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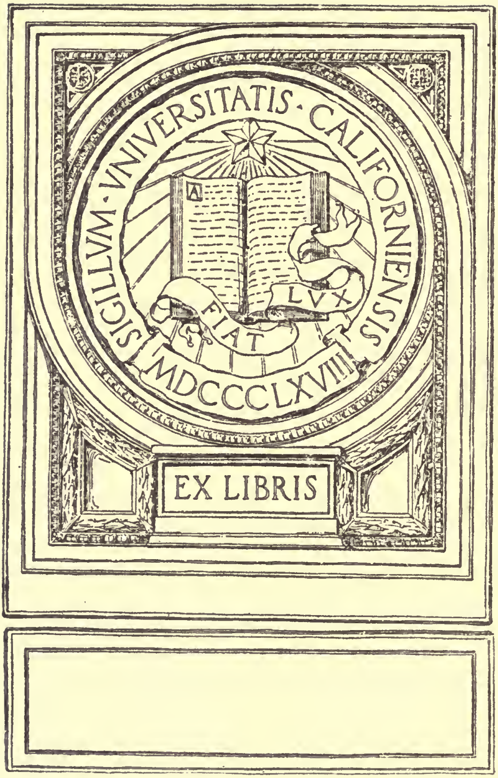

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SERVICE CHEMISTRY

FIG. 1. DENDRITIC STRUCTURE OF ANTIMONY.

FIG. 2. EUTECTIC ALLOY OF BISMUTH AND TIN.

SERVICE CHEMISTRY

BEING

A SHORT MANUAL OF CHEMISTRY AND METALLURGY

AND THEIR APPLICATION IN THE NAVAL AND MILITARY SERVICES

BY

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PREFACE

At no time in the world's history has the need for scientific knowledge in our two great Services been more important than at the present, whilst probably at no time has the period which could be devoted to acquiring it been shorter; and this book is an attempt to supply, as far as may be, a rational treatise on the more chemical side of the many subjects with which Officers are brought in almost daily contact.

In the short time that can be devoted to subjects outside the professional Service routine, it is impossible to acquire a complete knowledge of any of the many branches of science that enter into modern Service work, but the authors have found from long experience that it is quite possible to so develop the purely theoretical side of a science as to lead naturally up to the more technical details of such Service questions as are necessary to a Naval or Military career.

The technical side of a science is merely its adaptation to our special needs, and without a knowledge of the facts and laws that govern the results we desire to attain, a Service technology would be a mere collection of data, useless in the future and of but little present value. On the other hand, to attempt to educate a busy Officer of any branch in all the modern theories, before he had grasped the importance to him of their application, would be to court failure, and we have attempted so to formulate the fundamental facts and theories of modern chemistry as to form a firm foundation for their application to such questions as modern explosives, fuel problems, the physical and chemical characteristics of the metals and alloys, military ballooning, boiler incrustations, corrosion, protective paints, anti-fouling compositions, and the host of other subjects on which knowledge is necessary to ensure progress, and which are dealt with as the scientific side of the book leads up to them.

The fact that this is the fourth edition of the book shows that it has been acceptable to many, and in order to keep up with the rapid advances made in science during the last few years, it has been largely re-written to bring it up-to-date, and embraces much material, not available in the ordinary text-books, of importance to engineers and others. The authors, therefore, hope it may appeal to an even larger circle of readers than the Service students for whom it was specially prepared.

V. B. L.
J. S. S. B.

Royal Naval College, Greenwich,
March, 1913.

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SERVICE CHEMISTRY

CHAPTER I

INTRODUCTORY

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

Physical Change.—Cold will convert water into ice, and heat will convert it into steam; yet the solid ice, the liquid water, and the gaseous steam have all the same composