; *felspar*, *granite*, *mica*, *alum-shale* or *schist*, all contain aluminium silicate. (ii) *Cryolite* is a double fluoride of aluminium and sodium. (iii) *Bauxite* is an impure form of aluminium hydrate. (iv) The precious stones, the *ruby* and the *sapphire*, and the polishing powder known as *emery-powder*, consist mainly of aluminium oxide or alumina (Al_2O_3).

Preparation and properties of the metal aluminium.—The oxide of aluminium cannot be deprived of its oxygen by means of charcoal at any temperature; the metal is therefore obtained by reducing aluminium chloride by means of the metal sodium; this is accomplished by passing the vapour of aluminium chloride over melted sodium, the sodium uniting with the chlorine, and the metal aluminium being set free. Aluminium is a light, white metal, remaining unchanged in both dry and moist air; it is mainly used in the preparation of *aluminium bronze*, an alloy of copper and aluminium. Dilute sulphuric and hydrochloric acids both act on the metal aluminium forming respectively the sulphate and chloride, with evolution of hydrogen.

ALUMINIUM SALTS.

Ammonia alum ($Al_2(SO_4)_3$, $(NH_4)_2SO_4$).—This is prepared by mixing solutions of aluminium sulphate and ammonium sulphate, evaporating the mixed solution and setting aside, when the alum crystallises out. The aluminium sulphate is obtained either by the action of strong sulphuric acid with heat on clay, or by roasting alum-shale in the air. Alum-shale consists of aluminium silicate and iron pyrites (FeS_2), and when roasted the sulphur becomes oxidised to sulphuric acid, which forms aluminium sulphate by its action on the silicate, ferric oxide being also produced; on boiling the roasted shale with water, the aluminium sulphate is dissolved out, ferric oxide being left insoluble.

Potash alum ($Al_2(SO_4)_3$, K_2SO_4).—This is prepared by a similar process to that used for making ammonia alum, with the substitution of potassium sulphate for ammonium sulphate.

Both ammonia and potash alums contain twenty-four molecules of water of crystallisation ($Al_2(SO_4)_3$, $(NH_4)_2SO_4$, $24H_2O$ — $Al_2(SO_4)_3$, K_2SO_4, $24H_2O$).

If potash alum be deprived of its water of crystallisation by heating, the anhydrous alum is known as *burnt alum*.

There are *alums* which contain no aluminium such as *iron alum* ($Fe_2(SO_4)_3$, K_2SO_4) and *chrome alum* ($Cr_2(SO_4)_3$, K_2SO_4); so that the term "alum" is used for bodies which may or may not contain aluminium. An "alum" is, in fact, merely a double sulphate crystallising in the octahedral form.

Aluminium oxide or **alumina** (Al_2O_3).—This oxide may be prepared either by heating the precipitated aluminium hydrate,—

$$\underset{\text{Aluminium hydrate.}}{Al_2(HO)_6} = \underset{\text{Aluminium oxide.}}{Al_2O_3} + \underset{\text{Water;}}{3H_2O}$$

or by heating ammonia alum, when ammonium sulphate and sulphur trioxide will be volatilised by the heat, the aluminium oxide being left,—

$$\underset{\text{Ammonia alum.}}{Al_2(SO_4)_3,(NH_4)_2SO_4} = \underset{\text{Aluminium oxide.}}{Al_2O_3} + \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4} + \underset{\text{Sulphur trioxide.}}{3SO_3}$$

Aluminium hydrate ($Al_2(HO)_6$) is prepared by the addition of an alkali to solution of ammonia alum or potash alum; it is a gelatinous precipitate, which possesses the power of fixing or combining with vegetable dyes, and hence is used as a mordant; it is also employed in the chemical treatment of sewage, on account of its property of entangling and carrying down suspended matters.

Aluminium chloride (Al_2Cl_6) is prepared by passing a stream of chlorine over a mixture of alumina and charcoal raised to a red heat, when the aluminium chloride volatilises and condenses on cooling to a solid.

$$\underset{\text{Aluminium oxide.}}{2Al_2O_3} + \underset{\text{Carbon.}}{3C_2} + \underset{\text{Chlorine.}}{6Cl_2} = \underset{\text{Aluminium chloride.}}{2Al_2Cl_6} + \underset{\text{Carbon monoxide.}}{6CO}$$

Tests for Aluminium.

(i) Aluminium salts give with solution of ammonia a white gelatinous precipitate of aluminium hydrate ($Al_2(HO)_6$), insoluble in excess of ammonia.

(ii) With ammonium sulphide aluminium salts also give a precipitate of aluminium hydrate, sulphuretted hydrogen being evolved. The reason that ammonium sulphide does not precipitate aluminium sulphide is due to the fact that aluminium sulphide is decomposed by water into the hydrate and sulphuretted hydrogen.

$$\underset{\text{Aluminium sulphide.}}{Al_2S_3} + \underset{\text{Water.}}{6H_2O} = \underset{\text{Aluminium hydrate.}}{Al_2(HO)_6} + \underset{\text{Sulphuretted hydrogen.}}{3H_2S}$$

(iii) With the fixed alkalies, caustic potash and caustic soda, aluminium salts yield a precipitate of aluminium hydrate, soluble in excess of either fixed alkali.

ZINC.

Symbol, Zn ; *formula*, Zn ; *dyad ; atomic weight*, 65 ; *molecular weight*, 65.

Zinc is one of the elements containing only one atom in the molecule.

Natural compounds of zinc.—(i) *Calamine* is the native carbonate of zinc ($ZnCO_3$) ; it is of a pink colour, from a small quantity of iron contained in it, and is used in surgery in the form of an ointment and lotion. (ii) *Blende* is the native sulphide of zinc (ZnS).

Preparation of the metal zinc.—The zinc ore, either calamine or blende, is first smelted or roasted in the air, to convert it into the zinc oxide, and this is then reduced to the metal by roasting with charcoal or fine coal. Since zinc is a volatile metal, it has to be prepared by a process of distillation, and the process employed is that of *downward distillation.* The mixture of zinc oxide and charcoal or coal (Fig. 21, A) is packed in a large crucible, provided with a pipe passing through a hole in the bottom of the crucible, and the lid of the crucible is then luted down. One of these crucibles ready charged is represented in section in Fig. 21.

Several of these crucibles are then placed in a furnace, with the distillation pipes projecting between and below the bars of the furnace (Fig. 22).

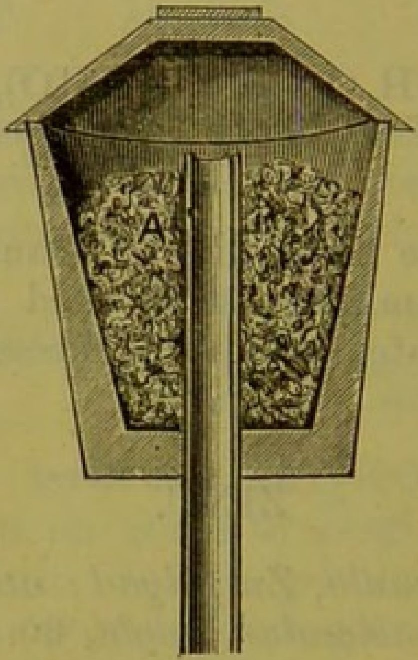


Fig. 21.—Section of Crucible for the Preparation of the Metal Zinc by Downward Distillation (A).

On strongly heating, the zinc is set free by the reducing action of the carbon on the zinc oxide, and passes down the pipe in the form of vapour, which in the lower and cooler portion of the pipe condenses to molten zinc ; this then immediately drops into iron vessels placed to receive it. Zinc prepared in this manner is generally impure, from the presence of small quantities of arsenic, from which it can be purified by well stirring with the molten zinc some potassium nitrate, which converts the arsenic into potassium arseniate.

Granulated zinc, the form in which the metal is commonly employed in the preparation of hydrogen, is obtained by pouring melted zinc from a height into water.

Properties of the metal zinc.—Zinc is a bluish-white hard metal; if heated to 100° C.—150° C.

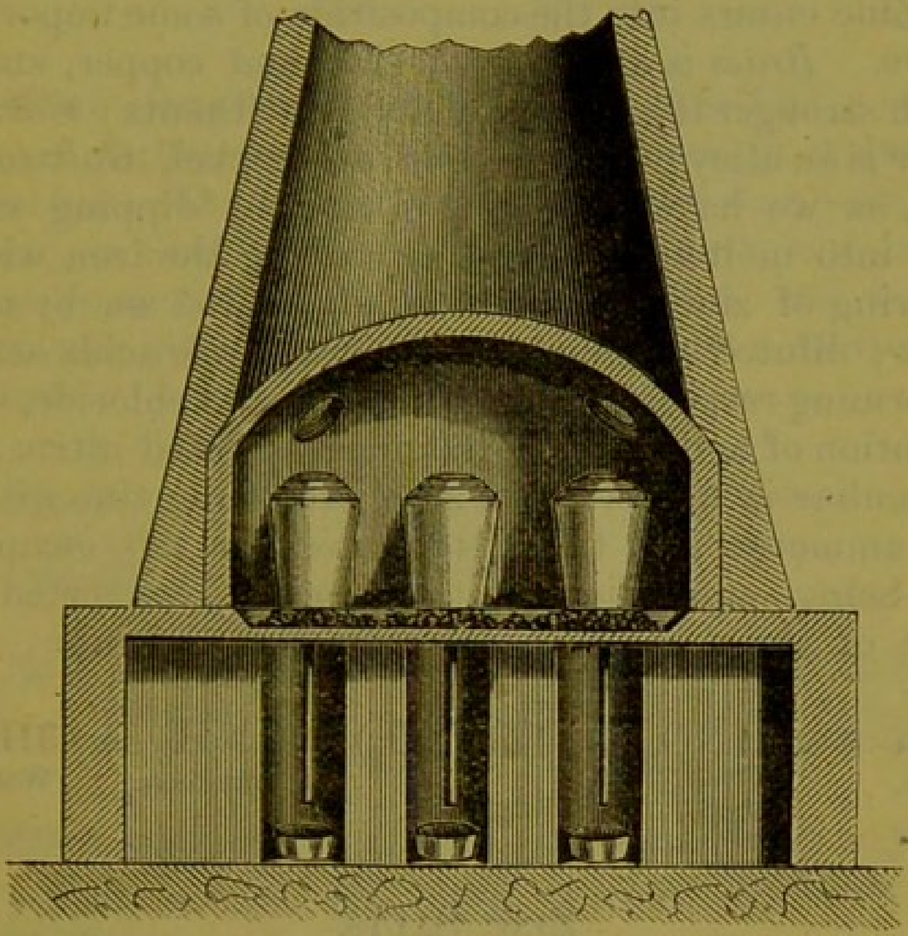


Fig. 22.—Section of Furnace for Distillation of the Metal Zinc.

it becomes soft and malleable, so that it can be rolled into thin plates; at 200° C. it is quite brittle, and can then be readily reduced to powder; at 412° C. it melts, and boils at a bright-red heat (about 1000° C.); when strongly heated in the air it burns with a bright bluish flame, forming light white flocks of zinc oxide. In moist air it oxidises, becoming covered with a very thin film of zinc oxide, which, however, is a very compact film, and effectually checks any further oxidation; in this respect it is very unlike the metal iron, which in moist air oxidises or rusts continuously, and so becomes in time thoroughly corroded. Zinc is, therefore, employed for coating iron vessels, etc., to prevent their rusting, such coated iron being known as *galvanised iron.*

Zinc enters into the composition of some important alloys. *Brass* is an alloy of zinc and copper, and is much stronger than either of its constituents ; *German silver* is an alloy of zinc, copper, and nickel. *Galvanised iron,* as we have seen, is prepared by dipping clean iron into molten zinc, and so coating the iron with a covering of zinc. Zinc is readily acted on by most acids ; diluted sulphuric and hydrochloric acids attack it, forming respectively zinc sulphate and chloride, with evolution of hydrogen. Moderately diluted nitric acid is peculiar in its action on zinc, producing zinc nitrate and ammonia gas, the latter, however, not escaping, but being, immediately it is formed, converted by some of the nitric acid into ammonium nitrate.

$$\begin{array}{ccccccccc} 4Zn & + & 9HNO_3 & = & 4Zn(NO_3)_2 & + & NH_3 & + & 3H_2O \\ \text{Zinc.} & & \text{Nitric} & & \text{Zinc} & & \text{Ammonia.} & & \text{Water.} \\ & & \text{acid.} & & \text{nitrate.} & & & & \end{array}$$

ZINC SALTS.

Zinc sulphate ($ZnSO_4$) is prepared by the action of diluted sulphuric acid on zinc.

$$\begin{array}{ccccccc} Zn & + & H_2SO_4 & = & ZnSO_4 & + & H_2 \\ \text{Zinc.} & & \text{Sulphuric} & & \text{Zinc} & & \text{Hydrogen.} \\ & & \text{acid.} & & \text{sulphate.} & & \end{array}$$

Zinc sulphate occurs in small crystals, very much resembling magnesium sulphate, for which it is apt to be mistaken. For the methods of distinguishing the two salts, *see* page 244.

Zinc sulphate is occasionally termed *white vitriol.*

Zinc chloride ($ZnCl_2$) is prepared by the action of hydrochloric acid on zinc.

$$\underset{\text{Zinc.}}{Zn} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Zinc}\\\text{chloride.}}}{ZnCl_2} + \underset{\text{Hydrogen.}}{H_2}$$

Zinc carbonate ($ZnCO_3, 2Zn(HO)_2$).—The normal carbonate ($ZnCO_3$) only occurs in nature as *calamine.* The precipitated carbonate is a basic carbonate, or double carbonate and hydrate, and is prepared by mixing solutions of zinc sulphate and sodium carbonate, when it is thrown down as a white precipitate.

$$\underset{\substack{\text{Zinc}\\\text{sulphate.}}}{3ZnSO_4} + \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{3Na_2CO_3} + \underset{\text{Water.}}{2H_2O} =$$

$$\underset{\substack{\text{Basic zinc}\\\text{carbonate.}}}{ZnCO_3,2Zn(HO)_2} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{3Na_2SO_4} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{2CO_2}$$

Zinc oxide (ZnO) is prepared either by burning the metal zinc in air, or by heating the basic zinc carbonate.

$$\underset{\substack{\text{Basic zinc}\\\text{carbonate.}}}{ZnCO_3,2Zn(HO)_2} = \underset{\substack{\text{Zinc}\\\text{oxide.}}}{3ZnO} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{2H_2O}$$

Zinc oxide under the name of *zinc-white* is used as a paint; it possesses this advantage over white-lead, that it is not blackened by sulphuretted hydrogen, whereas white-lead paint slowly blackens on account of the small quantities of sulphuretted hydrogen present in the air of towns and dwelling-houses. The covering power or "body" of zinc-white is, however, not nearly so great as that of white-lead.

Zinc acetate ($Zn(C_2H_3O_2)_2$) is prepared by the action of acetic acid on the basic zinc carbonate.

$$\underset{\substack{\text{Basic zinc}\\\text{carbonate.}}}{ZnCO_3,\ 2Zn(HO)_2} + \underset{\substack{\text{Acetic}\\\text{acid.}}}{6HC_2H_3O_2} =$$

$$\underset{\substack{\text{Zinc}\\\text{acetate.}}}{3Zn(C_2H_3O_2)_2} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{5H_2O}$$

Zinc valerianate ($Zn(C_5H_9O_2)_2$) is prepared by mixing strong and hot solutions of zinc sulphate and sodium valerianate; on cooling, the valerianate of zinc separates out as a crystalline white substance.

$$\underset{\substack{\text{Zinc}\\\text{sulphate.}}}{ZnSO_4} + \underset{\substack{\text{Sodium}\\\text{valerianate.}}}{2NaC_5H_9O_2} = \underset{\substack{\text{Zinc}\\\text{valerianate.}}}{Zn(C_5H_9O_2)_2} +$$

$$\underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4}$$

Tests for Zinc.

(i) Ammonium sulphide gives in neutral or alkaline zinc solutions a white precipitate of zinc sulphide (ZnS). This is a characteristic reaction, as zinc sulphide is the only white sulphide capable of being precipitated.

(ii) Solution of ammonia gives a white precipitate of zinc hydrate ($Zn(HO)_2$), readily soluble in excess of ammonia. From this solution in the excess of ammonia the zinc may be precipitated as the white sulphide by the addition of ammonium sulphide.

(iii) Caustic potash and caustic soda both precipitate the white zinc hydrate, which is soluble in excess of either alkali, provided it is free from carbonate.

(iv) Potassium ferrocyanide gives a white precipitate of zinc ferrocyanide.

CHAPTER V.

IRON.

Iron—Natural Compounds of Iron—Preparation and Properties of the Metal Iron—Cast Iron—Wrought Iron—Steel—Action of Acids on Iron—Preparation of the Ferrous and Ferric Salts—Tests for Iron—Distinguishing Tests between Ferrous and Ferric Salts.

IRON.

Symbol, Fe ; *formula*, Fe_2 ; *tetrad and dyad ;*
atomic weight, 56 ; *molecular weight*, 112.

Natural compounds of iron.—(i) The important ore *red hæmatite* consists of ferric oxide (Fe_2O_3) ; *brown hæmatite* is a ferric oxyhydrate. (ii) *Magnetic iron ore* or *loadstone* consists of ferroso-ferric oxide (FeO,Fe_2O_3). (iii) *Iron pyrites*, an iron ore widely distributed in nature, consists of iron disulphide (FeS_2). (iv) *Spathic iron ore* is an impure ferrous carbonate ($FeCO_3$); it is found in England mixed with clay, and constitutes *clay ironstone.* (v) Iron occurs to a small extent in the free state in nature in the form of meteorites, which are masses of iron that have fallen on to the earth's surface from extra-terrestrial space.

Preparation of the metal iron.—In connection with the preparation of this important metal separate descriptions must be given of the manufacturing processes employed in preparing cast iron, wrought iron, and steel.

Cast iron is obtained by first smelting or roasting the iron ore in air in order to completely convert it into ferric oxide, and then reducing the oxide to the metallic state by strongly heating with coke or coal in

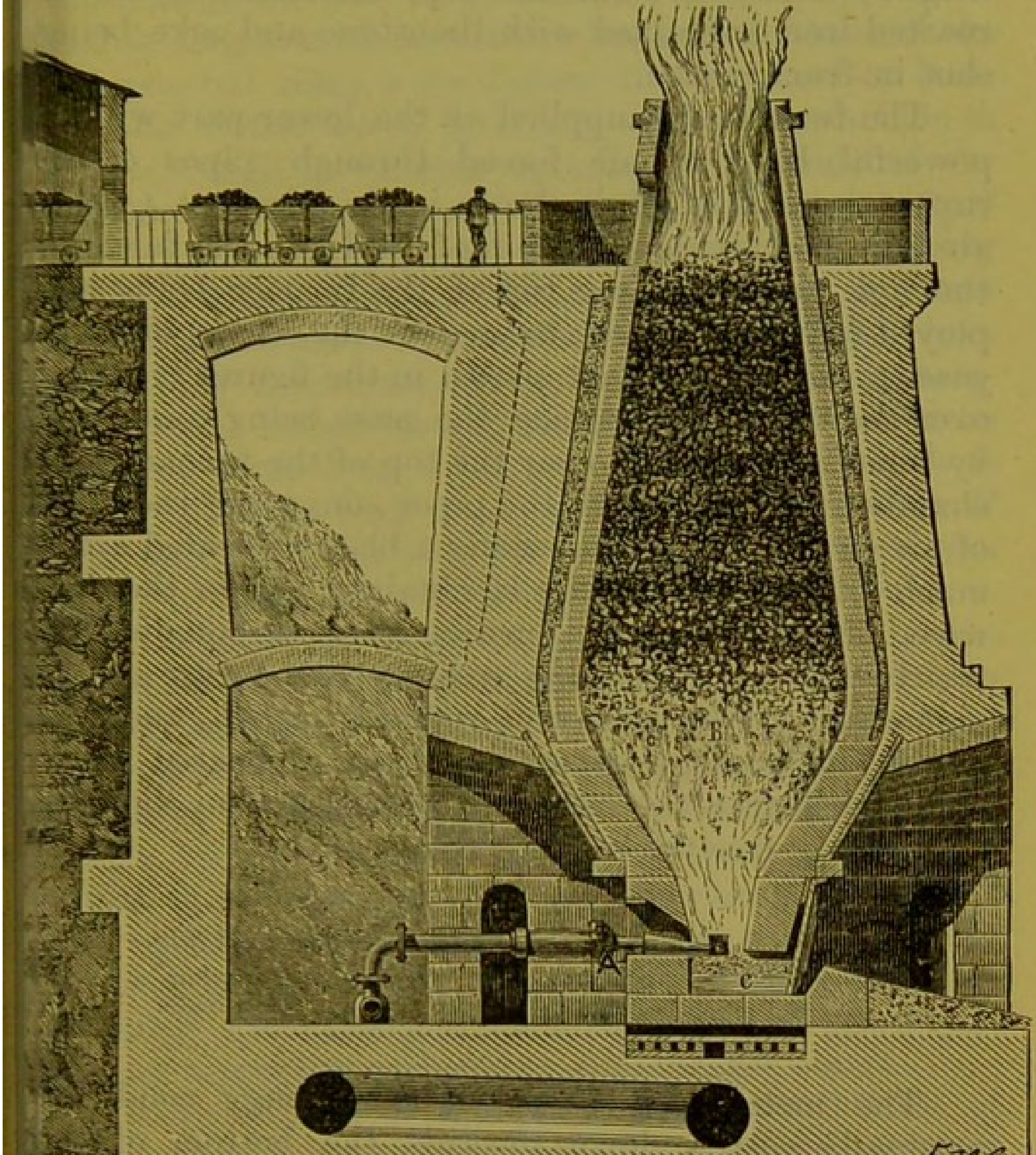


Fig. 23.—Section of a Blast Furnace.

presence of some limestone; this reduction of the ferric oxide requires a very high temperature, and is carried out in the *blast-furnace* (Fig. 23). This furnace is constructed of very solid masonry lined with firebricks, and reaches from 60 to 80 feet in height; it is fed from the top, alternate layers of roasted iron ore mixed with limestone and coke being shot in from trucks.

The furnace is supplied at the lower part with a powerful blast of air forced through pipes called tuyères, one of which is shown in the figure at A; this air is heated previous to being forced into the furnace, the hot gases from the top of the furnace being employed for this purpose; to prevent the escape of these gases a cap or hood (not shown in the figure) is placed over the top of the furnace, the gases being conducted by pipes issuing from near the top of the furnace to a chamber through which the pipes conveying the blast of air circulate; by thus using a blast of heated air a much higher temperature is obtained within the furnace. Some of the coke burning forms carbon dioxide, which with the remaining red-hot coke forms carbon monoxide, a very powerful reducing agent, and this gas in its passage over the lumps of heated ferric oxide abstracts the oxygen, forming carbon dioxide, and setting free the metal.

$$\underset{\text{Ferric oxide.}}{Fe_2O_3} + \underset{\text{Carbon monoxide.}}{3CO} = \underset{\text{Iron.}}{Fe_2} + \underset{\text{Carbon dioxide.}}{3CO_2}$$

The metal iron in a soft or spongy condition gradually settles down towards the bottom of the furnace, and arrived at the hottest part (B in figure) it melts, and trickling over the lumps of coke, takes up from 4 to 5 per cent. of the carbon into solution, and then settles down in the molten state at the bottom of the furnace (C in figure). The function of the limestone is to combine with impurities originally present in the iron ore (mainly silica and phosphates), which it does by forming a fusible silicate of calcium or *slag*, and so preventing the silica and phosphates from contaminating the iron, as they otherwise would do. This fusible slag also trickles down towards the base of the furnace, but being much lighter than the molten iron, it floats on the top of it, and is removed from time to time through a suitable opening in the side of the furnace. At the base of the furnace the molten cast iron is run out from time to time through an opening which is temporarily blocked up with clay; it is run into channels made in wet sand, and solidifies into bars technically known as *pig-iron*, which after being hammered and rolled constitutes *cast iron*. Cast iron contains from 4 to 5 per cent. of carbon, which is partly in union with some of the iron as carbide of iron, and partly in the free state as little crystals of graphite disseminated through the mass of the iron. These crystals of graphite have been formed by the carbon of the coke which dissolved in the molten iron and remained in the free state, and which crystallised out as graphite as the iron cooled and solidified. If cast iron be treated with diluted sulphuric or hydrochloric acid, the iron will dissolve in the acid with evolution of hydrogen, and the minute crystals of graphite will be left insoluble, whilst the carbon combined with the iron as carbide of iron will unite with some of the escaping hydrogen and form hydrocarbon gases possessing a peculiar and rather disagreeable odour.

Wrought iron is the purest commercial form of iron. It is cast iron deprived of the greater part of its carbon. It contains from 0·1 to 0·5 per cent. of carbon; but if more than 0·5 per cent. is present, it cannot be correctly termed wrought iron.

It is prepared by burning out the carbon from cast iron, which can be effected by melting the cast iron in the bed of a reverberatory furnace, and then, while a current of hot air is passing over the surface of the molten iron, well stirring or *puddling* it so as to freely expose it to the current of hot air; in this way the carbon of the cast iron is gradually burnt out, and as the less easily fusible wrought iron is produced, the metal assumes a pasty condition. The process is known as the "puddling process."

Steel is iron containing from 1 to 2 per cent. of carbon. Since it is intermediate in composition between cast iron (containing 4 to 5 per cent. of carbon) and wrought iron (containing 0·1 to 0·5 per cent. of carbon), it is obvious that it may be prepared (*a*) by abstracting part of the carbon from cast iron, till the percentage of carbon is reduced to 1—1·5; (*b*) by the addition of carbon to wrought iron, so as to raise the percentage to 1—1·5; (*c*) by mixing cast iron and wrought iron in such proportions that the mixture shall contain 1 to 1·5 per cent. of carbon. These are the three methods actually employed, the first being known as the Bessemer process, the second being the old or Cementation process, and the third being the Siemens-Martin process.

(*a*) *Bessemer process.*—This consists in burning out the greater part of the carbon in cast iron, by passing a current of air through melted cast iron. The Bessemer converter consists of a large egg-shaped vessel lined with fire-clay and provided with an opening at the base, through which a current of air can be forced; molten cast iron is run in, and the air then passed through it, the oxygen of the air rapidly burning away most of the carbon; some spiegeleisen (a variety of cast iron containing manganese) is then added to impart the necessary amount of carbon and manganese, a small quantity of the latter element notably increasing the hardness of the steel.

(*b*) *Cementation process.*—This, the old process for producing steel, consists in the addition of carbon to wrought iron, so as to raise the percentage of carbon to about 1 to 1·5. It is carried out by embedding bars of wrought iron in charcoal powder, and then heating to bright redness for some days; carbon is gradually taken up by the wrought iron, and steel is produced; the product is known as *cement-steel.*

(*c*) *Siemens-Martin process.*—This consists in fusing cast iron, and then adding to it wrought iron and a small quantity of spiegeleisen, until the percentage of carbon is brought to 1—1·5.

Properties of the metal iron.—*Cast iron* has a grey colour, and a crystalline or granular structure; as previously mentioned, its carbon exists partly in the form of minute crystals of graphite disseminated through the mass of the iron, and partly in union with some of the iron as a carbide of iron. Cast iron melts at a lower temperature than any other form of iron, but it is the most brittle form, owing partly to its granular structure, and partly to its homogeneity being interfered with by the crystals of graphite distributed through its mass; on account of its brittleness, articles of cast iron are not nearly so strong as those made of wrought iron or of steel. Cast iron contains from 4 to 5 per cent. of carbon; as the percentage of carbon diminishes in iron, the iron becomes less easily fusible, and its malleability increases; therefore steel and wrought iron are more difficult to fuse, and more malleable than cast iron.

Wrought iron is fibrous in structure, and therefore much stronger than the crystalline or granular cast iron, but the fibrous texture is apt to undergo a change into the granular condition when exposed to long-continued vibration; this explains the occasional sudden snapping of railway-carriage axles, the fibrous wrought iron of which they were made having become gradually changed into the granular and crystalline condition. All forms of iron are rendered extremely brittle by the presence of silica, sulphur or phosphorus, hence the importance of removing these impurities in the slag during the preparation of iron in the blast furnace. Pieces of wrought iron can be welded or joined together, by bringing their clean surfaces in contact at a red heat and then hammering them; to clean their surfaces from the film of oxide of iron, which is produced by the action of the air on the heated iron, the blacksmith uses some sand as a flux previous to hammering, the silica uniting with the oxide of iron to form a fusible silicate of iron, which is squeezed away during the process of hammering, and so allows of the absolutely clean metallic surfaces coming in contact and uniting.

Steel is of a pale grey colour, and capable of taking a high polish; it is finely granular, not fibrous in structure, and consequently is more brittle than wrought iron; it unites the hardness and fusibility of cast iron with the ductility and malleability of wrought iron. *Hard steel* is prepared by heating steel to redness and then rapidly cooling it by immersion in water; it is very brittle and highly elastic. To toughen or *temper* steel, it is again heated, and again rapidly cooled.

Reduced iron is pure iron in the form of powder, obtained by passing a stream of hydrogen over heated ferric oxide; the oxygen is abstracted as water, and the iron is left in a finely divided state.

$$\underset{\text{Ferric oxide.}}{Fe_2O_3} + \underset{\text{Hydrogen.}}{3H_2} = \underset{\text{Iron.}}{Fe_2} + \underset{\text{Water.}}{3H_2O}$$

All kinds of iron are magnetic, that is, capable of being attracted to and picked up by a magnet, and also capable of being magnetised; soft iron readily becomes magnetised when in contact with a magnet, but loses its magnetism when withdrawn from the magnet, whereas steel very slowly becomes magnetised, but when once magnetised, retains its magnetism for a long period.

Iron remains unchanged in dry air or oxygen at ordinary temperatures, but in moist air it readily unites with oxygen and moisture, forming reddish-brown *rust*, a ferric oxyhydrate. At a red-heat iron is more rapidly oxidised than by moist air at ordinary temperatures, as is well seen in the production of the forge-scales that collect around the blacksmith's anvil, which consist of the black magnetic oxide of iron.

Barff's process for the prevention of rusting of iron consists in coating the iron article with a film of the hard black magnetic oxide (ferroso-ferric oxide), which then effectually prevents further oxidation in damp air; to effect this a current of steam is passed for a few minutes over the iron article raised to a red-heat.

$$\underset{\text{Iron.}}{3Fe_2} + \underset{\text{Water.}}{8H_2O} = \underset{\substack{\text{Magnetic oxide}\\\text{of iron.}}}{2(FeO, Fe_2O_3)} + \underset{\text{Hydrogen}}{8H_2}$$

Action of acids on iron.—Dilute sulphuric acid acts on iron, forming ferrous sulphate and evolving hydrogen.

$$\underset{\text{Iron.}}{Fe_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Ferrous}\\\text{sulphate,}}}{2FeSO_4} + \underset{\text{Hydrogen.}}{2H_2}$$

Strong sulphuric acid, with heat, also acts on iron, but in this case with evolution of sulphur dioxide.

$$\underset{\text{Iron.}}{Fe_2} + \underset{\substack{\text{Sulphuric}\\\text{acid}}}{4H_2SO_4} = \underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{2FeSO_4} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2SO_2} + \underset{\text{Water.}}{4H_2O}$$

Hydrochloric acid acts on iron, forming ferrous chloride, and evolving hydrogen.

$$\underset{\text{Iron.}}{Fe_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{4HCl} = \underset{\substack{\text{Ferrous}\\\text{chloride.}}}{2FeCl_2} + \underset{\text{Hydrogen.}}{2H_2}$$

Nitric acid acts on iron, forming ferric nitrate, and evolving nitrogen dioxide.

$$\underset{\text{Iron.}}{Fe_2} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{8HNO_3} = \underset{\substack{\text{Ferric}\\\text{nitrate.}}}{Fe_2(NO_3)_6} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

IRON SALTS.

Two classes of iron salts exist, the ferrous and the ferric ; in the ferrous salts the iron is only exerting part of its atomicity, and acting as a dyad ; whereas in ferric salts it is exerting its full atomicity as a tetrad (*see* page 47).

FERROUS SALTS.

Ferrous sulphate ($FeSO_4$).—This salt is also known as *proto-sulphate of iron*, *green vitriol*, *copperas*, and *green copperas*. It is prepared (*a*) by the action of dilute sulphuric acid on iron—

$$\underset{\text{Iron.}}{Fe_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{2FeSO_4} + \underset{\text{Hydrogen ;}}{2H_2}$$

(*b*) by the action of dilute sulphuric acid on ferrous sulphide, this being the ordinary method employed for the preparation of sulphuretted hydrogen—

$$\underset{\substack{\text{Ferrous}\\\text{sulphide.}}}{\mathrm{FeS}} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{\mathrm{H_2SO_4}} = \underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{\mathrm{FeSO_4}} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen;}}}{\mathrm{H_2S}}$$

(*c*) by gently roasting iron pyrites (FeS_2) in the air.

If a strong aqueous solution of ferrous sulphate be poured into alcohol, the salt is precipitated in a granular condition, forming the granulated sulphate of iron (*Ferri sulphas granulata*, B. P.).

Both the ordinary ferrous sulphate and the granulated variety contain seven molecules of water of crystallisation ($FeSO_4$, $7H_2O$). By careful heating, six-sevenths of this water can be expelled, leaving the dried sulphate of iron (*Ferri sulphas exsiccata*, B. P.) of the composition ($FeSO_4$, H_2O). If further heat be employed, so as to expel this last molecule of water, then the salt is decomposed, ferric oxide being left and Nordhausen sulphuric acid evolved.

If ferrous sulphate be exposed for some time to the air, it loses its green colour and becomes brown, due to absorption of oxygen and conversion into ferric oxysulphate ($Fe_2O(SO_4)_2$).

Ferrous sulphate is very largely employed in the preparation of black writing-ink, the black colour of which is due to tannate of iron in a finely-divided state suspended in weak mucilage, the tannic acid being furnished by an infusion of galls.

Ferrous chloride ($FeCl_2$).—This salt, also known as protochloride of iron, is prepared by the action of hydrochloric acid on iron.

$$\underset{\text{Iron.}}{\mathrm{Fe_2}} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{\mathrm{4HCl}} = \underset{\substack{\text{Ferrous}\\\text{chloride.}}}{\mathrm{2FeCl_2}} + \underset{\text{Hydrogen}}{\mathrm{2H_2}}$$

Ferrous carbonate ($FeCO_3$) is prepared by mixing together solutions of ferrous sulphate and potassium carbonate, when it is thrown down as a precipitate.

$$\underset{\substack{\text{Ferrous}\\\text{sulphate}}}{FeSO_4} + \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} = \underset{\substack{\text{Ferrous}\\\text{carbonate.}}}{FeCO_3} + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4}$$

Ferrous carbonate is, when first precipitated, of a white colour, but quickly turns green, and ultimately brown from absorption of oxygen from the air, and conversion into ferric oxyhydrate.

The so-called Griffith's mixture (*Mistura ferri composita*, B. P.) contains green ferrous carbonate in suspension; the absorption of oxygen from the air may be, to a certain extent, prevented by mixing dried ferrous carbonate with sugar (*Ferri carbonas saccharata*, B. P.). Ferrous carbonate is appreciably soluble in water containing carbon dioxide in solution, such being the way in which the iron is kept in solution in *chalybeate* spring waters. If such a water be exposed to the air for some time, it becomes turbid from the formation and deposition of ferric hydrate.

Ferrous sulphide (FeS) is prepared by heating a mixture of iron filings and sulphur, or by rubbing a stick of roll sulphur against a bar of iron at a bright red heat.

Ferrous iodide (FeI_2) is prepared by warming together iron wire, iodine, and water.

Ferrous phosphate ($Fe_3(PO_4)_2$) is prepared by mixing together solutions of ferrous sulphate, sodium phosphate, and sodium bicarbonate.

$$\underset{\substack{\text{Ferrous}\\\text{sulphate}}}{3FeSO_4} + \underset{\substack{\text{Sodium}\\\text{phosphate.}}}{2Na_2HPO_4} + \underset{\substack{\text{Sodium}\\\text{bicarbonate.}}}{2NaHCO_3} =$$

$$\underset{\substack{\text{Ferrous}\\\text{phosphate.}}}{Fe_3(PO_4)_2} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{3Na_2SO_4} + \underset{\substack{\text{Carbon.}\\\text{dioxide.}}}{2CO_2} + \underset{\text{Water}}{2H_2O}$$

The ferrous phosphate comes down at first as a white precipitate, quickly changing to a bluish colour. The sodium bicarbonate is added to prevent the formation of free sulphuric acid, which would keep some of the ferrous phosphate in solution.

Ferrous arseniate ($Fe_3(AsO_4)_2$) is prepared by mixing together solutions of ferrous sulphate, sodium arseniate, and sodium bicarbonate.

$$\underset{\substack{\text{Ferrous}\\\text{sulphate}}}{3\mathrm{FeSO_4}} + \underset{\substack{\text{Sodium}\\\text{arseniate}}}{2\mathrm{Na_2HAsO_4}} + \underset{\substack{\text{Sodium}\\\text{bicarbonate.}}}{2\mathrm{NaHCO_3}} =$$

$$\underset{\substack{\text{Ferrous}\\\text{arseniate.}}}{\mathrm{Fe_3(AsO_4)_2}} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{3\mathrm{Na_2SO_4}} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{2\mathrm{CO_2}} + \underset{\text{Water.}}{2\mathrm{H_2O}}$$

The ferrous arseniate comes down at first as a white precipitate, quickly changing to a greenish colour. The sodium bicarbonate is added for a similar reason to that given in connection with ferrous phosphate.

FERRIC SALTS.

Ferric chloride, or **perchloride of iron** (Fe_2Cl_6).—This may be prepared (*a*) by passing chlorine over heated iron—

$$\underset{\text{Iron.}}{\mathrm{Fe_2}} + \underset{\text{Chlorine}}{3\mathrm{Cl_2}} = \underset{\text{Ferric chloride;}}{\mathrm{Fe_2Cl_6}}$$

(*b*) by passing chlorine through a solution of ferrous chloride—

$$\underset{\text{Ferrous chloride.}}{2\mathrm{FeCl_2}} + \underset{\text{Chlorine}}{\mathrm{Cl_2}} = \underset{\text{Ferric chloride;}}{\mathrm{Fe_2Cl_6}}$$

(*c*) by warming a solution of ferrous chloride with hydrochloric and nitric acids—

$$\underset{\substack{\text{Ferrous}\\\text{chloride.}}}{6FeCl_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} + \underset{\substack{\text{Nitric}\\\text{acid}}}{2HNO_3} = \underset{\substack{\text{Ferric}\\\text{chloride.}}}{3Fe_2Cl_6} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

This is the process employed in the preparation of the solution of perchloride of iron used in medicine (*Liquor ferri perchloridi*, B. P.). It really consists in the passage of chlorine into ferrous chloride, since the action of the nitric acid is to oxidise the hydrogen of the hydrochloric acid to water, thus liberating the chlorine, the nitrogen of the nitric acid being evolved as nitrogen dioxide.

Ferric sulphate, or **persulphate of iron** ($Fe_2(SO_4)_3$) is prepared by warming together a solution of ferrous sulphate with sulphuric and nitric acids.

$$\underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{6FeSO_4} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} =$$

$$\underset{\substack{\text{Ferric}\\\text{sulphate.}}}{3Fe_2(SO_4)_3} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

The action of the nitric acid is similar to that described in the last process for the preparation of ferric chloride.

Ferric nitrate or **pernitrate of iron** ($Fe_2(NO_3)_6$) is prepared by the action of nitric acid on iron.

$$\underset{\text{Iron.}}{Fe_2} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{8HNO_3} = \underset{\substack{\text{Ferric}\\\text{nitrate.}}}{Fe_2(NO_3)_6} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

Ferric acetate or **peracetate of iron** ($Fe_2(C_2H_3O_2)_6$) is prepared by dissolving freshly-precipitated ferric hydrate in glacial acetic acid.

$$\underset{\substack{\text{Ferric}\\\text{hydrate.}}}{Fe_2(HO)_6} + \underset{\text{Acetic acid.}}{6HC_2H_3O_2} = \underset{\text{Ferric acetate.}}{Fe_2(C_2H_3O_2)_6} + \underset{\text{Water.}}{6H_2O}$$

Ferric hydrate ($Fe_2(HO)_6$) is prepared by precipitating a solution of ferric sulphate or ferric chloride with an alkali, caustic soda being generally employed for the sake of cheapness.

$$\underset{\substack{\text{Ferric}\\\text{sulphate.}}}{Fe_2(SO_4)_3} + \underset{\substack{\text{Sodium}\\\text{hydrate.}}}{6NaHO} = \underset{\substack{\text{Ferric}\\\text{hydrate.}}}{Fe_2(HO)_6} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{3Na_2SO_4}$$

Freshly precipitated ferric hydrate is used as an antidote in cases of poisoning by arsenic, the reaction between the ferric hydrate and the arsenic resulting in the formation of the insoluble ferrous arseniate.

$$\underset{\text{Ferric hydrate.}}{2(Fe_2(HO)_6)} + \underset{\text{Arsenic.}}{As_2O_3} = \underset{\text{Ferrous arseniate.}}{Fe_3(AsO_4)_2} + \underset{\substack{\text{Ferrous}\\\text{hydrate.}}}{Fe(HO)_2} + \underset{\text{Water.}}{5H_2O}$$

Freshly precipitated ferric hydrate dissolves in a solution of perchloride of iron, forming a dark red solution of basic chloride of iron; if this solution be placed in a dialyzer, the greater proportion of the hydrochloric acid of this basic chloride passes through the dialyzer, leaving a still more basic chloride of iron, which constitutes the solution of dialyzed iron used in medicine (*Liquor ferri dialysatus*, B. P.).

Freshly precipitated ferric hydrate is also used in the preparation of the iron scale compounds, which are uncrystallisable bodies obtained in the solid form by the evaporation of their solutions to a syrup, and then allowing the syrup to dry in scales. Citrate of iron and ammonium (*Ferri et ammoniæ citras*, B. P.)

is prepared by dissolving ferric hydrate in a solution of citric acid, adding ammonia, evaporating to a syrup, and drying in scales; it is a double citrate of iron and ammonium. Citrate of iron and quinine (*Ferri et quinæ citras*, B. P.) is prepared by dissolving ferric hydrate and quinine in a solution of citric acid, adding ammonia (not in excess, or the quinine would be precipitated), evaporating to a syrup, and drying in scales; it is a triple citrate of iron, quinine, and ammonium. Tartarated iron (*Ferrum tartaratum*, B. P.) is prepared by dissolving ferric hydrate in a solution of potassium acid tartrate, evaporating to a syrup, and drying in scales; it is a double tartrate of iron and potassium.

Alkaline bicarbonates, which are incompatible with most iron preparations, can be prescribed with citrate of iron and ammonium, and with tartarated iron, without the iron being precipitated; they would not be compatible with citrate of iron and quinine, as the quinine would be thrown down by alkaline carbonates.

Ferric oxyhydrate ($Fe_2O_2(HO)_2$) si prepared by drying ferric hydrate at 100° C. It is the *Ferri peroxidum hydratum*, B. P.

$$\underset{\substack{\text{Ferric}\\\text{hydrate}}}{Fe_2(HO)_6} = \underset{\substack{\text{Ferric}\\\text{oxyhydrate.}}}{Fe_2O_2(HO)_2} + \underset{\text{Water.}}{2H_2O}$$

Ferric oxide (Fe_2O_3) is prepared by further heating ferric oxyhydrate.

$$\underset{\substack{\text{Ferric}\\\text{oxyhydrate.}}}{Fe_2O_2(HO)_2} = \underset{\substack{\text{Ferric}\\\text{oxide.}}}{Fe_2O_3} + \underset{\text{Water.}}{H_2O}$$

It may also be prepared by roasting crystals of ferrous sulphate until fumes of the Nordhausen sulphuric acid cease to be evolved; this variety of ferric oxide passes under the names of *red oxide of iron*, *mineral rouge*, *Venetian red*, *colcothar*, and *crocus*.

Ferroso-ferric oxide (FeO,Fe_2O_3) is also known as black oxide of iron and magnetic oxide of iron. It may be prepared (*a*) by passing steam over red-hot iron—

$$\underset{\text{Iron.}}{3Fe_2} + \underset{\text{Water.}}{8H_2O} = \underset{\text{Ferroso-ferric oxide.}}{2(FeO, Fe_2O_3)} + \underset{\text{Hydrogen ;}}{8H_2}$$

(*b*) by precipitating a mixed solution of ferric and ferrous sulphates with caustic soda, when the black ferroso-ferric hydrate is thrown down—

$$\underset{\substack{\text{Ferric}\\\text{sulphate.}}}{Fe_2(SO_4)_3} + \underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{FeSO_4} + \underset{\substack{\text{Sodium}\\\text{hydrate.}}}{8NaHO} =$$

$$\underset{\text{Ferroso-ferric hydrate.}}{Fe(HO)_2, Fe_2(HO)_6} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{4Na_2SO_4}$$

This when heated in a closed vessel loses water, and yields the ferroso-ferric oxide.

$$\underset{\text{Ferroso-ferric hydrate.}}{Fe(HO)_2, Fe_2(HO)_6} = \underset{\substack{\text{Ferroso-ferric}\\\text{oxide.}}}{FeO, Fe_2O_3} + \underset{\text{Water.}}{4H_2O}$$

(*c*) The black *forge-scales*, which collect around the blacksmith's anvil, consist of the ferroso-ferric oxide.

Iron and cyanogen compounds. (*See* pages 386, 392.)

General methods of raising ferrous salts to the ferric state.—(*a*) The passage of chlorine gas through a solution of a ferrous salt raises it to the ferric state, thus :

$$\underset{\substack{\text{Ferrous}\\\text{chloride.}}}{2FeCl_2} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Ferric}\\\text{chloride.}}}{Fe_2Cl_6}$$

$$\underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{6FeSO_4} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\substack{\text{Ferric}\\\text{sulphate.}}}{2Fe_2(SO_4)_3} + \underset{\substack{\text{Ferric}\\\text{chloride.}}}{Fe_2Cl_6}$$

(*b*) Nitric acid with heat will raise any ferrous salt to the ferric state, thus:

$$\underset{\substack{\text{Ferrous}\\\text{chloride.}}}{6FeCl_2} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{8HNO_3} = \underset{\substack{\text{Ferric}\\\text{chloride.}}}{2Fe_2Cl_6} + \underset{\substack{\text{Ferric}\\\text{nitrate.}}}{Fe_2(NO_3)_6} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

$$\underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{6FeSO_4} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{8HNO_3} = \underset{\substack{\text{Ferric}\\\text{sulphate.}}}{2Fe_2(SO_4)_3} + \underset{\substack{\text{Ferric}\\\text{nitrate.}}}{Fe_2(NO_3)_6} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

(*c*) Long-continued exposure to air will convert most, and heating in the air will convert all ferrous salts into ferric salts.

General methods of reducing ferric salts to the ferrous state.—(*a*) If to a solution of a ferric salt some zinc be added, and then sufficient hydrochloric acid to act on the zinc and liberate hydrogen, the nascent hydrogen will reduce the ferric salt to the ferrous state.

$$\underset{\substack{\text{Ferric}\\\text{chloride.}}}{Fe_2Cl_6} + \underset{\text{Hydrogen.}}{H_2} = \underset{\substack{\text{Ferrous}\\\text{chloride.}}}{2FeCl_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl}$$

(*b*) If sulphuretted hydrogen be passed through a solution of a ferric salt, the latter will be reduced to the ferrous state, sulphur being thrown down.

$$\underset{\text{Ferric chloride.}}{2Fe_2Cl_6} + \underset{\text{Sulphuretted hydrogen.}}{2H_2S} = \underset{\text{Ferrous chloride.}}{4FeCl_2} + \underset{\text{Hydrochloric acid.}}{4HCl} + \underset{\text{Sulphur.}}{S_2}$$

(*c*) If to a solution of a ferric salt, solution of stannous chloride be added, the former will be reduced to the ferrous state, the latter being raised to the stannic state.

$$\underset{\text{Ferric chloride.}}{Fe_2Cl_6} + \underset{\text{Stannous chloride.}}{SnCl_2} = \underset{\text{Ferrous chloride.}}{2FeCl_2} + \underset{\text{Stannic chloride.}}{SnCl_4}$$

Tests for iron occurring as a ferrous salt.

(i) Ammonium sulphide gives a black precipitate of ferrous sulphide.

(ii) Sulphuretted hydrogen gives no precipitate with a ferrous salt. This negative reaction is of value in the separation from iron of metals precipitated by sulphuretted hydrogen.

(iii) Potassium ferrocyanide (K_4FeCy_6) gives with ferrous salts a precipitate, at first almost white, but rapidly changing to a light blue colour, owing to absorption of oxygen from the air. This precipitate is a double ferrocyanide of iron in the ferrous state and potassium (FeK_2FeCy_6).

(iv) Potassium ferricyanide ($K_6Fe_2Cy_{12}$) gives with ferrous salts a dark blue precipitate of Turnbull's blue ($Fe_3Fe_2Cy_{12}$), exactly resembling in colour Prussian blue.

(v) Potassium sulphocyanide gives no colour with ferrous salts, provided they are quite free from ferric salts.

(vi) Alkalies, such as ammonia, potash, and soda, partially precipitate ferrous salts as ferrous hydrate, the precipitate being white at first, but rapidly turning to a greenish colour from absorption of oxygen from the air.

Tests for iron occurring as a ferric salt.

(i) Ammonium sulphide reduces a ferric salt to the ferrous state, producing a mixed precipitate of the black ferrous sulphide and sulphur.

(ii) Sulphuretted hydrogen passed through a solution of a ferric salt reduces it to the ferrous state, sulphur being precipitated.

(iii) Potassium ferrocyanide (K_4FeCy_6) gives a dark blue precipitate of Prussian blue ($Fe_4(FeCy_6)_3$).

(iv) Potassium ferricyanide gives with a solution of a ferric salt a brownish colour, no precipitate being produced.

(v) Potassium sulphocyanide gives with solutions of ferric salts a deep blood-red colour, due to the formation of the soluble ferric sulphocyanide.

(vi) The alkalies, ammonia, potash, and soda, precipitate from ferric solutions the reddish-brown ferric hydrate.

Distinguishing Tests between Ferrous and Ferric Salts.

	Ferrous Salts.	Ferric Salts,
Potassium ferrocyanide.	White precip., rapidly changing to light blue.	Dark blue precip. of Prussian blue.
Potassium ferricyanide.	Dark blue precip. of Turnbull's blue.	No precip.; brownish colour produced.
Potassium sulphocyanide.	No change of colour.	Dark blood-red colour.
Alkalies . .	Whitish precip., rapidly changing to green.	Reddish-brown precipitate.

CHAPTER VI.

MANGANESE—CHROMIUM—COBALT—NICKEL—COPPER.

Manganese—Manganese Salts—Tests for Manganese—Chromium—Chromium Compounds—Test for Chromium—Cobalt—Nickel—Copper—Natural Compounds of Copper—Preparation and Properties of the Metal Copper—Action of Acids on Copper—Preparation of the Copper Salts—Tests for Copper.

MANGANESE.

Symbol, Mn; *formula,* Mn_2; *hexad; atomic weight,* 55; *molecular weight,* 110.

The chief natural compound of manganese is the *black oxide of manganese* or *pyrolusite* (MnO_2). Manganese exerts its full atomicity as a hexad in the manganates and permanganates; in the black oxide of manganese it only exerts the atomicity of a tetrad, whilst in manganous sulphate ($MnSO_4$) and manganous chloride it acts as a dyad only. The metal is of but little interest.

Manganous sulphate ($MnSO_4$). — When manganese dioxide is heated with strong sulphuric acid, oxygen is evolved and manganous sulphate produced.

$$\underset{\text{Manganese dioxide.}}{2MnO_2} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Manganous sulphate.}}{2MnSO_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}$$

Manganous chloride ($MnCl_2$).—This compound is obtained as a bye-product in the preparation of chlorine from manganese dioxide and hydrochloric acid under the influence of heat. (*See* page 132.)

Potassium manganate and **permanganate.**—The latter of these compounds is the most important manganese preparation, from the medical point of view. (For their preparation and properties *see* pages 218, 219.)

Tests for Manganese.

(i) Ammonium sulphide throws down a flesh-coloured precipitate of manganous sulphide.

(ii) Solution of ammonia gives a white precipitate of manganous hydrate, which darkens on exposure to the air, owing to absorption of oxygen and conversion into the black oxide of manganese.

(iii) If any manganese salt is fused with sodium carbonate and potassium nitrate on a piece of platinum foil, the green sodium manganate is obtained; if this be boiled with water, a red solution is obtained, owing to the conversion of the manganate into the permanganate.

CHROMIUM.

Symbol, Cr; *formula*, Cr_2; *hexad*; *atomic weight*, 52·2; *molecular weight*, 104·4.

The principal compound of chromium occurring in nature is *chrome iron ore* (FeO, Cr_2O_3). The metal is only of scientific interest.

Potassium chromate (K_2CrO_4).—This compound, known also as *yellow chromate of potash*, is prepared from chrome iron ore by fusing it with potassium carbonate and potassium nitrate; ferric oxide and potassium chromate result, the latter being dissolved out by boiling the fused mass with water.

Potassium dichromate (K_2CrO_4,CrO_3).—This is more commonly called *bichromate of potash* or, on account of its colour, *red chromate of potash.* It is prepared by acidifying a solution of potassium chromate with sulphuric acid, concentrating and allowing the dichromate to crystallise out.

$$\underset{\text{Potassium chromate.}}{2K_2CrO_4} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Potassium dichromate.}}{K_2CrO_4, CrO_3} + \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Water.}}{H_2O}$$

Chromic oxide (Cr_2O_3).—This, the green oxide of chromium, may be prepared by strongly heating potassium dichromate; the potassium chromate portion remains unchanged by the heat, whilst the chromic anhydride (CrO_3) portion is decomposed into chromic oxide and oxygen.

$$\underset{\text{Potassium dichromate.}}{4(K_2CrO_4,CrO_3)} = \underset{\text{Potassium chromate.}}{4K_2CrO_4} + \underset{\text{Chromic oxide.}}{2Cr_2O_3} + \underset{\text{Oxygen.}}{3O_2}$$

Chromic anhydride (CrO_3).—This, the red oxide of chromium, is obtained by mixing together equal volumes of a saturated solution of potassium dichromate and strong sulphuric acid; as the mixture cools, the chromic anhydride crystallises out in long slender needles of a bright crimson colour.

$$\underset{\text{Potassium dichromate.}}{K_2CrO_4, CrO_3} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Chromic anhydride.}}{2CrO_3} + \underset{\text{Potassium sulphate.}}{K_2SO_4} + \underset{\text{Water.}}{H_2O}$$

Chromic anhydride is used as a powerful caustic under the name of chromic acid (*Acidum chromicum*, B. P.); it is the anhydride of chromic acid, into which it is converted by dissolving in water.

$$\underset{\text{Chromic anhydride.}}{CrO_3} + \underset{\text{Water.}}{H_2O} = \underset{\text{Chromic acid.}}{H_2CrO_4}$$

Chrome alum ($Cr_2(SO_4)_3$, K_2SO_4).—This is prepared by heating potassium dichromate with sulphuric acid in presence of some reducing agent such as alcohol, the alcohol uniting with the excess of oxygen of the dichromate to form acetic acid, the sulphuric acid then uniting with the two metals to form the double sulphate.

Test for Chromium.

If a chromium salt be fused with sodium carbonate and potassium nitrate on a piece of platinum foil, the yellow sodium chromate is formed; on dissolving this in boiling water, and acidifying the solution with acetic acid, a yellow precipitate (lead chromate) will be obtained on the addition of lead acetate.

COBALT AND NICKEL.

These metals exist in nature combined with arsenicum and with sulphur. Their compounds are not used in medicine. Cobalt salts are used for staining glass of a dark blue colour. Nickel is mainly employed in the preparation of certain alloys; the principal alloy is *German silver* or *nickel silver*, which consists of copper, zinc, and nickel. Nickel-plating, which is now largely employed, consists in coating metallic articles with a thin layer of nickel by means of an electric current;

the coating of nickel improves the appearance of the articles; it rusts or tarnishes but very slowly, and on articles made of iron, effectually prevents the rusting of the iron.

COPPER.

Symbol, Cu; *formula*, Cu_2; *dyad; atomic weight*, 63·5; *molecular weight*, 127.

Natural compounds of copper. — (i) The commonest copper ore is *copper pyrites*, a double sulphide of copper and iron ($CuFeS_2$), containing in addition some sulphide of arsenic. (ii) *Cuprite* or *red copper ore* consists of cuprous oxide (Cu_2O). (iii) *Malachite* is a double carbonate and hydrate of copper ($CuCO_3,Cu(HO)_2$). (iv) The metal copper is found to a certain extent free in nature, occurring especially in North America.

Preparation of the metal copper.—The separation of the metal copper from copper pyrites is a lengthy and complicated process; briefly described, the copper ore is first smelted in a reverberatory furnace to expel sulphur and arsenic, and to form copper oxide, which is then reduced to the metallic state by roasting with some form of carbon. Chemically pure copper may be obtained by passing hydrogen over copper oxide raised to a red heat.

$$\underset{\text{Copper oxide.}}{2CuO} + \underset{\text{Hydrogen.}}{2H_2} = \underset{\text{Copper.}}{Cu_2} + \underset{\text{Water.}}{2H_2O}$$

Properties of the metal copper.—Copper is one of the few metals possessing a distinctive colour—it is bright red; it is a very malleable and ductile metal, and is an extremely good conductor of both heat and electricity, hence its employment for lightning conductors. Copper remains unchanged in dry air, but in moist air it becomes gradually covered with a green layer of a basic copper carbonate, frequently mistaken for verdigris, which is an oxyacetate of copper. Water can be boiled in copper vessels without attacking them, but a solution of common salt slowly attacks copper, forming a green oxychloride of copper, and vinegar still more readily acts on copper vessels forming verdigris (oxyacetate of copper); hence the danger of using copper vessels for culinary purposes, the copper salts produced by the action of common salt and vinegar being poisonous. Copper does not decompose steam, even at a bright red heat; if copper be heated to redness in the air, it readily oxidises, forming the black copper oxide (CuO). The metal copper is deposited from its solutions by either iron or zinc, and it is also deposited at the negative pole when an electric current is passed through a solution of copper sulphate, a process employed in producing electrotypes or copies of objects in copper.

Copper enters into the formation of several very useful alloys. *Brass* contains about 70 parts of copper to 30 parts of zinc; a larger proportion of zinc yields an alloy of a pale yellow colour, known as *Muntz metal*, largely used for covering wooden ships; by increasing the amount of copper, and adding a little tin, *Dutch metal* is obtained. *Bronze*, *gun-metal*, and *bell-metal* are alloys of copper and tin containing from 80 to 90 per cent. of copper; *speculum metal* is a hard white alloy of 2 parts of copper to 1 part of tin; it is capable of taking a high polish, and is used for the mirrors of reflecting telescopes. *German silver* or *nickel silver* is an alloy of copper, zinc, and nickel; all silver articles and silver coins contain some copper, in order to render the silver harder; *aluminium bronze* or *aluminium gold* is an alloy of copper and aluminium.

Action of acids on copper.—Dilute sulphuric acid has no action on the metal copper. Strong sulphuric acid with heat readily acts on copper, forming the sulphate and evolving sulphur dioxide gas.

$$\underset{\text{Copper.}}{Cu_2} + \underset{\text{Sulphuric acid.}}{4H_2SO_4} = \underset{\text{Copper sulphate.}}{2CuSO_4} +$$

$$\underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Water.}}{4H_2O}$$

Nitric acid readily acts on copper forming copper nitrate, with evolution of nitrogen dioxide.

$$\underset{\text{Copper.}}{Cu_3} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Copper nitrate.}}{3Cu(NO_3)_2} +$$

$$\underset{\text{Nitrogen dioxide.}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

Hydrochloric acid has no action on the metal copper.

COPPER SALTS.

Copper forms two classes of compounds, *cupric* and *cuprous;* in both classes the copper is acting as a dyad, but all cuprous compounds contain in the molecule two atoms of copper, and as these two atoms are linked together by an atom-fixing power of each, the copper atoms only exert towards other elements the atom-fixing power of a monad; this will be rendered evident by inspection of the following graphic formula of cupric chloride ($CuCl_2$) and cuprous chloride (Cu_2Cl_2).

$$\underset{\text{Cupric chloride.}}{Cl - Cu - Cl} \qquad \underset{\text{Cuprous chloride.}}{Cl - Cu - Cu - Cl}$$

Copper sulphate ($CuSO_4$).—This, the commonest salt of copper, is also known as *blue vitriol* and *bluestone.* It is prepared (*a*) by the action of strong sulphuric acid on the metal copper—

$$\underset{\text{Copper.}}{Cu_2} + \underset{\text{Sulphuric acid.}}{4H_2SO_4} = \underset{\text{Copper sulphate.}}{2CuSO_4} + \underset{\text{Sulphur dioxide.}}{2SO_2} + \underset{\text{Water;}}{4H_2O}$$

(*b*) by the action of dilute sulphuric acid on cupric oxide—

$$\underset{\text{Cupric oxide.}}{CuO} + \underset{\text{Sulphuric acid.}}{H_2SO_4} = \underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Water;}}{H_2O}$$

(*c*) by roasting copper pyrites in the air, by which process it is obtained mixed with sulphate of iron.

Copper sulphate in its crystalline condition contains five molecules of water of crystallisation ($CuSO_4, 5H_2O$); these can be expelled by heat leaving the anhydrous copper sulphate ($CuSO_4$) which is of a white colour; if this anhydrous copper sulphate is shaken with liquids containing water, it unites with the water forming the blue crystalline variety, and hence becomes a valuable test for the detection of water in liquids which should, if pure, be free from it, such as absolute alcohol.

Cupric oxide (CuO).—This, the black copper oxide, may be obtained (*a*) by roasting the metal copper in air, (*b*) by heating copper nitrate—

$$\underset{\text{Copper nitrate.}}{2Cu(NO_3)_2} = \underset{\text{Cupric oxide.}}{2CuO} + \underset{\text{Nitrogen tetroxide.}}{2N_2O_4} + \underset{\text{Oxygen;}}{O_2}$$

(*c*) by adding caustic soda to a solution of copper sulphate to precipitate the light blue copper hydrate ($Cu(HO)_2$), and then boiling the liquid, when the copper hydrate decomposes into cupric oxide and water.

$$\underset{\text{Copper hydrate.}}{Cu(HO)_2} = \underset{\text{Cupric oxide.}}{CuO} + \underset{\text{Water.}}{H_2O}$$

Cuprous oxide (Cu_2O).—This, the red oxide of copper, is best prepared by boiling a mixed solution of copper sulphate, grape sugar, and caustic potash or soda; in the absence of the grape sugar, cupric oxide (CuO) would be thrown down, but the grape sugar possesses the property of abstracting one-half of the oxygen from the cupric oxide, with the consequent formation and precipitation of the red cuprous oxide. This constitutes the test for sugar in diabetic urine.

Copper nitrate ($Cu(NO_3)_2$) is prepared by the action of nitric acid on the metal copper.

$$\underset{\text{Copper.}}{Cu_3} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Copper nitrate.}}{3Cu(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

Copper oxyacetate (verdigris) ($Cu_2O(C_2H_3O_2)_2$) is prepared by exposing copper to the fumes of acetic acid and the action of the air.

Copper arsenite (Scheele's green) ($CuHAsO_3$) is prepared by mixing solutions of copper sulphate and sodium arsenite, when it is thrown down as a bright green precipitate.

$$\underset{\text{Copper sulphate.}}{CuSO_4} + \underset{\text{Sodium arsenite.}}{Na_2HAsO_3} = \underset{\text{Scheele's green.}}{CuHAsO_3} + \underset{\text{Sodium sulphate.}}{Na_2SO_4}$$

Scheele's green is very poisonous, mainly on account of the arsenic contained in it; it is a pigment frequently employed in the colouring of wall-papers, book-covers, etc. For the methods of detecting it in wall-papers, etc., *see* pages 318, 319, 321.

Tests for Copper.

(i) Sulphuretted hydrogen passed into copper solutions gives a black precipitate of copper sulphide (CuS).

(ii) Ammonium sulphide gives a similar precipitate of the black copper sulphide.

(iii) Potassium ferrocyanide gives a reddish-brown precipitate of copper ferrocyanide (Cu_2FeCy_6). This is the most delicate test for copper, as an extremely dilute solution of a copper salt is tinted reddish-brown on the addition of potassium ferrocyanide.

(iv) Solution of ammonia gives a light blue precipitate of copper hydrate ($Cu(HO)_2$), readily soluble in excess of ammonia and yielding an intensely dark-blue solution. This is a very delicate test for copper salts.

(v) Solution of caustic potash or caustic soda produces a light blue precipitate of copper hydrate, not soluble in excess of the fixed alkali; on boiling the liquid, the light blue precipitate turns black, due to decomposition of the copper hydrate into cupric oxide and water.

(vi) A piece of bright steel, such as the polished steel blade of a knife, if immersed in a solution of a copper salt, becomes in a short time coloured with a reddish deposit of the metal copper upon it. This is a ready and useful test for ascertaining whether a blue liquid contains copper or not.

CHAPTER VII.

MERCURY.

Mercury—Occurrence in Nature—Preparation and Properties of the Metal Mercury—Action of Acids on Mercury—Preparation of the Mercurous and Mercuric Salts—Test for Mercury—Distinguishing Tests between Mercurous and Mercuric Salts.

MERCURY.

Symbol, Hg ; *formula*, Hg ; *dyad ; atomic weight*, 200 ; *molecular weight*, 200.

Natural compounds of mercury.— (i) The chief natural compound of mercury is *cinnabar*, a sulphide of mercury (HgS), which is found in masses of a dark red colour. (ii) Mercury is occasionally found in the free state in small quantities.

Preparation of the metal mercury.—It is obtained from cinnabar by heating it with quicklime in retorts, when double decomposition first takes place between the cinnabar and the lime, resulting in the formation of mercuric oxide and calcium sulphide.

$$\underset{\text{Cinnabar.}}{HgS} + \underset{\text{Lime.}}{CaO} = \underset{\substack{\text{Mercuric}\\\text{oxide.}}}{HgO} + \underset{\substack{\text{Calcium}\\\text{sulphide.}}}{CaS}$$

The mercuric oxide is then decomposed by the heat into mercury and oxygen, the mercury distilling over, and being condensed in a suitable receiver.

Mercury may also be obtained by roasting cinnabar in excess of air, and passing the resulting vapours of mercury and sulphur dioxide through a series of condensing chambers to condense the mercury.

Properties of the metal mercury.—At ordinary temperatures mercury is a heavy lustrous liquid; it is the only metal that is liquid at ordinary temperatures, with the exception of the rare metal gallium; it is commonly known as *quicksilver*, on account of its possessing a white colour like silver, and from its being liquid. Its specific gravity is 13·55; it solidifies at —40° C., and boils at 357° C.; it volatilises slowly at ordinary temperatures; it remains unchanged in air at ordinary temperatures, but when heated to 300° C., in contact with air, it oxidises, forming the red oxide of mercury. It is capable of a very fine state of division, by being well rubbed with certain substances, and in this finely-divided state it is employed in some medicinal preparations. Those containing such finely-divided mercury are blue pill (*Pilula hydrargyri*, B. P.), grey powder (*Hydrargyrum cum cretâ*, B. P.), and mercury ointment (*Unguentum hydrargyri*, B. P.). Mercury unites with most of the metals, forming *amalgams*, the most useful of which is an amalgam of mercury and tin, which is used for silvering ordinary looking-glasses. Mercury does not unite or amalgamate with iron and platinum, hence it is generally stored in large iron bottles.

Action of acids on mercury.—Dilute sulphuric acid and hydrochloric acid have no action on mercury. Strongly sulphuric acid with heat acts on mercury, forming mercuric sulphate, and evolving sulphur dioxide.

$$\underset{\text{Mercury.}}{Hg} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Mercuric sulphate.}}{HgSO_4} + \underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Water.}}{2H_2O}$$

Nitric acid acts on mercury, producing different mercury salts, accordingly as strong or dilute nitric acid is employed with heat or without. Strong nitric acid with heat forms mercuric nitrate, with evolution of nitrogen dioxide.

$$\underset{\text{Mercury.}}{3Hg} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Mercuric nitrate.}}{3Hg(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

Moderately diluted nitric acid digested with mercury in the cold forms mercurous nitrate with evolution of nitrogen dioxide.

$$\underset{\text{Mercury.}}{6Hg} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Mercurous nitrate.}}{3Hg_2(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

Aqua regia (nitro-hydrochloric acid) dissolves mercury, forming mercuric chloride, and evolving nitrogen dioxide.

$$\underset{\text{Mercury.}}{3Hg} + \underset{\text{Hydrochloric acid.}}{6HCl} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Mercuric chloride.}}{3HgCl_2} + \underset{\text{Nitrogen dioxide.}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

MERCURY SALTS.

There are two classes of mercury salts, *mercuric* and *mercurous*, in both of which the mercury is acting as a dyad; but all mercurous compounds contain in the molecule two atoms of mercury, and as these two atoms are linked together by an atom-fixing power of each, the mercury atoms only exert towards other elements the atom-fixing power of a monad. This is rendered evident by inspection of the following graphic formulæ of mercuric chloride ($HgCl_2$) and mercurous chloride (Hg_2Cl_2).

$$\underset{\text{Mercuric chloride.}}{Cl—Hg—Cl} \qquad \underset{\text{Mercurous chloride.}}{Cl—Hg——Hg—Cl}$$

For a further description of the composition of mercurous salts, *see* page 51.

It will be convenient to describe the various mercuric and mercurous salts together in couples.

Mercuric sulphate ($HgSO_4$) is prepared by the action of strong sulphuric acid with heat on mercury.

$$\underset{\text{Mercury.}}{Hg} + \underset{\text{Sulphuric acid.}}{2H_2SO_4} = \underset{\text{Mercuric sulphate.}}{HgSO_4} + \underset{\text{Sulphur dioxide.}}{SO_2} + \underset{\text{Water.}}{2H_2O}$$

Mercuric sulphate is largely used in the preparation of mercuric chloride (corrosive sublimate), and also for preparing mercurous sulphate, from which calomel is made. Mercuric sulphate is decomposed by water, with production of a yellow oxysulphate of mercury ($Hg_3O_2SO_4$), formerly employed in medicine under the name of *Turpeth mineral.*

$$\underset{\text{Mercuric sulphate.}}{3HgSO_4} + \underset{\text{Water.}}{2H_2O} = \underset{\text{Turpeth mineral.}}{Hg_3O_2SO_4} + \underset{\text{Sulphuric acid.}}{2H_2SO_4}$$

Mercurous sulphate (Hg_2SO_4).—This is prepared by well rubbing mercuric sulphate with as much mercury as it already contains.

$$\underset{\text{Mercuric sulphate.}}{HgSO_4} + \underset{\text{Mercury.}}{Hg} = \underset{\text{Mercurous sulphate.}}{Hg_2SO_4}$$

This salt is used for the preparation of calomel; it is very apt to be contaminated with some unchanged mercuric sulphate.

Mercuric chloride ($HgCl_2$).—This important salt is also known as *perchloride of mercury*, *bichloride of mercury*, and *corrosive sublimate.* It is prepared by heating a mixture of mercuric sulphate and sodium chloride (common salt), and conveying the vapour of the mercuric chloride into a cool chamber, where it condenses to a white crystalline solid.

$$\underset{\substack{\text{Mercuric}\\\text{sulphate.}}}{HgSO_4} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl} = \underset{\substack{\text{Mercuric}\\\text{chloride}}}{HgCl_2} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4}$$

Mercuric chloride is a very poisonous substance; it is soluble in water, but if the solution is kept exposed to light it slowly decomposes, depositing mercurous chloride (calomel); to prevent this change, the solution employed in medicine (*Liquor hydrargyri perchloridi*, B. P.) contains equal weights of mercuric chloride and ammonium chloride in solution, by which means a stable double salt ($HgCl_2, 2NH_4Cl$) is formed, which does not decompose by keeping in the light, and in which the therapeutical properties of the mercuric chloride remain unaltered. A weak aqueous solution of mercuric chloride (1 part in 1,000 of water) is a powerful germicide, and is largely used in surgery as an antiseptic lotion; in using it, care should be taken not to dip articles of gold, such as rings, into it, as they would quickly become coated with metallic mercury.

Mercurous chloride (Hg_2Cl_2).—This largely-employed mercurial preparation is also known as *calomel* and *subchloride of mercury.* It is prepared by heating a mixture of mercurous sulphate and sodium chloride (common salt), when the calomel that is formed volatilises, and the vapour is conveyed into a cool chamber, within which it condenses to a white powder.

$$\underset{\substack{\text{Mercurous}\\\text{sulphate.}}}{Hg_2SO_4} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl} = \underset{\substack{\text{Mercurous}\\\text{chloride.}}}{Hg_2Cl_2} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4}$$

As the mercurous sulphate is apt to be contaminated with mercuric sulphate, so calomel is apt to be contaminated with corrosive sublimate formed from the mercuric sulphate ; the calomel must be freed from this impurity by thoroughly washing it with hot water, until the washings cease to show the presence of corrosive sublimate, as indicated by their ceasing to give a black precipitate with ammonium sulphide. As calomel is given in fairly large doses (5 to 10 grains), it is most important that it should be thoroughly freed from the poisonous corrosive sublimate. A simple test for the detection of the latter impurity in calomel is to place some of the calomel on a clean knife-blade, moisten it with a few drops of alcohol, and allow it to remain for a few minutes, when a black spot will be produced on the blade if corrosive sublimate is present.

Another method of preparing calomel is to precipitate it from a solution of mercurous nitrate by means of hydrochloric acid.

$$\underset{\substack{\text{Mercurous}\\\text{nitrate.}}}{Hg_2(NO_3)_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Mercurous}\\\text{chloride.}}}{Hg_2Cl_2} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3}$$

This process is not employed for the preparation of the calomel used in medicine, the sublimation process always being used for the commercial production of calomel.

Mercuric iodide (HgI_2), also known as the *biniodide of mercury* and the *red iodide of mercury*, is prepared by precipitating a solution of mercuric chloride with potassium iodide. It is thrown down at first as a yellow precipitate, rapidly changing to red.

$$\underset{\substack{\text{Mercuric}\\\text{chloride.}}}{HgCl_2} + \underset{\substack{\text{Potassium}\\\text{iodide.}}}{2KI} = \underset{\substack{\text{Mercuric}\\\text{iodide.}}}{HgI_2} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{2KCl}$$

The precipitated mercuric iodide is soluble in excess of either mercuric chloride or of iodide of potassium, but especially in the latter; with excess of potassium iodide it forms a soluble double iodide ($HgI_2,2KI$), which is a very convenient and frequently employed form of administering mercury internally. This is generally done by prescribing together a suitable dose of perchloride of mercury (*Liquor hydrargyri perchloride*, B. P.) with excess of potassium iodide. A weak solution of this double iodide (1 part in 2,000 or 3,000 of water) is also a powerful germicide and disinfectant, and is employed as an antiseptic lotion. *Nessler's solution* is a solution of this double iodide of mercury and potassium mixed with caustic potash. It constitutes an extremely delicate test for ammonia, and can be used for the detection of most minute quantities of ammonia in drinking waters, imparting a yellow or brownish tint to the water, according to the amount of ammonia present. This test is known as *Nessler's test.* The yellow or brownish colour is due to the precipitation of the dimercuric-ammonium iodide (NHg_2I)—*i.e.* ammonium iodide (NH_4I), from which the four atoms of the monad hydrogen have been displaced by two atoms of the dyad mercury.

$$\underset{\text{Ammonia.}}{NH_3} + \underset{\substack{\text{Mercuric}\\ \text{iodide.}}}{2HgI_2} = \underset{\substack{\text{Di-mercuric-}\\ \text{ammonium iodide.}}}{NHg_2I} + \underset{\substack{\text{Hydriodic}\\ \text{acid.}}}{3HI}$$

Mercurous iodide (Hg_2I_2), also known as the *green iodide of mercury*, is prepared by direct combination of its elements in suitable proportions—*i.e.* by rubbing 200 parts of mercury with 127 parts of iodine and a little alcohol, the latter being used to prevent elevation of temperature, due to the chemical action taking place.

Mercuric nitrate ($Hg(NO_3)_2$) is prepared by the action of strong nitric acid with heat on the metal mercury.

$$\begin{array}{ccccccccc} 3Hg & + & 8HNO_3 & = & 3Hg(NO_3)_2 & + & N_2O_2 & + & 4H_2O \\ \text{Mercury.} & & \text{Nitric} & & \text{Mercuric} & & \text{Nitrogen} & & \text{Water.} \\ & & \text{acid.} & & \text{nitrate.} & & \text{dioxide.} & & \end{array}$$

Mercurous nitrate ($Hg_2(NO_3)_2$) is prepared by the action of moderately diluted nitric acid in the cold on the metal mercury.

$$\begin{array}{ccccccccc} 6Hg & + & 8HNO_3 & = & 3Hg_2(NO_3)_2 & + & N_2O_2 & + & 4H_2O \\ \text{Mercury.} & & \text{Nitric} & & \text{Mercurous} & & \text{Nitrogen} & & \text{Water.} \\ & & \text{acid.} & & \text{nitrate.} & & \text{dioxide.} & & \end{array}$$

Mercuric oxide (HgO).—There are two varieties of this oxide—the *red* or crystalline variety, and the *yellow* or amorphous variety. The red mercuric oxide, commonly known as *red precipitate*, is obtained as a red crystalline powder by heating a mixture of mercuric nitrate and metallic mercury.

$$\begin{array}{ccccccc} Hg(NO_3)_2 & + & Hg & = & 2HgO & + & N_2O_4 \\ \text{Mercuric} & & \text{Mercury.} & & \text{Mercuric} & & \text{Nitrogen} \\ \text{nitrate.} & & & & \text{red oxide.} & & \text{tetroxide.} \end{array}$$

It may also be obtained by heating mercury with exposure to the air for some time at a temperature of 300° C.

The yellow mercuric oxide is obtained as a yellow amorphous powder by precipitating a solution of mercuric chloride with any of the fixed alkalies, potash, soda, or lime.

$$\begin{array}{ccccccccc} HgCl_2 & + & 2NaHO & = & HgO & + & 2NaCl & + & H_2O \\ \text{Mercuric} & & \text{Sodium} & & \text{Mercuric} & & \text{Sodium} & & \text{Water.} \\ \text{chloride.} & & \text{hydrate.} & & \text{yellow oxide.} & & \text{chloride.} & & \end{array}$$

The yellow mercuric oxide is contained in *yellow lotion* or *yellow wash* (*Lotio hydrargyri flava*, B. P.), in which it is made by precipitating a weak solution of mercuric chloride with lime-water.

$$\underset{\substack{\text{Mercuric}\\\text{chloride.}}}{HgCl_2} + \underset{\substack{\text{Calcium}\\\text{hydrate.}}}{Ca(HO)_2} = \underset{\substack{\text{Mercuric}\\\text{yellow oxide.}}}{HgO} + \underset{\substack{\text{Calcium}\\\text{chloride.}}}{CaCl_2} + \underset{\text{Water.}}{H_2O}$$

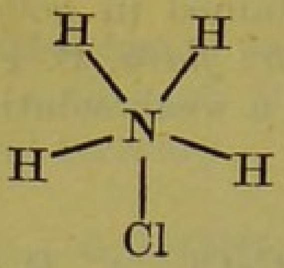
Mercurous oxide (Hg_2O) is also known as *black oxide of mercury*; it is prepared by the action of one of the fixed alkalies, potash, soda, or lime, on a mercurous salt; it is contained in *black lotion* or *black wash* (*Lotio hydrargyri nigra*, B. P.), in which it is obtained as a black precipitate by shaking together calomel (mercurous chloride) and lime-water.

$$\underset{\substack{\text{Mercurous}\\\text{chloride.}}}{Hg_2Cl_2} + \underset{\substack{\text{Calcium}\\\text{hydrate.}}}{Ca(HO)_2} = \underset{\substack{\text{Mercurous}\\\text{oxide.}}}{Hg_2O} + \underset{\substack{\text{Calcium}\\\text{chloride.}}}{CaCl_2} + \underset{\text{Water.}}{H_2O}$$

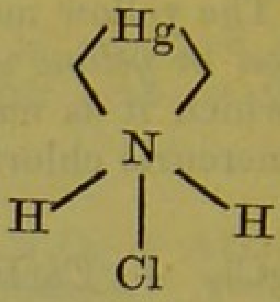
Mercuric cyanide ($Hg(CN)_2$).—If red mercuric oxide is digested in dilute hydrocyanic acid, it dissolves, and mercuric cyanide is afterwards deposited in crystals.

$$\underset{\substack{\text{Mercuric}\\\text{oxide.}}}{HgO} + \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{2HCN} = \underset{\substack{\text{Mercuric}\\\text{cyanide.}}}{Hg(CN)_2} + \underset{\text{Water.}}{H_2O}$$

Ammoniated mercury (NH_2HgCl). — This compound, commonly known as *white precipitate*, is mercuric ammonium chloride; that is, it consists of ammonium chloride (NH_4Cl) from which two atoms of the monad hydrogen have been displaced by one atom of the dyad mercury, as is rendered evident by inspection of their graphic formulæ.



Ammonium chloride.



Ammoniated mercury.

It is obtained as a white precipitate by pouring a solution of mercuric chloride into a solution of ammonia.

$$\underset{\text{Mercuric chloride.}}{HgCl_2} + \underset{\text{Ammonia.}}{2NH_3} = \underset{\text{Ammoniated mercury.}}{NH_2HgCl} + \underset{\text{Ammonium chloride.}}{NH_4Cl}$$

Mercuric sulphide (HgS).—This exists in nature as cinnabar; it constitutes the pigment *vermilion,* which is prepared by rubbing together mercury and sulphur, when the black amorphous mercuric sulphide is obtained, which on heating sublimes as vermilion; the composition of the sulphide is not changed by the heat, but the black amorphous sulphide becomes converted into the red crystalline variety. *Ethiop's mineral*, formerly employed in medicine, is a mixture of the black mercuric sulphide and free sulphur; it is obtained by rubbing mercury with excess of sulphur.

Mercuric oleate.—This substance, which is now frequently used as an external application in certain skin diseases, is prepared by dissolving yellow mercuric oxide in oleic acid.

Test for Mercury.

All solid mercury compounds if mixed with lime or sodium carbonate, and then heated in a dry test-tube, yield a sublimate of metallic mercury on the cool sides of the tube; this sublimate, when rubbed with a glass rod, produces the characteristic globules of mercury.

Tests for Mercuric Salts.

(i) Sulphuretted hydrogen gives a black precipitate of mercuric sulphide; if the solution of the mercuric salts is strong, the precipitate may at first come down of a yellowish-white colour; afterwards, as more sulphuretted hydrogen passes in, the light-coloured precipitate passes through successive stages of dark yellow, orange, and brown, to a black colour; these colour stages are due to the partial displacement, at first, of the acid radical of the mercury salt by the sulphur.

(ii) Ammonium sulphide also precipitates the black mercuric sulphide.

(iii) Potassium iodide gives with a solution of a mercuric salt a precipitate of red mercuric iodide, the precipitate being thrown down at first of a yellowish colour, rapidly changing to red; it is soluble in excess of either the mercuric salt or of potassium iodide, but especially so in the latter.

(iv) If a solution of a mercuric salt is acidified with a few drops of hydrochloric acid, and then boiled for a few minutes with a strip of bright copper foil, the metal mercury is deposited on the surface of the strip of copper, giving to it a characteristic lustre resembling polished silver; if the strip of copper is washed with water, carefully dried, and then heated in a dry test-tube, a sublimate of metallic mercury will be obtained on the sides of the tube; this sublimate, when rubbed with a glass rod, produces the characteristic globules of mercury.

(v) Caustic potash and caustic soda both give with solutions of mercuric salts a yellow precipitate of mercuric oxide.

Tests for Mercurous Salts.

(i) Hydrochloric acid gives with a solution of a mercurous salt, a white precipitate of mercurous chloride (calomel); this is blackened by the addition of ammonia, due to the formation of the black mercurous ammonium chloride (NH_2Hg_2Cl), the mercurous analogue of ammoniated mercury (NH_2HgCl).

(ii) Potassium iodide gives a dirty-green precipitate of mercurous iodide.

(iii) Caustic potash and caustic soda both give a black precipitate of mercurous oxide.

CHAPTER VIII.

LEAD.

Lead—Occurrence in Nature—Preparation and Properties of the Metal Lead—Action of Acids on Lead—Oxides of Lead—Preparation of the Lead Salts—Tests for Lead.

LEAD.

Symbol, Pb; *formula*, Pb_2; *dyad; atomic weight*, 207; *molecular weight*, 414.

Natural compounds of lead.—The principal lead compound occurring in nature is *galena*, sulphide of lead (PbS), which always contains small quantities of sulphide of silver; lead is also naturally found in small quantities as the sulphate and carbonate.

Preparation of the metal lead.—The principal process for the extraction of lead from galena is known as the *air reduction process*. It consists in roasting the galena in a furnace in a current of air, so as to convert it in part into the sulphate and oxide.

$$\underset{\text{Galena.}}{PbS} + \underset{\text{Oxygen.}}{2O_2} = \underset{\text{Lead sulphate.}}{PbSO_4}$$

$$\underset{\text{Galena.}}{2PbS} + \underset{\text{Oxygen.}}{3O_2} = \underset{\substack{\text{Lead}\\\text{oxide.}}}{2PbO} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2SO_2}$$

The current of air is then shut off, and the temperature of the furnace is raised, when the undecomposed galena reduces both the sulphate and oxide to the metallic state, with evolution of sulphur dioxide.

$$\underset{\substack{\text{Lead}\\\text{sulphate.}}}{PbSO_4} + \underset{\text{Galena.}}{PbS} = \underset{\text{Lead.}}{Pb_2} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2SO_2}$$

$$\underset{\substack{\text{Lead}\\\text{oxide.}}}{4PbO} + \underset{\text{Galena.}}{2PbS} = \underset{\text{Lead.}}{3Pb_2} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{2SO_2}$$

Lead thus prepared contains silver, which, if present in sufficient quantity to pay for its extraction, is obtained by converting the lead into lead oxide, which is removed, the silver remaining unchanged. The process by which this is effected is called the *cupellation process ;* it consists in roasting the lead in a reverberatory furnace (Fig. 24), the floor or hearth of which is lined with porous clay or bone-ash ; the lead (A) melts and oxidises to lead oxide under the influence of blasts of air admitted through openings (*a a*) ; most of this lead oxide in a molten condition flows away by side openings, whilst the remainder is absorbed by the porous clay or bone-ash, pure metal silver being finally left on the hearth of the furnace in a molten state. From the lead oxide produced in this process, the metal lead may be

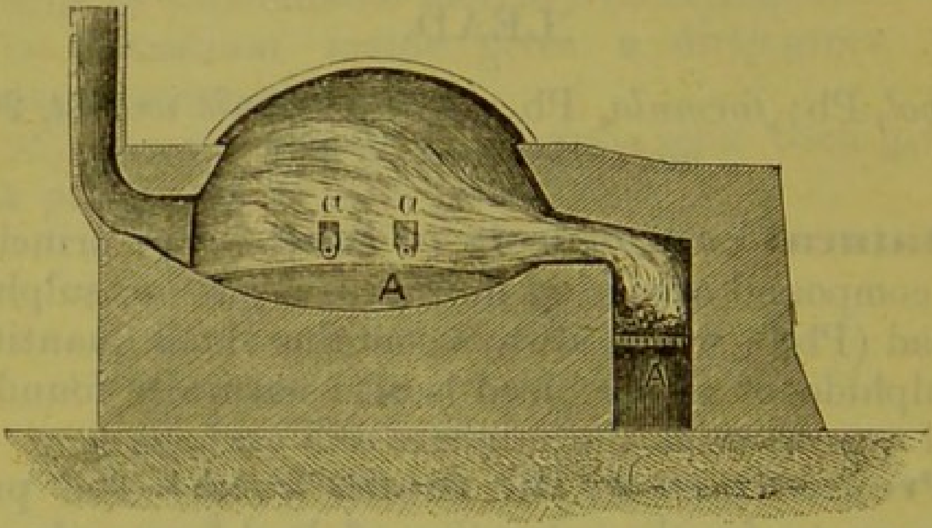


Fig 24.—Section of the Furnace Employed in the Cupellation Process.

obtained by reduction with charcoal or coal. The removal of a quantity of the lead in the metallic state from the silver may be effected by means of *Pattinson's process*, which depends upon the fact that the metal lead is less easily fusible than an alloy of silver and lead. The lead containing the silver is run in a melted condition into a large iron vessel, in which it is allowed to cool gradually; the part solidifying out first consists of crystals of pure lead, which can be raked out by means of a perforated iron ladle, and when about five-sixths of the lead has been so removed, the remaining rich alloy of silver and lead is submitted to the cupellation process.

Properties of the metal lead.—Lead is a lustrous, bluish-grey metal, soft enough to be cut with a knife, and to leave a mark on paper when drawn across it; it is malleable and ductile, and melts at 325° C.; it is not a good conductor of heat and electricity as compared with many other metals. If lead is exposed to perfectly dry air, it does not oxidise or tarnish, but if exposed to moist air, it soon becomes covered with a film of the double carbonate and hydrate of lead; similarly, if lead is immersed in distilled water which has been boiled to deprive it of all dissolved air, it remains unaffected by the water, but water containing air in solution attacks lead, the oxygen of the air forming lead oxide, which is then dissolved by the water as lead hydrate in small but appreciable quantities. This is one way in which a drinking water, passing through leaden pipes, may become contaminated with lead. The corrosive action of a water on lead is much increased by the presence in it of chlorides, nitrates, nitrites, and of ammonia, whereas the presence of sulphates and of calcic carbonate, held in solution as calcic bicarbonate by a moderate excess of carbon dioxide, hinders corrosion; in the latter case, a film of lead carbonate is formed within the pipe, which is but very slightly soluble in water. The presence, however, of an excess of carbon dioxide in a water would increase its solvent action on the lead, lead carbonate dissolving in water containing an excess of this gas, in the form of the soluble lead bicarbonate. The presence of vegetable matter in a water, as a rule, hinders corrosion of lead by the water, owing to the formation of an insoluble compound of lead oxide and organic matter. Some soft waters, notably some moorland waters, have a powerfully solvent action upon lead, due in some cases, perhaps, to the presence of acids in the water, either humic or ulmic acid derived from the soil, or, perhaps, in other cases to traces of sulphuric acid produced by oxidation of iron pyrites. Power has suggested that the action of a water upon lead is dependent upon organisms. Tidy, Odling, and Crookes attribute the lead-dissolving power to the absence of silica from the water, and have shown that when dissolved silica is present in a water, lead becomes coated with a film of insoluble lead silicate. As an actual fact, all drinking waters that have been allowed to flow through leaden pipes, or that have been stored in cisterns lined with lead, contain some lead in solution; if, however, the amount of lead carbonate does not exceed one-sixtieth of a grain per gallon, then its presence in a drinking water may be neglected.

The metal lead is largely used in the manufacture of pipes, as a covering for roofs, etc. Lead is contained in several alloys, the most important of which are, *type-metal*, an alloy of lead and antimony; *pewter* and *soft solder*, alloys of lead and tin; *shot*, an alloy of lead with a small quantity of arsenicum (not more than 0·8 part in 100), which possesses the property of hardening the lead.

Action of acids on the metal lead.—Hydrochloric acid has but very little action on lead. Concentrated sulphuric acid only slightly attacks lead, with formation of lead sulphate. Nitric acid readily acts on lead, forming lead nitrate, and evolving nitrogen dioxide.

$$\underset{\text{Lead.}}{Pb_3} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Lead nitrate.}}{3Pb(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

LEAD SALTS.

Lead oxides.—There are three oxides of lead, the *suboxide*, *oxide*, and *dioxide*, and a compound of the two latter oxides, known as *red lead.*

Pb_2O . .	Lead suboxide.
PbO . .	Lead oxide.
$2PbO, PbO_2$.	Red lead.
PbO_2 . .	Lead dioxide or peroxide.

Lead suboxide (Pb_2O) is prepared by heating lead oxalate out of contact with the air.

$$\underset{\text{Lead oxalate.}}{2PbC_2O_4} = \underset{\text{Lead suboxide.}}{Pb_2O} + \underset{\text{Carbon dioxide.}}{3CO_2} + \underset{\text{Carbon monoxide.}}{CO}$$

Lead oxide (PbO) is prepared by oxidation of the metal lead, by roasting it in air. In the amorphous state it forms a dirty yellow powder (*massicot*); if fused and solidified, it forms brighter, reddish-yellow scales (*litharge*).

This oxide is largely used in the manufacture of flint glass, and as a cheap glaze for earthenware. Nitric acid dissolves litharge, forming lead nitrate and water.

$$\underset{\substack{\text{Lead}\\\text{oxide.}}}{PbO} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} = \underset{\substack{\text{Lead}\\\text{nitrate.}}}{Pb(NO_3)_2} + \underset{\text{Water.}}{H_2O}$$

Hydrochloric acid and litharge form lead chloride and water.

$$\underset{\substack{\text{Lead}\\\text{oxide.}}}{PbO} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Lead}\\\text{chloride.}}}{PbCl_2} + \underset{\text{Water.}}{H_2O}$$

Red lead ($2PbO, PbO_2$), also known as *minium*, is prepared by heating lead oxide (PbO) in air to 400° C. for some time, when it absorbs oxygen and, becoming of a bright red colour, produces red lead. If red lead be strongly heated, it liberates the oxygen absorbed from the air, and returns to the condition of litharge; nitric acid decomposes it, dissolving the lead oxide (PbO) portion, and leaving unattacked the lead dioxide (PbO_2) portion; hydrochloric acid warmed with red lead forms lead chloride with evolution of chlorine, the latter being produced by the action of the hydrochloric acid on the lead dioxide (*see* below).

Lead dioxide (PbO_2) is also known as *lead peroxide*, and, on account of its brown colour with a purple-tinge, is sometimes called the *puce-coloured oxide of lead.* It is obtained, as previously stated, by the action of nitric acid on red lead, in which it already exists combined with lead oxide, the nitric acid merely dissolving out the latter, and leaving the higher oxide undissolved.

$$\underset{\text{Red lead.}}{2PbO, PbO_2} + \underset{\text{Nitric acid.}}{4HNO_3} = \underset{\text{Lead nitrate.}}{2Pb(NO_3)_2} +$$

$$\underset{\text{Lead dioxide.}}{PbO_2} + \underset{\text{Water.}}{2H_2O}$$

Lead dioxide if heated loses one-half of its oxygen, and is converted into the monoxide; hydrochloric acid acts on it forming lead chloride, with evolution of chlorine.

$$\underset{\text{Lead dioxide.}}{PbO_2} + \underset{\text{Hydrochloric acid.}}{4HCl} = \underset{\text{Lead chloride.}}{PbCl_2} + \underset{\text{Chlorine.}}{Cl_2} + \underset{\text{Water.}}{2H_2O}$$

Lead acetate ($Pb(C_2H_3O_2)_2$).—This salt, on account of its sweet taste, is commonly known as *sugar of lead;* it is prepared by dissolving litharge in acetic acid with heat.

$$\underset{\text{Lead oxide.}}{PbO} + \underset{\text{Acetic acid.}}{2HC_2H_3O_2} = \underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2} + \underset{\text{Water.}}{H_2O}$$

Lead oxyacetate ($Pb_2O(C_2H_3O_2)_2$).—This basic lead acetate is prepared by boiling a solution of lead acetate with lead oxide.

$$\underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2} + \underset{\text{Lead oxide.}}{PbO} = \underset{\text{Lead oxyacetate.}}{Pb_2O(C_2H_3O_2)_2}$$

Liquor plumbi subacetatis, B. P., is a strong solution of this oxyacetate, and is frequently termed *Goulard's extract;* a weaker solution of it is the *Liquor plumbi subacetatis dilutus,* B. P., which is frequently used as a lotion, and is commonly known as *Goulard water*.

Lead nitrate ($Pb(NO_3)_2$) is prepared either by the action of nitric acid on litharge, or on the metal lead.

$$\underset{\text{Litharge.}}{PbO} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Lead nitrate.}}{Pb(NO_3)_2} + \underset{\text{Water.}}{H_2O}$$

$$\underset{\text{Lead}}{Pb_3} + \underset{\text{Nitric acid.}}{8HNO_3} = \underset{\text{Lead nitrate.}}{3Pb(NO_3)_2} + \underset{\text{Nitrogen dioxide.}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

White lead or **basic lead carbonate** ($2PbCO_3, Pb(HO)_2$).—This lead compound, which is so largely used as a white paint, is not the normal lead carbonate ($PbCO_3$), but a double carbonate and hydrate of lead. There are two methods of preparing it.

(i) *The English* or *French process* consists in passing carbon dioxide gas through a solution of lead oxyacetate, when that portion of the lead not in union with the acetic radical is precipitated as *white lead*.

$$\underset{\text{Lead oxyacetate.}}{3Pb_2O(C_2H_3O_2)_2} + \underset{\text{Carbon dioxide.}}{2CO_2} + \underset{\text{Water.}}{H_2O} = \underset{\text{White lead.}}{2PbCO_3, Pb(HO)_2} + \underset{\text{Lead acetate.}}{3Pb(C_2H_3O_2)_2}$$

The lead acetate remaining in solution can then be boiled with litharge, and so a fresh batch of the oxyacetate will be obtained for further treatment with carbon dioxide.

(ii) *The Dutch process* also consists in decomposing lead oxyacetate with carbon dioxide in presence of moisture, but an entirely different arrangement is adopted. The metal lead is cast into spirals or gratings, so as to expose as large a surface of the metal as possible, and these are suspended in earthenware pots containing a layer of vinegar at the bottom; the pots are embedded in spent tan spread on the floor of a room, which is then closed for some weeks. The acetic acid of the vinegar and the oxygen of the air attack the lead, forming an oxyacetate, which is immediately decomposed by the carbon dioxide and moisture evolved from the fermenting spent tan into white lead; after several weeks the spirals or gratings are found covered with a loose layer of white lead, which is removed, and the spirals or gratings are returned to the pots, and the action allowed to go on until they are completely corroded away. White lead prepared by this process is more compact, or has more *body*, than that made by the English or French process, and is therefore preferred for painting purposes; when used as a paint white lead slowly darkens, from traces of sulphuretted hydrogen in the air forming the black sulphide of lead.

Lead iodide (PbI_2) is prepared by precipitating a solution of lead acetate or lead nitrate with potassium iodide.

$$\underset{\text{Lead acetate.}}{Pb(C_2H_3O_2)_2} + \underset{\text{Potassium iodide.}}{2KI} = \underset{\text{Lead iodide.}}{PbI_2} + \underset{\text{Potassium acetate.}}{2KC_2H_3O_2}$$

Iodide of lead is a bright yellow-coloured precipitate, insoluble in cold water, but soluble in hot water; in cases of chronic lead poisoning occurring amongst workers in white lead, iodide of potassium is administered as a medicine, with the view of removing the lead deposited as an albuminate of lead throughout the tissues; this it does by converting the albuminate of lead into iodide of lead, which is soluble in the warm blood and so is eliminated in the urine.

Lead chromate ($PbCrO_4$) is prepared by precipitating a solution of lead acetate or lead nitrate with potassium chromate.

$$\underset{\substack{\text{Lead}\\\text{nitrate.}}}{Pb(NO_3)_2} + \underset{\substack{\text{Potassium}\\\text{chromate.}}}{K_2CrO_4} = \underset{\substack{\text{Lead}\\\text{chromate.}}}{PbCrO_4} + \underset{\substack{\text{Potassium}\\\text{nitrate.}}}{2KNO_3}$$

Lead chromate is a bright yellow precipitate, and is used as a pigment under the name of *chrome-yellow;* if boiled with caustic potash or soda it yields *chrome-red* (Pb_2OCrO_4), an orange-red pigment.

Tests for Lead.

(i) Sulphuretted hydrogen gives a black precipitate of lead sulphide. This is the test employed for the detection of lead in a drinking water, the absence of other metals yielding precipitates with sulphuretted hydrogen being proved; if lead is present in the water, a brownish or blackish colour, according to the amount present, will be produced on the addition of sulphuretted hydrogen.

(ii) Ammonium sulphide also precipitates the black lead sulphide.

(iii) Potassium iodide gives a bright yellow precipitate of lead iodide, soluble in boiling water, and crystallising out in golden-coloured spangles as the solution cools.

(iv) Potassium chromate gives a yellow precipitate of lead chromate, changing to an orange-red colour on boiling with caustic potash or caustic soda.

(v) Hydrochloric acid gives, with moderately strong solutions of lead salts, a white precipitate of lead chloride; this precipitate remains unaltered on the addition of solution of ammonia, thus distinguishing it from mercurous chloride, which is also thrown down as a white precipitate by hydrochloric acid from a solution of a mercurous salt. Hydrochloric acid does not completely precipitate lead from its solutions, as lead chloride is appreciably soluble in cold water, and more so in hot water. As previously mentioned (*see* page 301), a water containing chlorides is very apt to dissolve lead from leaden pipes.

(vi) Sulphuric acid gives with solutions of lead salts a white precipitate of lead sulphate. This also is not a very delicate test for lead, as lead sulphate is slightly soluble in water.

CHAPTER IX.

ARSENICUM—ANTIMONY.

Arsenicum—Occurrence in Nature—Arsenious and Arsenic Compounds—Tests for Arsenicum—Antimony—Occurrence in Nature—Preparation of the Antimony Salts—Tests for Antimony.

ARSENICUM.

Symbol, As; *formula*, As_4; *pentad and triad; atomic weight*, 75; *molecular weight*, 300.

Arsenicum and phosphorus are the only elements containing four atoms in the molecule; their molecular weights are, therefore, four times their atomic weights.

Natural compounds of arsenicum.—(i) The commonest arsenical ore is the *arsenio-sulphide of iron* (FeSAs). (ii) Two compounds of arsenicum and sulphur occur in nature, a yellow sulphide named *orpiment* (As_2S_3), and a red sulphide named *realgar* (As_2S_2). (iii) *Arsenious acid* (H_3AsO_3) occurs in minute amounts in several mineral springs, as in those of Ems, Kissingen, Pyrmont, and Schwalbach. The quantity of arsenious acid present in these waters is too small to confer poisonous properties on them when drunk, but it is quite possible that their therapeutic properties are in part due to the minute quantities of arsenic present. (iv) The *metal arsenicum* occurs native to a small extent in laminated lumps, and occasionally in the crystalline state.

Preparation of the metal arsenicum.—The metal arsenicum is obtained as a sublimate by passing the vapour of arsenious oxide or white arsenic (As_2O_3) over heated charcoal.

$$\underset{\text{Arsenious oxide.}}{2As_2O_3} + \underset{\text{Carbon.}}{3C_2} = \underset{\text{Arsenicum.}}{As_4} + \underset{\text{Carbon monoxide.}}{6CO}$$

Properties of the metal.—Arsenicum possesses a steel-grey colour and a metallic lustre; it is very brittle, and is therefore easily pulverised. When heated in the air, arsenicum volatilises and burns, forming arsenious oxide or white arsenic (As_2O_3), and emitting at the same time an unpleasant garlic-like odour, possibly due to the arsenicum in a partial state of oxidation. The only use to which the metal arsenicum is put is in the manufacture of shot, which consists of lead alloyed with a small amount of arsenicum.

COMPOUNDS OF ARSENICUM.

Two classes of arsenical compounds exist, viz. the *arsenious compounds*, in which the arsenicum is only exerting the atomicity of a triad, and the *arsenic compounds* in which the arsenicum is exerting its full atomicity as a pentad.

There are two oxides of arsenicum, arsenious oxide or arsenicum trioxide, and arsenic oxide or arsenicum pentoxide.

Arsenious oxide or **arsenicum trioxide** (As_2O_3).—This oxide constitutes the *white arsenic* of commerce; it is also known as *arsenious anhydride.* It is obtained during the smelting or roasting of arsenical iron pyrites and other ores containing arsenicum united with sulphur, the latter element burning away as sulphur dioxide, whilst the arsenicum volatilises and oxidises to arsenious oxide, which is then condensed to a solid in long condensing flues attached to the smelting furnace.

$$\underset{\substack{\text{Arsenious}\\\text{sulphide.}}}{2As_2S_3} + \underset{\text{Oxygen.}}{9O_2} = \underset{\substack{\text{Arsenious}\\\text{oxide.}}}{2As_2O_3} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{6SO_2}$$

There are two varieties of arsenious oxide—(*a*) a crystalline variety which can be obtained in small octahedra, and (*b*) a vitreous variety constituting the deposit in the condensing flues attached to the furnaces in which arsenical ores are being roasted; this vitreous variety is obtained at first as a semi-transparent, glass-like solid, becoming after a time opaque like porcelain. The *white arsenic* of commerce is obtained by grinding this vitreous variety to a powder. Arsenious oxide or white arsenic is a white, odourless, and almost tasteless substance, possessing just a very faint sweetish taste; it is very poisonous, and it is on account of its practically tasteless character that, if introduced into food for homicidal purposes, it will be swallowed by the victim without its presence being detected by taste; in cases of poisoning with arsenic the administration of freshly-precipitated ferric hydrate or of solution of dialysed iron will act as an antidote, although not a very efficacious one, by forming the insoluble arseniate of iron. Arsenious oxide or white arsenic is soluble in cold water to the extent of half a grain in a fluid ounce, and in boiling water to the extent of 6 grains in a fluid ounce; when dissolved in water it forms arsenious acid (H_3AsO_3).

Arsenic oxide or **arsenicum pentoxide** (As_2O_5).—This, the higher oxide of arsenicum, is obtained by the further oxidation of arsenious oxide with nitric acid; if ordinary white arsenic be heated with nitric acid, reddish-brown fumes of nitrogen trioxide are evolved, and the residue, if dried and raised to a low red heat to expel water, leaves the arsenic oxide.

$$\underset{\substack{\text{Arsenious}\\\text{oxide.}}}{As_2O_3} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3} = \underset{\substack{\text{Arsenic}\\\text{oxide.}}}{As_2O_5} + \underset{\substack{\text{Nitrogen}\\\text{trioxide.}}}{N_2O_3} + \underset{\text{Water}}{H_2O}$$

Arsenic oxide or arsenic anhydride is a white amorphous substance, dissolving in water to form arsenic acid (H_3AsO_4); although more soluble in water than arsenious oxide, yet it is less poisonous than that substance. At temperatures above a red heat arsenic anhydride breaks up into arsenious anhydride and oxygen.

There are two acids of arsenicum corresponding to the two oxides or anhydrides, viz. arsenious acid and arsenic acid.

Arsenious acid (H_3AsO_3).—This is prepared by dissolving white arsenic (arsenious anhydride) in water.

$$\underset{\substack{\text{Arsenious}\\\text{anhydride.}}}{As_2O_3} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Arsenious}\\\text{acid.}}}{2H_3AsO_3}$$

It is a weak acid, and is only slightly soluble in water; it is too weak an acid to decompose solutions of the alkaline carbonates; arsenious acid is contained in two solutions used in medicine, both of them containing 1 per cent. of arsenic in solution; these are Fowler's solution (*Liquor arsenicalis*, B. P.), and the Hydrochloric solution of arsenic (*Liquor arsenici hydrochloricus*, B. P.). Although arsenious acid is so sparingly soluble in cold water, yet it is much more soluble in a dilute solution of an alkaline carbonate, or in a weak mineral acid. On this account Fowler's solution contains some potassium carbonate, which merely increases the solubility of the arsenious acid without forming a potassium arsenite; and the Hydrochloric solution of arsenic contains some diluted hydrochloric acid, which also increases the solubility of arsenious acid, but without forming a chloride of arsenicum.

Two compounds of arsenious acid are not uncommonly employed as pigments, viz. Scheele's green (arsenite of copper) and emerald green (aceto-arsenite of copper).

Scheele's green is prepared by mixing together solutions of copper sulphate and sodium arsenite, when it is thrown down as a bright green precipitate.

$$\underset{\substack{\text{Copper}\\\text{sulphate.}}}{CuSO_4} + \underset{\substack{\text{Sodium}\\\text{arsenite.}}}{Na_2HAsO_3} = \underset{\substack{\text{Copper}\\\text{arsenite.}}}{CuHAsO_3} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4}$$

Wall-papers printed with bright green colours are frequently surfaced with Scheele's green or emerald green, the arsenic contained in which may exercise a very injurious influence on people living or sleeping in rooms so papered. The arsenical pigment may become brushed off the paper as dust, and so become disseminated through the atmosphere of the room. But it is not only by this mechanical means that the arsenic can be dispersed into the atmosphere of the room; the papers are fastened to the walls with starch-paste, which easily ferments and sets free nascent hydrogen; and since the paper is originally saturated with the paste, this nascent hydrogen comes directly into contact with the arsenical compounds, and produces gaseous arseniuretted hydrogen, which escapes into and poisons the air of the room. It is true that the quantity of the gas so produced is very minute; but as arseniuretted hydrogen is more poisonous than any other compound of arsenicum, very small quantities may be sufficient to produce very injurious effects.

For the methods of detecting arsenic in wall-papers, *see* pages 318, 320, 321.

Arsenic acid (H_3AsO_4).—This is obtained by dissolving arsenic anhydride in water.

$$\underset{\substack{\text{Arsenic}\\\text{anhydride.}}}{As_2O_5} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Arsenic}\\\text{acid.}}}{2H_3AsO_4}$$

It may also be prepared by the action of chlorine on a solution of arsenious acid, the chlorine uniting with the hydrogen of some of the water to form hydrochloric acid, and setting free oxygen, which in the nascent state oxidises the arsenious acid to arsenic acid.

$$\underset{\substack{\text{Arsenious}\\\text{acid.}}}{H_3AsO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Arsenic}\\\text{acid.}}}{H_3AsO_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl}$$

A similar action occurs when iodine is added to a solution of arsenious acid.

$$\underset{\substack{\text{Arsenious}\\\text{acid.}}}{H_3AsO_3} + \underset{\text{Water.}}{H_2O} + \underset{\text{Iodine.}}{I_2} = \underset{\substack{\text{Arsenic}\\\text{acid.}}}{H_3AsO_4} + \underset{\substack{\text{Hydriodic}\\\text{acid.}}}{2HI}$$

Arsenic acid is a stronger acid as regards its action on litmus paper, and its power of forming salts, than arsenious acid, and is much more soluble in water, but it is not so powerful a poison as arsenious acid. Arsenic acid is employed in the preparation of magenta and some other aniline dyes, becoming reduced to arsenious acid during the process. If the dye is not properly freed from the arsenious acid, then injurious effects may follow from the employment of articles coloured with such dyes, such as socks, gloves, Cretonne and other hangings. Red aniline dyes are also sometimes used for giving a colour to liqueurs, syrups, sweetmeats, and raspberry vinegar; and here, again, injurious effects might follow from the taking of such coloured articles if the dye contained arsenic. A potassium arseniate (K_2HAsO_4) is contained in some fly-papers, flies being readily killed by imbibing a small quantity of a solution of this salt.

Two salts of arsenic acid are used in medicine, viz. sodium arseniate (*see* page 229) and ferrous arseniate (*see* page 269).

Arsenicum chloride ($AsCl_3$) is prepared by burning powdered arsenicum in dry chlorine, or by distilling a mixture of arsenious anhydride, sodium chloride, and concentrated sulphuric acid. It is a colourless volatile liquid, decomposed by water into arsenious and hydrochloric acids.

$$\underset{\substack{\text{Arsenicum}\\\text{chloride.}}}{AsCl_3} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Arsenious}\\\text{acid.}}}{H_3AsO_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3HCl}$$

It is on account of this immediate decomposition of arsenicum chloride by water that its existence in the Hydrochloric solution of arsenic (*Liquor arsenici hydrochloricus*, B. P.) is rendered impossible.

Arsenicum iodide (AsI_3) is prepared by direct union of its elements, or by dissolving arsenious anhydride in hydriodic acid. An aqueous solution, containing 1 per cent. of this arsenicum iodide and 1 per cent. of mercuric iodide, with an excess of potassium iodide, forms Donovan's solution (*Liquor arsenici et hydrargyri iodidi*, B. P.).

Tests for Arsenicum.

(i) Sulphuretted hydrogen gives, with an acid solution of arsenious acid, a yellow precipitate of arsenous sulphide, which is soluble in alkalies and in ammonium sulphide.

(ii) If a small quantity of white arsenic is mixed with a reducing agent containing carbon, such as *black flux* (a mixture of potassium carbonate and charcoal, obtained by heating acid tartrate of potassium in a covered vessel), and the mixture introduced into a Berzelius's reduction tube, and then heat applied to the bulb containing the mixture, a sublimate of metallic arsenicum of an iron-grey colour will be obtained on the cool part of the tube just above the constriction. (Fig. 25, A being the sublimate of the metallic arsenicum.)

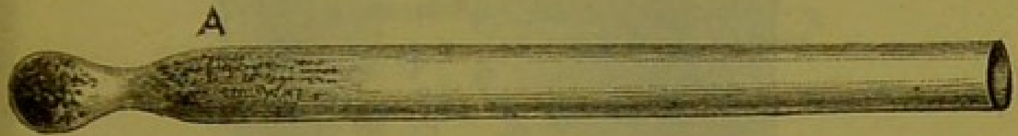


Fig. 25.—Sublimate of Metallic Arsenicum in a Berzelius's Reduction Tube.

If the portion of the tube containing the sublimate A be cut off with a file, and then broken into fragments, and the fragments introduced into a dry test-tube, on applying heat to the bottom of the latter, whilst holding it in an almost horizontal position, with the mouth of the tube partially covered by the thumb, the arsenicum will volatilise and oxidise to the arsenious oxide, which will deposit on the cool part of the tube in small brilliant crystals, consisting of perfect and imperfect octahedra. If the portion of the tube containing the sublimate be viewed under a microscope, using a $\frac{1}{4}$ in. or $\frac{1}{5}$ in. objective, the crystals will present the characteristic appearances shown in Fig. 26.

(iii) *Reinsch's test.*—This very delicate test for arsenic consists in boiling, for a short time, a strip of bright copper foil in a solution of arsenious acid, to which a few drops of hydrochloric acid have been added. The metal arsenicum deposits on the surface of the copper as a dull grey film. The acid liquid is then poured off from the slip of copper, and the latter washed two or three times with water and dried, firstly by pressure between folds of blotting-paper, and lastly by carefully warming it some distance above the Bunsen flame. The strip of copper, with the deposit of arsenicum on it, is now transferred to a dry test-tube, and heat is applied in a manner similar to that described in the previous test, when the arsenicum volatilises and oxidises to arsenious oxide, which forms a crystalline deposit on the cool part of the tube, presenting under the microscope the characteristic appearances shown in Fig. 26.

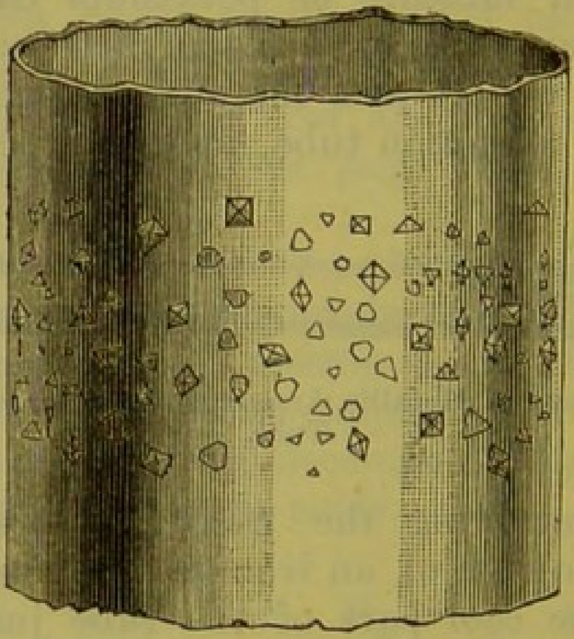


Fig. 26.—Crystals of Arsenic Obtained in Reinsch's Test (magnified).

Reinsch's test may be employed for the detection of arsenic in wall-paper. Some of the paper is cut into small pieces, which are then digested in diluted hydrochloric acid with heat for a few minutes; the acid liquid is then poured off, and boiled with a strip of bright copper, and the test proceeded with in the manner just described.

(iv) *Marsh's test.*—This delicate test for arsenic

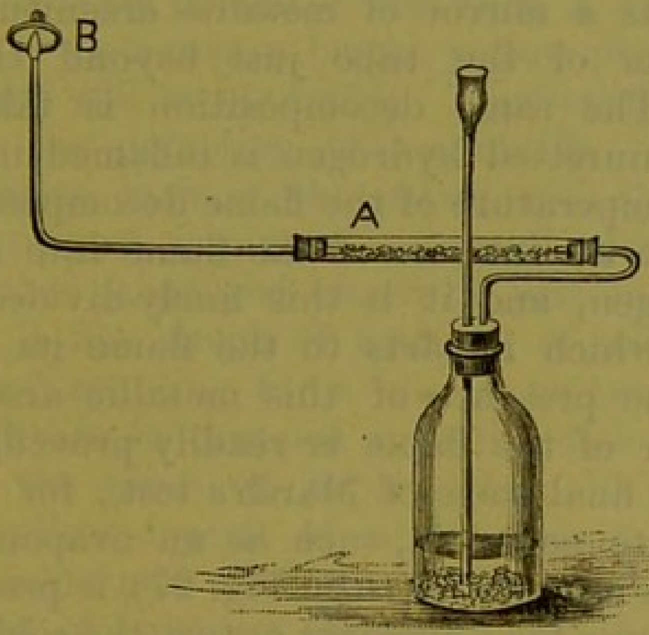


Fig. 27.—Apparatus for Marsh's Test.

depends upon the conversion of the arsenic into arseniuretted hydrogen, and obtaining from the latter a deposit of metallic arsenicum. Hydrogen is generated in a suitable apparatus (Fig. 27) from zinc and dilute sulphuric acid, the gas is dried by passing through a calcium chloride tube (A in Fig. 27), and is then ignited as it escapes from the end of the tube bent at right angles.

If some solution of arsenious acid is now poured into the apparatus by means of the long funnel, the nascent hydrogen produces arseniuretted hydrogen (AsH_3), the production of which is quickly indicated by the hydrogen flame becoming a pale livid colour.

$$\underset{\text{Arsenious acid.}}{H_3AsO_3} + \underset{\text{Hydrogen.}}{3H_2} = \underset{\text{Arseniuretted hydrogen.}}{AsH_3} + \underset{\text{Water.}}{3H_2O}$$

In arseniuretted hydrogen the two constituents are so loosely combined that a low red-heat is sufficient to decompose the compound into metallic arsenicum and hydrogen; the gas, therefore, when passed through a glass tube, the central portion of which is made red-hot, deposits a mirror of metallic arsenicum on the cooler parts of the tube just beyond the heated portion. The same decomposition is taking place when arseniuretted hydrogen is inflamed in the air; the high temperature of the flame decomposes the unburnt gas in the interior of the flame into arsenicum and hydrogen, and it is this finely-divided metallic arsenicum which imparts to the flame its pale livid colour. The presence of this metallic arsenicum in the interior of the flame is readily proved, and constitutes the final stage of Marsh's test; for if a piece of cold white porcelain, such as an evaporating dish or porcelain crucible lid (B in Fig. 27), is pressed down upon the flame for a moment or two, the cold porcelain becomes coated with a blackish-grey round stain of metallic arsenicum at the spot where the flame touched it. This spot of metallic arsenicum readily dissolves in solution of chlorinated lime or chlorinated soda, and so can be distinguished from the antimony spot, which is obtained under similar conditions (*see* page 326). To detect arsenic in wall-paper by means of Marsh's test, it is simply necessary to introduce into Marsh's apparatus some of the acid liquid obtained by digesting pieces of the paper in diluted hydrochloric acid with heat, the test being then proceeded with in the usual way.

In employing Marsh's test, care must be taken that no unburnt arseniuretted hydrogen escapes into the atmosphere of the laboratory, as it is a most powerful poison, being, in fact, more poisonous than any other arsenical compound.

(v) If to an aqueous solution of arsenious acid some copper sulphate be added, and then a drop or two of solution of ammonia, a bright green precipitate (Scheele's green) will be thrown down.

(vi) If to an aqueous solution of arsenious acid some silver nitrate be added, and then a drop or two of solution of ammonia, a bright yellow precipitate of silver arsenite will be obtained. This reaction may be applied to the detection of arsenic in wall-paper; about a square inch of the paper, with the coloured surface uppermost, is placed in a small porcelain dish, distilled water is poured on so as just to cover the paper, and a few drops of solution of ammonia are added; after standing for a minute or two, a crystal of silver nitrate is dropped into the dish on to the surface of the piece of paper, when, if arsenic be present, a yellow deposit of silver arsenite will occur around the edge and over the surface of the crystal. The working of this test depends upon the solubility of Scheele's green (copper arsenite) in a weak solution of ammonia, and the precipitation from this solution of the yellow silver arsenite, in presence of an excess of silver nitrate.

Distinction of Arsenious and Arsenic Acids.

If to an aqueous solution of arsenic acid some silver nitrate be added, and then a drop or two of solution of ammonia, a chocolate-coloured precipitate of silver arseniate will be obtained; this test serves to distinguish between the two acids, as in similar circumstances arsenious acid will give a bright yellow precipitate. In like manner, neutral solutions of arseniates will at once give a chocolate precipitate, and neutral solutions of arsenites a yellow precipitate with silver nitrate.

ANTIMONY.

Symbol, Sb; *formula*, Sb_2; *pentad and triad; atomic weight*, 120; *molecular weight*, 240.

Natural compounds of antimony.—The sulphide of antimony (Sb_2S_3) is the principal natural compound of this metal; it is known as *grey antimony ore*, and in the form of powder as *black antimony*.

Preparation and properties of the metal antimony.—This is obtained by heating together the native sulphide of antimony and metallic iron, the iron uniting with the sulphur to form ferrous sulphide, and setting free the antimony.

$$\underset{\substack{\text{Antimony}\\\text{sulphide.}}}{2Sb_2S_3} + \underset{\text{Iron.}}{3Fe_2} = \underset{\text{Antimony.}}{2Sb_2} + \underset{\substack{\text{Ferrous}\\\text{sulphide.}}}{6FeS}$$

Crude antimony contains arsenicum, from which it can be purified by fusing with some sodium carbonate and potassium nitrate, and well stirring the mixture, when the arsenicum becomes converted into sodium arseniate.

The metal antimony is contained in *type-metal*, an alloy of lead and antimony, and in *britannia-metal*, an alloy of tin and antimony.

ANTIMONY SALTS.

There are two classes of antimony compounds, the *antimonious* and *antimonic*, resembling the two classes of arsenical compounds; in the antimonious compounds the antimony is only exerting part of its atomicity as a triad, whereas in the antimonic compounds it is exerting its full atomicity as a pentad.

Antimony trichloride or **antimonious chloride** ($SbCl_3$).—(i) This may be prepared by direct union of the elements; if powdered metallic antimony is thrown into a jar of chlorine, it will catch fire, producing antimony trichloride.

$$\underset{\text{Antimony.}}{Sb_2} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\substack{\text{Antimony}\\\text{trichloride.}}}{2SbCl_3}$$

(ii) The usual method of preparing this chloride is by the action of strong hydrochloric acid with heat on the native sulphide of antimony.

$$\underset{\substack{\text{Antimony}\\\text{sulphide.}}}{Sb_2S_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{6HCl} = \underset{\substack{\text{Antimony}\\\text{trichloride.}}}{2SbCl_3} + \underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{3H_2S}$$

Prepared in this way it is generally of a reddish-brown colour from the presence of iron salts; it is a strongly acid liquid, constituting *Liquor antimonii chloridi*, B. P., and is commonly known as *butter of antimony*, but it is actually a solution of antimony trichloride in hydrochloric acid, since the chloride itself is of a buttery consistence, whence its common name. The true butter of antimony is obtained by evaporating the acid solution to a low bulk, and distilling the residue, when the antimony trichloride condenses in the neck of the retort as a white, semi-transparent mass.

Antimony pentachloride or **antimonic chloride** ($SbCl_5$) is prepared by acting on the trichloride with chlorine.

$$\underset{\substack{\text{Antimony}\\\text{trichloride.}}}{SbCl_3} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Antimony}\\\text{pentachloride.}}}{SbCl_5}$$

Antimony trioxide or **antimonious oxide** (Sb_2O_3) is prepared by pouring the acid solution of antimony trichloride into water, by which means a white precipitate of oxychloride of antimony is thrown down.

$$\underset{\substack{\text{Antimony}\\ \text{trichloride.}}}{12SbCl_3} + \underset{\text{Water.}}{15H_2O} = \underset{\substack{\text{Antimony}\\ \text{oxychloride.}}}{2SbCl_3, 5Sb_2O_3} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{30HCl}$$

This precipitate is then stirred up with solution of sodium carbonate, which abstracts the chlorine from the oxychloride, producing the pure antimony trioxide, which is of a light buff colour.

$$\underset{\substack{\text{Antimony}\\ \text{oxychloride.}}}{2SbCl_3, 5Sb_2O_3} + \underset{\substack{\text{Sodium}\\ \text{carbonate.}}}{3Na_2CO_3} = \underset{\substack{\text{Antimony}\\ \text{trioxide.}}}{6Sb_2O_3} + \underset{\substack{\text{Sodium}\\ \text{chloride.}}}{6NaCl} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{3CO_2}$$

Antimony pentoxide or **antimonic oxide** (Sb_2O_5) is prepared by the action of nitric acid on the metal antimony.

Tartarated antimony ($KSbOC_4H_4O_6$).—This compound, commonly known as *tartar emetic*, is an oxytartrate of potassium and antimony. It is prepared by mixing antimony trioxide and potassium acid tartrate with sufficient water to form a paste, leaving it for twenty-four hours, as the two substances are somewhat sluggish in uniting, and then boiling the paste with water; on filtering, and concentrating the solution by evaporation, the tartar emetic is obtained in crystals.

$$\underset{\substack{\text{Antimony}\\ \text{trioxide.}}}{Sb_2O_3} + \underset{\substack{\text{Potassium}\\ \text{acid tartrate.}}}{2KHC_4H_4O_6} = \underset{\substack{\text{Tartar}\\ \text{emetic.}}}{2KSbOC_4H_4O_6} + \underset{\text{Water.}}{H_2O}$$

Sulphurated antimony.—Prepared by boiling native black sulphide of antimony and sulphur with solution of caustic soda, filtering and precipitating the sulphurated antimony with diluted sulphuric acid, when it is thrown down as an orange-red precipitate. It is a mixture of the sulphides and oxides of antimony, and is one of the many varieties of *mineral kermes*, so called from their similarity in colour to the *insect kermes; kermes* being the old name of the cochineal insect, which at one time was used for dyeing.

Tests for Antimony.

(i) Hydrochloric acid gives, with a neutral solution of an antimony salt (such as tartar emetic), a white precipitate of oxychloride of antimony, soluble in excess of hydrochloric acid.

(ii) Sulphuretted hydrogen gives, with an acid solution of an antimony salt, an orange-red precipitate of antimony sulphide (Sb_2S_3), soluble in alkalies and in ammonium sulphide.

(iii) If a solution of an antimony salt, to which sufficient hydrochloric acid is added to dissolve any precipitate at first thrown down, be boiled with a strip of bright copper foil, a dark grey film of metallic antimony will be deposited on the copper; if the strip of copper be now treated in a precisely similar manner to that described in connection with Reinsch's test for arsenic (*see* page 318), a white sublimate of antimony oxide will be obtained, but differing from the arsenic sublimate in that it is amorphous, and that it is deposited on the sides of the tube much nearer to the copper than the arsenic sublimate is, on account of the antimony being less volatile than arsenicum.

(iv) If the operations described under Marsh's test for arsenic (*see* page 319) be repeated, substituting the addition of an antimony salt for an arsenical compound, then antimoniuretted hydrogen (SbH_3) will be evolved, also communicating a livid colour to the burning hydrogen flame; this antimoniuretted hydrogen is decomposed like arseniuretted hydrogen at a low red heat, and a black spot of metallic antimony can be obtained on a cool porcelain dish or crucible-lid introduced for a moment into the flame. As previously mentioned, this antimony spot can be distinguished from the arsenicum spot obtained in similar circumstances by being insoluble in solution of chlorinated lime or chlorinated soda, whereas the arsenicum spot readily dissolves in either of these solutions.

CHAPTER X.

TIN—BISMUTH—SILVER—PLATINUM—GOLD.

Tin—Preparation and Properties of the Metal Tin—Tin Salts—Tests for Tin—Bismuth—Preparation of the Bismuth Salts—Tests for Bismuth—Silver—Extraction and Properties of the Metal Silver—Silver Salts—Tests for Silver—Platinum—Gold.

TIN.

Symbol, Sn; *formula*, Sn_2; *dyad and tetrad; atomic weight*, 118; *molecular weight*, 236.

Natural compounds of tin.—The principal tin ore is *tinstone* or stannic oxide (SnO_2), which is found in Cornwall, Saxony, Bohemia, Peru, Mexico, and Australia.

Preparation and properties of the metal tin.—The tin ore is first roasted to expel arsenic and sulphur, and the stannic oxide is then reduced to the metallic state by roasting it with anthracite coal or powdered charcoal. Tin is a soft and very malleable metal; it can therefore be hammered out into thin foil (tin-foil). It does not lose its lustre on exposure to the air at ordinary temperatures, and is used to coat iron to prevent the latter from rusting, *tin-plate* consisting of thin sheets of iron coated with tin. A bar of tin when bent emits a peculiar noise, the so-called *cry of tin*, produced by the friction of the crystals of the metal against one another. Tin enters into the composition of several very useful alloys; *bronze* is an alloy of copper and tin; *britannia-metal* is composed of tin and antimony; *solder* consists of tin and lead; *pewter* is also an alloy of tin and lead.

Action of acids on the metal tin.—Hot concentrated hydrochloric acid forms stannous chloride ($SnCl_2$) with evolution of hydrogen.

$$\underset{\text{Tin.}}{Sn_2} + \underset{\substack{\text{Hydrochloric}\\ \text{acid.}}}{4HCl} = \underset{\substack{\text{Stannous}\\ \text{chloride.}}}{2SnCl_2} + \underset{\text{Hydrogen.}}{2H_2}$$

Hot strong sulphuric acid forms stannous sulphate $SnSO_4$), and liberates sulphur dioxide.

$$\underset{\text{Tin.}}{Sn_2} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{4H_2SO_4} = \underset{\substack{\text{Stannous}\\ \text{sulphate.}}}{2SnSO_4} + \underset{\substack{\text{Sulphur}\\ \text{dioxide.}}}{2SO_2} + \underset{\text{Water.}}{4H_2O}$$

Strong nitric acid acts energetically on tin with the production of a white powder, metastannic acid, and the evolution of nitrogen tetroxide.

$$\underset{\text{Tin.}}{Sn_5} + \underset{\substack{\text{Nitric}\\ \text{acid.}}}{20HNO_3} = \underset{\substack{\text{Metastannic}\\ \text{acid.}}}{H_{10}Sn_5O_{15}} + \underset{\substack{\text{Nitrogen}\\ \text{tetroxide.}}}{10N_2O_4} + \underset{\text{Water.}}{5H_2O}$$

TIN SALTS.

There are two classes of tin salts, *stannous* and *stannic*; in the former the tin is only exerting one-half of its atomicity, viz. as a dyad; in the latter it is exerting its full atomicity as a tetrad.

Stannous chloride ($SnCl_2$) is prepared by the action of hot concentrated hydrochloric acid on tin. This salt is used commercially, under the name of *tin-salt*, in dyeing and for purposes of reduction.

Stannic chloride ($SnCl_4$) is prepared by passing chlorine into a solution of stannous chloride.

Stannic oxide (SnO_2) is prepared by heating metastannic acid, the product of the action of nitric acid on tin.

$$\underset{\substack{\text{Metastannic}\\\text{acid.}}}{H_{10}Sn_5O_{15}} = \underset{\substack{\text{Stannic}\\\text{oxide.}}}{5SnO_2} + \underset{\text{Water.}}{5H_2O}$$

Stannic oxide is used, under the name of *putty powder*, as a polishing powder for plate.

Tests for Tin.

(i) Sulphuretted hydrogen gives with an acidified solution of a stannous salt a brown precipitate of stannous sulphide, and with an acidified solution of a stannic salt a yellow precipitate of stannic sulphide.

(ii) Soluble stannous salts act as reducing agents, whereas stannic salts have no reducing action. For instance, if solution of stannous chloride be added to a solution of mercuric chloride, calomel (mercurous chloride) will be thrown down, owing to the stannous chloride abstracting one-half of the chlorine from the mercuric chloride to form stannic chloride.

$$\underset{\substack{\text{Mercuric}\\\text{chloride.}}}{2HgCl_2} + \underset{\substack{\text{Stannous}\\\text{chloride.}}}{SnCl_2} = \underset{\substack{\text{Mercurous}\\\text{chloride.}}}{Hg_2Cl_2} + \underset{\substack{\text{Stannic}\\\text{chloride.}}}{SnCl_4}$$

If more stannous chloride be now added, it will abstract all the chlorine from the precipitated calomel, forming the metal mercury in a fine state of division, and more stannic chloride.

$$\underset{\substack{\text{Mercurous}\\\text{chloride.}}}{Hg_2Cl_2} + \underset{\substack{\text{Stannous}\\\text{chloride.}}}{SnCl_2} = \underset{\text{Mercury.}}{2Hg} + \underset{\substack{\text{Stannic}\\\text{chloride.}}}{SnCl_4}$$

On account of the white and subsequently grey appearances of the precipitate this test was formerly known as the *magpie test for mercury.*

BISMUTH

Symbol, Bi ; *formula,* Bi_2 ; *triad ; atomic weight,* 210 ; *molecular weight,* 420.

Occurrence in nature.—Bismuth occurs in the metallic state in nature, mixed with quartz and other earthy substances ; it is separated by melting it away from the earthy impurities. Bismuth obtained in this way is generally contaminated with variable quantities of the metal arsenicum, from which it may be purified by melting it with potassium nitrate, and well stirring the mixture, when the arsenicum is oxidised to potassium arseniate.

BISMUTH SALTS.

Bismuth nitrate ($Bi(NO_3)_3$) is prepared by the action of strong nitric acid on bismuth.

$$\underset{\text{Bismuth.}}{Bi_2} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{8HNO_3} = \underset{\substack{\text{Bismuth}\\\text{nitrate.}}}{2Bi(NO_3)_3} +$$

$$\underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

Bismuth oxynitrate ($BiONO_3$).—This compound is derived from bismuth nitrate, by the displacement of two univalent nitric radicals by the dyad oxygen ; it is prepared by pouring bismuth nitrate into water, when it is thrown down as a white precipitate.

$$\underset{\substack{\text{Bismuth}\\\text{nitrate.}}}{Bi(NO_3)_3} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Bismuth}\\\text{oxynitrate.}}}{BiONO_3} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{2HNO_3}$$

This compound is largely used in medicine under the name of subnitrate of bismuth (*Bismuthi subnitras*, B. P.); it is also employed as a cosmetic or face-powder under the name of *Pearl white* (Blanc de Perle).

Bismuth oxide (Bi_2O_3) is prepared by boiling bismuth oxynitrate with solution of caustic soda; it is a yellow powder.

$$\underset{\substack{\text{Bismuth}\\ \text{oxynitrate.}}}{2BiONO_3} + \underset{\substack{\text{Sodium}\\ \text{hydrate.}}}{2NaHO} = \underset{\substack{\text{Bismuth}\\ \text{oxide.}}}{Bi_2O_3} + \underset{\substack{\text{Sodium}\\ \text{nitrate.}}}{2NaNO_3} + \underset{\text{Water.}}{H_2O}$$

Bismuth oxycarbonate ($Bi_2O_2CO_3$).—This compound may be regarded as bismuth oxide (Bi_2O_3), from which one atom of oxygen is displaced by an equivalent quantity of the dyad carbonic radical. It is prepared by pouring bismuth nitrate into a solution of ammonium carbonate.

$$\underset{\substack{\text{Bismuth}\\ \text{nitrate.}}}{2Bi(NO_3)_3} + \underset{\substack{\text{Ammonium}\\ \text{carbonate.}}}{3(NH_4)_2CO_3} = \underset{\substack{\text{Bismuth}\\ \text{oxycarbonate.}}}{Bi_2O_2CO_3} + \underset{\substack{\text{Ammonium}\\ \text{nitrate.}}}{6NH_4NO_3} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{2CO_2}$$

This compound is also extensively used in medicine under the name of carbonate of bismuth (*Bismuthi carbonas*, B. P.).

Bismuth citrate ($BiC_6H_5O_7$).—If an acid solution of bismuth nitrate be diluted with water until the oxynitrate just begins to be precipitated, and then a solution of sodium citrate be added, a precipitate of bismuth citrate (*Bismuthi citras*, B. P.) will be thrown down.

$$\underset{\substack{\text{Bismuth}\\ \text{nitrate.}}}{Bi(NO_3)_3} + \underset{\substack{\text{Sodium}\\ \text{citrate.}}}{Na_3C_6H_5O_7} = \underset{\substack{\text{Bismuth}\\ \text{citrate.}}}{BiC_6H_5O_7} + \underset{\substack{\text{Sodium}\\ \text{nitrate.}}}{3NaNO_3}$$

A solution of citrate of bismuth and ammonium (*Liquor bismuthi et ammonii citratis,* B. P.) is prepared by dissolving citrate of bismuth in a weak solution of ammonia; if this solution is evaporated to the consistence of a syrup, and then spread on plates and dried in scales, the solid double salt (*Bismuthi et ammonii citras,* B. P.) is obtained.

Tests for Bismuth.

(i) If any acid salt of bismuth is concentrated and then poured into an excess of water, a white oxysalt is precipitated.

(ii) Hydrochloric acid added to a neutral solution of a bismuth salt gives a white precipitate of bismuth oxychloride, soluble in excess of hydrochloric acid. The only other metal yielding a white precipitate with hydrochloric acid, soluble in excess of the acid, is antimony; the two metals can be readily distinguished by the different colours of their sulphides, as precipitated by sulphuretted hydrogen, the sulphide of bismuth being black and the sulphide of antimony orange-red.

(iii) Sulphuretted hydrogen gives with bismuth salts a black precipitate of bismuth sulphide.

SILVER.

Symbol, Ag; *formula*, Ag_2; *monad; atomic weight*, 108; *molecular weight*, 216.

Occurrence in nature.—Silver mainly occurs free in nature; *horn silver* is chloride of silver ($AgCl$); *sulphide of silver* (Ag_2S) is frequently contained in other native sulphides, notably in those of lead, copper, and antimony.

Extraction of the metal silver.—The *cupellation process* for extracting silver from lead has already been described in connection with the latter metal (*see* page 300). The *amalgamation process* for the extraction of silver consists in roasting the silver ores with common salt (sodium chloride), by which means silver chloride is formed; the roasted ores are then agitated in barrels with water and scrap iron, the iron abstracting the chlorine from the silver chloride to form ferrous chloride, and setting free the metal silver; mercury is then introduced into the barrels and they are again thoroughly agitated, when an amalgam of mercury and silver is formed; this amalgam is removed and heated in retorts, when the mercury distils over, the metal silver being left in the retort.

Properties of the metal silver.—Silver is a white, lustrous metal; it is soft, and so malleable that it can be beaten into extremely thin leaves (*silver leaf*). It does not oxidise at any temperature in the air, but in the molten state it possesses the peculiar power of dissolving about 20 times its volume of oxygen from the air; this oxygen is given off on the cooling and solidifying of the silver, producing the phenomenon known as the *spitting* of silver. Sulphuretted hydrogen blackens silver, and hence polished silver articles slowly tarnish when exposed to the air. Pure silver is too soft for use, but by the admixture of a small amount of copper with it a hard alloy is obtained; hence commercial silver and silver coins contain from 5 to 10 per cent. of copper.

Action of acids on silver.—Hydrochloric acid does not attack silver. Nitric acid forms silver nitrate, with evolution of nitrogen dioxide.

$$\underset{\text{Silver.}}{3Ag_2} + \underset{\substack{\text{Nitric}\\\text{acid.}}}{8HNO_3} = \underset{\substack{\text{Silver}\\\text{nitrate.}}}{6AgNO_3} + \underset{\substack{\text{Nitrogen}\\\text{dioxide.}}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

Strong sulphuric acid acts on silver, forming silver sulphate and evolving sulphur dioxide.

$$\underset{\text{Silver.}}{Ag_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Silver}\\\text{sulphate.}}}{Ag_2SO_4} + \underset{\substack{\text{Sulphur}\\\text{dioxide.}}}{SO_2} + \underset{\text{Water.}}{2H_2O}$$

SILVER SALTS.

Silver nitrate ($AgNO_3$) is prepared by the action of nitric acid on silver (*see* above). If silver nitrate is carefully melted, and then poured into moulds, it solidifies in the form of sticks, known as *lunar caustic*, which is frequently employed for external application as a caustic. The blackening produced on the skin after the application of silver nitrate is due to the reduction of the salt to metallic silver. A weaker caustic known as *mitigated caustic* is a mixture of silver and potassium nitrates (*Argenti et potassii nitras*, B. P.), and is prepared by fusing together one part of silver nitrate with two parts of potassium nitrate.

Silver oxide (Ag_2O) is prepared by precipitating a solution of silver nitrate with a solution of one of the fixed alkalies, potash, soda, or lime; lime-water is the preferable alkali to be employed on account of its freedom from chlorides.

$$\underset{\substack{\text{Silver}\\ \text{nitrate.}}}{2AgNO_3} + \underset{\substack{\text{Calcium}\\ \text{hydrate.}}}{Ca(HO)_2} = \underset{\substack{\text{Silver}\\ \text{oxide.}}}{Ag_2O} +$$

$$\underset{\substack{\text{Calcium}\\ \text{nitrate.}}}{Ca(NO_3)_2} + \underset{\text{Water.}}{H_2O}$$

Silver oxide is a brown powder, which is reduced to the metallic state either by heat or by contact with organic matter; on account of this last-mentioned property it should not be used in medicine combined with an essential oil or other organic substance.

Silver chloride, bromide, and **iodide**.—These compounds are obtained as precipitates when the corresponding potassium salts are added to a solution of silver nitrate. They are all very sensitive to the action of light, becoming reduced to a sub-salt after exposure, and this sub-salt, if afterwards treated with a reducing agent, becomes converted into metallic silver. It is on account of their sensitiveness to light that these silver salts are used in the production of photographs. The dry plates now used in photography consist of glass plates covered with a film of silver iodide or bromide suspended in gelatine; these plates are then exposed in the camera to the light reflected from the object to be photographed, when the silver salt where the light falls on it, is more or less reduced to a sub-salt, according to the intensity of the light. If the exposed plate is now placed in a solution of a reducing agent, such as pyrogallic acid, the sub-salt is completely reduced to metallic silver; this is the process known as *developing*. To preserve this picture and to prevent the undecomposed silver salt from blackening when exposed to the light, it must now be *fixed*; this process consists in dissolving out the undecomposed bromide or iodide of silver by immersing the plate in a solution of sodium thiosulphate (hyposulphite of soda).

In this way a *negative* is obtained, showing the bright parts of the object dark and the dark parts light; to *print* an ordinary photograph on to paper, the negative is placed over a sheet of paper prepared with silver chloride, and then exposed to the light.

Tests for Silver.

(i) Hydrochloric acid gives, with solutions of silver salts, a white curdy precipitate of silver chloride, insoluble in nitric acid, but soluble in solution of ammonia.

(ii) Potassium chromate gives, with a neutral solution of a silver salt, a red precipitate of silver chromate.

(iii) Lime-water produces a brown precipitate of silver oxide.

(iv) Sodium phosphate gives, with a neutral solution of a silver salt, a yellow precipitate of silver phosphate.

PLATINUM.

Symbol, Pt; *formula*, Pt_2; *tetrad; atomic weight*, 195; *molecular weight*, 390.

Platinum occurs in nature in the metallic state mixed with quartz. It is a very tough metal, and on account of a very high temperature being required to melt it, it is very suitable for the manufacture of crucibles, dishes, etc., used for analytical work. Platinum may be obtained as a grey spongy mass, called *spongy platinum*, by heating the double chloride of platinum and ammonium ($PtCl_4, 2NH_4Cl$); this spongy platinum is very porous, and possesses the power of occluding, or condensing within its pores, oxygen from the atmosphere. This occluded oxygen is so active that, if a stream of hydrogen is directed on to spongy platinum, the platinum first becomes red-hot, and then ignites the hydrogen. Döbereiner's hydrogen lamp depends upon this property of spongy platinum igniting a jet of hydrogen.

Platinum is not attacked by sulphuric, hydrochloric, or nitric acids separately; it is acted on by aqua regia (nitro-hydrochloric acid), platinic chloride ($PtCl_4$) being formed, and nitrogen dioxide evolved.

GOLD.

Symbol, Au; *formula*, Au_2; *triad; atomic weight*, 197; *molecular weight*, 394.

Gold occurs in nature in the free state. It is found in masses called nuggets, and also, in a more finely-divided state, in quartz rocks and in alluvial quartz sand which has been deposited by the disintegration of the older rocks.

Gold is one of the few metals possessing a decided tint, and is distinguished by its yellow colour. It is soft and very malleable, and can be beaten out into thin leaves (*gold-leaf*). It can be hammered so thin as to transmit light, the light being of a bluish-green colour. Gold is too soft a metal for general use, and is therefore alloyed with copper, in order to produce a hard alloy, which does not so readily wear away when used. The fineness of a sample of gold is in England expressed in *carats*, pure gold being said to be 24 carats. Thus 18-carat gold consists of 18 parts of gold alloyed with 6 parts of copper; 15-carat gold consists of 15 parts of gold alloyed with 9 parts of copper, and so on. English sovereigns and half-sovereigns are made of 22-carat gold, that is, of 22 parts of gold alloyed with 2 parts of copper.

Gold is not attacked by sulphuric, hydrochloric, or nitric acids separately; it is acted on by aqua regia (nitro-hydrochloric acid), auric chloride ($AuCl_3$) being formed, and nitrogen dioxide evolved.

$$\underset{\text{Gold.}}{Au_2} + \underset{\text{Hydrochloric acid.}}{6HCl} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Auric chloride.}}{2AuCl_3} + \underset{\text{Nitrogen dioxide.}}{N_2O_2} + \underset{\text{Water.}}{4H_2O}$$

Tables for the analytical detection of the metals and acids will be found at the end of this book.

Part IV.

ORGANIC CHEMISTRY.

CHAPTER I.

ORGANIC COMPOUNDS.

Organic Compounds—Organic Radicals—Destructive or Dry Distillation—Decay—Fermentation—Putrefaction—Classification of Organic Compounds—Isomeric Bodies.

Organic chemistry includes the chemistry of the organic compounds. The term *organic* is derived from ὄργανον, *an organ*. Originally organic chemistry only included the chemistry of those compounds formed in plants and animals as the result of the vital processes occurring in their cells and tissues; at that time it was believed that organic compounds could not be prepared artificially, but were only the result of the vital processes taking place in plants and animals. This distinction is now well known to be erroneous, a number of organic substances having been artificially prepared, either from their elements or from inorganic compounds. For instance, *cyanogen* C_2N_2) and *acetylene* (C_2H_2) have both been prepared by direct union of their elements; *urea* (CH_4N_2O), an organic body present in urine, has been artificially prepared from ammonium cyanate. Briefly stated, an organic compound is simply a carbon compound, and strictly the chemistry of the carbon compounds (*i.e.* organic chemistry) should be included in the chemistry of carbon and its compounds; but on account of the number and complexity of the organic compounds, it is found convenient to describe them separately; but it should be clearly understood that such a separation is a purely conventional one, adopted to facilitate the description and study of this extensive series of compounds.

Definition of the term 'organic compound.'—If by an organic compound is simply meant a carbon compound, then such inorganic substances as carbon dioxide (CO_2) and the metallic carbonates (Na_2CO_3, $CaCO_3$, $FeCO_3$, etc.) would have to be included amongst organic bodies. Such, however, is not intended in the conventional arrangement adopted, and we must therefore adopt some better and more exclusive definition of the term *organic compound* than that of its being simply "a carbon compound." A definition which applies to all organic compounds, and only to them, is that employed by Frankland. It begins by stating that an organic compound is a carbon compound; but this statement is then qualified by enumerating the elements that the carbon must be directly united with in order to form an organic body. Frankland defines an organic body as "a substance where one or more atoms of the carbon of a molecule are *directly* combined with carbon, hydrogen, or nitrogen."

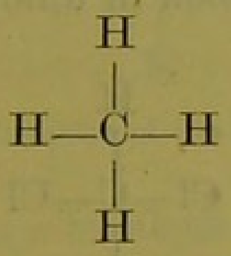
This definition does not exclude the presence of other elements, such as oxygen, chlorine, bromine, iodine, sulphur, phosphorus, etc., as it merely requires that an organic body must contain in its molecule carbon, which carbon is in direct union with carbon, or with hydrogen, or with nitrogen. According to this definition, carbon dioxide (CO_2) and the metallic carbonates ($CaCO_3$, etc.) are not organic compounds, since though they contain carbon, yet this carbon is not in union with carbon, or with hydrogen, or with nitrogen. On the other hand, it will be found that this definition applies to all true organic bodies, as the following examples will demonstrate.

Charcoal (C_2) is an organic body, for its molecule consists of carbon in union with carbon.

$$C—C$$

Graphic formula of carbon.

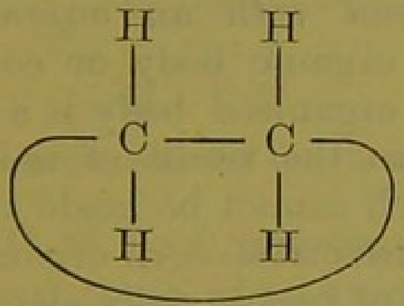
Methane (CH_4) is an organic body, for its molecule contains carbon in union with hydrogen.



$$\begin{array}{c} H \\ | \\ H—C—H \\ | \\ H \end{array}$$

Graphic formula of methane

Ethene (C_2H_4) is an organic body, for its molecule contains carbon in union with carbon and hydrogen.



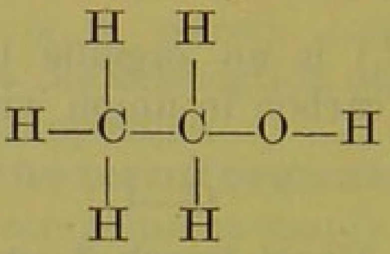
Graphic formula of ethene.

Cyanogen (C_2N_2) is an organic body, for its molecule contains carbon in union with carbon and nitrogen.

$$C \equiv N - N \equiv C$$

Graphic formula of cyanogen.

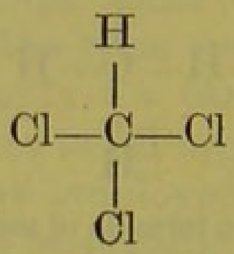
Ethyl alcohol (C_2H_6O) is an organic body, for its molecule contains carbon in union with carbon and hydrogen.



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & — & C & — & C & — & O & — & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

Graphic formula of ethyl alcohol.

Chloroform ($CHCl_3$) is an organic body, for its molecule contains carbon in union with hydrogen.



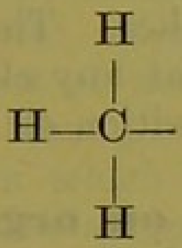
$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ Cl & — & C & — & Cl \\ & & | & & \\ & & Cl & & \end{array}$$

Graphic formula of chloroform.

It is very important not to confuse an *organic body* or *compound* with an *organised body.* The definition of an organic body or compound has just been given; an organised body is a tissue of fibrous or cellular nature, the result of animal or vegetable growth, and which cannot be made artificially.

Organic radicals.—An organic radical is composed of a group of two or more elements, which must contain carbon directly united with carbon, hydrogen, or nitrogen, and the elements of which group do not completely saturate one another; such a radical, therefore, requires to be saturated by some other body, or bodies, in order to be capable of existing. The quantivalence or atomicity of the radical will be determined by its degree of unsaturation; thus, a univalent radical would require one atom of a univalent element to combine with and saturate it, a bivalent radical would require two atoms of a univalent element to saturate it, a trivalent radical would require three atoms of a univalent element, and so on.

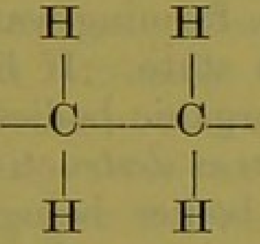
Examples.—Methyl $(CH_3)^{i}$ is a univalent organic radical, since in the group one atom-fixing power of the carbon is left unsaturated.



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{H—C—} \\ | \\ \mathrm{H} \end{array}$$

Graphic representation of the methyl radical.

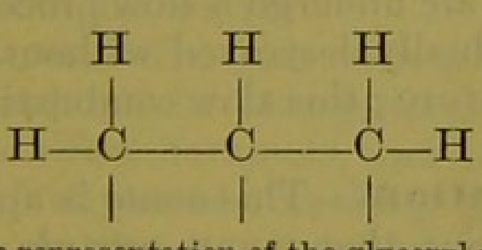
Ethene $(C_2H_4)^{ii}$ is a bivalent organic radical, since in the group two atom-fixing powers of the carbon atoms are left unsaturated.



$$\begin{array}{ccc} \mathrm{H} & & \mathrm{H} \\ | & & | \\ \mathrm{—C} & \mathrm{——} & \mathrm{C—} \\ | & & | \\ \mathrm{H} & & \mathrm{H} \end{array}$$

Graphic representation of the ethene radical.

Glyceryl $(C_3H_5)^{iii}$ is a trivalent organic radical, since in the group three atom-fixing powers of the carbon atoms are left unsaturated.



$$\begin{array}{ccccc} & \mathrm{H} & \mathrm{H} & \mathrm{H} & \\ & | & | & | & \\ \mathrm{H—} & \mathrm{C——} & \mathrm{C——} & \mathrm{C} & \mathrm{—H} \\ & | & | & | & \end{array}$$

Graphic representation of the glyceryl radical.

Elements composing organic compounds.—Although the number of organic compounds far exceeds that of the inorganic bodies, yet the actual number of elements entering into the composition of the great majority of organic substances is small. The four elements, carbon, hydrogen, nitrogen, and oxygen, combine to form a very large proportion of organic bodies; chlorine, bromine, iodine, sulphur, and phosphorus enter into the composition of a few, whilst metallic elements are contained in a very small number of organic bodies. The fact, however, should be borne in mind that any element can be made to enter into the composition of an artificially prepared organic compound.

Action of heat on organic bodies.—With the exception of those organic substances that volatilise unchanged when heated, most organic bodies are distinguished by the facility with which they are decomposed on the application of heat. If heated to a sufficiently high temperature with free contact of air, they burn away, the carbon forming carbon dioxide, the hydrogen forming water, and the nitrogen escaping in the free state. If heated out of contact with the air, most organic bodies undergo a complex decomposition, known as *destructive* or *dry distillation*, a number of fresh bodies being produced by a re-arrangement of the atoms of the organic molecule under the influence of dry heat, without contact of air. For examples of destructive or dry distillation *see* pages 399, 420.

Decay.—Many moist organic substances when exposed to the air undergo a slow process of oxidation, and so are gradually destroyed without sensible elevation of temperature; this slow combustion or oxidation is called *decay*.

Fermentation.—This name is applied to a class of decompositions that many organic bodies undergo in presence of a ferment. There are two classes of ferments, the *organised* and the *non-organised.* The *organised ferments* are microscopic fungoid organisms, the principal of which are *yeast* or *torula cerevisiæ*, which produces alcoholic or vinous fermentation, *mycoderma aceti*, which produces acetous fermentation, and *penicillium glaucum*, which produces lactic and probably butyric fermentation.

The various micro-organisms (bacilli, etc.) that have been discovered in connection with several of the zymotic diseases, and which are apparently the primary causative factors of the diseases, possibly act as ferments within the human body, producing organic poisons, the presence of which in the system may be the direct cause of the symptoms of the various diseases. The *non-organised* or *soluble ferments* act only in solution, and when isolated are obtained as amorphous powders, the principal of which are *pepsin*, the ferment contained in gastric juice, *ptyalin*, the ferment contained in saliva, and *trypsin*, the ferment contained in pancreatic juice.

In the case of the organised ferments, the fermentative process is probably due to the ferment growing and multiplying at the expense of part of the substance that is being acted on, the remaining part breaking up into simpler bodies, which are the products of fermentation; in other words, the ferment is regarded as feeding, for its growth and multiplication, on a small portion of the substance undergoing fermentation, and thus destroying the chemical balance of the remaining portion, so as to cause its resolution into simpler bodies.

Putrefaction.—This process is practically one of fermentation produced in nitrogenised organic bodies by bacteria and other ferments, and accompanied by the evolution of unpleasant-smelling gases, which are mainly compounds of sulphur and phosphorus, and in part, possibly, complex hydrocarbon gases and volatile nitrogenous bases. The conditions necessary for putrefaction are (*a*) the presence of a certain amount of air to start the process, (*b*) moisture, and (*c*) warmth. If air is excluded, as in the proper tinning of tinned provisions, and if bacteria and other ferments are previously destroyed by heat, then putrefaction does not occur. Disinfectants prevent putrefaction by their germicidal action; that is, by destroying the ferments that set up the putrefactive changes.

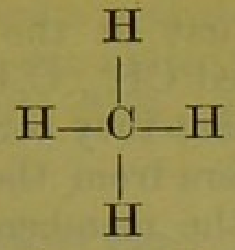
CLASSIFICATION OF ORGANIC COMPOUNDS.

The following are the chief groups of organic compounds, with illustrations of each :—

Hydrocarbons. — Compounds of carbon and hydrogen only. A very large number of hydrocarbons exist; they are divided into two groups; (*a*) *paraffins*, in which the carbon is completely saturated with hydrogen, (*b*) *olefines*, in which the carbon is only partly saturated with hydrogen.

Paraffins, on account of being completely saturated bodies, have but little affinity for other elements, hence the derivation of their name (from *parum affinis*, little affinity); olefines derive their name from olefiant gas or ethene (C_2H_4), the first known member of the group of unsaturated hydrocarbons.

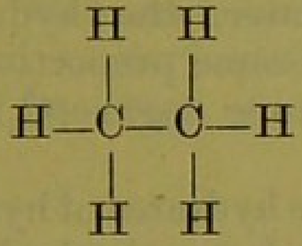
All paraffins are referable to the general formula CnH_{2n+2}, that is, by doubling the number of the carbon atoms, and adding two, the number of the hydrogen atoms will always be obtained. The simplest *paraffin* is methane or marsh gas (CH_4).



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

Graphic formula of methane.

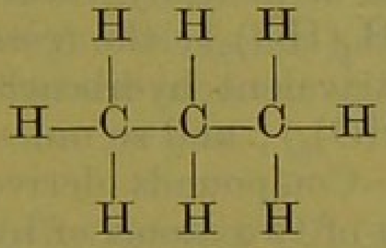
The two carbon atom *paraffin* is ethane (C_2H_6).



$$\begin{array}{ccccccc} & & H & & H & & \\ & & | & & | & & \\ H & - & C & - & C & - & H \\ & & | & & | & & \\ & & H & & H & & \end{array}$$

Graphic formula of ethane.

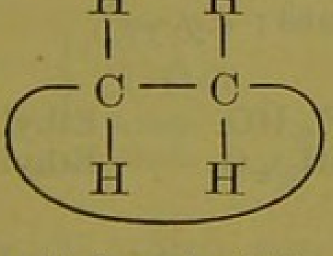
The three carbon atom *paraffin* is propane (C_3H_8).



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & \\ & & H & & H & & H & & \end{array}$$

Graphic formula of propane.

The simplest *olefine* is ethene or olefiant gas (C_2H_4). The graphic formula shows that two of the atom-fixing powers of the carbon atoms are not united with hydrogen, but these, when the olefine is in the free state, unite with one another, and so neutralise their grasping or fixing powers.



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & - & C \\ | & & | \\ H & & H \end{array}$$

Graphic formula of ethene.

It will be seen that in the cases of the three paraffins just mentioned CH_4, C_2H_6, C_3H_8, and therefore of all paraffins, that they constitute a series, any member of which differs from the succeeding one by CH_2; such a series, the members of which differ in composition by a constant quantity, is called a *homologous series*.

Carbohydrates.—Compounds of carbon and the elements of water, the hydrogen and oxygen being present in the same proportion as in water: *e.g.* starch ($C_6H_{10}O_5$), grape sugar ($C_6H_{12}O_6$), cane sugar ($C_{12}H_{22}O_{11}$).

Alcohols.—The hydrates of hydrocarbon radicals; the *monatomic alcohols* are the hydrates of univalent hydrocarbon radicals: *e.g.* methyl alcohol (CH_3HO) and ethyl alcohol (C_2H_5HO); the *diatomic alcohols* are the hydrates of bivalent hydrocarbon radicals: *e.g.* ethene glycol ($C_2H_4(HO)_2$); the *triatomic alcohols* are the hydrates of trivalent hydrocarbon radicals: *e.g.* glycerine ($C_3H_5(HO)_3$); and so on.

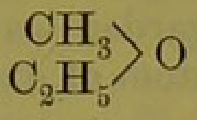
Aldehydes.—Compounds derived from alcohols by the abstraction of two atoms of hydrogen from the molecule of an alcohol, *e.g.*—

Ethyl alcohol	C_2H_6O
Ethyl aldehyde	C_2H_4O

Ethers.—The oxides of hydrocarbon radicals. As alcohols are the hydrates of hydrocarbon radicals, so to every alcohol there is a corresponding ether, the ether being the oxide of the radical, of which the alcohol is the hydrate: *e.g.*—

Methyl alcohol	$CH_3.HO.$	Ethyl alcohol	$C_2H_5.HO.$
Methyl ether	$(CH_3)_2.O.$	Ethyl ether	$(C_2H_5)_2.O.$

If the ether is an oxide of only one hydrocarbon radical, then it is called a *simple ether* ; if two different hydrocarbon radicals are united with the oxygen, then it is called a compound ether : *e.g.*—

Methyl-ethyl ether 

$$\left.\begin{matrix}CH_3\\C_2H_5\end{matrix}\right>O$$

Ethereal salts.—Compounds of the hydrocarbon or alcohol radicals with acid radicals. An ethereal salt may be regarded as derived from an alcohol, the hydroxyl of which has been displaced by an acid radical : *e.g.*—

Ethyl nitrite or nitrous ether	$C_2H_5.NO_2$.
Ethyl acetate or acetic ether	$C_2H_5.C_2H_3O_2$.

If the acid radical united with the alcohol radical is one of the halogen elements (chlorine, bromine, iodine, fluorine), then the ethereal salt bears the special name of a *haloid ether : e.g.*—

Methyl chloride	$CH_3.Cl$.
Ethyl iodide	C_2H_5I.

Organic acids.—Compounds containing the radical oxatyl or carbonyl (COHO) united with some other radical. The radical united with the oxatyl may be simply hydrogen, as in the case of formic acid, or it may be an alcohol radical, as in the case of acetic acid, or it may be oxatyl itself, as in the case of oxalic acid.

$$\begin{array}{ccc} \left\{\begin{matrix}H\\COHO\end{matrix}\right. & \left\{\begin{matrix}CH_3\\COHO\end{matrix}\right. & \left\{\begin{matrix}COHO\\COHO\end{matrix}\right. \\ \text{Formic acid.} & \text{Acetic acid.} & \text{Oxalic acid.} \end{array}$$

Those organic acids which can be obtained by oxidation of alcohols are produced by the abstraction of two atoms of hydrogen from the molecule of the alcohol, and the substitution of one atom of oxygen for the hydrogen withdrawn ; or, in other words, they may be regarded as aldehydes to the molecule of which one atom of oxygen has been added : *e.g.*—

Methyl alcohol	CH_4O.	Ethyl alcohol	C_2H_6O.
Methyl aldehyde	CH_2O.	Ethyl aldehyde	C_2H_4O.
Formic acid	CH_2O_2.	Acetic acid	$C_2H_4O_2$.

Ketones.—Compounds of the bivalent radical carbonyl (CO) with two hydrocarbon or alcohol radicals ; *e.g.*—

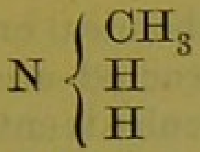
$$CH_3—CO—CH_3$$

Dimethyl ketone or acetone.

Alkaloids.—Organic bases derived from plants, All alkaloids contain nitrogen, and they are, in fact, complex derivatives of ammonia, the hydrogen of which has been partially or entirely displaced by various radicals. Since alkaloids are organic bases, they possess the property of uniting with and neutralising acids, to form salts. The best-known alkaloids are quinine, morphine, strychnine, atropine, etc.

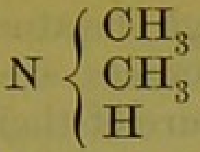
A group of alkaloids of animal origin, known as *animal alkaloids*, have within the last few years been discovered ; some of them are amongst the products of the putrefaction of animal substances, and are called *ptomaines*.

Compound ammonias.—Compounds derived from ammonia by the displacement of part or all of the hydrogen by an organic radical or radicals. If the radical is an alcohol or hydrocarbon one, then the resulting compound ammonia is called an *amine ;* if the radical is an acid one, then the resulting compound ammonia is called an *amide ; e.g.*—



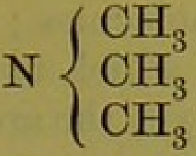
$N\left\{\begin{matrix}CH_3\\H\\H\end{matrix}\right.$

Methylamine.



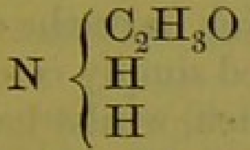
$N\left\{\begin{matrix}CH_3\\CH_3\\H\end{matrix}\right.$

Dimethylamine.



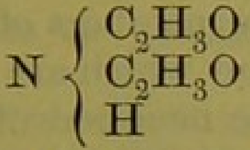
$N\left\{\begin{matrix}CH_3\\CH_3\\CH_3\end{matrix}\right.$

Trimethylamine.



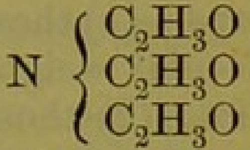
$N\left\{\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right.$

Acetamide.



$N\left\{\begin{matrix}C_2H_3O\\C_2H_3O\\H\end{matrix}\right.$

Diacetamide.



$N\left\{\begin{matrix}C_2H_3O\\C_2H_3O\\C_2H_3O\end{matrix}\right.$

Triacetamide.

Those compound ammonias derived by the displacement of all the hydrogen of the ammonia are sometimes called *nitrils.*

Glucosides.—Certain organic substances (either nitrogenous or non-nitrogenous) derived from plants, and splitting up when boiled with dilute sulphuric acid, or under the influence of a ferment, into glucose and some other substance or substances.

ISOMERIC BODIES.

The term *isomeric* (from ἴσος, equal; μέρος, part) is applied to those bodies that have the same percentage composition, but which differ in their properties. In other words, isomeric bodies are composed of the same elements, and in the same proportions, but yet they are entirely different bodies, as indicated by their entirely different properties. These different properties are due to a different arrangement of the atoms in the molecules of isomeric bodies; so that although isomeric bodies have the same composition, they have a different constitution. For instance, oil of turpentine and oil of lemons are isomeric bodies; they both possess the formula $C_{10}H_{16}$, yet they differ markedly in their properties, and this difference is due to different arrangements of the atoms in their respective molecules; although the atoms, or chemical bricks, out of which two substances are constructed are the same, yet the architecture of their molecules is entirely different.

Isomeric bodies are generally divided into two groups—(1) those the members of which have the same molecular weight, and which are called simply *isomeric bodies;* (2) those the members of which, whilst having the same percentage composition, yet differ in molecular weight, and which are called *polymeric bodies* (from πολύς, many, and μέρος, part).

As examples of *isomeric bodies* may be mentioned urea (CH_4N_2O) and ammonium cyanate (NH_4CNO), which both have the same composition; starch ($C_6H_{10}O_5$), dextrine ($C_6H_{10}O_5$), and cellulose ($C_6H_{10}O_5$); and oil of turpentine ($C_{10}H_{16}$) and oil of lemons ($C_{10}H_{16}$). As examples of *polymeric bodies* may be mentioned acetylene (C_2H_2) and benzene (C_6H_6), which both have the same percentage composition, whilst the molecular weight of the latter is three times that of the former; and lactic acid ($C_3H_6O_3$) and glucose ($C_6H_{12}O_6$), which both have the same percentage composition, whilst the molecular weight of the latter is twice that of the former.

CHAPTER II.

ULTIMATE ANALYSIS OF ORGANIC COMPOUNDS.

Determination of Carbon, Hydrogen, Oxygen, Nitrogen, Chlorine, Sulphur, and Phosphorus in Organic Bodies—Calculation of Formulæ from Percentage Composition—Empirical, Molecular, and Constitutional Formulæ.

SINCE so large a number of organic compounds only contain carbon, hydrogen, and oxygen, their ultimate analysis consists in determining the amount of carbon in the form of carbon dioxide, the amount of hydrogen in the form of water, the amount of oxygen being always determined by difference. The determinations of the amounts of other elements, such as nitrogen, chlorine, bromine, iodine, sulphur, and phosphorus, are always done separately.

Determination of the carbon and hydrogen in an organic compound containing carbon, hydrogen, and oxygen.—A weighed quantity of the dried organic compound (sugar, for instance) is taken, and its carbon is converted into carbon dioxide, and its hydrogen into water, by burning it in a stream of oxygen in a tube containing copper oxide ; the water is collected in a previously-weighed calcium chloride tube (Fig. 28), and the carbon dioxide in a strong solution of caustic potash contained in a series of bulbs (Fig. 29), which are weighed with the caustic potash previous to the operation.

The combustion is carried out in a thick combustion tube, about 24 inches long, made of hard glass (Fig. 30), the fore part of which is charged with well-dried granular copper oxide (c), a plug of asbestos (D) being placed in front of it to prevent the mechanical carrying over of any of the copper oxide. The weighed quantity of sugar is placed in a small platinum boat (B), which is then slipped into the tube as shown in the figure, and the tube is then placed in a gas combustion-furnace, with the ends projecting from either extremity of the furnace; the weighed calcium chloride tube (E) is then connected to the D end of the combustion tube by means of a perforated cork, and the weighed potash bulbs (Fig. 29) are next connected to the calcium chloride tube at F by means of a small piece of india-rubber

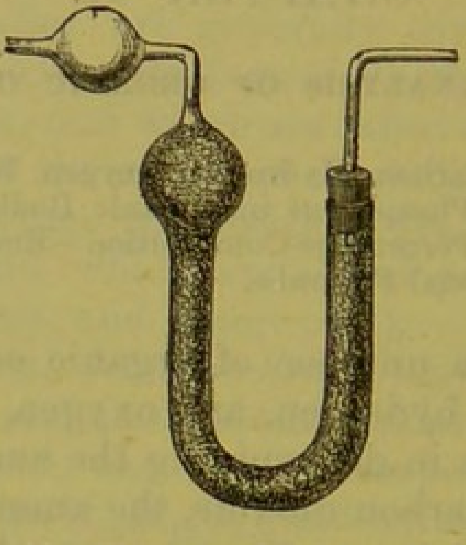


Fig. 28.—Chloride of Calcium Tubes.

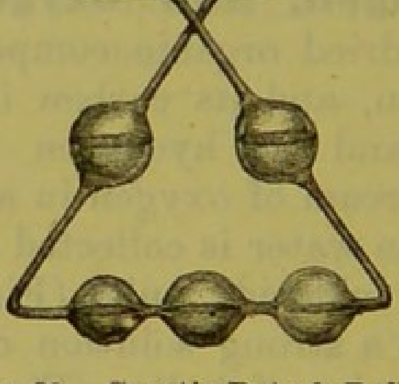


Fig. 29.—Caustic Potash Bulbs.

tubing; the hinder extremity of the tube at A is connected with a reservoir or gasometer, from which pure dry oxygen can be passed through the apparatus.

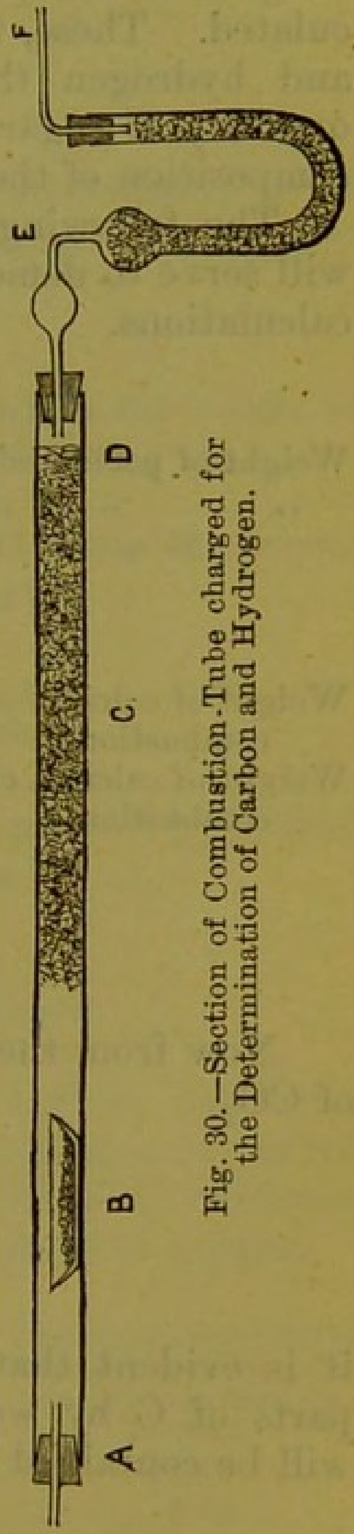


Fig. 30.—Section of Combustion-Tube charged for the Determination of Carbon and Hydrogen.

The fore part of the tube containing the copper oxide is first made red-hot, and oxygen is allowed to pass slowly through the tube; heat is then applied to the part B where the platinum boat containing the sugar has been placed, when the sugar is burnt by the oxygen to carbon dioxide and water, any hydrocarbon vapours that may escape combustion by the oxygen becoming completely oxidised during their transit over the red-hot copper oxide, some of which becomes reduced to cuprous oxide or to metallic copper. The water in the form of aqueous vapour (steam) and the carbon dioxide are carried onwards by the stream of oxygen, the water being entirely absorbed by the calcium chloride, and the carbon dioxide passing on to become completely absorbed by the caustic potash in the potash bulbs. When all the sugar is completely burnt away, and nothing but oxygen bubbles through the potash bulbs, the operation is stopped, and the potash bulbs and the calcium chloride tube are detached and carefully weighed; the increase in weight of the latter gives the amount of water produced, and the increase in weight of the former gives the amount of carbon dioxide produced; from these the actual weights of carbon and hydrogen can easily be calculated. These, then, will be the weights of carbon and hydrogen that were present in the weighed quantity of sugar taken; from which the percentage composition of the sugar can then be calculated.

The following account of a combustion of sugar will serve to demonstrate the method of making these calculations.

Weight of sugar employed 0·4 gramme.

Weight of potash bulbs after the combustion	52·7425 grammes.
,, ,, ,, before ,,	52·1250 ,,
	·6175 gramme of CO_2 produced.
Weight of calcium chloride tube after the combustion.	33·4895 grammes.
Weight of calcium chloride tube before the combustion.	33·2575 ,,
	·2320 gramme of H_2O produced.

Now from the calculation of the molecular weight of CO_2

$$\begin{aligned} C &= 12 \\ O_2 = 16 \times 2 &= 32 \\ &\overline{44} \end{aligned}$$

it is evident that every 44 parts of CO_2 contain 12 parts of C by weight; therefore what weight of C will be contained in ·6175 gramme of CO_2?

$44 : \cdot6175 :: 12 : x$

$x = \cdot1684$ gramme of carbon, which is the weight of carbon present in ·4 gramme of sugar.

Similarly from the calculation of the molecular weight of H_2O

$$\begin{array}{lr} H_2 = 1 \times 2 = & 2 \\ O \qquad\quad = & 16 \\ \hline & 18 \end{array}$$

it is evident that every 18 parts of H_2O contain 2 parts of H by weight; therefore what weight of H will be contained in ·232 gramme of H_2O?

$18 : {\cdot}232 :: 2 : x$

$x = {\cdot}0257$ gramme of hydrogen, which is the weight of hydrogen present in ·4 gramme of sugar.

If ·4 parts of sugar contain ·1684 parts of carbon, what will 100 parts of sugar contain?

$${\cdot}4 : 100 :: {\cdot}1684 : x$$

$x = 42{\cdot}10$ per cent. of carbon.

If ·4 parts of sugar contain ·0257 parts of hydrogen, what will 100 parts of sugar contain?

$${\cdot}4 : 100 :: {\cdot}0257 : x$$

$x = 6{\cdot}42$ per cent. of hydrogen.

As sugar is composed only of carbon, hydrogen, and oxygen, if the sum of the percentages of carbon and hydrogen be deducted from 100, the difference, viz. 51·48, will represent the percentage of oxygen.

	Percentage composition of sugar as obtained by analysis.	Percentage composition of sugar as obtained by calculation from its formula.
Carbon . .	42·10	42·11
Hydrogen . .	6·42	6·43
Oxygen . .	51·48	51·46
	100·00	100·00

Determination of the carbon and hydrogen in an organic compound containing nitrogen.—The carbon and hydrogen are determined separately from the nitrogen; the process of combustion just described is adopted, but it is necessary to insert in the fore part of the tube at D (Fig. 30) a roll of metal copper gauze about 3 or 4 inches long; this is made red hot before commencing the combustion, and then serves to reduce any oxides of nitrogen that may be evolved, converting them by abstraction of their oxygen into free nitrogen, which then passes unabsorbed through the calcium chloride tube and potash bulbs, and so escapes. If this were not done, any oxides of nitrogen formed would be absorbed by the caustic potash, and so would vitiate the determination of the carbon.

Determination of the carbon and hydrogen in an organic compound containing chlorine, bromine, or iodine.—Lead chromate should be substituted for the copper oxide, and the combustion proceeded with in the usual manner; the lead chromate keeping back either of the halogen elements.

Determination of the carbon and hydrogen in an organic liquid.—If it is required to determine the amounts of carbon and hydrogen in an organic liquid, such as alcohol, a bulb is blown on the end of a piece of fine capillary glass tubing, the whole being of about the size shown in Fig. 31, so that it can be easily slipped into the combustion-tube. The bulb is first accurately weighed, and is then warmed over a spirit or Bunsen flame to expand the air within it, and its open end is then quickly inverted beneath some of the alcohol or whatever organic liquid is being submitted to analysis; as the air in the bulb cools and contracts, the alcohol is forced up into it by atmospheric pressure, and when the bulb is full of alcohol up to A, the end B is inserted for a moment or two into a spirit or Bunsen flame in order to seal it. The sealed bulb is now again weighed, and the increase of weight represents the amount of alcohol contained in it; the sealed end B is then broken off and is placed together with the bulb in the platinum boat (B, Fig. 30), which is then pushed into the combustion-tube, and the combustion is proceeded with in the ordinary way, care being taken to apply heat very gradually to the part of the tube under the platinum boat, so that the alcohol shall be slowly converted into vapour, which, carried by the current of oxygen over the red hot copper oxide, becomes completely oxidised to carbon dioxide and water.

Fig. 31.—Bulb for weighing Organic Liquids

Determination of the nitrogen in an organic nitrogenous compound.—The nitrogen of an organic compound is always determined separately from the carbon and hydrogen by a special process. There are two methods in use:—(i) *The ammonia process*, by which the nitrogen is converted into ammonia, the amount of which is estimated; and

(ii) *the free nitrogen process*, by which the nitrogen of the organic substance is obtained in the free state, and its amount determined by collecting it in a graduated tube.

(i) *The ammonia process*, or *Will and Varrentrapp's method.*—This process depends upon the fact that if an organic nitrogenous body is heated with a solid caustic alkali, the nitrogen is converted into and is completely evolved as ammonia. A piece of stout combustion-tubing, about 15 inches long, is drawn out to a point at one end, which is bent nearly to a right angle (Fig. 32); the posterior third of this (A, Fig. 33) is filled with the granular soda-lime (a mixture of sodium and calcium hydrates, produced by slaking lime with a strong solution of caustic soda); the weighed quantity of the nitrogenous organic substance is then thoroughly mixed with more soda-lime, and the mixture introduced into the combustion-tube so as to occupy the middle third (B, Fig. 33); the anterior third of the tube is then filled up with soda-lime (C, Fig. 33), in front of which is placed a plug of asbestos, D, to prevent the mechanical carrying over of any of the soda-lime. To the charged combustion-tube is now fitted, by means of a perforated cork, the piece of apparatus, E (Fig. 33), consisting of three bulbs, and containing a measured quantity of a standardised sulphuric acid. Heat is then applied to the fore part of the tube (C and D), and when this has become red-hot the other portions of the tube are

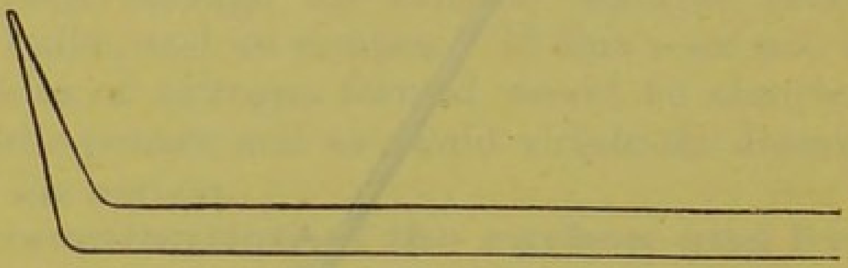


Fig. 32.—Combustion-Tube for the Determination of Nitrogen by the Ammonia Process.

gradually heated, until the whole is red-hot. The nitrogen of the organic substance is converted by the soda-lime into ammonia, which as it bubbles through the diluted sulphuric acid contained in the bulbs is absorbed, neutralising some of the sulphuric acid. When no more bubbles pass through the acid, the turned-up extremity of the combustion-tube is broken off, and air is drawn through the apparatus, so as to displace any ammonia remaining within the combustion-tube into the acid. The bulbs are then withdrawn and the acid turned out into an evaporating-dish; the amount of free acid left is then determined by seeing what quantity of a standard solution of caustic soda is required to neutralise the acid left unneutralised by the ammonia; the difference (since a measured quantity of standardised sulphuric acid was taken) represents the amount of acid neutralised by the ammonia, from which the amount of ammonia required to neutralise it can easily be calculated. The weight of nitrogen contained in this amount of ammonia then represents the actual weight of nitrogen contained in the weighed quantity of the organic nitrogenous substance operated on, from which the percentage of nitrogen is easily calculated.

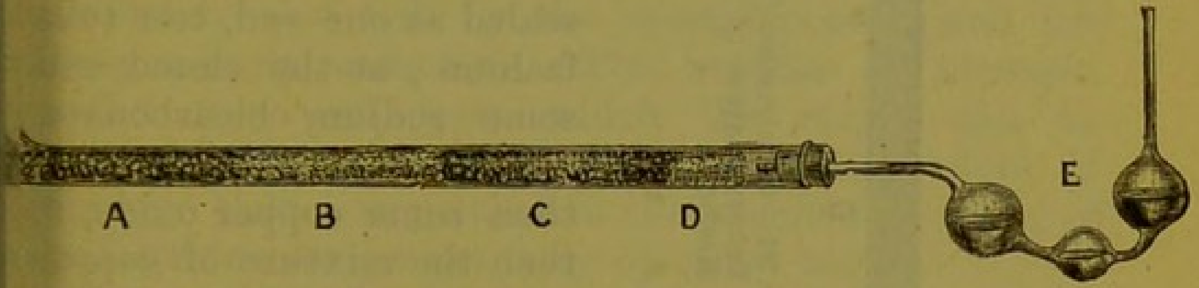


Fig. 33.—Combustion-Tube charged for the Determination of Nitrogen by the Ammonia Process.

(ii) *The free nitrogen process*, or *Duma's method.*—This consists in burning the organic nitrogenous substance with copper oxide, passing the oxides of nitrogen formed over heated metallic copper, to reduce them to nitrogen, and collecting the nitrogen in a graduated tube over a strong solution of caustic potash, which absorbs carbon dioxide, but not nitrogen. Before commencing the combustion, the air within the charged combustion-tube is expelled by means of carbon dioxide. To carry out this process, a piece of combustion-tubing, about 20 inches long, is sealed at one end, test tube fashion; at the closed end some sodium bicarbonate, A (Fig. 34), is introduced, then some copper oxide, B, then the mixture of copper oxide and the weighed quantity of the organic nitrogenous substance, C; after this some more copper oxide, D, and finally a roll of metallic copper gauze, E. A piece of bent tubing, dipping beneath the surface of mercury in a pneumatic trough, is then connected to the charged combustion-tube by means of a perforated cork. Before the graduated tube F is placed over the delivery tube, heat is applied to the sodium bicarbonate at A, so that the carbon dioxide evolved shall chase out all the air in the combustion and delivery tubes. When this is effected,

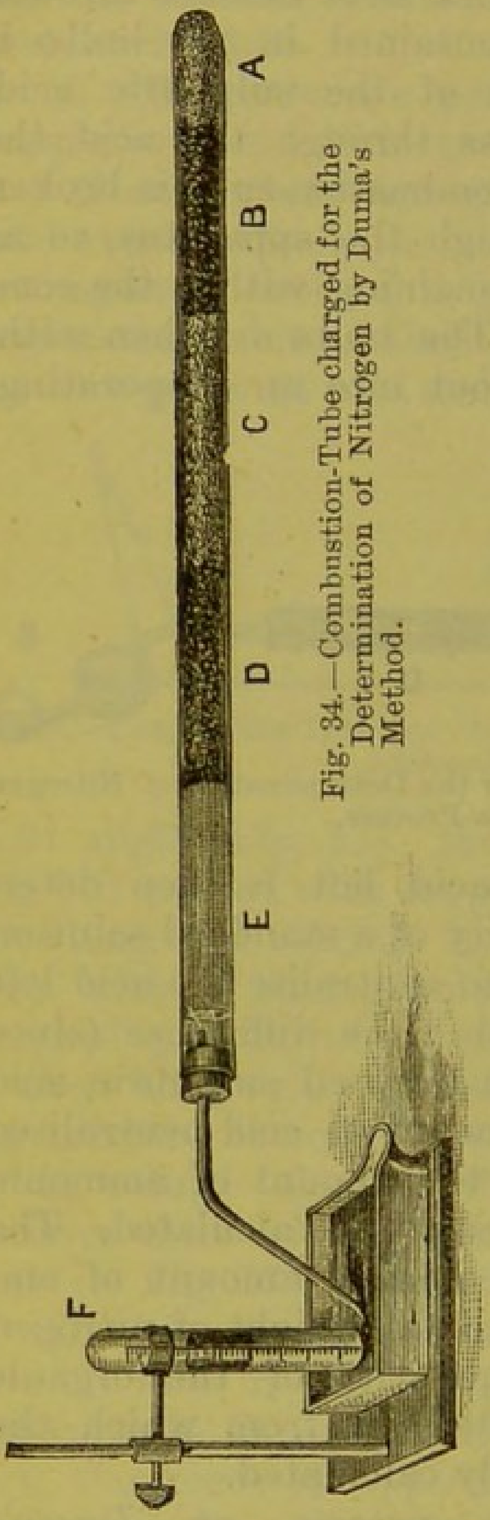


Fig. 34.—Combustion-Tube charged for the Determination of Nitrogen by Duma's Method.

the graduated tube F is filled two-thirds with mercury and one-third with a strong solution of caustic potash, and is then inverted over the end of the delivery tube —that is, beneath the surface of the mercury in the trough. The combustion is then carried on by first making the fore part of the combustion-tube at F red-hot, and gradually extending the heat to the hinder part till it is red-hot throughout. Any oxides of nitrogen formed are reduced by the metallic copper to free nitrogen, which, along with carbon dioxide, bubbles up through the mercury and caustic potash in the graduated tube, the carbon dioxide becoming completely absorbed by the caustic potash, and the nitrogen only collecting. The volume of nitrogen is then read off, from which the weight can be calculated, and this represents the actual weight of nitrogen that was present in the weighed quantity of the organic nitrogenous body operated on.

Determination of chlorine in organic compounds.—A weighed quantity of the organic compound is roasted with pure quicklime (CaO) in a combustion-tube, by which means the chlorine of the organic compound is converted into calcium chloride; the contents of the tube are then dissolved in water and nitric acid, and silver nitrate added to precipitate all the chlorine as silver chloride, which is then collected, washed, dried, and weighed. From the weight of silver chloride the amount of chlorine present is calculated, and this will be the actual amount of chlorine present in the weighed quantity of the organic compound operated on.

Iodine and *bromine* in organic compounds are estimated in a precisely similar manner to chlorine.

Determination of sulphur in organic compounds.—A weighed quantity of the organic compound is heated in a porcelain dish with potassium chlorate and nitric acid, by which means the sulphur is oxidised to sulphuric acid ; the contents of the dish are boiled with water, and filtered, and, to the filtrate, barium nitrate is added to precipitate the sulphuric acid as barium sulphate, which is then collected, washed, dried, and weighed. From the weight of barium sulphate the amount of sulphur present is calculated.

Phosphorus in organic compounds is oxidised to phosphoric acid in a similar manner, and is precipitated as the magnesium ammonium phosphate.

CALCULATION OF THE FORMULA OF AN ORGANIC COMPOUND FROM THE PERCENTAGE COMPOSITION.

The percentage composition represents the proportions of the elements in the compound by weight ; as a formula represents the proportions of the elements as atoms. Since the atoms of different elements have different weights, to change the proportions by weight into proportions by atoms, it will be necessary to divide the percentage weights of the elements by their respective atomic weights. The procedure is best demonstrated by taking an example ; that of acetic acid will be taken.

The percentage composition of acetic acid is :—

Carbon	40·00
Hydrogen	6·66
Oxygen	53·34
	100·00

These proportions of the elements by weight are divided by their respective atomic weights to find their relative proportions as atoms.

Carbon	$40{\cdot}00 \div 12 = 3{\cdot}33$
Hydrogen	$6{\cdot}66 \div 1 = 6{\cdot}66$
Oxygen	$53{\cdot}34 \div 16 = 3{\cdot}33$

The numbers representing the atomic proportions, are then by a common divisor reduced to the simplest possible whole numbers. It is obvious that in the present case 3·33 is a common divisor, giving the proportions of 1 atom of carbon to 2 atoms of hydrogen and 1 atom of oxygen, which represented as a formula is:—

$$CH_2O.$$

This is the *empirical formula* of acetic acid; that is, it is the simplest possible expression of its composition, representing the elements of which it is composed, and their relative proportions as atoms to one another. A *molecular formula* indicates the number of atoms in the molecule of a body, and may be the same as the empirical formula, or some simple multiple of it. To ascertain the molecular formula of acetic acid, its vapour-density must be taken; that is, it must be converted into vapour, and the specific gravity of its vapour determined. The molecular weight is obtained by doubling the vapour-density, since the specific gravity of any gas or vapour is half its molecular weight (*see* page 49); it can then be easily ascertained whether this molecular weight is the same as that calculated from the empirical formula, or some multiple of it.

Now, the vapour-density of acetic acid is 30 (that is, its vapour is 30 times heavier than hydrogen at the same temperature and pressure), therefore the molecular weight of acetic acid is 60. The formula CH_2O only gives a weight of 30.

$$\begin{array}{lr} C & = 12 \\ H_2 = 1 \times 2 & = \;\;2 \\ O & = 16 \\ \hline & 30 \end{array}$$

Therefore, the double of the empirical formula, viz. $C_2H_4O_2$, must be the molecular formula of acetic acid, since it yields the molecular weight of acetic acid, viz. 60.

$$\begin{array}{lrcr} C_2 = & 12 \times 2 & = & 24 \\ H_4 = & 1 \times 4 & = & 4 \\ O_2 = & 16 \times 2 & = & 32 \\ \hline & & & 60 \end{array}$$

A constitutional or rational formula indicates not only the number of atoms in the molecule of a body, but also the way in which those atoms are arranged; that is, it exhibits the constitution or architecture of the body. A constitutional formula can only be arrived at by a series of experiments, which may require to be very elaborate, and the description of which would be out of place here; in fact, the constitution of many organic bodies has not yet been ascertained.

In the case of acetic acid, it is found that out of the four atoms of hydrogen one can be displaced by metals, and therefore has a different arrangement to the other three; this may be expressed by a constitutional formula represented thus :—

$$HC_2H_3O_2,$$

which indicates the different position of the hydrogen atom that can be displaced by metals, and also shows the grouping of the remaining atoms together to form the *acetic radical*, $C_2H_3O_2$.

It is also found, as the result of experiments, that the three hydrogen atoms are present in acetic acid as a methyl group, CH_3; this may be expressed by a constitutional formula represented thus :—

$$\left\{\begin{array}{l} CH_3 \\ COHO, \end{array}\right.$$

which shows that acetic acid is composed of the radical *methyl* (CH_3) united with the radical *oxatyl* (COHO).

CHAPTER III.

HYDROCARBONS.

Paraffin Series — Methane — Ethane — Petroleum — Benzoline — Olefine Series—Ethene—Acetylene Series—Acetylene—Coal Gas—Structure of Gas or Candle Flame.

(I.) PARAFFIN SERIES.

Methane (CH_4).—Known also as *marsh gas*, *fire-damp*, and *light carburetted hydrogen*.

Modes of preparation.—(i) By heating a mixture of sodium acetate and caustic soda, the latter being most conveniently employed in the form of soda-lime.

$$\underset{\substack{\text{Sodium}\\\text{acetate.}}}{NaC_2H_3O_2} + \underset{\substack{\text{Sodium}\\\text{hydrate.}}}{NaHO} = \underset{\text{Methane.}}{CH_4} + \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3}$$

(ii) By passing a mixture of sulphuretted hydrogen and the vapour of carbon disulphide over red-hot copper.

$$\underset{\substack{\text{Sulphuretted}\\\text{hydrogen.}}}{2H_2S} + \underset{\substack{\text{Carbon}\\\text{disulphide.}}}{CS_2} + \underset{\text{Copper.}}{4Cu_2} = \underset{\text{Methane.}}{CH_4} + \underset{\substack{\text{Cuprous}\\\text{sulphide.}}}{4Cu_2S}$$

(iii) Methane is produced by the slow decomposition of vegetable substances, as in marshes and stagnant pools from decaying vegetable matter, when it is known as *marsh gas*, and is also found in coal mines, where it is known as *fire-damp*.

(iv) Methane is formed by the dry or destructive distillation of various organic substances, and is one of the constituents of coal gas.

Properties of methane.—A colourless, inodorous, and tasteless gas; its specific gravity is 8, and it is therefore much lighter than air; it is but very slightly soluble in water, and is combustible, but not a supporter of combustion. It burns with a partially luminous flame, producing carbon dioxide and water; if mixed with oxygen or air, and a light applied to the mixture, an explosion will take place; this is the cause of the frequent disastrous explosions that occur in coal mines. Methane is not poisonous, but it is incapable of supporting life. A mixture of methane and excess of chlorine exposed to bright sunshine explodes, forming hydrochloric acid and setting free carbon; but in diffused daylight chlorine acts upon methane slowly and quietly, forming a series of substitution products according to the amount of chlorine used. Thus, if equal volumes of methane and chlorine are employed, methyl chloride or monochlormethane (CH_3Cl) is formed.

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\text{Methyl chloride.}}{CH_3Cl} + \underset{\text{Hydrochloric acid.}}{HCl}$$

If 1 volume of methane and 2 volumes of chlorine are employed, bichloride of methylene or dichlormethane (CH_2Cl_2) is formed.

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Chlorine.}}{2Cl_2} = \underset{\text{Methylene bichloride.}}{CH_2Cl_2} + \underset{\text{Hydrochloric acid.}}{2HCl}$$

If 1 volume of methane and 3 volumes of chlorine are employed, chloroform or trichlormethane ($CHCl_3$) is formed.

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Chloroform.}}{CHCl_3} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3HCl}$$

Lastly, if 1 volume of methane and 4 volumes of chlorine are employed, carbon tetrachloride or tetrachlormethane (CCl_4) is formed.

$$\underset{\text{Methane.}}{CH_4} + \underset{\text{Chlorine.}}{4Cl_2} = \underset{\substack{\text{Carbon}\\\text{tetrachloride.}}}{CCl_4} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{4HCl}$$

Test for methane.—The formation of chloroform by the exposure of a mixture of 1 volume of the gas and 3 volumes of chlorine to diffused daylight constitutes the best test for methane.

Ethane (C_2H_6).—This paraffin is di-methyl $(CH_3)_2$, and may be obtained by heating together methyl iodide and zinc.

$$\underset{\substack{\text{Methyl}\\\text{iodide.}}}{2CH_3I} + \underset{\text{Zinc.}}{Zn} = \underset{\text{Ethane.}}{C_2H_6} + \underset{\substack{\text{Zinc}\\\text{iodide.}}}{ZnI_2}$$

Some of the higher paraffins or saturated hydrocarbons are found in natural *petroleum*, and in coal-oil paraffins obtained by the dry or destructive distillation of various kinds of coal; *benzoline* is petroleum spirit, a very volatile and inflammable liquid obtained by distillation from petroleum, and consisting of a mixture of liquid hydrocarbons. Benzoline must not be compounded with benzol or benzene (*see* page 432).

(II.) OLEFINE SERIES.

Ethene (C_2H_4).—Known also as *ethylene*, *olefiant gas*, and *heavy carburetted hydrogen*.

Modes of preparation.—(i) By heating a mixture of equal volumes of alcohol and strong sulphuric acid. The action of the sulphuric acid is simply that of dehydration, or withdrawal of the elements of water from the alcohol.

$$\underset{\text{Alcohol.}}{C_2H_6O} \quad - \quad \underset{\text{Water.}}{H_2O} \quad = \quad \underset{\text{Ethene.}}{C_2H_4}$$

(ii) By passing acetylene (C_2H_2) through a mixture of zinc and an alkali generating nascent hydrogen.

$$\underset{\text{Acetylene.}}{C_2H_2} \quad + \quad \underset{\text{Hydrogen.}}{H_2} \quad = \quad \underset{\text{Ethene.}}{C_2H_4}$$

(iii) Ethene is produced during the dry or destructive distillation of many organic bodies—coal, for instance—and is present to the amount of about ·5 or 6 per cent. in coal gas.

Properties of ethene.—A colourless, inodorous, and tasteless gas; its specific gravity is 14, and it is therefore a little lighter than air; it is but very slightly soluble in water, and is combustible, but not a supporter of combustion. It burns with a very luminous flame, producing carbon dioxide and water; the luminosity of coal gas when burnt is in great part due to the presence of ethene in the gas. A mixture of ethene and oxygen or air explodes on the application of a light. Ethene is not a direct poison, but it is incapable of supporting life. It unites with chlorine, bromine, and iodine, forming oily liquids, and hence its old name of olefiant gas (from *oleum*, oil, and *fians*, forming); its compound with chlorine, ethene or ethylene chloride ($C_2H_4Cl_2$), was discovered by some Dutch chemists, and is known as *Dutch liquid.* Ethene dissolves in strong sulphuric acid, forming ethylsulphuric acid.

$$\underset{\text{Ethene.}}{C_2H_4} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Ethylsulphuric}\\\text{acid.}}}{HC_2H_5SO_4}$$

This, when boiled with water, splits up into alcohol and sulphuric acid.

$$\underset{\substack{\text{Ethylsulphuric}\\\text{acid.}}}{HC_2H_5SO_4} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5HO} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4}$$

Tests for ethene.—The luminosity with which the gas burns, combined with its being inodorous, and with the fact that it forms an oily liquid with chlorine, constitutes the best means for the identification of this gas.

Propene (C_3H_6).—This olefine may be prepared by heating propyl iodide (C_3H_7I) with an alcoholic solution of caustic potash.

$$\underset{\substack{\text{Propyl}\\\text{iodide.}}}{C_3H_7I} + \underset{\substack{\text{Caustic}\\\text{potash.}}}{KHO} = \underset{\text{Propene.}}{C_3H_6} + \underset{\substack{\text{Potassium}\\\text{iodide.}}}{KI} + \underset{\text{Water.}}{H_2O}$$

(III.) Acetylene Series.

Acetylene (C_2H_2).—This body is of interest, in that it is the only hydrocarbon that can be prepared by direct union of its elements.

Modes of preparation.—(i) By synthesis; if the electric arc is produced in an atmosphere of hydrogen, the two elements will unite at the very high temperature produced, and acetylene is formed.

$$\underset{\text{Carbon.}}{C_2} + \underset{\text{Hydrogen.}}{H_2} = \underset{\text{Acetylene.}}{C_2H_2}$$

(ii) By passing the vapour of chloroform over red-hot copper.

$$\underset{\text{Chloroform.}}{2CHCl_3} + \underset{\text{Copper.}}{3Cu_2} = \underset{\text{Acetylene.}}{C_2H_2} + \underset{\text{Cuprous chloride.}}{3Cu_2Cl_2}$$

(iii) By the incomplete combustion of ethene (C_2H_4), as when the coal gas in a Bunsen burner catches fire at the bottom of the burner; on account of the insufficient supply of air under such conditions, only part of the hydrogen of the ethene undergoes combustion, acetylene being produced.

$$\underset{\text{Ethene.}}{2C_2H_4} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetylene.}}{2C_2H_2} + \underset{\text{Water.}}{2H_2O}$$

Properties of acetylene.—A colourless gas, possessing an unpleasant odour; its specific gravity is 13, and it is lighter than air. It burns with a very bright and smoky flame, on account of the large amount of carbon contained in it; if mixed with chlorine it explodes almost instantly.

A description of the other hydrocarbons, of medical interest and importance, will be found in connection with the benzene series.

COAL GAS.

Coal gas is a mixture of gases, consisting mainly of hydrogen and hydrocarbons, produced by the dry or destructive distillation of coal. The coal is heated, without contact of air, in iron retorts, and the products of its destructive distillation are made to pass, firstly, through condensers in which, as a result of the cooling they are subjected to, the heavy coal-tar and the lighter ammoniacal tar-liquor are condensed, and are then collected in tanks; and, secondly, the gas is led through purifying chambers, containing either moist slaked lime or ferric oxyhydrate spread on shelves, either of which removes the gaseous impurities containing sulphur, the former removing carbon dioxide as well; finally the gas is passed into a gasometer for storing purposes.

The constituents of coal gas may be divided into three groups—the *diluents*, *illuminants*, and *impurities*. The *diluents* are gases which, without conferring much luminosity on coal gas when burnt, yet serve the important purpose of diluting down the heavy hydrocarbons, which by themselves would yield a smoky flame; they constitute about 90 per cent. by volume of the coal gas. The *illuminants* are hydrocarbon gases or vapours rich in carbon, and to their presence the luminosity of coal gas when burnt is due; they constitute about 6 per cent. by volume of the coal gas. The *impurities* consist of nitrogen derived from a little air getting into the retorts when opened for the purpose of recharging, and of some carbon dioxide, and traces of sulphur compounds which may have escaped removal in the purifiers.

Composition of coal gas.—

		By volume.
Diluents	Hydrogen	50 per cent.
	Methane or marsh gas	35 ,, ,,
	Carbonic oxide	5 ,, ,,
Illuminants	Ethene or olefiant gas	6 ,, ,,
	Acetylene	
	Benzene vapour	
Impurities	Nitrogen	4 ,, ,,
	Sulphuretted hydrogen	
	Carbon disulphide vapour	
	Carbon dioxide	

STRUCTURE OF GAS OR CANDLE FLAME.

A gas or candle flame consists of three layers (Fig. 35)—an outer or colourless layer, A, consisting of completely burnt gases; a middle or luminous layer, B, consisting of partially-burnt gases, and containing floating in it minute particles of carbon; and an inner or colourless layer, C, consisting of unburnt gases.

Taking the gas flame by way of illustration, in the outer layer A, both the hydrogen and the carbon of the gaseous constituents are completely oxidised by the oxygen of the air to water and carbon dioxide; to the middle layer, B, only a limited supply of oxygen from the air can gain access, most of it being used up in the outer layer, and this limited amount of oxygen has, therefore, the choice of oxidising either the hydrogen or the carbon. On account of the greater affinity of oxygen for hydrogen, this constituent of the hydrocarbons is oxidised to water, and the carbon is set free in the form of small particles which remain floating in the middle layer; these particles of carbon are rendered incandescent by the heat of the flame, and so emit the white light to which the luminosity of the flame is due.

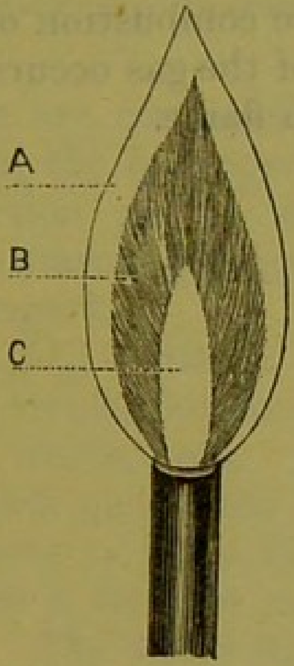


Fig. 35.—Structure of Gas or Candle Flame.

The presence of the free carbon in the middle layer can be demonstrated by inserting a piece of white porcelain into the flame, when the carbon is deposited on it as soot or lamp-black. The inner layer of the flame must necessarily consist of unburnt gas, since as there is insufficient oxygen reaching the middle layer for the complete combustion of its constituents, none can gain access to the inner layer. If air is introduced with the gas from within the flame, as in the Bunsen burner, then complete combustion of both the hydrogen and the carbon of the gas occurs, and the result is the colourless Bunsen flame.

CHAPTER IV.

CARBOHYDRATES.

Starch—Glycogen—Dextrin—Cellulose — Cellulose Derivatives—Cane Sugar—Grape Sugar—Levulose—Milk Sugar—Maltose.

THESE substances are compounds of carbon and the elements of water, the hydrogen and oxygen being in the same proportion as in water. The principal carbohydrates are starch, glycogen, dextrin, cellulose, and the various sugars.

Starch ($C_6H_{10}O_5$).—Starch is contained in certain roots, seeds, soft stems, potatoes, and various grains, such as wheat, maize, etc. Arrowroot and rice contain considerable quantities of starch. Starch is prepared from roots or seeds by crushing them and placing them upon a sieve or strainer, through which water is flowing. The water mechanically carries the starch through the sieve, leaving fibrous and cellular substances behind. The water is then allowed to stand, and the starch deposits as a white sediment, from which the water is poured off, and which is finally dried. Starch may be prepared from wheat flour and other flours by placing the flour in a muslin or calico bag and wringing it out several times with water, when the starch is again mechanically carried away by the water, a sticky substance, gluten, being left in the bag.

Properties of starch.—The different starches are white powders, which, when examined under the microscope, are seen to consist of granules, the granules of the various starches differing in size and shape. Starch is insoluble in cold water, the granules being unaffected by it, but in hot water the granules break up, being in part dissolved and in part remaining in suspension, forming what is called "decoction or mucilage of starch." Starch, as employed for laundry purposes, is coloured a light-blue with indigo, which is introduced in order to neutralise the faint yellow colour of recently-washed linen. If a solution of free iodine is added to a cold decoction of starch, a dark-blue colour, due to a molecular compound of iodine and starch, is developed. If heat be applied to the blue liquid, the blue colour disappears, owing to the dissociation of the starch and iodine by the heat. If the heat be quickly withdrawn, the blue colour reappears on cooling, but if the heat be long continued then the iodine is volatilised, and no blue colour reappears on cooling. A solution of starch does not reduce an alkaline copper solution when boiled with it. If starch is boiled with dilute sulphuric acid, it is first converted into dextrin and then, by assimilation of water, into grape sugar. Starch is also converted firstly into dextrin and finally into grape sugar under the influence of certain ferments such as yeast, diastase in malt, ptyalin in saliva, and the pancreatic ferments in pancreatic juice.

Test for starch.—The blue colour produced by a solution of free iodine constitutes an extremely delicate test for starch.

Glycogen ($C_6H_{10}O_5$).—This substance, which is an isomer of starch, is found in the livers of man and animals. It is prepared by finely chopping up fresh liver and boiling it with water, which dissolves out the glycogen; from this solution it is precipitated by the addition of alcohol.

Properties of glycogen.—Glycogen is a white powder, soluble in water, in which it forms an opalescent solution. A solution of free iodine gives a mahogany-brown colour to a solution of glycogen. This colour disappears on the application of heat, but reappears on cooling. Glycogen does not reduce an alkaline copper solution, and it does not undergo fermentation in contact with yeast. It is readily converted into grape sugar by boiling with dilute sulphuric acid, or when in contact with such ferments as ptyalin, pancreatic ferments, and diastase. In each of these cases the conversion of the glycogen into grape sugar merely consists in the assimilation of water.

$$\underset{\text{Glycogen.}}{C_6H_{10}O_5} + \underset{\text{Water.}}{H_2O} = \underset{\text{Grape sugar.}}{C_6H_{12}O_6}$$

Test for glycogen.—The mahogany-brown colour produced on the addition of iodine, disappearing when heat is applied and reappearing on cooling, constitutes a good test for glycogen.

Dextrin ($C_6H_{10}O_5$).—This substance is an isomer of starch and glycogen. It is prepared from starch either by baking it in an oven, or by boiling it with dilute sulphuric acid, or by the action of ferments such as yeast and diastase upon it. The first-mentioned method is the best one, as by the other methods the dextrin is quickly converted into grape sugar.

Properties of dextrin.—Dextrin is a whitish powder, readily soluble in cold water, in which it forms a sticky or mucilaginous solution. It is commonly employed under the name of *British gum.*

Test for dextrin.—A solution of free iodine gives, with a solution of dextrin, a mahogany-brown colour, which disappears on the application of heat, and does not reappear on cooling, thus distinguishing it from glycogen.

Cellulose ($C_6H_{10}O_5$).—This substance is an isomer of starch, glycogen, and dextrin. It is also called *lignin.* It is obtained in its purest form as *cotton wool*, the hairs surrounding the seeds of various species of Gossypium. Cellulose is insoluble in both cold and boiling water. Three nitro-derivatives of cellulose can be obtained, one of which is used in surgery, and another constitutes ordinary gun-cotton. The three nitro-derivatives are xyloidin, pyroxylin, and gun-cotton.

Xyloidin, or *mono-nitrocellulose* ($C_6H_9(NO_2)O_5$). —This is prepared by steeping cellulose in commercial nitric acid.

$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Xyloidin.}}{C_6H_9(NO_2)O_5} + \underset{\text{Water.}}{H_2O}$$

Pyroxylin, or *di-nitrocellulose.* ($C_6H_8(NO_2)_2O_5$). —This is prepared by steeping cellulose in a mixture of sulphuric and nitric acids, the sulphuric acid being employed to absorb the water produced by the action of the nitric acid on the cellulose.

$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{2HNO_3} = \underset{\text{Pyroxylin.}}{C_6H_8(NO_2)_2O_5} + \underset{\text{Water.}}{2H_2O}$$

This substance, dissolved in a mixture of alcohol and ether, constitutes *collodion*, which is employed for producing a covering or artificial skin to abrasions, etc., of the skin.

Gun-cotton, or *tri-nitrocellulose* ($C_6H_7(NO_2)_3O_5$). —This substance is prepared by steeping gun-cotton in the strongest sulphuric and nitric acids, the sulphuric acid being employed to absorb the water produced in the process.

$$\underset{\text{Cellulose.}}{C_6H_{10}O_5} + \underset{\text{Nitric acid.}}{3HNO_3} = \underset{\text{Gun-cotton.}}{C_6H_7(NO_2)_3O_5} + \underset{\text{Water.}}{3H_2O}$$

This is the ordinary gun-cotton employed for blasting purposes and in gun-cotton cartridges. It is an explosive, in that it contains sufficient oxygen for the combustion of the carbon and hydrogen contained in it. It produces, when exploded, large volumes of the two oxides of carbon, steam, and nitrogen, which are, in addition, greatly expanded by the heat produced by the chemical decomposition. It is the sudden production and violent expansion of these gases that cause the explosion of gun-cotton when fired.

SUGARS.

The principal sugars are cane sugar, grape sugar, milk sugar, and maltose or malt sugar.

Cane sugar, sucrose, or saccharose ($C_{12}H_{22}O_{11}$).—This sugar exists in the sugar cane, beet root, and in the sap of the sugar maple. It is extracted from the sugar cane by crushing the canes in order to squeeze out the juice, to which is then added some slaked lime; the mixture is then boiled, and the mechanical impurities are allowed to settle; the liquor, poured off from these impurities, is then concentrated by evaporation and set aside to cool, when crystals of *raw or brown sugar* settle out, the viscid mother liquid constituting *molasses.* To obtain the *white or loaf sugar*, the brown sugar is dissolved in water, and some serum of blood and a little slaked lime are added; the liquid is heated, and allowed to stand, when the coagulum produced from the serum of blood settles down, carrying with it impurities. The solution is next filtered through animal charcoal to decolorise it, and is then evaporated to a syrup, which is poured into conical moulds, within which, on cooling, the white or loaf sugar crystallises.

Properties of cane sugar.—Cane sugar is readily soluble in both cold and hot water ; its solution does not reduce an alkaline copper solution. If boiled with dilute sulphuric acid, water is assimilated, and grape sugar is formed, or rather invert sugar, which is a mixture of dextrose and levulose.

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}$$

Yeast also converts cane sugar into grape sugar. If solid cane sugar is carefully heated, a reddish-brown liquid is obtained, which is *burnt sugar* or *caramel.*

Test for cane sugar.—Cane sugar does not reduce the alkaline copper solution, and hence is distinguished from grape sugar and milk sugar; but after boiling a solution of cane sugar with dilute sulphuric acid, the solution will reduce the alkaline copper solution, on account of the conversion of the cane sugar into grape sugar.

Grape sugar, ordinary glucose, or dextrose ($C_6H_{12}O_6$).—This sugar is contained in grapes, in honey, the solid portion of which consists of glucose, and in diabetic urine. It may be extracted from any of these sources, and may also be obtained by the hydration of starch under the influence of dilute sulphuric acid or of diastase.

Properties of glucose.—Glucose is readily soluble in both cold and hot water. Its most important property is that in contact with yeast it undergoes alcoholic or vinous fermentation, the yeast causing the decomposition of the glucose into alcohol and carbon dioxide, together with the production of small quantities of some other substances (*see* page 402).

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\text{Ethyl alcohol.}}{2C_2H_6O} + \underset{\text{Carbon dioxide.}}{2CO_2}$$

Test for glucose.—A solution of glucose reduces an alkaline copper solution when boiled with it, causing the precipitation of the red cuprous oxide. This is the ordinary *copper test for grape sugar*, and is the method employed for the detection of sugar in urine. The alkaline copper solution is prepared and used under the name of *Fehling's solution.* To prepare this, a solution of copper sulphate is first made, and another solution of potassium sodium tartrate and caustic soda is made. If equal quantities of these solutions are mixed, a dark blue clear liquid is obtained, which is Fehling's solution. If some of this is boiled with a small quantity of grape sugar, the cupric salt is reduced and precipitated as red cuprous oxide.

Levulose ($C_6H_{12}O_6$). — This is an isomer of ordinary grape sugar or dextrose. It occurs in small quantities in honey, and in many fruits mixed with dextrose. It is distinguished from dextrose by its solution turning a ray of polarised light to the left, whereas a solution of dextrose turns it always to the right. It is best prepared by the inversion of cane sugar, which consists in boiling the cane sugar with dilute sulphuric acid, when a mixture of dextrose and levulose is obtained.

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Levulose.}}{C_6H_{12}O_6}$$

To separate the two sugars advantage is taken of the fact that they both form compounds with lime, the dextrose-lime compound being soluble, while the levulose-lime compound is insoluble. To the solution of the two sugars slaked-lime is therefore added, and the mixture filtered; on passing carbon dioxide through the filtrate, the lime is precipitated as calcium carbonate, and the glucose only is left in solution. If the insoluble levulose-lime compound is suspended in water and carbon dioxide passed through, calcium carbonate is precipitated, and the levulose, in a pure state, is left in solution.

Tests for levulose.—Levulose reduces Fehling's solution in a similar manner to dextrose, and can only be distinguished from dextrose, as previously mentioned, by its action on polarised light.

Milk sugar or lactose ($C_{12}H_{22}O_{11}$, H_2O).—This sugar is contained in milk, from which it may be prepared by precipitating the curds by the addition of rennet or some acid, filtering, and evaporating the clear whey to a low bulk, when the milk sugar crystallises out on cooling.

Properties of milk sugar.—It is less soluble in water than any of the other sugars, and also less sweet. It does not undergo fermentation in contact with yeast, or only after a very long time; in contact with the ferment *penicillium glaucum* it undergoes lactic acid fermentation; it is this conversion of milk sugar into lactic acid which is the cause of the souring of milk when exposed to the air, the spores of penicillium glaucum being always present in the air, and settling on the exposed surface of the milk.

Test for milk sugar.—A solution of milk sugar reduces Fehling's solution when boiled with it, and in this respect it resembles glucose. It can be distinguished from glucose, in the solid state, by its being so much less soluble in water, and in solution, by not undergoing fermentation in contact with yeast; whereas a solution of glucose readily ferments in contact with yeast when the mixture is left in a warm place.

Maltose ($C_{12}H_{22}O_{11}$, H_2O).—This substance is isomeric with lactose. It is obtained by the action of malt extract on starch.

CHAPTER V.

CYANOGEN GROUP.

Cyanogen—Potassium Ferrocyanide—Potassium Cyanide—Hydrocyanic Acid—Tests for Hydrocyanic Acid and Cyanides—Potassium Ferricyanide—Methyl Cyanide—Ethyl Cyanide—Potassium Cyanate—Ammonium Cyanate—Potassium Sulphocyanate.

Cyanogen (C_2N_2).—The name cyanogen (from κύανος, *blue ;* γεννάω, *to generate*) is due to the fact that some of the double cyanogen compounds possess brilliant blue colours.

Preparation of cyanogen.—Cyanogen is a gas, and is obtained by heating either mercuric cyanide or silver cyanide.

$$\underset{\text{Mercuric cyanide.}}{Hg(CN)_2} = \underset{\text{Mercury.}}{Hg} + \underset{\text{Cyanogen.}}{C_2N_2}$$

$$\underset{\text{Silver cyanide.}}{2AgCN} = \underset{\text{Silver.}}{Ag_2} + \underset{\text{Cyanogen.}}{C_2N_2}$$

Properties of cyanogen. — Cyanogen is a colourless gas, possessing a peculiar odour somewhat resembling that of the essential oil of bitter almonds ; it is soluble in water, and is very poisonous. It burns with a characteristic coloured flame, the colour resembling that of the peach blossom, and it produces carbon dioxide and free nitrogen when burnt. Its specific gravity is 26, and it is therefore much heavier than air.

Tests for cyanogen.—The odour of the gas, combined with the peculiar colour of its flame when burnt, constitute the best means for the recognition of cyanogen.

Potassium ferrocyanide (K_4FeCy_6).—This body is the ancestor of the cyanogen compounds. Since no cyanogen compounds exist in nature, it is necessary that one or more of them should be made by some artificial process, and the cyanogen compound that is prepared artificially is potassium ferrocyanide. To prepare this substance it is necessary to employ some potassium salt to furnish the potassium, the metal iron to furnish the iron, and some organic substance, rich in carbon and nitrogen, to furnish the elements for the production of the cyanogen. It is made, therefore, by roasting together potassium carbonate, iron filings, and animal matter, such as hoofs, horns, and scraps of hide, substances that are rich in both carbon and nitrogen. Under the influence of the heat, and in presence of the other substances, the carbon and nitrogen unite to form cyanogen, which, with the potassium carbonate, forms potassium cyanide (KCy), and with the iron forms ferrous cyanide ($FeCy_2$). On boiling the roasted mass with water, these two cyanides unite to form potassium ferrocyanide.

$$\underset{\text{Potassium cyanide.}}{4KCy} + \underset{\text{Ferrous cyanide.}}{FeCy_2} = \underset{\text{Potassium ferrocyanide.}}{K_4FeCy_6}$$

Properties.—Potassium ferrocyanide occurs in yellow crystals, and is commonly known as *yellow prussiate of potash.* Although the powerful poisons hydrocyanic acid and potassium cyanide are made from it, yet potassium ferrocyanide itself is non-poisonous. It is decomposed by very strong heat, with production of potassium cyanide and carbide of iron. Potassium ferrocyanide is decomposed by both strong and dilute sulphuric acid, but with different results in the two cases. If heated with strong sulphuric acid, carbon monoxide is copiously evolved.

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{K_4Fe(CN)_6} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{6H_2SO_4} + \underset{\text{Water.}}{6H_2O} = \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{2K_2SO_4} +$$

$$\underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{FeSO_4} + \underset{\substack{\text{Ammonium}\\\text{sulphate.}}}{3(NH_4)_2SO_4} + \underset{\substack{\text{Carbon}\\\text{monoxide.}}}{6CO}$$

If heated with dilute sulphuric acid, hydrocyanic acid only is evolved.

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{2K_4FeCy_6} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{3H_2SO_4} = \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{6HCy} +$$

$$\underset{\substack{\text{Ferro-potassium}\\\text{ferrocyanide.}}}{FeK_2FeCy_6} + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{3K_2SO_4}$$

Potassium ferrocyanide is used in the manufacture of *Prussian blue*, which is ferric ferrocyanide, and which is prepared by adding potassium ferrocyanide to a solution of ferric chloride or ferric sulphate.

$$\underset{\substack{\text{Ferric}\\\text{chloride.}}}{2Fe_2Cl_6} + \underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{3K_4FeCy_6} = \underset{\substack{\text{Prussian}\\\text{blue.}}}{Fe_4(FeCy_6)_3} + \underset{\substack{\text{Potassium}\\\text{chloride.}}}{12KCl}$$

Tests.—(i) Potassium ferrocyanide gives with a solution of ferric chloride a dark blue precipitate of Prussian blue.

(ii) A solution of copper sulphate gives with potassium ferrocyanide a reddish-brown precipitate of copper ferrocyanide. This is the most delicate test for the salt.

(iii) Potassium ferrocyanide heated with dilute sulphuric acid evolves the odour of hydrocyanic acid.

Potassium cyanide (KCy).—This salt is prepared in the form of commercial cyanide of potassium used for photographic purposes, and also as the pure cyanide of potassium. The commercial cyanide of potassium may be prepared by strongly heating potassium ferrocyanide (*see* page 386), but it is most conveniently prepared at a lower temperature by fusing together potassium ferrocyanide and potassium carbonate. The cyanide of potassium prepared by this process is, however, always mixed with some cyanate.

$$\underset{\substack{\text{Potassium}\\ \text{ferrocyanide.}}}{K_4FeCy_6} + \underset{\substack{\text{Potassium}\\ \text{carbonate.}}}{K_2CO_3} = \underset{\substack{\text{Potassium}\\ \text{cyanide.}}}{5KCy} + \underset{\substack{\text{Potassium}\\ \text{cyanate.}}}{KCyO} + \underset{\text{Iron.}}{Fe} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2}$$

Pure cyanide of potassium may be prepared by neutralising hydrocyanic acid with caustic potash; this is most conveniently effected by passing the vapour of hydrocyanic acid into an alcoholic solution of caustic potash, when the potassium cyanide crystallises out as it is formed.

$$\underset{\substack{\text{Hydrocyanic}\\ \text{acid.}}}{HCy} + \underset{\substack{\text{Caustic}\\ \text{potash.}}}{KHO} = \underset{\substack{\text{Potassium}\\ \text{cyanide.}}}{KCy} + \underset{\text{Water.}}{H_2O}$$

Pure potassium cyanide may also be prepared by utilising the nitrogen of the air. This is effected by passing air over a mixture of potassium carbonate and charcoal strongly heated, when potassium cyanide is formed and carbon monoxide evolved.

Properties.—Potassium cyanide is a white solid evolving, on exposure to the air, the odour of hydrocyanic acid. It is very poisonous and is readily acted on by acids, hydrocyanic acid being evolved. Both strong and dilute sulphuric acid decompose it, forming potassium sulphate and evolving hydrocyanic acid.

$$\underset{\substack{\text{Potassium}\\\text{cyanide.}}}{2KCy} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{2HCy} + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4}$$

Tests.—The tests for potassium cyanide are the same as those for hydrocyanic acid (*see* page 391).

Hydrocyanic acid (HCN or HCy).—This acid is commonly known as *prussic acid*, on account of its first having been prepared from Prussian blue; it may be prepared from potassium ferrocyanide or from any metallic cyanides. The hydrocyanic acid used in medicine (*Acidum hydrocyanicum dilutum*, B. P.) is prepared by distilling potassium ferrocyanide with dilute sulphuric acid (*see* page 387), and diluting the distillate to the required strength. It may also be prepared by shaking together solutions of potassium cyanide and tartaric acid, when the potassium acid tartrate is deposited on standing, leaving the hydrocyanic acid in solution.

$$\underset{\substack{\text{Potassium}\\\text{cyanide.}}}{KCy} + \underset{\substack{\text{Tartaric}\\\text{acid.}}}{H_2C_4H_4O_6} = \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{HCy} + \underset{\substack{\text{Potassium}\\\text{acid tartrate.}}}{KHC_4H_4O_6}$$

Pure hydrocyanic acid, which is seldom prepared on account of its extremely poisonous nature and the danger incurred by the operator in the preparation of it, may be obtained by passing dried sulphuretted hydrogen gas over heated mercuric cyanide, the hydrocyanic acid vapour being condensed in a suitable apparatus surrounded by a freezing mixture.

$$\underset{\substack{\text{Mercuric}\\ \text{cyanide.}}}{HgCy_2} + \underset{\substack{\text{Sulphuretted}\\ \text{hydrogen.}}}{H_2S} = \underset{\substack{\text{Hydrocyanic}\\ \text{acid.}}}{2HCy} + \underset{\substack{\text{Mercuric}\\ \text{sulphide.}}}{HgS}$$

Hydrocyanic acid is present in the *essential oil of bitter almonds*, being produced from the decomposition of the glucoside amygdalin under the influence of the ferment emulsin present in the bitter almonds, the presence of water being necessary for the emulsin to act on the amygdalin.

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Oil of}\\ \text{bitter almonds.}}}{C_7H_6O} +$$

$$\underset{\substack{\text{Hydrocyanic}\\ \text{acid.}}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

Properties.—Hydrocyanic acid is an extremely powerful and rapidly acting poison ; only a very dilute solution of it is employed in medicine, the Diluted Hydrocyanic Acid, B. P., being of only 2 per cent. strength. If dilute hydrocyanic acid be kept for some time with exposure to light it slowly decomposes, becoming converted into ammonium formate.

$$\underset{\substack{\text{Hydrocyanic}\\ \text{acid.}}}{HCN} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Ammonium}\\ \text{formate.}}}{NH_4CHO_2}$$

Hydrocyanic acid is contained in essential oil of bitter almonds, essence of peach kernels, essence of cherry kernels, bitter almond water and cherry laurel water. The strength of a sample of hydrocyanic acid can be determined by ascertaining the weight of silver cyanide precipitated by adding a solution of silver nitrate to a known quantity of the diluted hydrocyanic acid. The antidote, in cases of poisoning by hydrocyanic acid, is to convert the soluble and diffusible hydrocyanic acid into the insoluble Prussian blue. This is effected by giving a draught containing a mixture of sodium carbonate, ferrous sulphate, and ferric chloride. The sodium carbonate forms sodium cyanide.

$$\underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{2\mathrm{HCy}} + \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{\mathrm{Na_2CO_3}} = \underset{\substack{\text{Sodium}\\\text{cyanide.}}}{2\mathrm{NaCy}} + \underset{\text{Water.}}{\mathrm{H_2O}} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{\mathrm{CO_2}}$$

This, with the ferrous sulphate, forms sodium ferrocyanide :

$$\underset{\substack{\text{Sodium}\\\text{cyanide.}}}{6\mathrm{NaCy}} + \underset{\substack{\text{Ferrous}\\\text{sulphate.}}}{\mathrm{FeSO_4}} = \underset{\substack{\text{Sodium}\\\text{ferrocyanide.}}}{\mathrm{Na_4FeCy_6}} + \underset{\substack{\text{Sodium}\\\text{sulphate ;}}}{\mathrm{Na_2SO_4}}$$

and this, with the ferric chloride, forms Prussian blue.

$$\underset{\substack{\text{Ferric}\\\text{chloride.}}}{2\mathrm{Fe_2Cl_6}} + \underset{\substack{\text{Sodium}\\\text{ferrocyanide.}}}{3\mathrm{Na_4FeCy_6}} = \underset{\substack{\text{Prussian}\\\text{blue.}}}{\mathrm{Fe_4(FeCy_6)_3}} + \underset{\substack{\text{Sodium}\\\text{chloride.}}}{12\mathrm{NaCl}}$$

Tests for hydrocyanic acid.—(i) *Prussian blue test.*—This consists in adding to the hydrocyanic acid, caustic soda, solution of ferrous sulphate, solution of ferric chloride, and, finally, hydrochloric acid. The first three reagents act as described in connection with the antidote (*see* above) ; the hydrochloric acid is finally added to neutralise any excess of caustic alkali, which would, if present, prevent the development of the Prussian blue.

(ii) *Sulphocyanide test.*—This consists in the conversion of the hydrocyanic acid into ferric sulphocyanide, which is of a deep blood-red colour. This conversion is effected by adding to the hydrocyanic acid, solution of ammonia and then a few drops of yellow ammonium sulphide, and evaporating the mixture to a low bulk; to the concentrated liquid hydrochloric acid and ferric chloride are then added, when the deep blood-red colour of ferric sulphocyanide is produced. The solution of ammonia converts the hydrocyanic acid into ammonium cyanide.

$$\underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{\mathrm{HCy}} + \underset{\text{Ammonia.}}{\mathrm{NH_3}} = \underset{\substack{\text{Ammonium}\\\text{cyanide.}}}{\mathrm{NH_4Cy}}$$

The free sulphur contained in the yellow ammonium sulphide then converts this ammonium cyanide into ammonium sulphocyanide.

$$\underset{\substack{\text{Ammonium}\\\text{cyanide.}}}{\mathrm{2NH_4Cy}} + \underset{\text{Sulphur.}}{\mathrm{S_2}} = \underset{\substack{\text{Ammonium}\\\text{sulphocyanide.}}}{\mathrm{2NH_4CyS}}$$

This sulphocyanide, on the addition of ferric chloride, forms the blood-red ferric sulphocyanide. The hydrochloric acid is merely added to neutralise any excess of ammonia that may be present, which would otherwise prevent the formation of the ferric sulphocyanide.

$$\underset{\substack{\text{Ferric}\\\text{chloride.}}}{\mathrm{Fe_2Cl_6}} + \underset{\substack{\text{Ammonium}\\\text{sulphocyanide.}}}{\mathrm{6NH_4CyS}} = \underset{\substack{\text{Ferric}\\\text{sulphocyanide.}}}{\mathrm{Fe_2(CyS)_6}} + \underset{\substack{\text{Ammonium}\\\text{chloride.}}}{\mathrm{6NH_4Cl}}$$

Potassium ferricyanide ($K_6Fe_2Cy_{12}$).—This is prepared from potassium ferrocyanide by raising the iron from the ferrous state, in which it exists in the ferrocyanide, into the ferric state, in which it exists in the ferricyanide; this is most conveniently effected by passing chlorine into a solution of potassium ferrocyanide.

$$\underset{\substack{\text{Potassium}\\ \text{ferrocyanide.}}}{2K_4FeCy_6} + \underset{\substack{\text{Chlorine.}}}{Cl_2} = \underset{\substack{\text{Potassium}\\ \text{ferricyanide.}}}{K_6Fe_2Cy_{12}} + \underset{\substack{\text{Potassium}\\ \text{chloride.}}}{2KCl}$$

Properties.—Potassium ferricyanide occurs in reddish-brown crystals, and is commonly known as *red prussiate of potash.* With a solution of a ferrous salt potassium ferricyanide gives a dark blue precipitate of *Turnbull's blue.* With ferric salts it gives no precipitate at all, but merely a dark olive-green colour, and hence it is readily distinguished from potassium ferrocyanide, which with ferric chloride gives a dark blue precipitate of Prussian blue.

ALCOHOLIC CYANIDES.

Methyl cyanide (CH_3CN).—This alcoholic cyanide is prepared by distilling the potassium salt of methyl sulphuric acid with potassium cyanide.

$$\underset{\substack{\text{Potassium}\\ \text{methyl sulphate.}}}{KCH_3SO_4} + \underset{\substack{\text{Potassium}\\ \text{cyanide.}}}{KCN} = \underset{\substack{\text{Methyl}\\ \text{cyanide.}}}{CH_3CN} + \underset{\substack{\text{Potassium}\\ \text{sulphate.}}}{K_2SO_4}$$

Ethyl cyanide (C_2H_5CN).—This is prepared in a similar manner to the above by distilling the potassium salt of ethyl sulphuric acid with potassium cyanide.

$$\underset{\substack{\text{Potassium}\\ \text{ethyl sulphate.}}}{KC_2H_5SO_4} + \underset{\substack{\text{Potassium}\\ \text{cyanide.}}}{KCN} = \underset{\substack{\text{Ethyl}\\ \text{cyanide.}}}{C_2H_5CN} + \underset{\substack{\text{Potassium}\\ \text{sulphate.}}}{K_2SO_4}$$

CYANATES AND SULPHOCYANATES.

Potassium cyanate ($KCNO$).—This may be prepared by exposing fused potassium cyanide for some time to the air, when oxygen is absorbed and the cyanate formed; or it may be prepared by dropping a metallic oxide, such as lead oxide, into the fused potassium cyanide; the latter unites with the oxygen of the lead oxide, forming potassium cyanate, and the metal lead is set free.

Ammonium cyanate (NH_4CNO).—This salt is prepared by mixing solutions of potassium cyanate and ammonium sulphate, when double decomposition takes place.

$$\underset{\text{Potassium cyanate.}}{2KCNO} + \underset{\text{Ammonium sulphate.}}{(NH_4)_2SO_4} = \underset{\text{Ammonium cyanate.}}{2NH_4CNO} + \underset{\text{Potassium sulphate.}}{K_2SO_4}$$

Alcohol is then added to precipitate the potassium sulphate, leaving the ammonium cyanate in solution. This salt is of interest as its isomer *urea* (CH_4N_2O) can be prepared from it. The conversion of ammonium cyanate into urea is effected by simply evaporating its solution to dryness on the water-bath, when urea is left; the temperature of boiling water is therefore sufficient to change ammonium cyanate into urea. The urea, in its turn, may be reconverted into ammonium cyanate by raising it to a dull red heat, when ammonia gas is evolved and cyanuric acid formed.

$$\underset{\text{Urea.}}{3CH_4N_2O} = \underset{\text{Cyanuric acid.}}{H_3C_3N_3O_3} + \underset{\text{Ammonia.}}{3NH_3}$$

If the cyanuric acid be more strongly heated, it splits up into cyanic acid, which distils over.

$$\underset{\text{Cyanuric acid.}}{H_3C_3N_3O_3} = \underset{\text{Cyanic acid.}}{3HCNO}$$

If the cyanic acid is neutralised with ammonia, ammonium cyanate is reproduced.

Potassium sulphocyanate or sulphocyanide (KCNS).—This may be prepared by fusing together potassium ferrocyanide and sulphur.

$$\underset{\substack{\text{Potassium}\\\text{ferrocyanide.}}}{K_4FeCy_6} + \underset{\text{Sulphur.}}{3S_2} = \underset{\substack{\text{Potassium}\\\text{sulphocyanide.}}}{4KCyS} + \underset{\substack{\text{Ferrous}\\\text{sulphocyanide.}}}{Fe(CyS)_2}$$

The fused mass is then boiled with water and potassium carbonate added to convert the ferrous sulphocyanide into potassium sulphocyanide and ferrous carbonate, the latter being precipitated.

$$\underset{\substack{\text{Ferrous}\\\text{sulphocyanide.}}}{Fe(CyS)_2} + \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{K_2CO_3} = \underset{\substack{\text{Potassium}\\\text{sulphocyanide.}}}{2KCyS} + \underset{\substack{\text{Ferrous}\\\text{carbonate}}}{FeCO_3}$$

The soluble sulphocyanides may also be prepared by direct union of the soluble cyanides and sulphur, as in the sulphocyanide test for hydrocyanic acid (*see* page 392). Potassium sulphocyanide is present in minute quantities in the saliva of man.

Test.—Potassium sulphocyanide gives with ferric chloride a deep blood-red colour. This colour is not discharged on the addition of strong hydrochloric acid, being thus distinguishable from the blood-red colour given by ferric chloride with an acetate; the colour of ferric acetate being discharged by strong hydrochloric acid (*see* page 422). The colour of ferric sulphocyanide is discharged on the addition of a solution of mercuric chloride, and in this way it is distinguished from the blood-red colour given by ferric chloride with meconic acid or a meconate; the red colour of ferric meconate not being discharged by mercuric chloride (*see* page 447).

CHAPTER VI.

ALCOHOLS AND THEIR DERIVATIVES.

1. Monatomic Alcohols—Methyl Alcohol—Methyl Compounds—Ethyl Alcohol—Ethyl Compounds—Ether—Chloral—Chloroform—Iodoform—Propyl Alcohol—Butyl Alcohol—Amyl Alcohol — 2. Diatomic Alcohols — Ethene Glycol — 3. Triatomic Alcohols—Glycerine.

1. MONATOMIC ALCOHOLS.

These are the hydrates of the univalent hydrocarbon radicals, and therefore contain in the molecule only one equivalent of hydroxyl. The alcohols of principal medical importance are those containing the radicals (C_nH_{2n+1}) homologous with methyl.

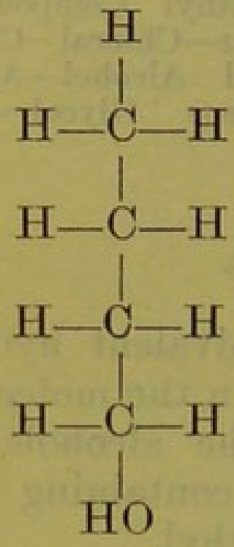
The principal members of this series are :

Methyl alcohol	CH_3HO.
Ethyl ,,	C_2H_5HO.
Propyl ,,	C_3H_7HO.
Butyl ,,	C_4H_9HO.
Amyl ,,	$C_5H_{11}HO$.

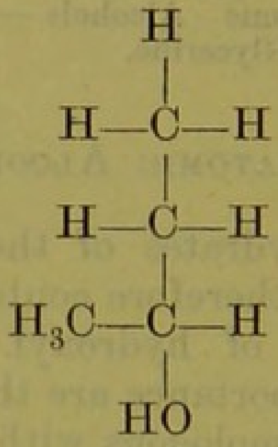
Another nomenclature for these alcohols is that of designating methyl alcohol as *carbinol*, and the alcohols formed by successive substitution of methyl, ethyl, etc., for an atom of hydrogen in the carbinol, are then named according to the radicals which they contain. Thus :

Carbinol or methyl alcohol	CH_3. HO.
Methyl carbinol or ethyl alcohol	$CH_2(CH_3)$. HO.
Ethyl carbinol or propyl alcohol	$CH_2(C_2H_5)$. HO.
Propyl carbinol or butyl alcohol	$CH_2(C_3H_7)$. HO.
Butyl carbinol or amyl alcohol	$CH_2(C_4H_9)$. HO.

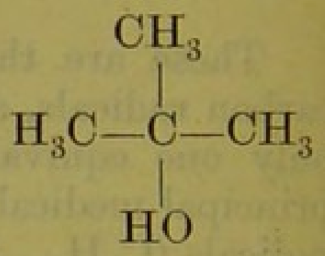
The graphic formula of butyl alcohol may be constructed in three different ways, according as the carbon atom in union with the hydroxyl is directly united with one, two, or three other carbon atoms. These are the primary, secondary, and tertiary butyl alcohols. Thus :—



Primary butyl alcohol.



Secondary butyl alcohol.



Tertiary butyl alcohol.

Thus, a *primary* alcohol is one in which the carbon atom in union with the hydroxyl is only directly united with one other carbon atom ; a *secondary* alcohol is one in which the carbon atom in union with the hydroxyl is directly united with two other carbon atoms ; a *tertiary* alcohol is one in which the carbon atom in union with the hydroxyl is directly united with three other carbon atoms.

Alcohols of the (C_nH_{2n+1}) or Methyl Series.

METHYL ALCOHOL AND METHYL COMPOUNDS.

Methyl alcohol (CH_3HO).—This alcohol may be prepared from methane or marsh gas (CH_4) by acting on it with chlorine to form methyl chloride (CH_3Cl); if this is decomposed with moist silver oxide, methyl alcohol is produced.

$$\underset{\substack{\text{Methyl}\\\text{chloride.}}}{2CH_3Cl} + \underset{\substack{\text{Silver}\\\text{oxide.}}}{Ag_2O} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Methyl}\\\text{alcohol.}}}{2CH_3HO} + \underset{\substack{\text{Silver}\\\text{chloride.}}}{2AgCl}$$

Pure methyl alcohol may also be prepared from the *oil of winter green*, which is pure methyl salicylate; by distilling this with caustic potash or soda methyl alcohol is obtained. Impure methyl alcohol, commonly known as *wood spirit or wood naphtha*, is obtained by the dry or destructive distillation of wood (*see* page 420); 10 per cent. of this wood spirit mixed with rectified spirits forms the *methylated spirit* of commerce.

Properties.—Methyl alcohol is a colourless, inflammable liquid; it produces carbon dioxide and water when burnt. In the pure state it is free from the disagreeable smell possessed by wood spirit. Methyl alcohol is converted by oxidation into formic acid; this oxidation may be effected either by dropping methyl alcohol on to platinum black, the occluded oxygen of which oxidises the alcohol, or by distillation with potassium bichromate and sulphuric acid.

$$\underset{\substack{\text{Methyl}\\\text{alcohol.}}}{CH_3HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Formic}\\\text{acid.}}}{HCHO_2} + \underset{\text{Water.}}{H_2O}$$

The test for methyl alcohol is to convert it by the last-mentioned process into formic acid (for the detection of which *see* page 419).

Methyl chloride (CH_3Cl).—This may be prepared by exposing equal volumes of methane and chlorine to sunlight (*see* page 369). It may also be prepared by the action of phosphorous chloride on methyl alcohol.

$$\underset{\substack{\text{Methyl}\\\text{alcohol.}}}{3CH_3HO} + \underset{\substack{\text{Phosphorous}\\\text{chloride.}}}{PCl_3} = \underset{\substack{\text{Methyl}\\\text{chloride.}}}{3CH_3Cl} + \underset{\substack{\text{Phosphorous}\\\text{acid.}}}{H_3PO_3}$$

Methyl iodide (CH_3I).—This is prepared by the action of phosphorus tri-iodide on methyl alcohol.

$$\underset{\substack{\text{Methyl}\\\text{alcohol.}}}{3CH_3HO} + \underset{\substack{\text{Phosphorous}\\\text{iodide.}}}{PI_3} = \underset{\substack{\text{Methyl}\\\text{iodide.}}}{3CH_3I} + \underset{\substack{\text{Phosphorous}\\\text{acid.}}}{H_3PO_3}$$

Methyl oxide, or **methyl ether** ($(CH_3)_2O$).—This is prepared by heating a mixture of equal volumes of methyl alcohol and strong sulphuric acid, when it passes over as a colourless gas.

Methyl sulphuric acid (HCH_3SO_4).—This is prepared by the action of sulphuric acid on methyl alcohol, with moderate heat.

Methyl mercaptan, or **methyl hydrosulphide** (CH_3HS).—This is prepared by distilling a mixture of potassium hydrosulphide and calcium methylsulphate.

Dimethyl-ketone, or **acetone** ($CH_3-CO-CH_3$).—This ketone is prepared by the action of dry heat on any metallic acetate.

$$\underset{\substack{\text{Sodium}\\\text{acetate.}}}{2NaC_2H_3O_2} = \underset{\substack{\text{Sodium}\\\text{carbonate.}}}{Na_2CO_3} + \underset{\text{Acetone.}}{CH_3-CO-CH_3}$$

It may also be prepared by the action of sodium methide on carbonyl chloride.

$$\underset{\substack{\text{Carbonyl}\\\text{chloride.}}}{Cl-CO-Cl} + \underset{\substack{\text{Sodium}\\\text{methide.}}}{2NaCH_3} = \underset{\substack{\text{Sodium}\\\text{chloride.}}}{2NaCl} + \underset{\text{Acetone.}}{CH_3-CO-CH_3}$$

ETHYL ALCOHOL AND ETHYL COMPOUNDS.

Ethyl alcohol (C_2H_5HO).—This constitutes the ordinary alcohol of commerce, as contained in proof spirit, rectified spirit, absolute alcohol, wines, and beers. It may be prepared by a synthetical process, which is of interest as showing the building up of the alcohol from its elements. To effect this, acetylene is first prepared by direct union of its elements, by the production of the electric arc in an atmosphere of hydrogen; the acetylene (C_2H_2) is then converted into ethylene by passing it through an alkaline mixture generating nascent hydrogen, such as zinc and ammonia solutions.

$$\underset{\text{Acetylene.}}{C_2H_2} \quad + \quad \underset{\text{Hydrogen.}}{H_2} \quad = \quad \underset{\text{Ethylene.}}{C_2H_4}$$

The ethylene is then agitated with strong sulphuric acid, which converts it into ethyl sulphuric acid.

$$\underset{\text{Ethylene.}}{C_2H_4} \quad + \quad \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} \quad = \quad \underset{\substack{\text{Ethyl sulphuric}\\\text{acid.}}}{HC_2H_5SO_4}$$

The ethyl sulphuric acid, if distilled with water, yields ethyl alcohol as a distillate.

$$\underset{\substack{\text{Ethyl sulphuric}\\\text{acid.}}}{HC_2H_5SO_4} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5HO} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4}$$

The various forms of ethyl alcohol met with in commerce are obtained by the fermentation of sugar under the influence of the yeast or diastase ferments. If a solution of ordinary sugar ($C_{12}H_{22}O_{11}$) is mixed with yeast, and the mixture kept in a covered vessel in a warm place, the cane sugar is first converted into glucose.

$$\underset{\text{Cane sugar.}}{C_{12}H_{22}O_{11}} + \underset{\text{Water.}}{H_2O} = \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

The glucose is then decomposed, by the fermentative action of the yeast, into alcohol and carbon dioxide, small quantities of other bodies (such as glycerine, succinic acid, etc.) also being produced.

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{2C_2H_6O} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{2CO_2}$$

When the fermentative process is finished, the alcohol is obtained in a weak state from the mixture by distillation. This weak spirit is then strengthened by the process known as *fractional distillation*, which consists in distilling it in portions, the greater quantity of the alcohol being contained in the first distillate. It is not possible to remove all the water by the process of fractional distillation; the strongest spirit that can be so obtained is rectified spirit, which contains 16 per cent. of water. To prepare *absolute alcohol* from this, that is, alcohol quite free from water, the rectified spirit is mixed with well-burnt lime, and allowed to stand for some hours. The lime unites with the water, forming slaked lime, and the pure or absolute alcohol can then be obtained by distillation. In the preparation of malt alcoholic liquors (beer, stout, and porter), the ferment diastase, which is contained in malted grain, is employed in place of yeast to produce the alcoholic fermentation. Starch, as contained in grain, is employed in place of sugar in the preparation of this and some other alcoholic liquids, the starch being converted by the action of the ferment, firstly, into dextrin, then into glucose, which substance finally undergoes the alcoholic fermentation.

Properties.—Ethyl alcohol is a colourless liquid with a faint pleasant smell, and is readily inflammable, producing, when burnt, carbon dioxide and water. *Proof spirit* contains 49 per cent. of alcohol, and is of sp. gr. 0·920. *Rectified spirit* contains 84 per cent. of alcohol, and is of sp. gr. 0·838. *Absolute alcohol* contains no water, and is of sp. gr. 0·793. The various wines and beers met with in commerce contain different amounts of alcohol, as shown in the following table :

Brandy Gin Whisky	... From 40 to 50 per cent.
Port Sherry	... About 18 per cent.
Champagne	... About 12 per cent.
Claret Hock	... From 8 to 12 per cent.
Beer	... From 3 to 8 per cent.

By the oxidation of alcohol two bodies are obtained, according to the strength of the oxidising agent employed. If the oxidising agent be a weak one, ethyl aldehyde (C_2H_4O) is produced. If the oxidising agent be a strong one, acetic acid ($C_2H_4O_2$) is produced. Thus, by distilling ethyl alcohol with manganese dioxide and sulphuric acid, ethyl aldehyde is formed, the action of this weak oxidising mixture being merely to abstract two atoms of hydrogen from the alcohol molecule.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{2C_2H_6O} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Ethyl}\\\text{aldehyde.}}}{2C_2H_4O} + \underset{\text{Water.}}{2H_2O}$$

If the alcohol be distilled with potassium bichromate and sulphuric acid, then the action of this more powerful oxidising mixture is not only to abstract two atoms of hydrogen from the molecule, but, in addition, to replace them by one atom of oxygen, thus forming acetic acid.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_6O} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Acetic}\\\text{acid.}}}{C_2H_4O_2} + \underset{\text{Water.}}{H_2O}$$

The metals potassium and sodium act on ethyl alcohol, displacing one atom of hydrogen from the molecule, and forming respectively potassium ethylate (C_2H_5KO) and sodium ethylate (C_2H_5NaO), the latter being sometimes employed as a caustic. If chlorine gas be passed into rectified spirit, a variety of bodies may be produced :

(i) Aldehyde may be formed by the direct withdrawal of hydrogen by the chlorine.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_6O} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Ethyl}\\\text{aldehyde.}}}{C_2H_4O} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl}$$

(ii) Chloral may be formed by the further action of the chlorine on this aldehyde.

$$\underset{\substack{\text{Ethyl}\\\text{aldehyde.}}}{C_2H_4O} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Chloral.}}{C_2HCl_3O} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3HCl}$$

(iii) Ethyl chloride may be formed by the action of the hydrochloric acid, produced in the former reactions, upon some of the undecomposed alcohol.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5HO} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl} = \underset{\substack{\text{Ethyl}\\\text{chloride.}}}{C_2H_5Cl} + \underset{\text{Water.}}{H_2O}$$

(iv) Acetic acid may be produced by the oxidation of some of the alcohol by oxygen, this gas being liberated by the action of chlorine on the water contained in the rectified spirit.

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetic acid.}}{C_2H_4O_2} + \underset{\text{Water}}{H_2O}$$

(v) Finally, ethyl acetate or acetic ether may be formed by the action of the acetic acid, produced in the former reaction, upon some undecomposed alcohol.

$$\underset{\text{Ethyl alcohol.}}{C_2H_5HO} + \underset{\text{Acetic acid.}}{HC_2H_3O_2} = \underset{\text{Ethyl acetate.}}{C_2H_5C_2H_3O_2} + \underset{\text{Water.}}{H_2O}$$

ETHYL COMPOUNDS.

Ethyl chloride (C_2H_5Cl).—This is prepared by the action of phosphorus trichloride on ethyl alcohol.

$$\underset{\text{Ethyl alcohol.}}{3C_2H_5HO} + \underset{\text{Phosphorus trichloride.}}{PCl_3} = \underset{\text{Ethyl chloride.}}{3C_2H_5Cl} + \underset{\text{Phosphorous acid.}}{H_3PO_3}$$

Ethyl iodide (C_2H_5I).—This is prepared by the action of phosphorus tri-iodide on ethyl alcohol.

$$\underset{\text{Ethyl alcohol.}}{3C_2H_5HO} + \underset{\text{Phosphorus tri-iodide.}}{PI_3} = \underset{\text{Ethyl iodide.}}{3C_2H_5I} + \underset{\text{Phosphorous acid.}}{H_3PO_3}$$

Ethyl ether ($(C_2H_5)_2O$).—This is commonly known as *ether* or *sulphuric ether*. It is the oxide of ethyl, but the process for its preparation will be rendered more intelligible by regarding it as ethyl alcohol partially dehydrated. Thus, if from two molecules of ethyl alcohol one molecule of water be abstracted, ether is obtained.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol}}}{2C_2H_6O} - \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Ethyl}\\\text{ether.}}}{(C_2H_5)_2O}$$

The process for preparing ether on a commercial scale, which is known as the *continuous etherification process*, consists in partially dehydrating ethyl alcohol by means of strong sulphuric acid. This process is carried out by distilling a mixture of sulphuric acid and rectified spirit, the latter being in excess. The ether, as it is formed, distils over, the sulphuric acid remaining in the retort, and therefore, to prevent the sulphuric acid from becoming in excess, it is necessary that as fast as the ether distils over more alcohol should be run into the retort. If this is effected the process becomes a continuous one; hence its name. The sulphuric acid does not directly withdraw the water from the alcohol, but indirectly, in the two following stages:

(i) The sulphuric acid first forms with the alcohol sulphethylic acid.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5HO} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sulphethylic}\\\text{acid.}}}{HC_2H_5SO_4} + \underset{\text{Water.}}{H_2O}$$

(ii) This sulphethylic acid then reacts with more alcohol, forming ether and sulphuric acid.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5HO} + \underset{\substack{\text{Sulphethylic}\\\text{acid.}}}{HC_2H_5SO_4} = \underset{\text{Ether.}}{(C_2H_5)_2O} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4}$$

It is essential, for the production of ether by this process, that the alcohol should be kept in excess; otherwise, if the sulphuric acid become in excess, it will first completely dehydrate the alcohol, forming ethylene or olefiant gas.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_6O} \quad - \quad \underset{\text{Water.}}{H_2O} \quad = \quad \underset{\text{Ethylene.}}{C_2H_4}$$

And, secondly, if the sulphuric acid accumulate in great excess, it will then act on the alcohol as upon an ordinary hydrate, producing an impure ethyl sulphate (the old *oil of wine*).

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{2C_2H_5HO} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Ethyl}\\\text{sulphate.}}}{(C_2H_5)_2SO_4} + \underset{\text{Water.}}{2H_2O}$$

Properties of ether.—The ether obtained by the process just given contains about 8 per cent. of alcohol, from which it can be purified by agitating with water; on standing, the ether rises to the surface of the water, leaving the alcohol in solution; the ether is then removed from the surface of the water, and distilled with some well-burnt quicklime to free it from the little water that it contains.

Pure ether is a colourless, transparent, very mobile liquid, with a characteristic fragrant smell, and extremely volatile. Its specific gravity is 0·720. It is very combustible, producing carbon dioxide and water when burnt. When dropped on the hand it occasions a sharp sensation of cold from its rapid evaporation. Ether is miscible with alcohol in all proportions, but in water it dissolves to a very small extent only. It dissolves fats and oils generally.

Ethyl nitrite or **nitrous ether** ($C_2H_5NO_2$).—In the pure state this may be made by the action of nitrous anhydride on absolute alcohol.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{2C_2H_5HO} + \underset{\substack{\text{Nitrous}\\\text{anhydride.}}}{N_2O_3} = \underset{\substack{\text{Ethyl}\\\text{nitrite.}}}{2C_2H_5NO_2} + \underset{\text{Water.}}{H_2O}$$

Mixed with aldehyde, alcohol and other substances, it is contained in Sweet Spirits of Nitre (*Spiritus ætheris nitrosi*, B. P.), which contains 10 per cent. of nitrous ether. This preparation is made by distilling together rectified spirit, copper turnings, sulphuric acid and nitric acid. The copper reduces the nitric acid to nitrous acid.

$$\underset{\substack{\text{Nitric}\\ \text{acid.}}}{\mathrm{HNO_3}} + \underset{\text{Copper.}}{\mathrm{Cu}} = \underset{\substack{\text{Nitrous}\\ \text{acid.}}}{\mathrm{HNO_2}} + \underset{\substack{\text{Copper}\\ \text{oxide.}}}{\mathrm{CuO}}$$

The nitrous acid then acts upon the alcohol, forming nitrous ether.

$$\underset{\substack{\text{Ethyl}\\ \text{alcohol.}}}{\mathrm{C_2H_5HO}} + \underset{\substack{\text{Nitrous}\\ \text{acid.}}}{\mathrm{HNO_2}} = \underset{\substack{\text{Nitrous}\\ \text{ether.}}}{\mathrm{C_2H_5NO_2}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

The function of the sulphuric acid is merely to unite with the copper oxide and to prevent its union with some of the nitric acid.

$$\underset{\substack{\text{Copper}\\ \text{oxide.}}}{\mathrm{CuO}} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{\mathrm{H_2SO_4}} = \underset{\substack{\text{Copper}\\ \text{sulphate.}}}{\mathrm{CuSO_4}} + \underset{\text{Water.}}{\mathrm{H_2O}}$$

The preparation of nitrous ether by this process constitutes a fairly good test for alcohol, the peculiar apple-like odour of nitrous ether being readily recognised.

Ethyl acetate or **acetic ether** ($C_2H_5C_2H_3O_2$).—This is prepared by distilling rectified spirit with sodium acetate and sulphuric acid. The two latter bodies set free acetic acid, which then immediately acts upon the alcohol producing acetic ether.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5HO} + \underset{\substack{\text{Acetic}\\\text{acid.}}}{HC_2H_3O_2} = \underset{\substack{\text{Ethyl}\\\text{acetate.}}}{C_2H_5C_2H_3O_2} + \underset{\text{Water.}}{H_2O}$$

Ethyl oxalate or **oxalic ether** ($(C_2H_5)_2C_2O_4$).—This is prepared by distilling a mixture of ethyl alcohol, potassium oxalate and sulphuric acid. The oxalic acid set free by the action of the sulphuric acid on the oxalate unites with the alcohol to form oxalic ether.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{2C_2H_5HO} + \underset{\substack{\text{Oxalic}\\\text{acid.}}}{H_2C_2O_4} = \underset{\substack{\text{Ethyl}\\\text{oxalate.}}}{(C_2H_5)_2C_2O_4} + \underset{\text{Water.}}{2H_2O}$$

Sulphethylic acid or **sulphovinic acid** ($HC_2H_5SO_4$) is prepared by warming a mixture of equal parts of ethyl alcohol and sulphuric acid.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{C_2H_5HO} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Sulphethylic}\\\text{acid.}}}{HC_2H_5SO_4} + \underset{\text{Water.}}{H_2O}$$

Ethyl hydrosulphide or **ethyl-mercaptan** (C_2H_5HS).—This is prepared by distilling a mixture of potassium hydrosulphide and calcium ethyl sulphate.

$$\underset{\substack{\text{Calcium}\\\text{ethylsulphate.}}}{Ca(C_2H_5SO_4)_2} + \underset{\substack{\text{Potassium}\\\text{hydrosulphide.}}}{2KHS} = \underset{\substack{\text{Ethyl}\\\text{mercaptan.}}}{2C_2H_5HS} +$$

$$\underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4} + \underset{\substack{\text{Potassium}\\\text{sulphate.}}}{K_2SO_4}$$

It is a liquid with an extremely unpleasant nauseating odour.

Ethyl aldehyde or **ordinary aldehyde** (C_2H_4O).—This body is also known as *acetic aldehyde.* It may be prepared—

(i) By the oxidation of ethyl alcohol by means of manganese dioxide and sulphuric acid.

$$\underset{\substack{\text{Manganese}\\\text{dioxide.}}}{2MnO_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{2H_2SO_4} = \underset{\substack{\text{Manganous}\\\text{sulphate.}}}{2MnSO_4} +$$

$$\underset{\text{Water.}}{2H_2O} + \underset{\text{Oxygen.}}{O_2}$$

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{2C_2H_6O} + \underset{\text{Oxygen}}{O_2} = \underset{\substack{\text{Ethyl}\\\text{aldehyde.}}}{2C_2H_4O} + \underset{\text{Water.}}{2H_2O}$$

(ii) By the action of chlorine upon a mixture of ethyl alcohol and water, the chlorine uniting with the hydrogen of the water, the oxygen of which oxidises the alcohol to aldehyde.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol.}}}{2C_2H_6O} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Ethyl}\\\text{aldehyde.}}}{2C_2H_4O} + \underset{\text{Water.}}{2H_2O}$$

Properties.—Aldehyde is a colourless liquid with a peculiar fragrant smell. Its name is derived from an abbreviation of the expression *alcohol dehydrogenated,* as it is alcohol deprived of part of its hydrogen. By exposure to the air it absorbs oxygen and becomes converted into acetic acid. Chlorine acts upon it, forming chloral (*see* below). A polymeric modification of it, viz. *paraldehyde* ($C_6H_{12}O_3$), is prepared by adding a few drops of concentrated sulphuric acid to aldehyde, when the liquid becomes hot, and, on cooling, crystals of paraldehyde form.

Trichloraldehyde or **chloral** (C_2HCl_3O).—This body constitutes what is commonly known as chloral, the hydrate of which is *chloral hydrate,* a substance largely used in medicine as a hypnotic. Chloral is prepared by the prolonged action of chlorine upon absolute alcohol. The reaction, although actually a somewhat complex one, may, for the sake of simplicity, be regarded as taking place in the two following stages:

(i) Chlorine first converts the alcohol into aldehyde.

$$\underset{\substack{\text{Ethyl}\\\text{alcohol}}}{C_2H_6O} + \underset{\text{Chlorine.}}{Cl_2} = \underset{\substack{\text{Ethyl}\\\text{aldehyde.}}}{C_2H_4O} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl}$$

(ii) The chlorine then acts upon the aldehyde, abstracting three-fourths of the hydrogen, replacing it by chlorine, and so producing chloral.

$$\underset{\substack{\text{Ethyl}\\\text{aldehyde.}}}{C_2H_4O} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Chloral.}}{C_2HCl_3O} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{3HCl}$$

Properties.—Chloral is a heavy liquid, with an extremely pungent, irritating odour. It is converted by the action of alkalies into chloroform and a formate of the alkali metal. Thus with caustic potash it yields chloroform and potassium formate.

$$\underset{\text{Chloral.}}{C_2HCl_3O} + \underset{\substack{\text{Caustic}\\\text{potash.}}}{KHO} = \underset{\text{Chloroform.}}{CHCl_3} + \underset{\substack{\text{Potassium}\\\text{formate.}}}{KCHO_2}$$

With slaked lime it yields chloroform and calcium formate.

$$\underset{\text{Chloral.}}{2C_2HCl_3O} + \underset{\text{Slaked lime.}}{Ca(HO)_2} = \underset{\text{Chloroform.}}{CHCl_3} + \underset{\text{Calcium formate.}}{Ca(CHO_2)_2}$$

Just as aldehyde is oxidised by nitric acid to acetic acid, so chloral or trichloraldehyde is oxidised by nitric acid to trichloracetic acid, thus:—

$$\underset{\text{Aldehyde.}}{2C_2H_4O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Acetic acid.}}{2HC_2H_3O_2}$$

$$\underset{\text{Chloral.}}{2C_2HCl_3O} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Trichloracetic acid.}}{2HC_2Cl_3O_2}$$

Chloral, when mixed with water, produces a crystalline mass of *chloral hydrate.*

Chloral hydrate (C_2HCl_3O, H_2O).—This body, as previously mentioned, is prepared by the action of water on chloral. It is a white crystalline solid, with a very faint odour of the liquid chloral attached to it. It is largely used in medicine as a hypnotic, and has been stated by Liebriech to be decomposed by the sodium carbonate of the blood into chloroform, though it is very doubtful whether such a decomposition takes place.

Chloral hydrate is decomposed by contact with caustic alkalies into chloroform and formate of the alkali metal. Chloral hydrate is therefore incompatible with alkalies, and should never be prescribed with them in medicine.

Chloroform ($CHCl_3$).—This body is actually a derivative of methane (CH_4), from which it may be obtained by the action of chlorine (*see* page 369); but since all the chloroform of commerce is prepared by the decomposition of chloral, it is more convenient to describe its preparation in the present section.

Chloroform, on the commercial scale, is prepared by distilling a mixture of rectified spirit, chlorinated lime (bleaching powder), and slaked lime. The formation of chloroform takes place in the three following stages :—

(i) Some of the oxygen of the chlorinated lime ($CaCl_2$, $CaCl_2O_2$) oxidises the alcohol to aldehyde.

$$\underset{\text{Ethyl alcohol.}}{C_2H_6O} + \underset{\text{Oxygen.}}{O} = \underset{\text{Ethyl aldehyde.}}{C_2H_4O} + \underset{\text{Water.}}{H_2O}$$

(ii) The aldehyde is then converted, by some of the chlorine of the chlorinated lime, into chloral.

$$\underset{\text{Aldehyde.}}{C_2H_4O} + \underset{\text{Chlorine.}}{3Cl_2} = \underset{\text{Chloral.}}{C_2HCl_3O} + \underset{\text{Hydrochloric acid.}}{3HCl}$$

(iii) The chloral is then decomposed by the slaked lime into chloroform and calcium formate, the chloroform distilling over.

$$\underset{\text{Chloral.}}{2C_2HCl_3O} + \underset{\text{Slaked lime.}}{Ca(HO)_2} = \underset{\text{Chloroform.}}{2CHCl_3} + \underset{\text{Calcium formate.}}{Ca(CHO_2)_2}$$

Properties of chloroform.—The sp. gr. of chloroform is 1·5. The medicinal chloroform contains a minute amount of alcohol, and is of sp. gr. 1·497. It is a thin, colourless liquid, with a sweetish taste and a pleasant characteristic odour. It is readily soluble in alcohol and ether, and slightly so in water (*Aqua chloroformi*, B. P.). It is difficult to kindle and burns with a greenish smoky flame.

Iodoform (CHI_3).—This body is analogous in constitution to chloroform. It is prepared by warming together sodium carbonate, alcohol, water, and iodine.

The production of iodoform constitutes a very delicate test for alcohol. Iodoform occurs in yellow, shiny scales, almost insoluble in water, but soluble in alcohol and ether. It has a characteristic penetrating and somewhat unpleasant smell.

PROPYL ALCOHOL.

Propyl alcohol (C_3H_7HO).—This alcohol is contained in fusel oil of brandy. It is of no medical importance.

BUTYL ALCOHOL.

Butyl alcohol (C_4H_9HO).—This may be prepared by acting on butane (C_4H_{10}) with chlorine, which forms butyl chloride, and then decomposing this chloride with moist silver oxide.

$$\underset{\substack{\text{Butyl}\\\text{chloride.}}}{2C_4H_9Cl} + \underset{\substack{\text{Silver}\\\text{oxide.}}}{Ag_2O} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Butyl}\\\text{alcohol.}}}{2C_4H_9HO} + \underset{\substack{\text{Silver}\\\text{chloride.}}}{2AgCl}$$

Butyl chloral $\left(C_4H_5Cl_3O \text{ or } \left\{\begin{array}{l} C_3H_4.Cl_3 \\ COH \end{array}\right.\right)$.—A hydrate of this body is used in medicine under the name of *croton chloral*, which was the original name erroneously applied to it. It is a body corresponding in its constitution to ordinary chloral, since it is trichlor-butyl-aldehyde, that is, it is butyl aldehyde (C_4H_8O), from the molecule of which three atoms of hydrogen have been displaced by three atoms of chlorine. It is a product of the action of dry chlorine on ordinary aldehyde in the cold. Its hydrate, $C_4H_5Cl_3O, H_2O$ (*Butyl chloral hydras*, B. P.) is the ordinary *croton chloral* used in medicine.

Amyl Alcohol.

Amyl alcohol ($C_5H_{11}HO$).—This body (which derives its name from *amylum*—starch) is the *fusel oil* obtained in the preparation of ordinary alcohol from the different forms of starch. It is contained in crude or raw whisky, but the sugar obtained from potato starch yields a more considerable amount, and hence this alcohol is sometimes called *potato oil.*

Properties.—Amyl alcohol is an oily colourless liquid having a peculiar unpleasant odour. It is not appreciably soluble in water, but floats on the surface of it like an oil; hence its name *fusel oil.* When oxidised it yields *valerianic acid.*

Amyl nitrite ($C_5H_{11}NO_2$).—This compound is prepared by a process similar to that employed in the preparation of ethyl nitrite, namely, by distilling a mixture of amyl alcohol, copper turnings, sulphuric and nitric acids.

Amyl acetate ($C_5H_{11}C_2H_3O_2$).—This substance is prepared by distilling amyl alcohol with sodium acetate and sulphuric acid. It constitutes the *jargonelle pear essence.*

2. Diatomic Alcohols.

These are hydrates of the bivalent hydrocarbon radicals, and therefore contain two equivalents of hydroxyl in the molecule. Several of them exist under the name of *glycols*, but as they are of no importance in medicine, a brief description of one of them only will be given here.

Ethene glycol ($C_2H_4(HO)_2$).—This is prepared by acting on ethene with bromine to form ethene dibromide ($C_2H_4Br_2$), and then decomposing this with moist silver oxide.

$$\underset{\substack{\text{Ethene}\\\text{dibromide.}}}{C_2H_4Br_2} + \underset{\substack{\text{Silver}\\\text{oxide.}}}{Ag_2O} + \underset{\text{Water.}}{H_2O} = \underset{\substack{\text{Ethene}\\\text{glycol.}}}{C_2H_4(HO)_2} + \underset{\substack{\text{Silver}\\\text{bromide.}}}{2AgBr}$$

3. TRIATOMIC ALCOHOLS.

These are the hydrates of the trivalent hydrocarbon radicals, and therefore contain in the molecule three equivalents of hydroxyl. Only one of them is employed in medicine, viz. *glycerine.*

Glycerine or glyceryl hydrate ($C_3H_5(HO)_3$).—Glycerine is prepared by the saponification of fats and oils. The radical glyceryl, in combination with the acidulous radicals of the higher fatty acids, forms most of the solid fats and oils. During the saponification of olive oil (glyceryl oleate) with caustic soda, glycerine is obtained.

$$\underset{\substack{\text{Glyceryl}\\\text{oleate.}}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\substack{\text{Sodium}\\\text{hydrate.}}}{3NaHO} = \underset{\substack{\text{Sodium}\\\text{oleate.}}}{3NaC_{18}H_{33}O_2} + \underset{\text{Glycerine.}}{C_3H_5(HO)_3}$$

Glycerine is more conveniently prepared by decomposing melted suet (glyceryl stearate) by means of superheated steam, when the glycerine and stearic acid are carried over in the current of steam, the stearic acid setting to a solid, and the glycerine, diluted with the condensed steam, being obtained as a liquid.

$$\underset{\substack{\text{Glyceryl}\\\text{stearate.}}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{Water.}}{3H_2O} = \underset{\substack{\text{Stearic}\\\text{acid.}}}{3HC_{18}H_{35}O_2} + \underset{\text{Glycerine.}}{C_3H_5(HO)_3}$$

Properties of glycerine.—Glycerine is a colourless and very viscid liquid of sp. gr. 1·27. It has a very sweet taste and mixes with water in all proportions. When exposed to heat it decomposes, losing the elements of water and yielding a substance *acrolein* (C_3H_4O), which has an intensely pungent odour.

Glycerine, treated with a mixture of strong nitric and sulphuric acids, forms *nitro-glycerine* ($C_3H_5(NO_2)_3O_3$), a heavy oily liquid, which produces by percussion a terrible explosion; on account of its liquid form it is very dangerous to handle, and is, therefore, for blasting and other purposes, made into *dynamite*, which simply consists of porous silica, in the form of infusorial earth, saturated with nitro-glycerine. Ordinary dynamite usually consists of 75 parts of nitro-glycerine and 25 parts of silica. Tablets of chocolate containing $\frac{1}{100}$th of a grain of nitro-glycerine are used in medicine (*Tabellæ nitro-glycerini*, B. P.).

CHAPTER VII.

ORGANIC ACIDS.

1. Monobasic Organic Acids—Formic Acid—Acetic Acid—Butyric Acid—Valerianic Acid—Lactic Acid—2. Dibasic Organic Acids—Oxalic Acid—Succinic Acid—Malic Acid—Tartaric Acid—3. Tribasic Organic Acids—Citric Acid.

THESE are compounds containing the radical *oxatyl* (COHO) united with some other radical; the simplest radical with which oxatyl can unite is hydrogen, as in the case of formic acid $\left\{\begin{matrix}\mathrm{H}\\ \mathrm{COHO}\end{matrix}\right.$. The series of so-called *fatty acids* are produced by the union of the hydrocarbon radicals of the methyl series with oxatyl, *e.g.*—

$\left\{\begin{matrix}\mathrm{CH_3}\\ \mathrm{COHO}\end{matrix}\right.$	$\left\{\begin{matrix}\mathrm{C_2H_5}\\ \mathrm{COHO}\end{matrix}\right.$	$\left\{\begin{matrix}\mathrm{C_3H_7}\\ \mathrm{COHO}\end{matrix}\right.$	$\left\{\begin{matrix}\mathrm{C_4H_9}\\ \mathrm{COHO}\end{matrix}\right.$	$\left\{\begin{matrix}\mathrm{C_5H_{11}}\\ \mathrm{COHO}\end{matrix}\right.$
Acetic acid.	Propionic acid.	Butyric acid.	Valerianic acid.	Caproic acid.

Monobasic organic acids contain one equivalent of oxatyl; dibasic acids two equivalents; tribasic acids three equivalents; and so on.

1. MONOBASIC ORGANIC ACIDS.

Formic acid $\left(\mathrm{HCHO_2}\text{ or }\left\{\begin{matrix}\mathrm{H}\\ \mathrm{COHO}\end{matrix}\right.\right)$.—This acid occurs in nature in red ants and in stinging nettles. It can be prepared by the oxidation of methyl alcohol, either by dropping it on to spongy platinum, the occluded oxygen of which oxidises it to formic acid; or by distilling methyl alcohol with potassium bichromate and sulphuric acid, which in presence of the alcohol evolve oxygen, with formation of potassium and chromium sulphates.

$$\begin{array}{ccccccc} CH_3HO & + & O_2 & = & HCHO_2 & + & H_2O \\ \text{Methyl alcohol.} & & \text{Oxygen.} & & \text{Formic acid.} & & \text{Water.} \end{array}$$

Properties of formic acid.—A clear, colourless liquid, with a very penetrating odour; in its concentrated state it produces a blister when painted or rubbed on the skin. The wheals produced on the skin by the sting of the stinging nettles are due to the injection beneath the skin of small quantities of formic acid, from the hair of the stinging glands penetrating the skin.

Test for formic acid.—A solution of silver nitrate is reduced to the metallic state on warming with formic acid, the silver forming a mirror-like deposit on the sides of the test-tube.

Acetic acid $\left(HC_2H_3O_2, \text{ or } \left\{\begin{array}{l} CH_3 \\ COHO \end{array}\right.\right)$.—There are two principal methods by which acetic acid is made: (i) The oxidation of alcohol; (ii) the dry or destructive distillation of wood. *Vinegar* is obtained by the former process; *pyroligneous acid*, or crude acetic acid, by the latter.

Brown or *malt vinegar* is prepared by exposing beer, mixed with a little yeast, to the air; under the influence of a ferment, *mycoderma aceti*, the alcohol of the beer becomes oxidised to acetic acid.

$$\begin{array}{ccccccc} C_2H_6O & + & O_2 & = & HC_2H_3O_2 & + & H_2O \\ \text{Alcohol.} & & \text{Oxygen.} & & \text{Acetic acid.} & & \text{Water.} \end{array}$$

The vinegar so prepared contains about 5½ per cent. of acetic acid; a small quantity of sulphuric acid is added at the last to destroy the ferment, and so prevent any further changes from taking place in the vinegar. It is to this development of acetic acid that the souring of beer is due when exposed to the air.

White-wine vinegar is prepared by the oxidation of the alcohol contained in the light white wines; the oxidation is facilitated by allowing the wine to trickle over the surface of wood-shavings contained in towers; in this way the alcohol of the wine becomes freely exposed to the action of the oxygen of the air, and so is rapidly converted into acetic acid.

Acetic acid may be prepared from ordinary alcohol by distilling it with potassium bichromate and sulphuric acid; the two last-mentioned bodies liberate oxygen, which in the nascent state immediately oxidises the alcohol to acetic acid, which then distils over.

Dry or destructive distillation of wood.—Although wood contains no acetic acid, yet it contains the elements necessary for the formation of that body, and under the influence of dry heat, without exposure to air, a re-arrangement of the elements of the wood takes place, with the formation of several fresh bodies, amongst which is acetic acid. This process is the dry or destructive distillation of wood, and if the products are collected in different portions, as they distil over, a rough separation of them is effected, since the bodies with low boiling-points will distil before those with higher boiling-points. Thus the first portion of the distillate from the destructive distillation of wood consists of impure methyl alcohol, or *wood spirit;* next comes over impure acetic acid, or *pyroligneous acid; creasote* and other bodies distil over afterwards; and lastly *wood tar.*

To obtain pure acetic acid from the pyroligneous acid, the latter is neutralised with sodium carbonate to form sodium acetate; the solution is then concentrated by evaporation, and, on cooling, crystals of sodium acetate separate out, leaving tarry and other impurities in the mother liquor. The crystals of sodium acetate are then carefully heated, so as to expel any tar carried down with them, and the sodium acetate is next distilled with sulphuric acid, when pure acetic acid will be obtained as a distillate.

$$\underset{\substack{\text{Sodium}\\\text{acetate.}}}{2NaC_2H_3O_2} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Acetic}\\\text{acid.}}}{2HC_2H_3O_2} + \underset{\substack{\text{Sodium}\\\text{sulphate.}}}{Na_2SO_4}$$

Properties of acetic acid.—Acetic acid is a clear, colourless liquid, with a penetrating, pleasant acid odour, and an acid taste. The pure acid applied to the skin produces a blister. Ordinary acetic acid (*Acidum aceticum*, B. P.) is a mixture of acetic acid and water, containing about 33 per cent. of real acid. Glacial acetic acid (*Acidum aceticum glaciale*, B. P.) is pure acetic acid, and solidifies to a crystalline mass at temperatures below 15·5° C.

Three derivatives of acetic acid (chloracetic acids) are obtained by the action of chlorine on acetic acid, 1, 2, or 3 atoms of hydrogen being displaced from the acetic acid molecule, according to the amount of chlorine used. The acids are respectively called monochloracetic acid, dichloracetic acid, and trichloracetic acid.

$$\underset{\text{Acetic acid.}}{\left\{\begin{matrix}CH_3\\COHO\end{matrix}\right.} \qquad \underset{\substack{\text{Monochloracetic}\\\text{acid.}}}{\left\{\begin{matrix}CH_2Cl\\COHO\end{matrix}\right.} \qquad \underset{\substack{\text{Dichloracetic}\\\text{acid.}}}{\left\{\begin{matrix}CHCl_2\\COHO\end{matrix}\right.} \qquad \underset{\substack{\text{Trichloracetic}\\\text{acid.}}}{\left\{\begin{matrix}CCl_3\\COHO\end{matrix}\right.}$$

Trichloracetic acid is used as a delicate test for the detection of albumen in urine.

Tests for acetic acid and acetates.—(i) If an acetate is boiled with sulphuric acid, the odour of acetic acid is evolved.

(ii) If an acetate is boiled with sulphuric acid and alcohol, the sweet smell of ethyl acetate (acetic ether) is obtained.

(iii) If ferric chloride is added to a solution of a neutral acetate, a blood-red colour is produced, due to the formation of ferric acetate ; the colour is discharged by the addition of strong hydrochloric acid.

(iv) If a dry acetate be heated in a test tube, the characteristic odour of acetone is evolved (*see* page 400).

Butyric acid $\left(HC_4H_7O_2, \text{ or } \left\{\begin{matrix} C_3H_7 \\ COHO \end{matrix}\right.\right)$.—This acid is contained in human perspiration, and is also produced when butter becomes rancid. It can be prepared by the oxidation of butyl alcohol, by distilling it with potassium bichromate and sulphuric acid.

$$\underset{\text{Butyl alcohol.}}{C_4H_9HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Butyric acid.}}{HC_4H_7O_2} + \underset{\text{Water.}}{H_2O}$$

Butyric acid can also be obtained from lactic acid by a fermentation process (*see* page 424).

Valerianic or **valeric acid** $\left(HC_5H_9O_2, \text{ or } \left\{\begin{matrix} C_4H_9 \\ COHO \end{matrix}\right.\right)$.—This acid is obtained by the oxidation of amyl alcohol or fusel oil, by distilling it with potassium bichromate and sulphuric acid.

$$\underset{\text{Amyl alcohol.}}{C_5H_{11}HO} + \underset{\text{Oxygen.}}{O_2} = \underset{\text{Valerianic acid.}}{HC_5H_9O_2} + \underset{\text{Water.}}{H_2O}$$

Test for valerianic acid.—This acid is distinguished by its powerful and characteristic smell, resembling that of valerian root.

Lactic acid $\left(HC_3H_5O_2 \text{ or } \left\{\begin{array}{l} C_2H_4(HO) \\ COHO \end{array}\right.\right)$.—It will be seen from the formula given below that this acid differs from propionic acid in containing one atom of oxygen more; it is therefore oxypropionic acid, and can be prepared by the substitution of hydroxyl (HO) for one atom of hydrogen in propionic acid.

$$\underset{\text{Propionic acid.}}{\left\{\begin{array}{l} C_2H_5 \\ COHO \end{array}\right.} \qquad \underset{\text{Lactic or oxypropionic acid.}}{\left\{\begin{array}{l} C_2H_4(HO) \\ COHO \end{array}\right.}$$

An isomer of lactic acid is the *sarcolactic acid* found in muscle.

Preparation of lactic acid.—This acid is best obtained by the process known as the *lactic acid fermentation* of sugar, which is effected by the action of the ferment, *penicillium glaucum*, on either glucose or milk sugar. Under the influence of this ferment, both these sugars split up into lactic acid ; the glucose molecule becoming resolved into two molecules of lactic acid, thus :—

$$\underset{\text{Glucose.}}{C_6H_{12}O_6} = \underset{\text{Lactic acid ;}}{2C_3H_6O_3}$$

the milk-sugar molecule becoming in its turn resolved into four molecules of lactic acid—

$$\underset{\text{Lactose or milk sugar.}}{C_{12}H_{22}O_{11}, H_2O} = \underset{\text{Lactic acid.}}{4C_3H_6O_3}$$

The production of lactic acid by fermentation is best effected by taking a mixture of sugar, mouldy cheese (the mould of which is *penicillium glaucum*), chalk, and water, and leaving the mixture for some time in a warm place; the lactic acid as it is formed is converted by the chalk into calcium lactate, which is deposited as a crystalline mass. From the calcium lactate the lactic acid may be set free by the addition of sulphuric or oxalic acid; on filtering from the insoluble calcium sulphate or oxalate, and evaporating the filtrate, the lactic acid is obtained as a syrupy liquid.

If the fermentation is allowed to continue too long, then the lactic acid becomes decomposed by a further fermentative process into butyric acid, thus:

$$\underset{\substack{\text{Lactic}\\\text{acid}}}{2C_3H_6O_3} = \underset{\substack{\text{Butyric}\\\text{acid.}}}{C_4H_8O_2} + \underset{\substack{\text{Carbon}\\\text{dioxide.}}}{2CO_2} + \underset{\text{Hydrogen.}}{2H_2}$$

As butyric acid can also be obtained from butter or fat, this conversion of lactic acid into butyric acid is of physiological interest, as indicating a possible method by which starchy foods become converted into fat when consumed as articles of diet. The starch is converted partly by the ptyalin of the saliva, but mainly by the ferment of the pancreatic juice, into sugar, this probably undergoes the lactic acid fermentation, the lactic acid possibly in its turn undergoes the butyric acid fermentation, and the butyric acid, after absorption into the circulation, may afterwards be deoxidised, and so yield fat, which is then deposited in the various tissues.

The souring of milk on exposure to the air is due to the conversion of the milk sugar into lactic acid, the fermentation being induced by the spores of *penicillium glaucum*, which are always present in the air, settling on the surface of the exposed milk.

2. Dibasic Organic Acids.

Oxalic acid $\left(H_2C_2O_4 \text{ or } \left\{\begin{matrix} COHO \\ COHO \end{matrix}\right.\right)$.—This acid is present in the form of potassium and calcium salts in a few plants, such as the wood-sorrel, rhubarb, and common dock. There is not, however, a sufficient quantity of it in these plants to render its extraction from them a commercial success, and it is therefore obtained by an artificial process. It may be prepared—

(i) In the form of its sodium salt by passing carbon dioxide over carefully heated metallic sodium.

$$\begin{array}{ccccc} Na_2 & + & 2CO_2 & = & Na_2C_2O_4 \\ \text{Sodium.} & & \text{Carbon} & & \text{Sodium} \\ & & \text{dioxide.} & & \text{oxalate.} \end{array}$$

(ii) It may also be prepared by boiling cane sugar with strong nitric acid, some of the oxygen of which oxidises the sugar to oxalic acid.

$$\begin{array}{ccccccc} C_{12}H_{22}O_{11} & + & 9O_2 & = & 6H_2C_2O_4 & + & 5H_2O \\ \text{Cane sugar.} & & \text{Oxygen.} & & \text{Oxalic acid.} & & \text{Water.} \end{array}$$

(iii) On the manufacturing scale, oxalic acid is prepared from sawdust; it does not pre-exist in sawdust, but the elements necessary for its formation do, and by roasting the sawdust with a caustic alkali, these elements unite to form oxalic acid, which is then converted by the alkali into an oxalate. The process is carried out on a large scale by roasting sawdust with caustic soda on iron plates, care being taken not to use sufficient heat to char the sawdust; the sodium oxalate is then extracted by means of boiling water, and decomposed by slaked lime into the insoluble calcium oxalate and caustic soda, which latter can then be used for roasting with a fresh portion of sawdust.

$$\underset{\substack{\text{Sodium}\\\text{oxalate.}}}{Na_2C_2O_4} + \underset{\substack{\text{Slaked}\\\text{lime.}}}{Ca(HO)_2} = \underset{\substack{\text{Calcium}\\\text{oxalate.}}}{CaC_2O_4} + \underset{\substack{\text{Caustic}\\\text{soda.}}}{2NaHO}$$

The calcium oxalate is then decomposed with sulphuric acid and water, with formation of insoluble calcium sulphate and soluble oxalic acid; on filtering from the calcium sulphate, and concentrating the filtrate by evaporation, crystals of oxalic acid are deposited.

$$\underset{\substack{\text{Calcium}\\\text{oxalate.}}}{CaC_2O_4} + \underset{\substack{\text{Sulphuric}\\\text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Oxalic}\\\text{acid.}}}{H_2C_2O_4} + \underset{\substack{\text{Calcium}\\\text{sulphate.}}}{CaSO_4}$$

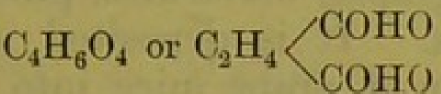
Properties of oxalic acid.—Oxalic acid is a white crystalline solid, with a very acid taste; it is an irritant poison, the antidote for it being chalk or lime-water, either of which neutralises the oxalic acid, and forms the insoluble calcium oxalate.

Salt of sorrel ($KHC_2O_4, H_2C_2O_4$) is an acid potassium oxalate combined with oxalic acid; it exists in the sorrel plant, and may be made by one-fourth neutralising oxalic acid with potassium carbonate; salt of sorrel and oxalic acid are both used for removing ink-stains from linen, the tannate of iron of the ink-stain being soluble in a solution of oxalic acid. Heat decomposes oxalic acid into water and the two oxides of carbon; a similar decomposition, but at a lower temperature, takes place when oxalic acid is heated with strong sulphuric acid (*see* page 163). Oxalates of the alkaline metals when heated yield carbonates, with evolution of carbon monoxide, thus—

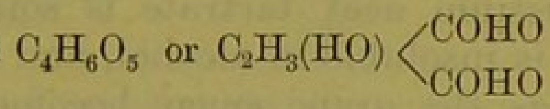
$$\underset{\substack{\text{Sodium}\\ \text{oxalate.}}}{Na_2C_2O_4} = \underset{\substack{\text{Sodium}\\ \text{carbonate.}}}{Na_2CO_3} + \underset{\substack{\text{Carbon}\\ \text{monoxide.}}}{CO}$$

Test for oxalic acid.—If a solution of oxalic acid be neutralised with ammonia, and calcium chloride be added, a white precipitate of calcium oxalate will be thrown down; this precipitate is insoluble in acetic acid, but is soluble in hydrochloric acid.

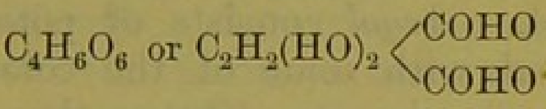
Succinic acid $\left(H_2C_4H_4O_4 \text{ or } C_2H_4\begin{cases}COHO\\COHO\end{cases}\right)$.—This acid can be obtained from amber by heat, hence its name (from *succinum*, amber). Although not employed at all in medicine, it is of interest on account of its relationship to malic and tartaric acids, as will be seen from the following formulæ.



Succinic acid $C_4H_6O_4$ or $C_2H_4\begin{cases}COHO\\COHO\end{cases}$



Malic acid $C_4H_6O_5$ or $C_2H_3(HO)\begin{cases}COHO\\COHO\end{cases}$



Tartaric acid $C_4H_6O_6$ or $C_2H_2(HO)_2\begin{cases}COHO\\COHO\end{cases}$

Malic acid is therefore oxysuccinic acid, since it contains one atom of oxygen more than succinic acid; tartaric acid is di-oxysuccinic acid, since it contains two atoms of oxygen more than succinic acid. Succinic acid may be prepared from both malic and tartaric acids, by withdrawal of the extra oxygen; this may be effected by the action upon them of hydriodic acid, the hydrogen of which unites with the extra oxygen to form water, the iodine being liberated, thus:—

$$\underset{\substack{\text{Malic}\\ \text{acid.}}}{C_4H_6O_5} + \underset{\substack{\text{Hydriodic}\\ \text{acid}}}{2HI} = \underset{\substack{\text{Succinic}\\ \text{acid.}}}{C_4H_6O_4} + \underset{\text{Water.}}{H_2O} + \underset{\text{Iodine}}{I_2}$$

$$\underset{\text{Tartaric acid.}}{C_4H_6O_6} + \underset{\text{Hydriodic acid.}}{4HI} = \underset{\text{Succinic acid.}}{C_4H_6O_4} + \underset{\text{Water.}}{2H_2O} + \underset{\text{Iodine.}}{2I_2}$$

Malic acid $\left(H_2C_4H_4O_5 \text{ or } C_2H_3(HO)\Big\langle\begin{matrix}COHO\\COHO\end{matrix}\right)$.—This acid is present in the free state in apples, pears, cherries, berries of the mountain ash, and various other fruits; it is also present in considerable quantities in green garden rhubarb, the sourness of which is due to malic acid. It is not used in medicine, but is of interest as being intermediate in composition between succinic and tartaric acids (*see* above).

Tartaric acid $\left(H_2C_4H_4O_6 \text{ or } C_2H_2(HO)_2\Big\langle\begin{matrix}COHO\\COHO\end{matrix}\right)$.—This acid occurs as potassium acid tartrate (cream of tartar) in grapes, tamarinds, pine-apples, and several other fruits. It is deposited as *argol* during the fermentation of grape juice into wine; for although the potassium acid tartrate is soluble in the grape juice, it is insoluble in alcohol, and is therefore precipitated as the grape sugar becomes converted into alcohol. *Argol* consists of potassium acid tartrate coloured with some of the colouring matter of the wine; it also constitutes the *crust*, formed as a sediment, in old port and other wines. *Cream of tartar*, or *bitartrate of potash*, as it is sometimes called, is argol deprived of its colouring matter by means of animal charcoal.

Preparation.—Tartaric acid is prepared by dissolving cream of tartar in boiling water, and adding chalk till effervescence ceases, when one-half of the tartaric radical is precipitated as calcium tartrate, the other half remaining in solution as potassium tartrate.

$$\underset{\text{Potassium acid tartrate.}}{2KHC_4H_4O_6} + \underset{\text{Calcium carbonate.}}{CaCO_3} = \underset{\text{Calcium tartrate.}}{CaC_4H_4O_6} +$$

$$\underset{\substack{\text{Potassium}\\ \text{tartrate.}}}{K_2C_4H_4O_6} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} + \underset{\text{Water.}}{H_2O}$$

Calcium chloride is then added to decompose the potassium tartrate, so that the whole of the cream of tartar is converted into the insoluble calcium tartrate.

$$\underset{\substack{\text{Potassium}\\ \text{tartrate.}}}{K_2C_4H_4O_6} + \underset{\substack{\text{Calcium}\\ \text{chloride.}}}{CaCl_2} = \underset{\substack{\text{Calcium}\\ \text{tartrate.}}}{CaC_4H_4O_6} + \underset{\substack{\text{Potassium}\\ \text{chloride.}}}{2KCl}$$

The calcium tartrate is finally decomposed with sulphuric acid and water, with the production of insoluble calcium sulphate and soluble tartaric acid; on filtering from the calcium sulphate, and concentrating the filtrate by evaporation, crystals of tartaric acid are deposited.

$$\underset{\substack{\text{Calcium}\\ \text{tartrate.}}}{CaC_4H_4O_6} + \underset{\substack{\text{Sulphuric}\\ \text{acid.}}}{H_2SO_4} = \underset{\substack{\text{Tartaric}\\ \text{acid.}}}{H_2C_4H_4O_6} + \underset{\substack{\text{Calcium}\\ \text{sulphate.}}}{CaSO_4}$$

Properties.—Tartaric acid is a white crystalline solid, with a very acid taste. Two isomeric varieties of tartaric acid exist, viz. dextro-tartaric acid and lævo-tartaric acid, a solution of the former twisting a ray of polarised light to the right, and of the latter to the left. Ordinary tartaric acid is the dextro-tartaric acid. *Racemic acid* is a mixture of the two varieties, and, in the form of the acid potassium salts, exists to a certain extent in grapes.

Test for tartaric acid.—If to a solution of tartaric acid neutralised with ammonia some silver nitrate be added, a white precipitate of silver tartrate is thrown down; on boiling the mixture, the precipitate blackens from reduction to metallic silver, which forms a mirror-like deposit on the sides of the test-tube.

3. TRIBASIC ORGANIC ACIDS.

Citric acid ($H_3C_6H_5O_7$).—This acid is present in lemons, limes, currants, gooseberries, raspberries, etc. It is prepared from lemon-juice or lime-juice by first boiling the juice and filtering from any suspended matters, and then adding chalk until effervescence ceases; the precipitated calcium citrate is then collected and is decomposed with sulphuric acid in a similar manner to that employed in the preparation of tartaric acid.

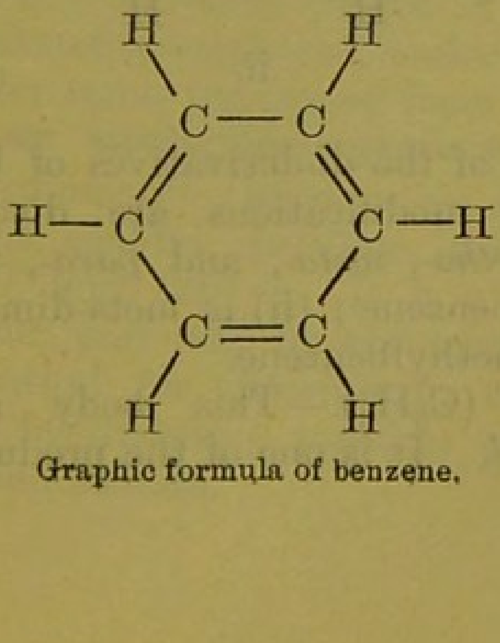
Properties and test.—Citric acid is a white crystalline solid, with a very acid taste. The best test for the solid acid is the peculiar way in which it chars when treated with strong sulphuric acid; it first turns of a pale lemon colour, passing successively to a darker yellow colour, a sherry colour, a port colour, and finally to a black colour.

CHAPTER VIII.

BENZENE DERIVATIVES, OR THE AROMATIC GROUP.

Benzene—Toluene—Nitrobenzene—Phenol or Carbolic Acid—Sulphocarbolic Acid—Picric Acid—Resorcin—Essential Oil of Bitter Almonds—Benzoic Acid—Hippuric Acid—Salicylic Acid—Gallic Acid—Pyrogallic Acid—Tannin—Terpenes—Camphor.

Benzene and its homologues constitute a group bearing to one another the same relation that methane or marsh gas bears to the group of paraffin derivatives. The members of this group are called aromatic bodies, on account of the fragrant odours possessed by some of them, such as essential oil of bitter almonds, benzoic acid, etc. The members of the benzene series are unsaturated hydrocarbons, from which their derivatives are obtained by the displacement of hydrogen by various radicals. Although in the molecule of benzene (C_6H_6) the carbon atoms are not completely saturated as regards their possible union with hydrogen, yet benzene may be regarded as a saturated molecule, as indicated by the following graphic formula, which shows the carbon atoms united together by one and two atom-fixing powers alternately. This graphic representation is known as the benzene ring:

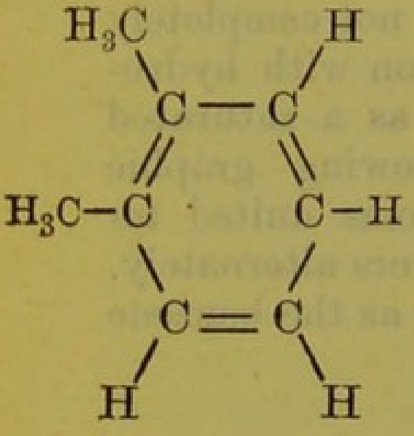


Graphic formula of benzene.

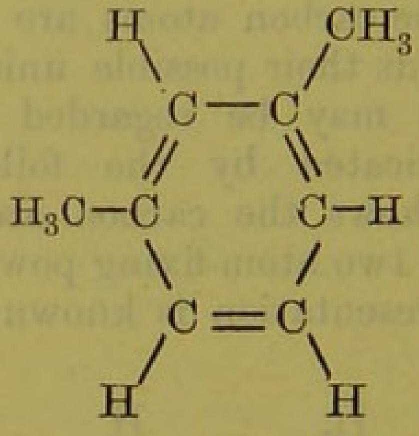
The other hydrocarbons of the series may be derived from benzene by the substitution of univalent hydrocarbon radicals for hydrogen, thus:

C_6H_6	Benzene.
$C_6H_5(CH_3)$	Methyl-benzene.
$C_6H_4(CH_3)_2$	Dimethyl-benzene.
$C_6H_3(CH_3)_3$	Trimethyl-benzene.

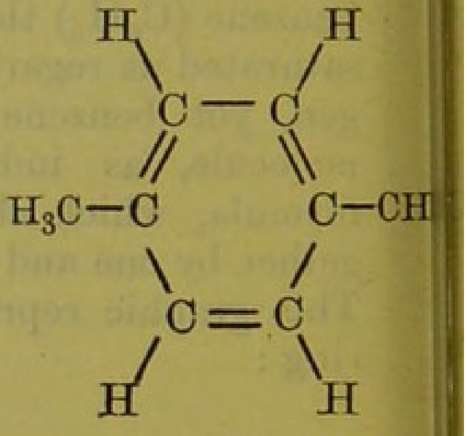
If two or more hydrogen atoms are displaced from the benzene ring by univalent elements or radicals, isomeric modifications are obtained according to the relative positions that those elements or radicals bear to one another in the benzene ring. Thus, taking the case of dimethyl-benzene, the two methyl radicals may be contiguous in the benzene ring (i), or may be separated by one atom of hydrogen (ii), or may be separated by two atoms of hydrogen (iii):



i.



ii.



iii.

In the case of the di-derivatives of benzene, these three isomeric modifications are distinguished by the prefixes *ortho-*, *meta-*, and *para-*, thus:—(i) is ortho-dimethylbenzene; (ii) is meta-dimethylbenzene; (iii) is para-dimethylbenzene.

Benzene (C_6H_6).—This body is commonly known as *benzol*. It is one of the products of the dry or destructive distillation of coal, and is obtained from the coal-tar by fractional distillation, being contained in that portion of the coal-tar distilling below 100° C. It may also be prepared by passing acetylene through red-hot tubes, a reaction of interest, because, as acetylene can be prepared from its elements, therefore benzene can also be indirectly prepared from its elements.

$$\underset{\text{Acetylene.}}{3C_2H_2} = \underset{\text{Benzene.}}{C_6H_6}$$

Pure benzene may also be prepared by the abstraction of carbon dioxide from benzoic acid, which is effected by heating benzoic acid with quicklime.

$$\underset{\text{Benzoic acid.}}{\left\{\begin{matrix} C_6H_5 \\ COHO \end{matrix}\right.} + \underset{\text{Lime.}}{CaO} = \underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Calcium carbonate.}}{CaCO_3}$$

Properties.—Benzene is a thin, colourless, limpid liquid, with a peculiar odour. Its sp. gr. is 0·899. It is very inflammable, burning with a smoky flame on account of the large amount of carbon it contains. It is a powerful solvent of fats, and is on this account commonly employed, under the name of *benzene collas*, for removing grease from clothes.

Toluene or methylbenzene ($C_6H_5.CH_3$).—This body is commonly known as *toluol.* It is contained in the coal-tar distillate, and passes over at between 100° and 120° C. It is a liquid, smelling like benzene, and may be obtained by the substitution of methyl for chlorine in chlorobenzene. This is effected by distilling together chlorobenzene, methyl iodide, and sodium.

$$\underset{\text{Chlorobenzene.}}{C_6H_5Cl} + \underset{\text{Methyl iodide.}}{CH_3I} + \underset{\text{Sodium.}}{Na_2} = \underset{\text{Toluene.}}{C_6H_5 . CH_3} + \underset{\text{Sodium chloride.}}{NaCl} + \underset{\text{Sodium iodide.}}{NaI}$$

Nitrobenzene ($C_6H_5NO_2$).—This body is also known as *nitrobenzol* and *essence of mirbane.* It is obtained by the action of strong nitric acid on benzene.

$$\underset{\text{Benzene.}}{C_6H_6} + \underset{\text{Nitric acid.}}{HNO_3} = \underset{\text{Nitrobenzene.}}{C_6H_5NO_2} + \underset{\text{Water.}}{H_2O}$$

Properties.—Nitrobenzene is a yellow liquid, heavier than water, and possessing a strong odour resembling that of the *essential oil of bitter almonds*, and is on this account sometimes known as *artificial oil of bitter almonds.* It is a poisonous substance, and is extensively employed in commerce in the manufacture of aniline (*see* page 455).

Phenol or **carbolic acid** (C_6H_5HO).—This body, which is the ordinary carbolic acid, is also known as *phenic acid.* It is contained in coal tar, from which it is obtained for commercial purposes, being that portion of coal tar distilling between 180° and 190° C. It may be obtained in a chemically pure state by the withdrawal of the carbon dioxide from salicylic acid, which is effected by heating salicylic acid with quicklime.

$$\underset{\text{Salicylic acid.}}{\left\{\begin{matrix} C_6H_5O \\ COHO \end{matrix}\right.} + \underset{\text{Lime.}}{CaO} = \underset{\text{Carbolic acid.}}{C_6H_5HO} + \underset{\text{Calcium carbonate.}}{CaCO_3}$$

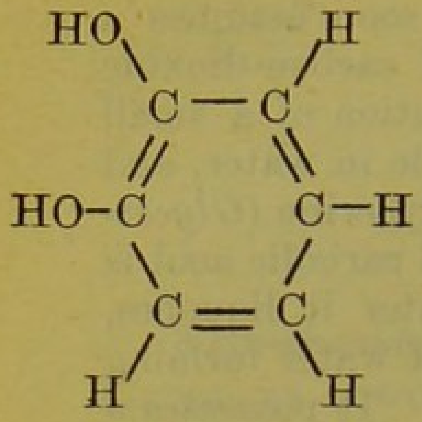
Properties.—Carbolic acid is, in the pure state, a colourless crystalline body, but it soon assumes a pink colour, due to the absorption of carbon dioxide from the air and the consequent formation of a small amount of aurin. It is slightly soluble in water, and readily soluble in alcohol, ether, and glycerine (*Glycerinum acidi carbolici*, B. P.). If solid carbolic acid is mixed with a small quantity of water it liquefies, 100 parts of the acid and 10 parts of water forming *Acidum carbolicum liquefactum*, B. P. It possesses a characteristic odour and taste, somewhat resembling creasote. It is a powerful antiseptic on account of its germicidal properties. It is a corrosive and irritant poison.

Tests.—(i) Carbolic acid gives, with bromine water, a white precipitate of tribromocarbolic acid ($C_6H_3Br_3O$). This constitutes a very delicate test for carbolic acid, and is the best method for its detection in the urine in cases of carbolic acid poisoning, and in cases of absorption of carbolic acid from wounds washed with carbolic acid lotion. (ii) Ferric chloride gives a violet colour with a solution of carbolic acid.

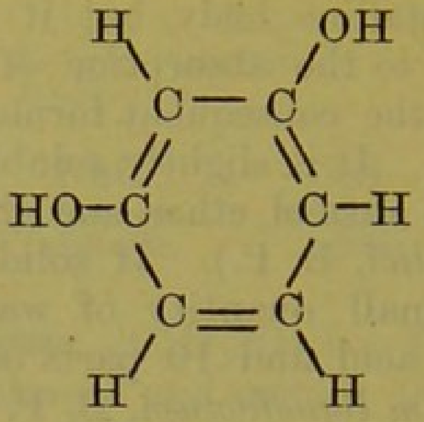
Sulphocarbolic acid ($HC_6H_5SO_4$).—This is prepared by dissolving carbolic acid in strong sulphuric acid. By mixing it with metallic hydrates or carbonates, sulphocarbolates are formed. Two of these salts are used in medicine, viz. sodium sulphocarbolate ($NaC_6H_5SO_4$), and zinc sulphocarbolate ($Zn(C_6H_5SO_4)_2$).

Trinitrophenol or **picric acid** ($C_6H_3(NO_2)_3O$).—This is obtained by dropping carbolic acid into fuming nitric acid. It is a yellow dye, known as *carbazotic acid* or *picric acid.*

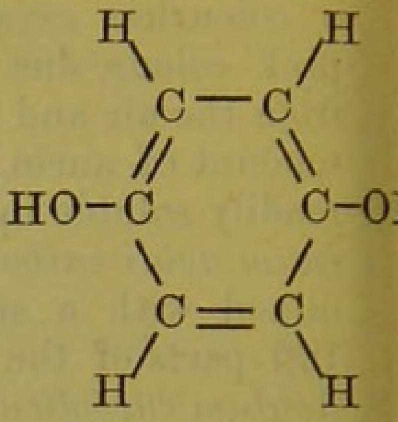
Resorcin ($C_6H_4(HO)_2$).—This body is dihydroxybenzene. Three such isomeric bodies exist, according to the relative positions of the hydroxyl groups in the benzene ring, viz.:—



Pyrocatechin.



Resorcin.



Hydroquinone.

Of these only the metaderivative (resorcin) is used in medicine. Resorcin is prepared by the action of melted caustic potash on chlorophenol, that is, by introducing a second hydroxyl group into phenol or carbolic acid (C_6H_5HO).

$$\underset{\text{Chlorophenol.}}{C_6H_4ClHO} + \underset{\text{Caustic potash.}}{KHO} = \underset{\text{Resorcin.}}{C_6H_4(HO)_2} + \underset{\text{Potassium chloride.}}{KCl}$$

Properties.—Resorcin is a white substance, soluble in water, alcohol, and ether. Its aqueous solution is coloured dark violet by ferric chloride, and gives a white precipitate with bromine water, in these properties resembling carbolic acid.

Benzoic aldehyde or **essential oil of bitter almonds** $\left(C_7H_6O \text{ or } \left\{\begin{matrix}C_6H_5\\COH\end{matrix}\right.\right)$.—This is obtained from the glucoside amygdalin present in the bitter almond seeds, by digesting the bitter almonds with water and afterwards distilling. The bitter almond seeds contain a ferment *emulsin*, which, in presence of water, causes the amygdalin to decompose into the essential oil of bitter almonds, hydrocyanic acid, and glucose.

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Essential oil of}\\\text{bitter almonds.}}}{C_7H_6O} + \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{HCN} + \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

The essential oil of bitter almonds therefore contains a considerable quantity of hydrocyanic acid (4 to 8 per cent.), unless specially purified from it. It may be freed from the hydrocyanic acid by distillation with slaked lime and ferrous chloride, by which means the volatile hydrocyanic acid is converted into the non-volatile calcium ferrocyanide. If the essential oil of bitter almonds is exposed to the air it absorbs oxygen, the benzoic aldehyde becoming converted into benzoic acid, which is deposited as white crystals.

$$\underset{\substack{\text{Essential oil of}\\\text{bitter almonds.}}}{2\left\{\begin{matrix}C_6H_5\\COH\end{matrix}\right.} + \underset{\text{Oxygen.}}{O_2} = \underset{\substack{\text{Benzoic}\\\text{acid.}}}{2\left\{\begin{matrix}C_6H_5\\COHO\end{matrix}\right.}$$

Benzoic acid $\left(HC_7H_5O_2 \text{ or } \left\{\begin{matrix}C_6H_5\\COHO\end{matrix}\right.\right)$.—This acid may be prepared (i) from gum benzoin, which contains from 12 to 15 per cent. of it, by heating the crushed benzoin, when the benzoic acid sublimes, or more economically by boiling the crushed benzoin with slaked lime and water, when the benzoic acid is extracted as the soluble calcium benzoate.

$$\underset{\substack{\text{Benzoic}\\\text{acid.}}}{2HC_7H_5O_2} + \underset{\substack{\text{Slaked}\\\text{lime.}}}{Ca(HO)_2} = \underset{\substack{\text{Calcium}\\\text{benzoate.}}}{Ca(C_7H_5O_2)_2} + \underset{\text{Water}}{2H_2O}$$

From the filtrate benzoic acid is precipitated by the addition of hydrochloric acid.

$$\underset{\substack{\text{Calcium}\\\text{benzoate.}}}{Ca(C_7H_5O_2)_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{2HCl} = \underset{\substack{\text{Benzoic}\\\text{acid.}}}{2HC_7H_5O_2} + \underset{\substack{\text{Calcium}\\\text{chloride.}}}{CaCl_2}$$

(ii) Benzoic acid may be prepared by the oxidation of oil of bitter almonds (*see* above).

(iii) Benzoic acid may also be obtained from hippuric acid, which can be extracted from the urine of cows or horses, by boiling that acid with hydrochloric acid (*see* below).

Hippuric acid or **benzoyl-amidacetic acid** $\left(\left\{\begin{array}{l}CH_2(NH.C_7H_5O)\\COHO\end{array}\right.\right)$.—This acid occurs in the urine of herbivorous animals, and is formed within them from the union of the benzoyl compounds contained in grass, fodder, etc., with amidacetic acid existing in some of the bile compounds. If benzoic acid is taken internally by man it appears in the urine as hippuric acid, the latter acid being produced by the union of benzoic acid with the amidacetic acid or glycocine present in a compound form in one of the bile salts (*see* page 461). Hippuric acid may be artificially produced by the action of benzoyl chloride on amidacetic acid (glycocine).

$$\underset{\substack{\text{Amidacetic}\\\text{acid.}}}{\left\{\begin{array}{l}CH_2(NH_2)\\COHO\end{array}\right.} + \underset{\substack{\text{Benzoyl}\\\text{chloride}}}{C_7H_5OCl} = \underset{\substack{\text{Hippuric}\\\text{acid.}}}{\left\{\begin{array}{l}CH_2(NH.C_7H_5O)\\COHO\end{array}\right.} +$$

$$\underset{\substack{\text{Hydrochloric}\\\text{acid.}}}{HCl}$$

Hippuric acid is decomposed by boiling with strong hydrochloric acid into benzoic acid and amidacetic acid (glycocine).

$$\underset{\text{Hippuric acid.}}{\left\{\begin{array}{l}CH_2(NH\,C_7H_5O)\\ COHO\end{array}\right.} + \underset{\text{Water.}}{H_2O} = \underset{\text{Amidacetic acid.}}{\left\{\begin{array}{l}CH_2(NH_2)\\ COHO\end{array}\right.} + \underset{\text{Benzoic acid.}}{HC_7H_5O_2}$$

Salicylic acid or **hydroxybenzoic acid** $\left(\left\{\begin{array}{l}C_6H_4(HO)\\ COHO\end{array}\right.\right)$.—Two kinds of salicylic acid occur in commerce, namely, the *natural* and *artificial* salicylic acids. The natural salicylic acid is obtained from oil of winter green or methyl salicylate, by distilling it with caustic soda, when methyl alcohol distils over and sodium salicylate is left behind. If the sodium salicylate is dissolved in water, salicylic acid can be precipitated by the addition of hydrochloric acid to the solution. Artificial salicylic acid is prepared from carbolic acid. It will be seen that if carbon dioxide is added to the molecule of carbolic acid salicylic acid is produced, thus:—

$$\underset{\text{Carbolic acid.}}{C_6H_6O} + \underset{\text{Carbon dioxide.}}{CO_2} = \underset{\text{Salicylic acid.}}{C_7H_6O_3}$$

This is effected by converting the carbolic acid into sodium carbolate by the addition of caustic soda, and then heating the sodium carbolate in a stream of carbon dioxide at 180° C., when it becomes converted into sodium salicylate.

$$\underset{\text{Sodium carbolate.}}{NaC_6H_5O} + \underset{\text{Carbon. dioxide.}}{CO_2} = \underset{\text{Sodium salicylate.}}{NaC_7H_5O_3}$$

Salicylic acid is precipitated from an aqueous solution of the sodium salicylate by the addition of hydrochloric acid.

Properties.—Salicylic acid is a white solid, free from smell, slightly soluble in cold water and readily soluble in hot water, alcohol and ether. It is an antiseptic. It is largely used in medicine in the form of its sodium salt, the preparation of which has been described in the two processes given above.

Tests.—(i) A solution of salicylic acid gives, with ferric chloride, a violet colour. (ii) Salicylic acid, heated with quicklime, evolves the odour of carbolic acid, the quicklime extracting the carbon dioxide from the salicylic acid, and so reducing it to carbolic acid.

Gallic acid, or **tri-hydroxybenzoic acid,** or **di-hydroxysalicylic acid** $\left(\left\{\begin{matrix}C_6H_2(HO)_3\\ COHO\end{matrix}\right.\right)$.—Gallic acid occurs in small quantity in oak galls, but is generally prepared from tannic acid by the union of that body with the elements of water. As tannic acid is contained to a considerable extent in oak galls, gallic acid is prepared by boiling the crushed galls with dilute sulphuric acid for about half an hour, when the tannin unites with the elements of water and forms gallic acid. If the liquid is filtered while hot, it deposits crystals of gallic acid on cooling.

Test.—A solution of gallic acid gives, with ferric chloride, a bluish-black precipitate of ferric gallate.

Pyrogallic acid ($C_6H_6O_3$).—This substance sublimes when gallic acid is heated, and is formed by the gallic acid losing carbon dioxide.

$$\underset{\substack{\text{Gallic}\\ \text{acid.}}}{C_7H_6O_5} = \underset{\substack{\text{Pyrogallic}\\ \text{acid.}}}{C_6H_6O_3} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2}$$

An aqueous solution of potassium pyrogallate possesses the property of rapidly absorbing oxygen, and hence is used in the analysis of air (*see* page 105).

Tannin or **tannic acid** ($C_{14}H_{10}O_9$).—This substance is a constituent of oak galls, from which it is obtained by macerating the galls in a mixture of ether, alcohol and water. The strained liquor, if evaporated, deposits tannin. The relationship of tannin to gallic acid is represented in the following equation, which shows that two molecules of gallic acid, deprived of one molecule of water, yield tannin.

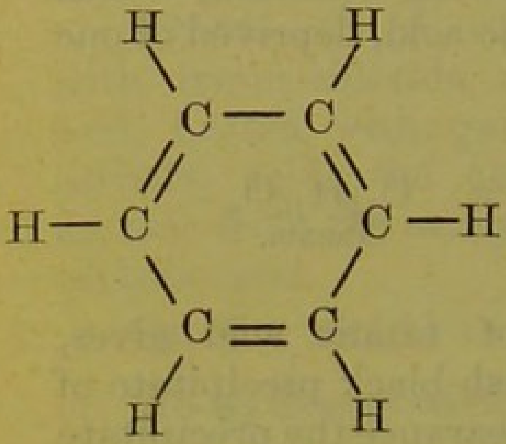
$$\underset{\text{Gallic acid.}}{2C_7H_6O_5} \quad - \quad \underset{\text{Water.}}{H_2O} \quad = \quad \underset{\text{Tannin.}}{C_{14}H_{10}O_9}$$

Tests.—(i) A solution of tannic acid gives, with ferric chloride, a dark bluish-black precipitate of ferric tannate resembling in appearance the precipitate of ferric gallate. (ii) An aqueous solution of tannin precipitates an aqueous solution of gelatine. This test serves to distinguish tannic acid from gallic acid, as the latter does not precipitate gelatine.

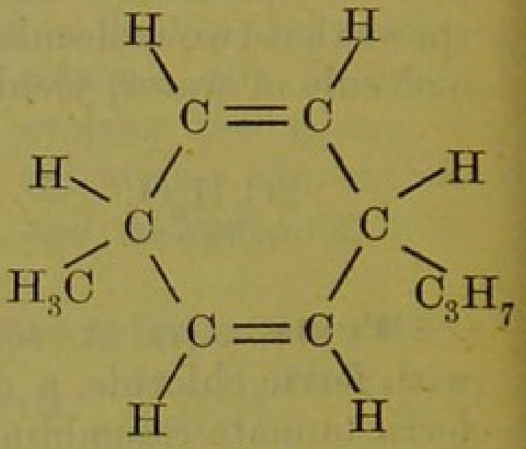
TERPENES.

Terpenes of the formula $C_{10}H_{16}$ are isomeric hydrocarbons occurring as volatile oils in plants, from which they may be obtained by a process of distillation. The commonest terpene is oil of turpentine; other terpenes isomeric with this are the volatile or essential oils of lemon, orange, citron and bergamot.

Essential oil of turpentine ($C_{10}H_{16}$) is also known as oil of turpentine, spirits of turpentine, turpentine, and "turps." It is prepared by distillation from the crude turpentine or oleo-resin, obtained from various species of pine trees; the volatile oil of turpentine distilling over, common resin being left in the retort. The relationship of oil of turpentine to benzene is shown in the following graphic formulæ, from which it is evident that the molecule of oil of turpentine consists of benzene, to which the radicals methyl (CH_3) and propyl (C_3H_7) have been added, by the loosening of a pair of atom-fixing powers in the benzene ring :—



Benzene.



Oil of Turpentine.

Camphor ($C_{10}H_{16}O$).—This substance is a partially-oxidised terpene ; it is a solid volatile substance obtained from the camphor plant.

CHAPTER IX.

FATS—SOAPS—ALKALOIDS.

Fats and Fixed Oils—Soaps—Saponification—Vegetable Alkaloids—Morphine—Apomorphine—Quinine—Strychnine—Brucine—Rarer Alkaloids—Ptomaines or Animal Alkaloids.

FATS AND FIXED OILS.

A FAT or oil is a compound of the radical glyceryl with the acid radical of one of the higher fatty acids. The large majority of fats and oils consist of the radical glyceryl united with the oleic, stearic, and palmitic radicals. The compound of glyceryl and the oleic radical is glyceryl oleate or *olein*; the compound of glyceryl and the stearic radical is glyceryl stearate or *stearin*; and the compound of glyceryl and the palmitic radical is glyceryl palmitate or *palmitin*. As the glyceryl radical is trivalent, and the fatty acid radicals are univalent, it follows that three equivalents of the latter are required to saturate one of the former; the formulæ of these fats and oils are, therefore, as follows:—

Glyceryl oleate or olein	$C_3H_5(C_{18}H_{33}O_2)_3$.
Glyceryl stearate or stearin	$C_3H_5(C_{18}H_{35}O_2)_3$.
Glyceryl palmitate or palmitin	$C_3H_5(C_{16}H_{31}O_2)_3$.

Olein is a liquid, stearin and palmitin are solids; therefore the larger the proportion of olein in a mixed fat the softer it will be; and the larger the proportion of stearin (which is harder than palmitin) the harder the mixed fat will be.

Olein in its pure form constitutes olive oil and almond oil, and is also contained in castor oil. *Stearin* forms the bulk of beef-suet and mutton-suet. *Palmitin* is present in palm oil. Human fat is a mixture of olein, stearin, and palmitin. *Margarine*, which was formerly believed to be a simple fat, is now known to be a mixture of stearin and palmitin.

SOAPS AND SAPONIFICATION.

A soap is a compound of a metal with one of the radicals of oleic, stearic, or palmitic acid, and is therefore obtained by the displacement of the glyceryl of an oil or fat by a metal. The following list shows the composition of the commonly used soaps :—

Common, yellow, or hard soap is *sodium oleate*	$NaC_{18}H_{33}O_2$
Soft soap is *potassium oleate* . .	$KC_{18}H_{33}O_2$
Curd soap is *sodium stearate* . .	$NaC_{18}H_{35}O_2$

Saponification is the process by which oils or fats are converted into soaps, and consists in decomposing the oil or fat with an alkali, when double decomposition takes place, resulting in the formation of a soap and glycerine.

Common, yellow, or hard soap.—This is prepared by boiling olive oil (glyceryl oleate) with caustic soda, when double decomposition occurs as follows :—

$$\underset{\text{Glyceryl oleate.}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\text{Sodium hydrate.}}{3NaHO} = \underset{\text{Sodium oleate.}}{3NaC_{18}H_{33}O_2} + \underset{\text{Glycerine.}}{C_3H_5(HO)_3}$$

When the process of saponification is completed, common salt is added to separate the soap from the glycerine; the soap being insoluble in a solution of common salt, it is thrown out of solution on the addition of the salt, and rises to the surface of the liquid, when it can be removed.

Soft soap.—This is prepared by boiling olive oil (glyceryl oleate) with caustic potash, when double decomposition occurs as follows :—

$$\underset{\text{Glyceryl oleate.}}{C_3H_5(C_{18}H_{33}O_2)_3} + \underset{\substack{\text{Potassium}\\\text{hydrate.}}}{3KHO} = \underset{\text{Potassium oleate.}}{3KC_{18}H_{33}O_2} + \underset{\text{Glycerine.}}{C_3H_5(HO)_3}$$

Common salt cannot be used to throw this soap out of solution, as it would convert it into the soda soap; the solution is therefore evaporated to a soft consistence, the glycerine being left in the soap.

Curd soap.—This is prepared by boiling suet (glyceryl stearate) with caustic soda, when double decomposition occurs as follows :—

$$\underset{\text{Glyceryl stearate.}}{C_3H_5(C_{18}H_{35}O_2)_3} + \underset{\text{Sodium hydrate.}}{3NaHO} = \underset{\text{Sodium stearate.}}{3NaC_{18}H_{35}O_2} + \underset{\text{Glycerine.}}{C_3H_5(HO)_3}$$

Common salt is added, as in the case of ordinary hard soap, to separate the soap from the glycerine; the soap is thrown out of solution by the addition of the salt, and rises to the surface, when it can be removed.

VEGETABLE ALKALOIDS.

These bodies are organic bases, resembling the alkalies in their properties of turning red litmus paper blue, and of uniting with acids to form salts; hence the derivation of the name "alkaloid," from *alkali*, and εἶδος, likeness. All alkaloids contain nitrogen, and are, in fact, derivatives of ammonia, the hydrogen of which has been partially or entirely displaced by various radicals. Alkaloids unite with acids to form crystalline salts.

Morphine or **morphia** ($C_{17}H_{19}NO_3$, H_2O).—This alkaloid exists in opium in combination with meconic acid as *meconate of morphine*; a fair sample of opium contains from 8 to 12 per cent. of morphine. It is extracted by the following process:—

(i) The opium is macerated in water and exhausted by percolation, by which means an aqueous extract of the meconate of morphine is obtained.

(ii) To this aqueous extract calcium chloride is added, when the meconic acid is precipitated as calcium meconate, the soluble hydrochlorate of morphine remaining in solution.

(iii) The liquid is filtered, and the filtrate, containing the hydrochlorate of morphine, is decolorised by boiling with animal charcoal.

(iv) The liquid is filtered from the animal charcoal, and evaporated to a low bulk; it is then set aside to cool, when it deposits crystals of the hydrochlorate of morphine.

(v) To obtain the free alkaloid, solution of ammonia is added to a strong aqueous solution of the hydrochlorate, when the morphine is thrown down as a white precipitate, the ammonia uniting with the hydrochloric acid.

Morphine hydrochlorate or **hydrochlorate of morphia** ($C_{17}H_{19}NO_3$, HCl).—This compound is prepared in the process just described.

Morphine acetate or **acetate of morphia** ($C_{17}H_{19}NO_3$, $C_2H_4O_2$).—This compound is prepared by dissolving the free alkaloid (precipitated by ammonia from the hydrochlorate) in acetic acid. Morphine acetate is the salt generally employed for hypodermic injection.

Tests for morphine.—(i) Ferric chloride gives, with a neutral solution of a morphine salt, a dingy blue colour. In the cases of the acetate and meconate of morphine, this blue colour is more or less neutralised by the production of the red colour that ferric chloride gives with an acetate and meconate.

(ii) Strong nitric acid gives an orange-red colour with morphine and its salts; this colour can also be obtained by the addition of sufficient nitric acid to a strong solution of a morphine salt.

(iii) Sulphomolybdic acid, rubbed with morphine or any of its salts in the solid state, gives a dark crimson colour, changing after a short time to a sapphire blue; this constitutes a very delicate test for morphine.

Detection of opium.—Apart from its characteristic smell, analytical evidence of the presence of opium is gained by obtaining the reactions for morphine (as detailed above) and for meconic acid. The reaction for meconic acid is that it gives a blood-red colour with ferric chloride, which colour is not discharged either by the addition of hydrochloric acid, or of solution of mercuric chloride; hence distinguishing it from similar red colours given by ferric chloride with acetates and sulphocyanides (*see* pages 396, 422).

Apomorphine ($C_{17}H_{17}NO_2$).—The molecule of this body differs from that of morphine by containing one molecule of water less. It is prepared by heating morphine with strong hydrochloric acid, when the elements of water are withdrawn from the morphine, and the hydrochlorate of apomorphine remains. This alkaloid possesses entirely different physiological properties to those of morphine; it is a very powerful and rapid emetic, and has none of the narcotic properties of morphine and its salts.

Codeine ($C_{18}H_{21}NO_3, H_2O$).—This is one of the alkaloids of opium; it is closely related to morphine, being *methyl-morphine;* that is, it consists of morphine, from the molecule of which one atom of hydrogen has been displaced by the radical methyl, as shown in the following formulæ:—

Morphine—$C_{17}H_{19}NO_3, H_2O$
Codeine or methyl-morphine—$C_{17}H_{18}(CH_3)NO_3, H_2O$.

Quinine or **quinia** ($C_{20}H_{24}N_2O_2,3H_2O$).—This, together with other alkaloids, exists in the different cinchona barks in combination with kinic acid. It is extracted by the following process:—

(i) The powdered cinchona bark is exhausted by percolation with water acidulated with hydrochloric acid, by which means the quinine is removed in solution as hydrochlorate of quinine.

(ii) The solution is decolorised by means of animal charcoal.

(iii) The quinine is precipitated from the solution of the hydrochlorate by the addition of caustic soda, which sets free the quinine as a white precipitate, by uniting with the hydrochloric acid to form sodium chloride.

Sulphate of quinine.—This is the form in which quinine is generally employed in medicine; it is made by dissolving the precipitated quinine in dilute sulphuric acid. The commercial sulphate of quinine, or *disulphate of quinine,* as it is sometimes called, has the composition $(C_{20}H_{24}N_2O_2)_2, H_2SO_4$; it is only slightly soluble in water, but may be readily dissolved by the addition of a little dilute sulphuric acid, which forms the neutral or soluble sulphate $C_{20}H_{24}N_2O_2, H_2SO_4$.

Tests for quinine.—(i) If to a solution of a quinine salt some chlorine water and then solution of ammonia be added, a green colour will be produced.

(ii) If the above-mentioned test be repeated, adding some potassium ferrocyanide solution previous to the addition of the ammonia, a red colour will be produced.

Cinchonine, *cinchonidine*, and *quinidine* are alkaloids also present in cinchona barks.

Strychnine or **strychnia** $(C_{21}H_{22}N_2O_2)$.—This alkaloid exists in nux vomica seeds in combination with igasuric acid, as strychnine igasurate; another alkaloid, *brucine* or *brucia*, is also present in the seeds as brucine igasurate.

Strychnine is extracted by the following process:—

(i) The crushed seeds are exhausted by maceration and percolation with rectified spirit, and from the tincture so obtained the spirit is recovered by distillation.

(ii) The soft extract left after the recovery of the spirit is mixed with water, to precipitate resinous matters, and acetate of lead added to throw down colouring matter and igasurate of lead, acetate of strychnine being left in solution.

(iii) The liquid is filtered from precipitated matters, and the filtrate is concentrated by evaporation; on the addition of ammonia, strychnine is precipitated together with brucine.

(iv) To separate the brucine from the strychnine the precipitate is dissolved in alcohol, and the solution is evaporated to a low bulk; on setting it aside to cool, the strychnine crystallises out, leaving the more soluble brucine in solution in the mother liquor.

Test for strychnine.—If a drop or two of strong sulphuric be added to a fragment of strychnine placed on a white porcelain dish or plate, and then if the mixture be touched with a glass rod dipped in a solution of potassium bichromate in strong sulphuric acid (made by adding a crystal or two of the bichromate to a few drops of sulphuric acid), a beautiful dark purple or violet colour will be developed, fading after a short time to a pale red colour.

Brucine or **brucia** ($C_{23}H_{26}N_2O_4$).—The separation of this alkaloid from strychnine has been described in the process just given.

Test for brucine.—Strong nitric acid gives a bright blood-red colour with brucine and its salts.

Rarer alkaloids.—Aconitine, atropine, cocaine, hyoscyamine, veratrine, etc., are prepared by separate processes, for a description of which the student is referred to the British Pharmacopœia. These rarer alkaloids are not, however, always prepared by the lengthy official processes of the B. P.; they may be obtained by the following general method.

General process for the extraction of alkaloids.—(i) The crushed roots, bark, leaves, fruits, or seeds are exhausted by maceration and percolation with alcohol containing tartaric acid; tartrates of the alkaloids being soluble in alcohol.

(ii) The alcohol is recovered by distillation, and the soft extract left is mixed with water to precipitate resinous matters.

(iii) The liquor is filtered from precipitated resinous matters, and the alkaloid precipitated by the addition of sodium carbonate.

(iv) The precipitated alkaloid is purified by solution in, and crystallisation from, a suitable solvent, such as ether, chloroform, or alcohol. If necessary, colouring matter is removed from the alkaloid by means of animal charcoal.

Liquid volatile alkaloids.—Conine (contained in the conium or hemlock plant), nicotine (contained in tobacco), and pilocarpine (contained in jaborandi leaves) are liquid volatile alkaloids; they may all be prepared by distilling the part of the plant containing the alkaloid with a dilute solution of caustic potash, when the alkaloid is set free, and being volatile distils over.

PTOMAINES OR ANIMAL ALKALOIDS.

Ptomaines are alkaloids produced by the decomposition of animal substances. The word *ptomaine*, which is derived from *πτῶμα*, a corpse, and *inus*, belonging to, was at first restricted to alkaloids produced by cadaveric decomposition; it is now also employed to designate alkaloids of animal origin formed during life as the result of chemical changes induced by some agency or other acting within the organism. The term *leucomaine* has recently been introduced to distinguish the animal alkaloids formed during life, from those produced by decomposition of dead animal matter. Such a distinction is, however, unnecessary, and it is probable that in the future the terms *ptomaines* and *leucomaines* will be dropped, and that these bases of animal origin will be classed in one category as *animal alkaloids.*

At the beginning of this century the formation of alkaloids by plants was clearly established; but until 1872 the power of producing alkaloids was believed to be restricted to plants, and not to be shared by animal organisms. Gautier, as the result of his researches on putrefying albuminous substances, was the first to clearly establish the fact that plants possess no monopoly of producing alkaloids, but that this productive power is equally shared by animal substances. The various forms of albumen are the common ancestors of alkaloids, whether animal or vegetable; and it is by various changes in the albumen molecule that animal alkaloids are produced.

The following is a list of the principal ptomaines that have been extracted from putrefying animal matters:—

Collodine, $C_8H_{11}N$, from putrefying horseflesh and mackerel.
Parvoline, $C_9H_{13}N$, from putrefying horseflesh and mackerel.
Unnamed base, $C_{10}H_{15}N$, from putrefying fibrin of bullock's blood.
Hydrocollodine, $C_8H_{13}N$, from putrefying horseflesh and mackerel.
Putrescine, $C_4H_{12}N_2$, from human corpses.
Neuridine, $C_5H_{14}N_2$, from human corpses and from putrefying fish and cheese.
Tyrotoxicon, $C_6H_5N_2$, from decomposing cheese, milk, and cream.
Cadaverine, $C_5H_{16}N_2$, from human corpses.
Neurine, $C_5H_{13}NO$, from cadaveric putrefaction.
Muscarine, $C_5H_{13}NO_2$, from putrid fish.
Choline, $C_5H_{15}NO_2$, from cadaveric putrefaction.
Gadinine, $C_7H_{16}NO_2$, from putrid cod-fish.

The following is a list of the principal animal alkaloids obtained from the secretions of living beings, and from fresh animal tissues:—

Creatinine, $C_4H_7N_3O$, from urine.
Pseudoxanthine, $C_4H_5N_5O$, from urine and flesh.
Sarkine, $C_5H_4N_4O$, from urine and flesh.
Xanthine, $C_5H_4N_4O_2$, from urine and flesh.
Crusocreatinine, $C_5H_8N_4O$, from fresh meat.
Xanthocreatinine, $C_5H_{10}N_4O$, from fresh meat.
Guanine, $C_5H_5N_5O$, from flesh and guano.
Carnine, $C_7H_8N_4O_3$, from fresh meat.
Betanine, $C_5H_{11}NO_2$, from urine.

The poisonous effects of certain shell-fish (mussels, etc.) have been shown to be due to a ptomaine named *mytiloxine*, $C_6H_{15}NO_2$.

Animal alkaloids have recently been discovered in connection with some of the infectious fevers. From the fæces of a cholera patient an animal alkaloid has been obtained, apparently identical with one extracted from cultivations of Koch's cholera bacillus. From cultivations of the typhoid bacillus, from the viscera of a patient dying of typhoid fever, and from the urines of typhoid patients, small quantities of animal alkaloids have been extracted. From the urine of scarlet fever patients an animal alkaloid in small amount has been extracted.

CHAPTER X.

COMPOUND AMMONIAS.

Amines—Trimethylamine—Aniline— Amides—Urea — Estimation of Urea in Urine—Uric Acid—Amidic Acids—Glycocine—Hippuric Acid—Glycocholic Acid—Sarcosine—Tyrosine—Leucine—Taurine—Taurocholic Acid.

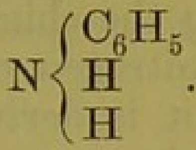
COMPOUND ammonias are compounds derived from ammonia by the displacement of part or all of the hydrogen by an organic radical or radicals. There are two classes of compound ammonias, viz. amines and amides. If the radical introduced into the ammonia is an alcohol or hydrocarbon radical, then the resulting compound ammonia is an *amine;* if the radical is an acid one, then the resulting compound ammonia is an *amide* (*see* page 350).

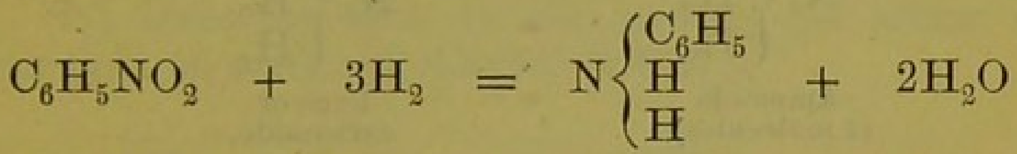
A *primary amine* is one produced by the displacement of one-third of the hydrogen of the ammonia by an alcohol radical; a *secondary amine* by the displacement of two-thirds of the hydrogen; a *tertiary amine* by the displacement of all the hydrogen. Thus:—

$$\begin{array}{ccc}
\text{Primary.} & \text{Secondary.} & \text{Tertiary.} \\
N\left\{\begin{matrix} CH_3 \\ H \\ H \end{matrix}\right. & N\left\{\begin{matrix} CH_3 \\ CH_3 \\ H \end{matrix}\right. & N\left\{\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\right. \\
\text{Methylamine.} & \text{Dimethylamine.} & \text{Trimethylamine.}
\end{array}$$

Very few of the amines have, at present, any medical interest.

Trimethylamine, $N\left\{\begin{matrix} CH_3 \\ CH_3 \\ CH_3 \end{matrix}\right.$, is a body with a strong fishy odour, and is contained in herring-brine. It is a deodorant and antiseptic, and is employed in the *amines process* for the treatment of sewage, which consists in treating the sewage with milk of lime and herring-brine; the trimethylamine contained in the latter acts as such an efficient deodorant and antiseptic as to yield a sterilised effluent, and a sludge which can be dried without evolving smell.

Aniline, or **phenylamine,**  $N\left\{\begin{matrix}C_6H_5\\H\\H\end{matrix}\right.$.—This important amine is prepared by the action of nascent hydrogen on nitrobenzene ($C_6H_5NO_2$); this is generally carried out by exposing nitrobenzene to the action of iron filings and acetic acid.

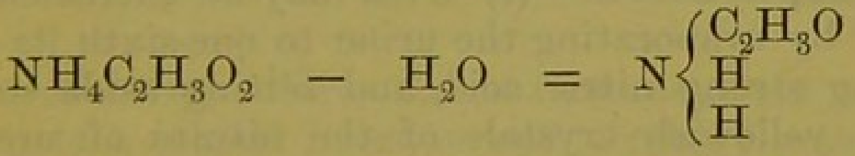


$$C_6H_5NO_2 + 3H_2 = N\left\{\begin{matrix}C_6H_5\\H\\H\end{matrix}\right. + 2H_2O$$

Nitrobenzene. Hydrogen. Aniline. Water.

Aniline, when first prepared, is a colourless liquid, gradually changing to a brownish colour by exposure to air. The aniline dyes are obtained by oxidising aniline with oxidising agents of different degrees of strength.

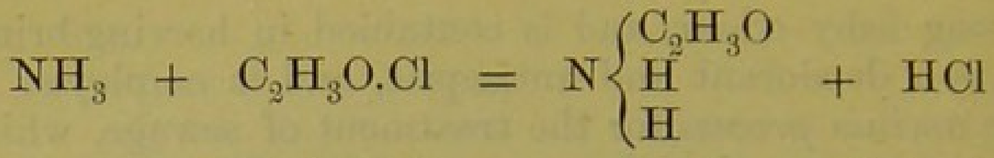
Amides.—These bodies may be derived from the ammonium salts of organic acids by the abstraction of water; thus :—



$$NH_4C_2H_3O_2 - H_2O = N\left\{\begin{matrix}C_2H_3O\\H\\H\end{matrix}\right.$$

Ammonium acetate. Water. Acetamide.

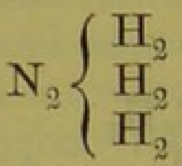
They are also obtained by the action of ammonia on acid chlorides; thus :—



$$NH_3 + C_2H_3O.Cl = N\begin{cases}C_2H_3O\\H\\H\end{cases} + HCl$$

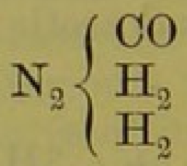
Ammonia. Acetyl chloride. Acetamide. Hydrochloric acid.

Urea, or **carbamide** (CH_4N_2O).—This important amide occurs as a normal constituent of urine, it being the chief form in which the waste or superfluous nitrogen of the system is eliminated. As an amide, it is derived from two molecules of ammonia by displacement of two out of the six atoms of hydrogen by the bivalent radical carbonyl (CO); thus :—



$$N_2\begin{cases}H_2\\H_2\\H_2\end{cases}$$

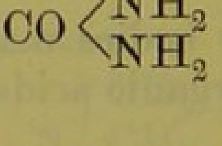
Ammonia (2 molecules)



$$N_2\begin{cases}CO\\H_2\\H_2\end{cases}$$

Urea or carbamide.

The formula and constitution of urea are more conveniently represented by showing the bivalent carbonyl radical (CO) in direct union with two equivalents of amidogen (NH_2); thus :—

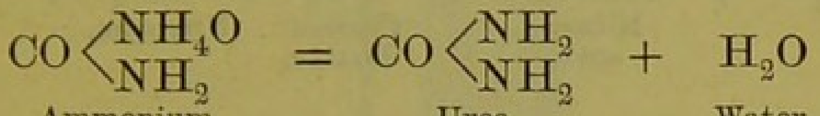


$$CO\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix}$$

Preparation.—(i) Urea may be extracted from urine by evaporating the urine to one-sixth its bulk, adding strong nitric acid, and setting aside to cool, when yellowish crystals of the nitrate of urea are deposited; these are collected on a filter, dissolved in boiling water, and barium carbonate added to form barium nitrate and free urea. The whole is then evaporated to dryness on a water-bath, and the dry residue exhausted with boiling alcohol, which dissolves out the urea, leaving the barium nitrate insoluble ; the filtered alcoholic solution, when evaporated, deposits crystals of urea.

(ii) Urea may be prepared from its isomer ammonium cyanate by simply evaporating a solution of that salt to dryness on a water-bath (*see* page 394).

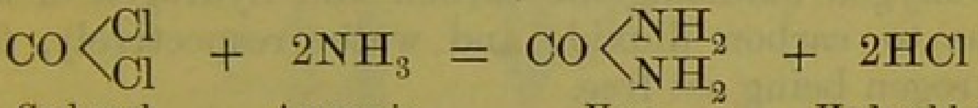
(iii) Urea is obtained by heating ammonium carbamate ($NH_4NH_2CO_2$), so as to deprive it of the elements of water.



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_4O}\\ \mathrm{NH_2}\end{matrix}\right. = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right. + \mathrm{H_2O}$$

Ammonium carbamate. Urea. Water.

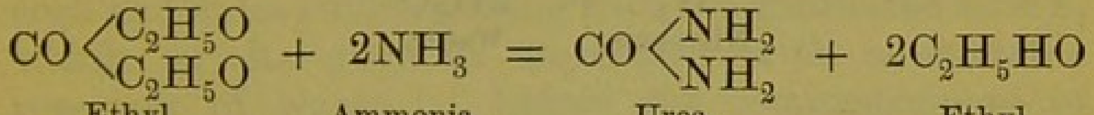
(iv) Urea can also be obtained by the action of ammonia on carbonyl chloride ($COCl_2$).



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix}\right. + 2\mathrm{NH_3} = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right. + 2\mathrm{HCl}$$

Carbonyl chloride. Ammonia. Urea. Hydrochloric acid.

(v) Urea is also produced by acting on ethyl carbonate ($(C_2H_5)_2CO_3$) with ammonia.



$$\mathrm{CO}\left\langle\begin{matrix}\mathrm{C_2H_5O}\\ \mathrm{C_2H_5O}\end{matrix}\right. + 2\mathrm{NH_3} = \mathrm{CO}\left\langle\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH_2}\end{matrix}\right. + 2\mathrm{C_2H_5HO}$$

Ethyl carbonate. Ammonia. Urea. Ethyl alcohol.

Properties.—Urea occurs in transparent colourless crystals, soluble in water and alcohol ; under the influence of heat it evolves ammonia, producing at first cyanuric acid, and finally cyanic acid (*see* p. 394). Urea is neutral to test-paper, but if urine is exposed to the air it soon becomes alkaline, from conversion of the urea into ammonium carbonate, which is formed by the union of urea with the elements of water.

$$\underset{\text{Urea.}}{CH_4N_2O} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Ammonium}\\ \text{carbonate.}}}{(NH_4)_2CO_3}$$

Urea is instantaneously decomposed by nitrous acid; carbon dioxide and nitrogen being evolved.

$$\underset{\text{Urea.}}{CH_4N_2O} + \underset{\substack{\text{Nitrous}\\ \text{acid.}}}{2HNO_2} = \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} + \underset{\text{Nitrogen.}}{2N_2} + \underset{\text{Water.}}{3H_2O}$$

It is also decomposed by the hypobromites and hypochlorites with evolution of carbon dioxide and nitrogen; thus sodium hypobromite ($NaBrO$) in presence of urea is reduced to sodium bromide ($NaBr$), its oxygen oxidising the carbon and hydrogen of the urea to carbon dioxide and water respectively, the nitrogen being set free.

$$\underset{\text{Urea.}}{CH_4N_2O} + \underset{\substack{\text{Sodium}\\ \text{hypobromite.}}}{3NaBrO} = \underset{\substack{\text{Sodium}\\ \text{bromide.}}}{3NaBr} + \underset{\substack{\text{Carbon}\\ \text{dioxide.}}}{CO_2} +$$

$$\underset{\text{Nitrogen.}}{N_2} + \underset{\text{Water.}}{2H_2O}$$

Estimation of urea in urine.—*Hypobromite process.* This process consists in decomposing the urea in a measured quantity of urine by means of sodium hypobromite, an excess of free caustic soda being present in the hypobromite solution, so that the carbon dioxide is absorbed by it, and only the nitrogen is evolved; the volume of nitrogen evolved is then measured. The apparatus (Fig. 36) consists of a bottle A, into which 25 c.c. of a strongly alkaline solution of sodium hypobromite are introduced; into this is carefully lowered a small test tube *b* containing 5 c.c. of the urine to be examined, care being taken not to spill any of the urine into the hypobromite solution. The bottle A is then connected by means of a perforated cork and india-rubber tubing with the graduated tube B, which in its turn is connected with a movable reservoir of water C; before the commencement of each experiment, the water in B is adjusted so as to be at the zero mark.

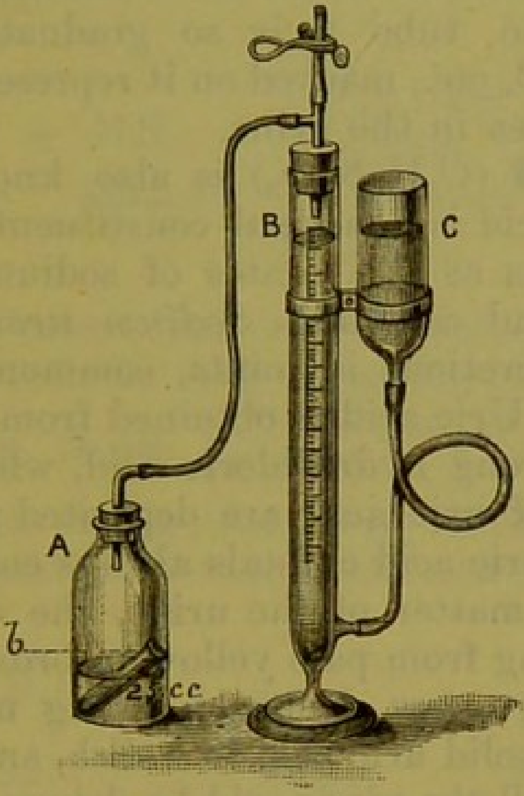


Fig. 36.—Apparatus for the Estimation of Urea in Urine by the Hypobromite Process.

The bottle A is then inclined to one side, so as to allow the urine contained in the small tube *b* to flow into the hypobromite solution, when the urea is immediately decomposed into carbon dioxide, nitrogen, and water; the carbon dioxide is instantly absorbed by the caustic soda present in the solution, and only the nitrogen escapes with effervescence. Whatever the amount of nitrogen evolved, there will be an equal volume of the air contained in the apparatus forced over into the measuring tube B, where the amount can be read off, and from its volume, the amount of urea contained in the 5 c.c. of urine can be determined. Employing 5 c.c. of urine in connection with each estimation, the tube B is so graduated that the numbers 1, 2, 3, etc., marked on it represent 1, 2, and 3 per cent. of urea in the urine.

Uric acid ($C_5H_4N_4O_3$) is also known as *lithic acid.* Uric acid is a normal constituent of urine, in which it exists as the urates of sodium, potassium, ammonium, and calcium. *Sodium urate* constitutes the gouty concretions in joints, commonly known as *chalk-stones.* Uric acid is obtained from urine by the addition of strong hydrochloric acid, when, on standing, crystals of uric acid are deposited ; prepared in this manner, uric acid crystals always contain some of the colouring matter of the urine, the colour of the crystals varying from pale yellow to brown.

Test.—If a few drops of strong nitric acid be added to some solid uric acid in a dish, and heat gently applied until all the nitric acid be driven off, a reddish coloured residue (alloxan) will be left. If, when the dish is cold, a few drops of solution of ammonia are added to this, a beautiful crimson purple colour is developed, due to the production of murexid by the action of the ammonia on alloxan. This test for uric acid is, on this account, known as the *murexid test.*

AMIDIC ACIDS.

These are derivatives of organic acids, in which hydrogen is displaced by amidogen (NH_2), or by an amidogen derivative. Several of the amidic acids are of physiological and pathological importance.

Glycocine, glycine, glycocoll, or **amidacetic acid** $\left\{\begin{matrix}CH_2(NH_2)\\COHO\end{matrix}\right.$.—This body consists of acetic acid $\left\{\begin{matrix}CH_3\\COHO\end{matrix}\right.$ from the molecule of which one atom of hydrogen has been displaced by amidogen. It may be obtained by the action of ammonia on chloracetic acid.

$$\underset{\text{Chloracetic acid.}}{\left\{\begin{matrix}CH_2.Cl\\COHO\end{matrix}\right.} + \underset{\text{Ammonia.}}{NH_3} = \underset{\text{Amidacetic acid.}}{\left\{\begin{matrix}CH_2(NH_2)\\COHO\end{matrix}\right.} + \underset{\text{Hydrochloric acid.}}{HCl}$$

Glycocine enters into the composition of hippuric acid and of glycocholic acid, one of the bile acids.

Hippuric acid $\left\{\begin{matrix}CH_2(NH.C_7H_5O)\\COHO\end{matrix}\right.$ is benzamidacetic acid, and is resolved by boiling with strong hydrochloric acid into benzoic acid and glycocine.

$$\underset{\text{Hippuric acid.}}{\left\{\begin{matrix}CH_2(NH.C_7H_5O)\\COHO\end{matrix}\right.} + \underset{\text{Water.}}{H_2O} = \underset{\text{Benzoic acid.}}{HC_7H_5O_2} + \underset{\text{Glycocine.}}{\left\{\begin{matrix}CH_2(NH_2)\\COHO\end{matrix}\right.}$$

Glycocholic acid, present as sodium glycocholate in bile, is a compound of glycocine and cholic acid; by boiling glycocholic acid with hydrochloric acid it splits up into glycocine and cholic acid.

Sarcosine or **methyl-glycocine** $\left\{\begin{matrix}CH_2(NH.CH_3)\\COHO\end{matrix}\right.$.—This body is glycocine, from which one atom of hydrogen of the amidogen has been displaced by methyl. Since glycocine is prepared by acting on chloracetic acid with ammonia, so sarcosine may be made by acting on chloracetic acid with methylamine, that is, with ammonia from which one atom of hydrogen has been displaced by methyl.

$$\underset{\text{Chloracetic acid.}}{\left\{\begin{array}{l}CH_2.Cl\\COHO\end{array}\right.} + \underset{\text{Methylamine.}}{NH_2.CH_3} = \underset{\text{Sarcosine.}}{\left\{\begin{array}{l}CH_2(NH.CH_3)\\COHO\end{array}\right.} + \underset{\text{Hydrochloric acid.}}{HCl}$$

Sarcosine is not met with in the animal body, but is a product of the decomposition of creatine.

Tyrosine ($C_9H_{11}NO_3$).—This body consists of amido-propionic acid from which one atom of hydrogen of the amidogen has been displaced by the radical oxyphenyl (C_6H_5O).

$$\underset{\text{Amido-propionic acid.}}{\left\{\begin{array}{l}C_2H_4(NH_2.)\\COHO\end{array}\right.} \qquad \underset{\text{Tyrosine.}}{\left\{\begin{array}{l}C_2H_4(NH.C_6H_5O)\\COHO\end{array}\right.}$$

Tyrosine is occasionally found in the urine together with leucine in connection with certain diseases of the liver.

Leucine or **amido-caproic acid** $\left\{\begin{array}{l}C_5H_{10}(NH_2)\\COHO\end{array}\right.$.—This body consists of caproic acid $\left\{\begin{array}{l}C_5H_{11}\\COHO\end{array}\right.$, from the molecule of which one atom of hydrogen has been displaced by amidogen. It is obtained by the action of ammonia on bromo-caproic acid.

$$\begin{cases} C_5H_{10}.Br \\ COHO \end{cases} + NH_3 = \begin{cases} C_5H_{10}(NH_2) \\ COHO \end{cases} + HBr$$

Bromo-caproic acid. Ammonia. Leucine. Hydrobromic acid.

Leucine is occasionally found in the urine in connection with certain diseases of the liver; it is one of the antecedents of urea.

Taurine or **amido-isethionic acid** $\begin{cases} C_2H_4(NH_2) \\ SO_2(HO) \end{cases}$ occurs in bile in union with cholic acid as taurocholic acid.

CHAPTER XI.

GLUCOSIDES—PROTEIDS.

Amygdalin—Cathartic Acid—Colocynthin—Digitalin—Jalapin—Myronic Acid—Salicin—Santonin—Proteids—Albumins—Globulins—Fibrin—Modified Albumins—Peptones—Albuminoids.

GLUCOSIDES.

THESE are certain organic substances (either nitrogenous or non-nitrogenous) derived from plants, and splitting up, when boiled with dilute sulphuric acid, or under the influence of a ferment, into glucose and some other substance or substances.

Amygdalin ($C_{20}H_{27}NO_{11}$).—This is a white crystalline substance present in bitter almond seeds, cherry laurel leaves, and the kernels of peaches, cherries, etc. Amygdalin is resolved, by boiling with dilute sulphuric acid, into essential oil of bitter almonds (benzoic aldehyde), hydrocyanic acid, and glucose. The same change is also produced by the action of a ferment named *emulsin* or *synaptase*, which is present together with amygdalin in bitter almond seeds, cherry laurel leaves, and the kernels of peaches, cherries, etc. This ferment is unable to act upon the amygdalin unless dissolved in water.

$$\underset{\text{Amygdalin.}}{C_{20}H_{27}NO_{11}} + \underset{\text{Water.}}{2H_2O} = \underset{\substack{\text{Essential}\\\text{oil of}\\\text{bitter almonds.}}}{C_7H_6O} + \underset{\substack{\text{Hydrocyanic}\\\text{acid.}}}{HCN} + \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Cathartic acid ($C_{180}H_{192}N_4SO_{82}$).—This very complex glucoside exists in senna leaves, of which it is the active purgative principle; it is decomposed by boiling with dilute sulphuric acid into glucose and a substance named cathartogenic acid.

Colocynthin ($C_{56}H_{84}O_{23}$).—This substance is the active purgative principle of colocynth pulp; it is decomposed by boiling with dilute sulphuric acid into glucose and a resinous substance.

Digitalin ($C_{27}H_{45}O_{15}$).—This glucoside is the active principle of digitalis leaves; by boiling with dilute sulphuric acid, it is decomposed into glucose, and a substance named digitaliretin.

Jalapin ($C_{31}H_{50}O_{16}$).—This substance is the active purgative principle of jalap root; it is decomposed by boiling with dilute sulphuric acid, into glucose and a substance named jalapinol.

Myronic acid ($C_{10}H_{19}NS_2O_{10}$).—This acid exists as a potassium salt in black mustard seeds; the salt is decomposed by boiling with dilute sulphuric acid, and also by the action of a ferment *myrosin* likewise contained in black mustard seeds, into volatile oil of mustard (allyl sulphocyanate), glucose, and potassium acid sulphate.

$$\underset{\substack{\text{Potassium}\\\text{myronate.}}}{KC_{10}H_{18}NS_2O_{10}} = \underset{\substack{\text{Allyl}\\\text{sulphocyanate.}}}{C_3H_5.CNS} + \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\substack{\text{Potassium}\\\text{acid sulphate.}}}{KHSO_4}$$

Salicin ($C_{13}H_{18}O_7$).—This is a crystalline bitter principle contained in the leaves and bark of the willow; it is resolved by boiling with dilute sulphuric acid into glucose and a substance named saligenin.

$$\underset{\text{Salicin.}}{C_{13}H_{18}O_7} + \underset{\text{Water.}}{H_2O} = \underset{\text{Glucose.}}{C_6H_{12}O_6} + \underset{\text{Saligenin.}}{C_7H_8O_2}$$

Santonin ($C_{15}H_{18}O_3$).—This glucoside is the active principle of santonica; it is resolved by boiling with dilute sulphuric acid into glucose and a substance named santoniretin.

PROTEIDS.

These substances are present in blood, muscle, and the various organs and tissues of man and animals; they are also present in vegetables and plants. Proteids contain from 15 to 16 per cent. of nitrogen, and small quantities of sulphur and phosphorus.

1. ALBUMINS.—Proteids soluble in pure water.

Serum albumin.—This is contained in blood serum; it is soluble in water, and the solution is coagulated by heat; it is precipitated by strong nitric acid, but is soluble in a large excess of the acid. It is not precipitated by sodium chloride, by acetic acid, or by ether.

Egg albumin.—This differs from the above in that it is precipitated by ether, and that it is insoluble in excess of strong nitric acid.

Plant albumin.—This occurs in most vegetable juices; it is coagulated by heat, and bears a close resemblance to egg albumin.

2. GLOBULINS.—Proteids insoluble in pure water, but soluble in dilute saline solutions, such as a dilute solution of sodium chloride.

Globulin.—This body is a constituent of the aqueous and vitreous humours of the eye. It is precipitated from its dilute solutions by passing a stream of carbon dioxide through them, also by the addition of alcohol; its solution is coagulated by heat.

Paraglobulin.—This body is a constituent of blood serum, from which it may be precipitated by complete saturation of the serum with magnesium sulphate. It is precipitated from dilute saline solutions by the addition of a small quantity of sodium chloride; on the addition of more sodium chloride the precipitate redissolves, to be again precipitated when the amount of sodium chloride added reaches about 20 per cent. It can also be precipitated from diluted blood serum by passing a stream of carbon dioxide through the latter. Its solution is coagulated by heat.

Fibrinogen.—This body is a constituent of blood.

Hæmoglobin.—This body is contained in red blood corpuscles, of which it constitutes the colouring matter.

Myosin.—This body is contained in muscle.

3. FIBRIN.—The proteid substance to which the clotting of blood is due; it is insoluble in water.

4. MODIFIED OR DERIVED ALBUMINS. — Proteids insoluble in water and dilute neutral saline solution, but soluble in dilute acids and alkalies.

Acid albumin or **syntonin.**—This body is obtained by gradually heating a weak solution of albumin with a small quantity of hydrochloric acid.

Alkali albumin or **casein.**—This body is obtained by gradually heating a weak solution of albumin with a small quantity of a caustic alkali. It is one of the constituents of milk.

5. PEPTONES.—Proteids soluble in water, not coagulated by heat, and very diffusible. They are obtained by the action of the peptic and pancreatic ferments on albumins, etc.

6. ALBUMINOIDS OR ALLIED ALBUMINS.— Proteids occurring in epithelial and connective tissues.

Mucin.—This body is insoluble in cold water, but soluble in alkaline solutions, from which it is precipitated by the addition of acetic acid; it is not coagulated by heat.

Gelatin.—This body is insoluble in cold, but soluble in hot water, the solution setting to a jelly on cooling; it is not precipitated by acetic acid.

Chondrin.—This body is soluble in hot water, the solution setting to a jelly on cooling; it is precipitated by acetic acid.

CHAPTER XII.

RARER ORGANIC COMPOUNDS.

Antifebrine—Antipyrine—Caffeine or Theine—Chrysophanic Acid—Hypnone—Ichthyol—Iodol—Iodo-Salicylic Acids—Kairine—Naphthalene—Naphthol—Saccharine—Salol—Sulphonal—Urethane.

Antifebrine ($NH.C_2H_3O.C_6H_5$). —This substance is also known as *acetanilide* and *phenyl-acetamide*. It consists of acetamide ($NH_2.C_2H_3O$), from the molecule of which one atom of hydrogen has been displaced by the phenyl radical (C_6H_5). It is obtained by the action of acetyl chloride on aniline.

$$\underset{\text{Aniline.}}{NH_2.C_6H_5} + \underset{\substack{\text{Acetyl}\\\text{chloride.}}}{C_2H_3OCl} = \underset{\text{Antifebrine.}}{NH.C_2H_3O.C_6H_5} + \underset{\substack{\text{Hydro-}\\\text{chloric}\\\text{acid.}}}{HCl}$$

Antifebrine occurs in small, white, odourless crystals, almost insoluble in cold water, but freely soluble in alcohol; it is an antipyretic.

Antipyrine.—This is a rather complex benzene derivative, prepared from aniline, aceto-acetic ether, and methyl iodide. It is a white crystalline powder, readily soluble in water; it is an antipyretic.

Caffeine or **theine** ($C_8H_{10}N_4O_2$).—This substance is an alkaloid occurring in tea leaves and coffee seeds. It is used in medicine in the form of the citrate of caffeine, a white powder readily soluble in water.

Chrysophanic acid.—This substance is also known as *pure chrysarobin*; it occurs in araroba or goa powder, and in rhubarb root. It crystallises in bright golden-yellow needles.

Hypnone.—This body is phenyl-methyl-ketone; that is, it consists of CO in union with the phenyl and methyl radicals; thus:—

$$C_6H_5—CO—CH_3$$

Hypnone.

It is obtained by distillation from a mixture of benzoate of calcium and acetate of calcium. At ordinary temperatures it is a colourless liquid, but below 14° C. it crystallises in white needles. It is insoluble in water, but soluble in alcohol.

Ichthyol.—This substance is an ammonium salt of sulpho-ichthyolic acid. It is obtained by treating the products of distillation of a bituminous quartz with sulphuric acid, and neutralising the sulpho-ichthyolic acid so produced with ammonia. The strata from which the bituminous quartz is obtained contain the remains of fishes and other animals, and the deposit probably consists of their decomposed and altered remains. No definite chemical composition can be assigned to ichthyol.

Iodol.—This substance is tetra-iodo-pyrrol (C_4HI_4N); that is, it is pyrrol (C_4H_5N), from the molecule of which four atoms of hydrogen have been displaced by four atoms of iodine.

It is obtained by the action of iodine on pyrrol, which is an oily liquid contained in bone-oil, produced by the dry or destructive distillation of bones.

Iodol is a brownish-white powder, insoluble in water, but soluble in glycerine, alcohol, ether, and chloroform. It is used as an antiseptic.

Iodo-salicylic acid and di-iodo-salicylic acid.—These bodies consist of salicylic acid, from which hydrogen has been displaced by iodine.

Salicylic acid	...	$C_7H_6O_3$
Iodo-salicylic acid	...	$C_7H_5IO_3$
Di-iodo-salicylic acid		$C_7H_4I_2O_3$

Kairine.—This substance is the hydrochlorate of a complex benzene derivative. It is a white crystalline powder, freely soluble in water, and possessing a very bitter and nauseous taste.

Naphthalene ($C_{10}H_8$).—This is a hydrocarbon, obtained as a bye-product in the preparation of coal gas; it occurs in white, shining, crystalline plates, insoluble in water, but soluble in alcohol and ether. It is an antiseptic.

Naphthol ($C_{10}H_7.HO$).—Two isomeric modifications, α-naphthol and β-naphthol, exist; they are derivatives of naphthalene, from the molecule of which one atom of hydrogen is displaced by hydroxyl. Naphthol occurs in white shining crystals, sparingly soluble in water, but soluble in alcohol and ether; it is a powerful antiseptic.

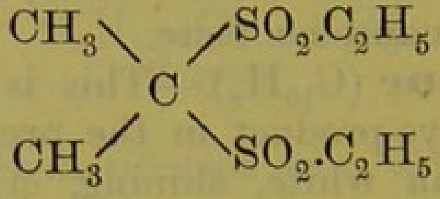
Saccharine.—This substance is a benzene derivative, obtained from toluene. It occurs as a white, minutely crystalline powder, with an intensely sweet taste; it is slightly soluble in water, and much more soluble in alcohol.

Salol.—This substance is salicylic phenol, that is, phenol (C_6H_5HO), from the molecule of which one atom of hydrogen is displaced by the salicylic radical ($C_7H_5O_2$); thus:—

$$\underset{\text{Salol.}}{C_6H_4.(C_7H_5O_2)HO}$$

It is a white crystalline substance, insoluble in water, but soluble in alcohol; it possesses antiseptic and antipyretic properties.

Sulphonal.—This body is a derivative of methane (CH_4), from the molecule of which two atoms of hydrogen are displaced by two equivalents of methyl (CH_3), and the other two atoms by two equivalents of the ethyl sulphonic acid radical ($C_2H_5.SO_2$); the constitution of sulphonal is therefore diethylsulphondimethyl methane, thus :—



Sulphonal.

It is produced by the oxidation of a mixture of ethyl-mercaptan and acetone. It occurs in white tabular crystals, tasteless and odourless, slightly soluble in water, and freely soluble in alcohol and ether. It is a hypnotic.

Urethane ($C_2H_5NH_2CO_2$).—This substance is ethyl carbamate; it occurs in colourless crystals, readily soluble in water. It is a hypnotic.

Part V.

CHEMICAL PROBLEMS.

In this section of the book illustrations will be given of the modes of working out the various chemical problems, which for the sake of convenience will be arranged in three groups, viz. :-- *Group I.* Chemical problems involving weight calculations only. *Group II.* Chemical problems involving both weight and volume calculations. *Group III.* Chemical problems involving volume calculations only.

GROUP I.—CHEMICAL PROBLEMS INVOLVING WEIGHT CALCULATIONS ONLY.

1. How many pounds of oxygen can be obtained from 100 lbs. of potassium chlorate?

The equation representing the effect of heat upon potassium chlorate shows that all the oxygen is evolved.

$$KClO_3 = KCl + O_3$$

The molecular weight of potassium chlorate is next calculated.

$$\begin{array}{lr} K & = 39 \\ Cl & = 35{\cdot}5 \\ O_3 = 16 \times 3 & = 48 \\ \hline & 122{\cdot}5 \end{array}$$

From this it is evident that 122·5 parts by weight of potassium chlorate contain 48 parts by weight of oxygen, and since all the oxygen is evolved by heat, therefore 122.5 parts by weight of potassium chlorate will evolve 48 parts by weight of oxygen, and therefore 122·5 lbs. of potassium chlorate will evolve 48 lbs. of oxygen. If 48 lbs. of oxygen can be obtained from 122·5 lbs. of potassium chlorate, how many lbs. of oxygen can be obtained from 100 lbs. of potassium chlorate?

$$122{\cdot}5 : 100 :: 48 : x.$$

$x = 39{\cdot}18$, the number of lbs. of oxygen that can be obtained from 100 lbs. of potassium chlorate.

2. How many grammes of carbon dioxide are evolved by heating 120 grammes of calcium carbonate?

The equation representing the effect of heat upon calcium carbonate shows that one molecule of calcium carbonate evolves one molecule of carbon dioxide.

$$CaCO_3 = CaO + CO_2$$

The molecular weights of these two bodies are next calculated.

$$\begin{array}{lll} Ca & & = 40 \\ C & & = 12 \\ O_3 & = 16 \times 3 & = 48 \\ \hline & & 100 \end{array} \qquad \begin{array}{lll} C & & = 12 \\ O_2 & = 16 \times 2 & = 32 \\ \hline & & 44 \end{array}$$

From these weights it is evident that 100 parts by weight of calcium carbonate evolve 44 parts by weight of carbon dioxide, and therefore 44 grammes of carbon dioxide are obtainable from 100 grammes of calcium carbonate. Therefore, how many grammes of carbon dioxide will be evolved from 120 grammes of calcium carbonate?

$$100 : 120 :: 44 : x$$

$x = 52 \cdot 80$, the number of grammes of carbon dioxide evolved by heating 120 grammes of calcium carbonate.

3. How many grains of sulphur dioxide are evolved by the action of 150 grains of sulphuric acid on copper?

The equation representing the action of sulphuric acid on copper shows that one molecule of sulphur dioxide is evolved from two molecules of the acid.

$$Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$$

Twice the molecular weight of sulphuric acid, and the molecular weight of sulphur dioxide are next calculated.

$$\begin{array}{llllllll} H_2 & = & 1 \times 2 & = & 2 \qquad & S & & = 32 \\ S & & & = & 32 \qquad & O_2 & = 16 \times 2 & = 32 \\ O_4 & = & 16 \times 4 & = & 64 \qquad & & & \overline{64} \\ & & & & \overline{98} & & & \end{array}$$

$$\therefore 2H_2SO_4 = 98 \times 2 = 196$$

From these weights it is evident that 64 parts by weight of sulphur dioxide are evolved from 196 parts by weight of sulphuric acid, by the action of that acid on copper, and therefore 64 grains of sulphur dioxide are evolved from 196 grains of sulphuric acid. Therefore, how many grains of sulphur dioxide will be evolved from 150 grains of sulphuric acid, under similar conditions?

$$196 : 150 :: 64 : x$$

$x = 48{\cdot}97$, the number of grains of sulphur dioxide evolved by the action of 150 grains of sulphuric acid on copper.

4. How many pounds of sodium carbonate are required to precipitate 100 lbs. of calcium chloride ?

The equation representing the action of sodium carbonate on calcium chloride shows that one molecule of sodium carbonate is required to precipitate one molecule of calcium chloride.

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$

The molecular weights of calcium chloride and sodium carbonate are next calculated.

$$\begin{array}{lr} Ca & = 40 \\ Cl_2 = 35{\cdot}5 \times 2 & = 71 \\ \hline & 111 \end{array} \qquad \begin{array}{lr} Na_2 = 23 \times 2 & = 46 \\ C & = 12 \\ O_3 = 16 \times 3 & = 48 \\ \hline & 106 \end{array}$$

From these weights it is evident that 106 parts by weight of sodium carbonate are required to precipitate 111 parts by weight of calcium chloride, and therefore 106 lbs. of sodium carbonate are required to precipitate 111 lbs. of calcium chloride. Therefore, how many pounds of sodium carbonate will be required to precipitate 100 lbs. of calcium chloride ?

$$111 : 100 :: 106 : x$$

$x = 95{\cdot}49$, the number of pounds of sodium carbonate required to precipitate 100 lbs. of calcium chloride.

5. How many grammes of nitric acid are required to convert 150 grammes of copper into copper nitrate ?

The equation representing the action of nitric acid on copper shows that eight molecules of nitric acid are required to convert 3 atoms of copper into copper nitrate.

$$Cu_3 + 8HNO_3 = 3Cu(NO_3)_2 + N_2O_2 + 4H_2O$$

Eight times the molecular weight of nitric acid, and three times the atomic weight of copper are next calculated.

$$\begin{array}{llll} H & & = & 1 \\ N & & = & 14 \\ O_3 & = 16 \times 3 & = & \underline{48} \\ & & & 63 \end{array} \qquad Cu_3 = 63{\cdot}5 \times 3 = 190{\cdot}5$$

$$\therefore 8HNO_3 = 63 \times 8 = 504$$

From these weights it is evident that 504 parts by weight of nitric acid are required to convert 190·5 parts by weight of copper into copper nitrate, and therefore that 504 grammes of nitric acid are required to act upon 190·5 grammes of copper. Therefore, how many grammes of nitric acid will be required to act upon 150 grammes of copper ?

$$190{\cdot}5 : 150 :: 504 : x$$

$x = 396{\cdot}85$, the number of grammes of nitric acid required to convert 150 grammes of copper into copper nitrate.

6. How many kilogrammes of mercuric

iodide can be prepared from 10 kilogrammes of mercuric chloride?

The equation representing the preparation of mercuric iodide from mercuric chloride shows that one molecule of mercuric iodide is prepared from one molecule of mercuric chloride.

$$HgCl_2 + 2KI = HgI_2 + 2KCl$$

The molecular weights of mercuric chloride and mercuric iodide are next calculated.

$$\begin{array}{lr} Hg & = 200 \\ Cl_2 = 35{\cdot}5 \times 2 & = \underline{\ 71} \\ & 271 \end{array} \qquad \begin{array}{lr} Hg & 200 \\ I_2 = 127 \times 2 & = \underline{254} \\ & 454 \end{array}$$

From these weights it is evident that 454 parts by weight of mercuric iodide are prepared from 271 parts by weight of mercuric chloride, and therefore that 454 kilogrammes of mercuric iodide would be prepared from 271 kilogrammes of mercuric chloride. Therefore, how many kilogrammes of mercuric iodide can be prepared from 10 kilogrammes of mercuric chloride?

$$271 : 10 :: 454 : x$$

$x = 16{\cdot}75$, the number of kilogrammes of mercuric iodide that can be prepared from 10 kilogrammes of mercuric chloride.

7. Calculate the percentage of sulphur in sulphuric acid.

The molecular weight of sulphuric acid is first calculated.

$H_2 = 1 \times 2 = 2$
$S = 32$
$O_4 = 16 \times 4 = 64$
$\overline{98}$

From this molecular weight it is evident that 98 parts by weight of sulphuric acid contain 32 parts by weight of sulphur. Therefore, what amount of sulphur will 100 parts of sulphuric acid contain?

$$98 : 100 :: 32 : x$$

$x = 32{\cdot}65$, the percentage of sulphur in sulphuric acid.

8. Calculate the percentage of iron in ferric oxide.

The molecular weight of ferric oxide is first calculated.

$Fe_2 = 56 \times 2 = 112$
$O_3 = 16 \times 3 = 48$
$\overline{160}$

From this molecular weight it is evident that 160 parts by weight of ferric oxide contain 112 parts by weight of iron. Therefore, what amount of iron will 100 parts of ferric oxide contain?

$$160 : 100 :: 112 : x$$

$x = 70{\cdot}00$, the percentage of iron in ferric oxide.

9. Calculate the percentage of carbon in starch.

The molecular weight of starch is first calculated.

$C_6 = 12 \times 6 = 72$
$H_{10} = 1 \times 10 = 10$
$O_5 = 16 \times 5 = 80$
$\overline{162}$

From this molecular weight it is evident that 162 parts by weight of starch contain 72 parts by weight of carbon. Therefore, what amount of carbon will 100 parts of starch contain?

$$162 : 100 :: 72 : x$$

$x = 44{\cdot}44$, the percentage of carbon in starch.

10. Calculate the percentage of nitrogen in urea.

The molecular weight of urea is first calculated.

$$\begin{array}{llrcrcr}
C & & & & & = & 12 \\
H_4 & = & 1 & \times & 4 & = & 4 \\
N_2 & = & 14 & \times & 2 & = & 28 \\
O & & & & & = & 16 \\
\hline
 & & & & & & 60
\end{array}$$

From this molecular weight it is evident that 60 parts by weight of urea contain 28 parts by weight of nitrogen. Therefore, what amount of nitrogen will be contained in 100 parts of urea?

$$60 : 100 :: 28 : x$$

$x = 46{\cdot}66$, the percentage of nitrogen in urea.

11. Calculate the percentage of chlorine in chloroform.

The molecular weight of chloroform is first calculated.

$$\begin{array}{llrcrcr}
C & & & & & = & 12 \\
H & & & & & = & 1 \\
Cl_3 & = & 35{\cdot}5 & \times & 3 & = & 106{\cdot}5 \\
\hline
 & & & & & & 119{\cdot}5
\end{array}$$

From this molecular weight it is evident that 119·5 parts by weight of chloroform contain 106·5 parts by weight of chlorine. Therefore, what amount of chlorine will be contained in 100 parts of chloroform?

$$119{\cdot}5 : 100 :: 106{\cdot}5 : x$$

$x = 89{\cdot}12$, the percentage of chlorine in chloroform.

GROUP II.—CHEMICAL PROBLEMS INVOLVING BOTH WEIGHT AND VOLUME CALCULATIONS.

For the conversion of the weights of gases into volumes, it is necessary to know either the weight of a litre of hydrogen, or the volume occupied by a gramme of hydrogen; the specific gravity of any given gas being known, it then becomes an easy matter to calculate the volume occupied by any given weight of it.

The *crith* is the weight of a litre of hydrogen at 0° C. and 760 mm. barometric pressure, and is 0·0896 of a gramme. The weight of a litre of oxygen, the specific gravity of which is 16, would be 0·0896 gramme × 16; the weight of a litre of carbon dioxide, the specific gravity of which is 22, would be 0·0896 gramme × 22; in fact, the weight of a litre of any gas is obtained by multiplying the crith by the specific gravity of the gas. The conversion of the weights of gases into volumes is, however, facilitated by bearing in mind that 1 gramme of hydrogen occupies 11·2 litres (at 0° C. and 760 mm. barometric pressure). Now since oxygen is 16 times heavier than hydrogen, 11·2 litres of oxygen must weigh 16 times as much as the same volume of hydrogen, that is, 16 grammes; again, since carbon dioxide is 22 times heavier than hydrogen, 11·2 litres of carbon dioxide must weigh 22 times as much as the same volume of hydrogen, that is, 22 grammes. In fact, the weight of 11·2 litres of any gas at 0° C. and 760 mm. barometric pressure is obtained by expressing its specific gravity as grammes.

1. How many litres of hydrogen will be evolved by the action of sulphuric acid on 10 grammes of zinc?

The equation representing the action of sulphuric acid on zinc shows that 2 atoms of hydrogen are liberated by the action of 1 atom of zinc on sulphuric acid.

$$Zn + H_2SO_4 = ZnSO_4 + H_2$$

The respective weights of zinc and hydrogen are—

$$Zn = 65 \qquad H_2 = 1 \times 2 = 2$$

Therefore 2 parts by weight of hydrogen are evolved by 65 parts by weight of zinc from the sulphuric acid, and therefore 2 grammes of hydrogen are evolved by 65 grammes of zinc. What weight of hydrogen then will be evolved by 10 grammes of zinc?

$$65 : 10 :: 2 : x$$

$x = 0·307$ gramme, the weight of hydrogen evolved by 10 grammes of zinc.

This weight of hydrogen must now be converted into litres. One gramme of hydrogen occupies 11·2 litres, therefore how many litres will 0·307 gramme of hydrogen occupy?

$$1 : ·307 :: 11·2 : x$$

$x = 3·43$ litres, the number of litres of hydrogen evolved by the action of sulphuric acid on 10 grammes of zinc.

2. How many litres of oxygen are evolved by heating 50 grammes of potassium chlorate?

The equation representing the decomposition of potassium chlorate by heat shows that 1 molecule of potassium chlorate yields 3 atoms of oxygen.

$$KClO_3 = KCl + O_3$$

The molecular weight of potassium chlorate and three times the atomic weight of oxygen are next calculated.

$$\begin{array}{lllll} K & & = 39 & & \\ Cl & & = 35{\cdot}5 & & O_3 = 16 \times 3 = 48 \\ O_3 & = 16 \times 3 & = \underline{48} & & \\ & & \ 122{\cdot}5 & & \end{array}$$

Therefore 48 parts by weight of oxygen are evolved from 122·5 parts by weight of potassium chlorate, and therefore 48 grammes of oxygen are evolved from 122·5 grammes of potassium chlorate. What weight of oxygen then will be evolved from 50 grammes of potassium chlorate?

$$122{\cdot}5 : 50 :: 48 : x$$

$x = 19{\cdot}59$ grammes, the weight of oxygen evolved from 50 grammes of potassium chlorate.

This weight of oxygen must now be converted into litres. 1 gramme of hydrogen occupies 11·2 litres, and as the specific gravity of oxygen is 16, therefore 16 grammes of oxygen occupy 11·2 litres. Therefore, how many litres will 19·59 grammes of oxygen occupy?

$$16 : 19{\cdot}59 :: 11{\cdot}2 : x$$

$x = 13{\cdot}71$ litres, the number of litres of oxygen evolved by heating 50 grammes of potassium chlorate.

3. How many litres of sulphur dioxide are produced by burning 5 grammes of sulphur?

The molecular weight of sulphur dioxide

$$\begin{array}{lcl} S & & = 32 \\ O_2 = 16 \times 2 & & = 32 \\ \hline & & \ 64 \end{array}$$

shows that sulphur produces twice its weight of sulphur dioxide, and, therefore, 5 grammes of sulphur, when burnt, would produce 10 grammes of sulphur dioxide.

This weight of sulphur dioxide must next be converted into litres. 1 gramme of hydrogen occupies 11·2 litres, and as the specific gravity of sulphur dioxide is 32 (half its molecular weight), therefore 32 grammes of sulphur dioxide occupy 11·2 litres. Therefore, how many litres will 10 grammes of sulphur dioxide occupy?

$$32 : 10 :: 11{\cdot}2 : x$$

$x = 3{\cdot}50$ litres, the number of litres of sulphur dioxide produced by burning 5 grammes of sulphur.

4. What volume of nitrogen dioxide will be produced by the action of nitric acid on 20 grammes of copper?

The equation representing the production of nitrogen dioxide by the action of nitric acid on copper shows that one molecule of nitrogen dioxide is set free by 3 atoms of copper.

$$Cu_3 + 8HNO_3 = 3Cu(NO_3)_2 + N_2O_2 + 4H_2O$$

Three times the atomic weight of copper and the molecular weight of nitrogen dioxide are next calculated.

$$Cu_3 = 63{\cdot}5 \times 3 = 190\ 5 \qquad \begin{array}{l} N_2 = 14 \times 2 = 28 \\ O_2 = 16 \times 2 = 32 \\ \hline \qquad\qquad\qquad\ \ 60 \end{array}$$

From these weights it is evident that 60 parts by weight of nitrogen dioxide are produced by the action of nitric acid on 190·5 parts by weight of copper; and, therefore, 60 grammes of nitrogen dioxide are evolved by means of 190·5 grammes of copper. Therefore, how many grammes of nitrogen dioxide will be evolved by means of 20 grammes of copper?

$$190{\cdot}5 : 20 :: 60 : x$$

$x = 6{\cdot}29$ grammes, the weight of nitrogen dioxide produced by the action of nitric acid on 20 grammes of copper.

This weight of nitrogen dioxide must now be converted into litres. 1 gramme of hydrogen occupies 11·2 litres, and as the specific gravity of nitrogen dioxide is 30, therefore 30 grammes of nitrogen dioxide occupy 11·2 litres. Therefore, how many litres will 6·29 grammes of nitrogen dioxide occupy?

$$30 : 6{\cdot}29 :: 11{\cdot}2 : x$$

$x = 2{\cdot}34$ litres, the volume of nitrogen dioxide produced by the action of nitric acid on 20 grammes of copper.

5. What volume of methane (marsh gas) will be produced by heating 30 grammes of sodium acetate with caustic soda ?

The equation representing the production of methane from sodium acetate and caustic soda shows that 1 molecule of sodium acetate takes part in the production of 1 molecule of methane.

$$NaC_2H_3O_2 + NaHO = Na_2CO_3 + CH_4$$

The molecular weights of sodium acetate and methane are next calculated.

$$\begin{array}{lr} Na & = 23 \\ C_2 = 12 \times 2 & = 24 \\ H_3 = 1 \times 3 & = 3 \\ O_2 = 16 \times 2 & = 32 \\ & — \\ & 82 \end{array} \qquad \begin{array}{lr} C & = 12 \\ H_4 = 1 \times 4 & = 4 \\ & — \\ & 16 \end{array}$$

From these weights it is evident that 16 parts by weight of methane are obtainable from 82 parts by weight of sodium acetate, and, therefore, 16 grammes of methane are obtainable from 82 grammes of sodium acetate. Therefore, how many grammes of methane will be obtained from 30 grammes of sodium acetate ?

$$82 : 30 :: 16 : x$$

$x = 5·85$ grammes, the weight of methane produced by heating 30 grammes of sodium acetate with caustic soda.

This weight of methane must now be converted into litres. 1 gramme of hydrogen occupies 11·2 litres, and as the specific gravity of methane is 8, therefore 8 grammes of methane occupy 11·2 litres. Therefore, how many litres will 5·85 grammes of methane occupy ?

$$8 : 5{\cdot}85 :: 11{\cdot}2 : x$$

$x = 8{\cdot}19$ litres, the volume of methane produced by heating 30 grammes of sodium acetate with caustic soda.

6. What volume of oxygen is required to burn 10 grammes of carbon to carbon dioxide?

The formula of carbon dioxide (CO_2) shows that 1 atom of carbon requires 2 atoms of oxygen to form carbon dioxide. The atomic weight of carbon and twice the atomic weight of oxygen are next taken.

$$C = 12 \qquad O_2 = 16 \times 2 = 32$$

From these weights it is evident that 32 parts by weight of oxygen are required for the combustion of 12 parts by weight of carbon, and, therefore, 32 grammes of oxygen are required by 12 grammes of carbon. Therefore, how many grammes of oxygen are required by 10 grammes of carbon?

$$12 : 10 :: 32 : x$$

$x = 26{\cdot}66$ grammes, the weight of oxygen required to burn 10 grammes of carbon to carbon dioxide.

This weight of oxygen must now be converted into litres. One gramme of hydrogen occupies 11·2 litres, and as the specific gravity of oxygen is 16, therefore 16 grammes of oxygen occupy 11·2 litres. Therefore, how many litres will 26·66 grammes of oxygen occupy?

$$16 : 26{\cdot}66 :: 11{\cdot}2 : x$$

$x = 18{\cdot}66$ litres, the volume of oxygen required to burn 10 grammes of carbon to carbon dioxide.

7. How many grammes of calcium carbonate will be precipitated by passing 20 litres of carbon dioxide through lime-water?

The equation representing the action of carbon dioxide on lime-water shows that 1 molecule of carbon dioxide is employed in the preparation of 1 molecule of calcium carbonate.

$$Ca(HO)_2 \quad + \quad CO_2 \quad = \quad CaCO_3 \quad + \quad H_2O$$

The molecular weights of carbon dioxide and calcium carbonate are next calculated.

$$\begin{array}{llr} C & & = 12 \\ O_2 & = 16 \times 2 & = 32 \\ \hline & & 44 \end{array} \qquad \begin{array}{llr} Ca & & = 40 \\ C & & = 12 \\ O_3 & = 16 \times 3 & = 48 \\ \hline & & 100 \end{array}$$

From these weights it is evident that 44 parts by weight of carbon dioxide precipitate 100 parts by weight of calcium carbonate, and therefore 44 grammes of carbon dioxide precipitate 100 grammes of calcium carbonate.

One gramme of hydrogen occupies 11·2 litres, and as the specific gravity of carbon dioxide is 22, therefore 22 grammes of carbon dioxide occupy 11·2 litres, and therefore 22 × 2, or 44 grammes of carbon dioxide will occupy 11·2 × 2 or 22·4 litres.

The previous calculation shows that 100 grammes of calcium carbonate are precipitated by 44 grammes of carbon dioxide, and as the latter occupy 22·4 litres, therefore 100 grammes of calcium carbonate are precipitated by 22·4 litres of carbon dioxide. Therefore, how many grammes of calcium carbonate will be precipitated by 20 litres of carbon dioxide?

$$22{\cdot}4 : 20 :: 100 : x$$

$x = 89{\cdot}28$ grammes, the weight of calcium carbonate precipitated by passing 20 litres of carbon dioxide through lime-water.

8. How many grammes of sodium chloride can be prepared from 50 litres of hydrochloric acid gas?

The formulæ of sodium chloride ($NaCl$) and hydrochloric acid gas (HCl) show that 1 molecule of the former can be prepared from 1 molecule of the latter. Their molecular weights are next calculated.

$$\begin{array}{lcr} Na & = & 23 \\ Cl & = & 35{\cdot}5 \\ \hline & & 58{\cdot}5 \end{array} \qquad\qquad \begin{array}{lcr} H & = & 1 \\ Cl & = & 35{\cdot}5 \\ \hline & & 36{\cdot}5 \end{array}$$

From these weights it is evident that 58·5 parts by weight of sodium chloride can be prepared from 36·5 parts by weight of hydrochloric acid gas, and therefore 58·5 grammes of sodium chloride can be prepared from 36·5 grammes of hydrochloric acid gas.

One gramme of hydrogen occupies 11·2 litres, and as the specific gravity of hydrochloric acid gas is 18·25, therefore 18·25 grammes of hydrochloric acid gas occupy 11·2 litres, and therefore $18{\cdot}25 \times 2$ or 36·5 grammes of hydrochloric acid gas will occupy $11{\cdot}2 \times 2$ or 22·4 litres.

The previous calculation shows that 58·5 grammes of sodium chloride can be prepared from 36·5 grammes of hydrochloric acid gas, and as the latter occupy 22·4 litres, therefore 58·5 grammes of sodium chloride can be prepared from 22·4 litres of hydrochloric acid gas. Therefore, how many grammes of sodium chloride can be prepared from 50 litres of hydrochloric acid gas?

$$22{\cdot}4 : 50 :: 58{\cdot}5 : x$$

$x = 130{\cdot}58$ grammes, the weight of sodium chloride that can be prepared from 50 litres of hydrochloric acid gas.

9. How many grammes of ammonium chloride are required to produce 30 litres of ammonia gas?

The formulæ of ammonium chloride (NH_4Cl) and ammonia gas (NH_3) show that 1 molecule of the former yields 1 molecule of the latter. Their molecular weights are next calculated.

$$\begin{array}{lcr} N & & = 14 \\ H_4 & = 1 \times 4 & = 4 \\ Cl & & = 35{\cdot}5 \\ \hline & & 53{\cdot}5 \end{array} \qquad \begin{array}{lcr} N & & = 14 \\ H_3 & = 1 \times 3 & = 3 \\ \hline & & 17 \end{array}$$

From these weights it is evident that 53·5 parts by weight of ammonium chloride are required to produce 17 parts by weight of ammonia gas, and therefore 53·5 grammes of ammonium chloride are required to produce 17 grammes of ammonia gas.

One gramme of hydrogen occupies 11·2 litres, and as the specific gravity of ammonia gas is 8·5, therefore 8·5 grammes of ammonia gas occupy 11·2 litres, and therefore 8·5 × 2 or 17 grammes of ammonia gas occupy 11·2 × 2 or 22·4 litres.

The previous calculation shows that 53·5 grammes of ammonium chloride are required to produce 17 grammes of ammonia gas, and as the latter occupy 22·4 litres, therefore 53·5 grammes of ammonium chloride are required to produce 22·4 litres of ammonia gas. Therefore, how many grammes of ammonium chloride are required to produce 30 litres of ammonia gas?

$$22{\cdot}4 : 30 :: 53{\cdot}5 : x$$

$x = 71{\cdot}65$ grammes, the weight of ammonium chloride required to produce 30 litres of ammonia gas.

GROUP III.—CHEMICAL PROBLEMS INVOLVING VOLUME CALCULATIONS ONLY.

The solution of problems of this class is a very simple matter. It is only necessary to write out a complete equation of the reaction involved in the problem, and to observe the relative numbers of the molecules of the gases taking part in the reaction; since the molecules of all gases occupy the same space, the relative numbers of molecules expressed in the equation represent the relative volumes of gases taking part in the reaction. It is quite immaterial whether the volumes of the gases are expressed in pints, litres, gallons, etc. (as will be seen from the following examples).

1. How many pints of oxygen are required for the combustion of 10 pints of hydrogen?

The equation representing the combustion of hydrogen is first written out.

$$\underset{\text{2 molecules.}}{2H_2} + \underset{\text{1 molecule.}}{O_2} = 2H_2O$$

From this equation it is evident that 1 molecule of oxygen is required for the combustion of 2 molecules of hydrogen, and since the molecules of all gases occupy the same space, therefore 1 pint of oxygen will be required for the combustion of 2 pints of hydrogen, and, therefore, for the combustion of 10 pints of hydrogen, 5 pints of oxygen will be required.

2. How many litres of oxygen are required for the combustion of 5 litres of sulphuretted hydrogen?

The equation representing the combustion of sulphuretted hydrogen is first written out.

$$\underset{\text{2 molecules.}}{2H_2S} + \underset{\text{3 molecules.}}{3O_2} = 2H_2O + 2SO_2$$

From this equation it is evident that 3 molecules of oxygen are required for the combustion of 2 molecules of sulphuretted hydrogen, and therefore 3 litres of oxygen are required for the combustion of 2 litres of sulphuretted hydrogen. Therefore, how many litres of oxygen will be required for the combustion of 5 litres of sulphuretted hydrogen?

3 litres of O required for combustion of 2 litres of H_2S
∴ $1\frac{1}{2}$ " " " " 1 " "
∴ $7\frac{1}{2}$ " " " " 5 " "

3. How many gallons of carbon dioxide are produced by burning 10 gallons of olefiant gas (ethylene)?

The equation representing the combustion of olefiant gas is first written out.

$$\underset{\text{1 molecule.}}{C_2H_4} + 3O_2 = \underset{\text{2 molecules.}}{2CO_2} + 2H_2O$$

From this equation it is evident that 2 molecules of carbon dioxide are produced by burning 1 molecule of olefiant gas, and therefore 2 gallons of carbon dioxide are produced by burning 1 gallon of olefiant gas.

1 gallon of C_2H_4 produces 2 gallons of CO_2
∴ 10 gallons " produce 20 " "

4. How many pints of oxygen are required for the combustion of 2 pints of marsh gas (methane)?

The equation representing the combustion of marsh gas is first written out.

$$\underset{\text{1 molecule.}}{CH_4} + \underset{\text{2 molecules.}}{2O_2} = CO_2 + 2H_2O$$

From this equation it is evident that 2 molecules of oxygen are required for the combustion of 1 molecule of marsh gas, and therefore 2 pints of oxygen are required for the combustion of 1 pint of marsh gas, and therefore 4 pints of oxygen will be required for the combustion of 2 pints of marsh gas.

5. How many pints of air are required for the combustion of 2 pints of marsh gas?

The problem is first worked out, as in the preceding case, to ascertain the number of pints of oxygen required for the combustion of 2 pints of marsh gas; it was found that 4 pints of oxygen were required. It now remains to ascertain in how many pints of air, 4 pints of oxygen will be contained.

Now 100 parts of air by volume contain 21 parts of oxygen by volume. Therefore, if 21 pints of oxygen are contained in 100 pints of air, in how many pints of air will 4 pints of oxygen be contained?

$$21 : 4 :: 100 : x$$

$x = 19{\cdot}04$ pints, the number of pints of air required for the combustion of 2 pints of marsh gas.

6. How many gallons of carbon monoxide are produced by passing 100 gallons of carbon dioxide over heated charcoal?

The equation representing the action of carbon dioxide on heated charcoal is first written out.

$$\underset{\text{2 molecules.}}{2CO_2} + C_2 = \underset{\text{4 molecules.}}{4CO}$$

From this equation it is evident that 4 molecules of carbon monoxide are produced from 2 molecules of carbon dioxide, and therefore 4 gallons of carbon monoxide will be produced from 2 gallons of carbon dioxide.

4 gallons of CO are produced from 2 gallons of CO_2
$\therefore$ 2 " " " 1 " "
$\therefore$ 200 " " " 100 " "

7. How many pints of chlorine are required to convert 10 pints of marsh gas (methane) into chloroform?

The equation representing the conversion of marsh gas into chloroform by the action of chlorine is first written out.

$$\underset{\text{1 molecule.}}{CH_4} + \underset{\text{3 molecules.}}{3Cl_2} = CHCl_3 + 3HCl$$

From this equation it is evident that 3 molecules of chlorine are required to convert 1 molecule of marsh gas into chloroform, and therefore 3 pints of chlorine are required to convert 1 pint of marsh gas into chloroform. Therefore 30 pints of chlorine are required to convert 10 pints of marsh gas into chloroform.

WEIGHTS AND MEASURES.

1 lb. Avoirdupois .. ... = 16 ozs. Av.
,, ,, ... = 7,000 grains.
1 oz. Avoirdupois... ... = 437·5 grains.
1 lb. Troy ... ... = 12 ozs. Troy.
,, ,, ... = 5,760 grains.
1 oz. Troy ... ... = 480 grains.
1 gallon ... ... = 8 pints.
1 pint ... ... = 20 fluid ozs.
1 fluid oz. ... ... = 8 fluid drachms.
1 fluid drachm ... ... = 60 minims.
1 gallon of water at 62° F.
weighs ... ... = 70,000 grains.

---

1 metre (m.) ... ... = 10 decimetres (dm.).
,, ,, ... = 100 centimetres (cm.).
,, ,, ... = 1,000 millimetres (mm.).
1 litre ... ... = 1,000 cubic centimetres (c.c.).
,, ... = 1·76 pints.
1 pint ... ... = 568 cubic centimetres.
1 fluid oz. ... ... = 28·4 ,, ,,
1 kilogramme (kg.) ... = 1,000 grammes (g.).
,, ,, ,, ... = 2·205 lbs. Av.
1 gramme ... ... = 10 decigrammes (dg.).
,, ... = 100 centigrammes (cg.).
,, ... = 1,000 milligrammes (mg.).
,, ... = 15·432 grains.
1 lb. Avoirdupois ... ... = 453·6 grammes.
1 oz. ,, ... = 28·35 ,,
1 grain ... ... = 64·8 milligrammes.

Directions for Examining a Salt or Solution containing not more than one Metal and one Acid.

Preliminary Examination.

If a solution, evaporate a small portion to dryness and submit the dry salt to the following examination.

(i) Carefully note the physical appearance of the salt, if necessary using a magnifying lens. Cautiously taste a minute fragment of the salt, being careful to afterwards spit it out.

(ii) Heat a small quantity in a dry tube and carefully notice if any of the following results occur.

Results.	Probably Indicative of
Salt sublimes	NH_4, Hg or As salt. Oxalic or Benzoic Acids. Sulphur.
Turns yellow and remains yellow on cooling	Pb or Bi salt.
Turns yellow, but becomes white again on cooling	Zn salt.
Brown fumes evolved	Nitrate.
Chars	Organic substance, such as Tartrate, Citrate, Acetate, Sugar, Urea, etc.

If no charring occurs, absence of organic compounds, with the exception of oxalates and cyanides, is indicated.

(iii) Heat a small quantity in a tube with strong H_2SO_4.

RESULT.	INDICATIVE OF
Brown fumes evolved	Bromide or Nitrate.
Violet ,, ,, ...	Iodide.
Greenish gas accompanied by explosions	Chlorate.
Colourless gas fuming in the air	Chloride or Nitrate.
Charring	Organic matter, such as Tartrate, Citrate, etc.

The evolution of gases or odorous vapours will be dealt with in Group I. for the detection of acids.

(iv) Moisten a platinum wire with dil. HCl, put it in the salt and then insert in the Bunsen flame. Observe if any of the following colours are communicated to the flame.

COLOUR OF FLAME.	INDICATIVE OF
Yellow (giving to the hand a livid colour)	Na.
Lasting bright crimson flame ...	Li.
Bright crimson flame, fading shortly to yellow	Sr.
Faint reddish flame rapidly fading	Ca.
Greenish flame	Cu, Ba, or Boracic Acid.
Lavender-tinted flame.	K.

EXAMINATION of the Solution, or of the Salt dissolved in water or in hydrochloric acid (afterwards diluted with water), for Metals.

GROUP I.

To the Solution add HCl. If a p.p. occurs, see if it is soluble in excess of cold strong HCl; if it is soluble, proceed to group II. as it will be Bi or Sb; if it is insoluble, add to the p.p. NH_4HO in excess.

SOLUBLE.	BLACKENS.	UNAFFECTED.
Ag. Confirm by KHO to orig. *Brown p.p.* K_2CrO_4 to orig. *Red p.p.*	Hg (-ous). Confirm by KHO to orig. *Black p.p.* KI to orig. *Green p.p.*	Pb. Confirm by KI to orig. *Yellow p.p.* H_2SO_4 to orig. *White p.p.*

GROUP II.

If no p.p. with HCl add to the same liquid H_2S water.

<table>
<tr><th colspan="3">Black p.p.</th><th colspan="3">Yellow p.p.</th><th>Orange p.p.</th><th>Brown p.p.</th></tr>
<tr><td colspan="3">Add KHO to orig.</td><td colspan="3">Collect p.p. on filter, wash, transfer to test tube and boil with equal parts of NH_4HO and NH_4HS.</td><td rowspan="3">Sb.
Confirm by Reinsch's Cu test with orig.</td><td rowspan="3">Sn (-ous).
Confirm by Borax & Cu bead test with orig.</td></tr>
<tr><td rowspan="2"><i>Yellow p.p.</i>
Hg (-ic).
Confirm by KI to orig.
<i>Red p.p.</i>
Cu sublimation test with orig.</td><td rowspan="2"><i>Blue p.p.</i>
Cu.
Confirm by NH_4HO to orig.
<i>Dark Blue colour.</i>
K_4 Fe Cy_6 to orig.
<i>Red-brown p.p.</i></td><td rowspan="2"><i>White p.p.</i>
Bi.</td><td rowspan="2"><i>Insoluble.</i>
Cd.</td><td colspan="2"><i>Soluble.</i>
Add KHO to orig.</td></tr>
<tr><td><i>White p.p.</i>
Sn (ic).
Confirm by Borax & Cu bead test with orig.</td><td><i>No p.p.</i>
As.
Confirm by Reinsch's Cu test with orig.</td></tr>
</table>

GROUP III.

If no p.p. with H_2S, add to the orig. NH_4Cl, NH_4HO and NH_4HS.

Black p.p.			White p.p.		Greenish p.p.	Flesh or Salmon Coloured p.p.
Collect p.p. on filter, wash and dissolve in HCl and HNO_3; to this sol. add NH_4HO in excess.			Add NH_4HO in excess to orig.		Cr. Confirm by KHO to orig.	Mn. Confirm by KHO to orig.
Red-brown p.p. Fe. To ascertain if Fe is in ferrous or ferric state, add to orig. K_4FeCy_6. *Dark Blue p.p.* Fe (-ic). *Light Blue p.p.* Fe (-ous). Confirm by $K_6Fe_2Cy_{12}$ to orig. *Dark Blue p.p.* Fe (-ous). *Dark Green colour.* Fe (-ic).	*No permanent p.p.* Add KHO to orig.		*Insoluble.* Al. Confirm by KHO to orig. *White p.p.* (Soluble in excess of KHO.)	*Soluble.* Zn. . Confirm by K_4FeCy6 to orig. *White p.p.*	*Green p.p.* (Soluble in excess of KHO.)	*White p.p.* (Turning brown on shaking with the air.)
	Red p.p. Co. Confirm by Borax bead. (Blue colour.)	*Green p.p.* Ni. Confirm by Borax bead. (Sherry colour)				

GROUP IV.

If no p.p. in Group III., add to orig. NH_4Cl and $(NH_4)C_2O_3$.

If a p.p. falls, add to orig. $CaSO_4$ solution or very dil. HS_2O_4.

Immediate White p.p.	White p.p. forms on Standing for some time.	No p.p. on Standing.
Ba. Confirm by K_2CrO_4 to orig. *Yellow p.p.*	Sr. Confirm by flame reaction. *Crimson colour.*	Ca. Confirm by NH_4HO and $(NH_4)_2C_2O_4$ to orig.
Flame reaction. *Green colour.*		*White p.p.*, insol. in $HC_2H_3O_2$. Sol. in HCl.

GROUP V.

If no p.p. in preceding groups, treat fresh portions of orig. sol. successively as follows:—

Add NH_4Cl, NH_4HO and Na_2HPO_4.	Add KHO and boil.	Add HCl, $PtCl_4$ and stir.	Dip a platinum wire in the orig. and insert in Bunsen flame.	
White granular p.p.	*Odour of Ammonia.*	*Yellow granular p.p.*	*Yellow flame.*	*Crimson flame.*
Mg.	**NH_4.**	K.	Na.	Li.
		Confirm by shaking orig. with strong sol. of tartaric acid. *White granular p.p.* Confirm by flame reaction. *Lavender tint.*		

EXAMINATION of the Solution or of the Salt dissolved in water (boiling if necessary) for an acid:—

Test the solution with both blue and red litmus-paper. If it is acid, neutralise it carefully with NH_4HO before you examine it by Tables II., III., and IV.; if it is alkaline, neutralise it carefully with dil. HNO_3 before you examine it by Tables III. and IV. There is no necessity to neutralise before examining by Table I.

TABLE I.

To orig. sol. add dil. HCl and heat; notice if any gas or odour is evolved.

ODOURLESS GAS (with effervescence).	ODOUR OF ROTTEN EGGS.	ODOUR OF BURNING SULPHUR.		ODOUR OF HYDROCYANIC ACID.	ODOUR OF ACETIC ACID.	WHITE JELLY FORMS.
Carbonate or *Bicarbonate.*	*Sulphide.*	Sol. remains clear. *Sulphite.*	Sol. becomes turbid. *Hyposulphite.*	*Cyanide.*	*Acetate.*	*Silicate.*
Prove that the gas is CO_2 by its turning lime-water turbid. Add to orig. $MgSO_4$. *Carbonate.* p.p. *Bicarbonate.*—No p.p. Add to orig. $HgCl_2$. *Carbonate.*—Red p.p. *Bicarbonate.*—White p.p. (turning red.)	Confirm by the gas blackening $Pb2C_2H_3O_2$.	Confirm by treating orig. with Zn and HCl, when H_2S should be evolved.	Confirm by adding $AgNO_3$ to orig. *White p.p. changing to yellow, orange, brown, and black.*	Confirm by adding to orig. the following reagents in the order mentioned—KHO, $FeSO_4$, Fe_2Cl_6 and HCl. *Dark blue p.p. of Prussian blue formed.*	Confirm by adding to orig. alcohol and H_2SO_4 and boiling. *Odour of Acetic Ether.*	

TABLE II.

SECTION I.		SECTION II.	
If no reaction occurs in Table I. add to orig. $Ba2NO_3$. If a p.p. falls, add to it strong HCl.		Add to orig. (previously neutralised with NH_4HO if acid) $CaCl_2$. If a p.p. falls, add to it strong $HC_2H_3O_2$.	
INSOLUBLE. *Sulphate.*	SOLUBLE. Pass on to Section II.	INSOLUBLE. *Oxalate.* Confirm by adding to this p.p. HCl, which should dissolve it.	SOLUBLE. Pass on to Table III.

TABLE III.

To orig. (previously neutralised if necessary) add $AgNO_3$.

White p.p. Add HNO_3 to p.p.				Yellow p.p. Add dil. HNO_3 to p.p.				Chocolate p.p.	Red p.p.
Insoluble. *Chloride.* Confirm by adding to the p.p. excess of NH_4HO, in which it should dissolve. Confirm by heating orig. with MnO_2 and strong H_2SO_4. *Chlorine evolved.*	Soluble. Refer to the Preliminary Examination of the Salt to see if it charred on heating it (both alone and with strong H_2SO_4).			Soluble. Acidify orig. with HCl and add H_2S.		Insoluble. Add to orig. Chlorine water and Starch decoction.		*Arseniate.* Confirm by NH_4Cl, NH_4HO, and $MgSO_4$ to orig. *White granular p.p.*	*Chromate.* Confirm by $Pb2C_2H_3O_2$ to orig. *Yellow p.p.*
	No Charring with Original Salt. *Borate.* Confirm by adding to orig. Salt H_2SO_4 and alcohol, and setting the alcohol on fire. *Green flame.*	Charring with Original Salt. Again add to orig. sol. (previously neutralised with NH_4HO if acid) $AgNO_3$ and boil.		Yellow p.p. *Arsenite.* Confirm by Reinsch's test with orig.	No p.p. *Phosphate.* Confirm by NH_4Cl, NH_4HO, and $MgSO_4$ to orig. *White granular p.p.*	Blue Colour. *Iodide.*	Orange Colour. *Bromide.*		
		P.p. blackens forming a mirror-like deposit. *Tartrate.*	*P.p. does not blacken.* *Citrate.*						

TABLE IV.

If no reaction occurs in previous tables add to orig. (rendered faintly acid with dil. HNO_3) Fe_2Cl_6.

CINNAMON COLOURED P.P.	DARK BLUE P.P.	DARK-GREENISH COLOUR.
Benzoate.	*Ferrocyanide.*	*Ferricyanide.*
Confirm by adding to orig. HCl which should give a white p.p., soluble on agitating with ether.	Confirm by $CuSO_4$ to orig.	Confirm by $FeSO_4$ to orig.
	Brick-red p.p.	*Dark-blue p.p.*

TABLE V.

If no reaction occurs in previous tables, add to orig. a drop or two of Sol. of Indigo Sulphate, and then strong H_2SO_4. If the colour of the Indigo is discharged, the presence of a *nitrate* or *chlorate* is indicated. To ascertain which, add to orig. Cu turnings, strong H_2SO_4 and warm.

GAS EVOLVED, TURNING REDDISH-BROWN IN THE AIR.	NO ACTION.
Nitrate.	*Chlorate.*
Confirm by adding a crystal or two of $FeSO_4$ and strong H_2SO_4 to orig.	
Dark colour.	

ADDITIONAL HINTS.

I. If the orig. solution is strongly alkaline, and carbonates are absent, the presence of an alkali such as ammonia, potash, soda, lime, or baryta is indicated. Ammonia would be detected by its smell, the other alkalies by a brown p.p. on addition of $AgNO_3$.

II. If the salt is insoluble in boiling water, attempts should be made to dissolve it in HCl. If it dissolves without effervescence, the absence of a carbonate is indicated. To prove an oxide, since the metal has been previously detected, the physical and chemical properties of the oxide of that metal must be borne in mind, and searched for; a few oxides, such as oxide of mercury, black oxide of manganese, and peroxide of lead, evolve oxygen on heating; litharge is of a characteristic yellow colour; oxide of bismuth of a lemon colour; oxide of copper black, forming with acids a green solution; oxide of antimony a buff colour, dissolving when boiled with cream of tartar and water; ferric oxide a reddish-brown colour; oxide of zinc a white colour, turning yellow when heated, but becoming white again on cooling.

III. The following are some of the reactions by which some of the more commonly occurring bodies, insoluble in HCl, may be recognised:—

Calomel by its turning black when treated with alkalies, and by its volatility.

Mercuric Iodide by its scarlet colour, and by its turning yellow on heating and scarlet again when the yellow modification is pressed.

Mercurous Iodide by its dirty-green colour, and by its yielding some yellow and scarlet mercuric iodide when heated in a dry tube.

Mercurous Oxide by its black colour, by its evolving oxygen, and by its yielding a sublimate of metallic mercury on heating.

Oxide of Silver by its brown colour, and by its evolving oxygen when heated, the metal silver being left.

Sulphur by its yellow colour, and by the peculiar odour when burnt.

Charcoal by its black colour, by its deflagrating when heated with KNO_3, and by its evolving SO_2 when boiled with strong H_2SO_4.

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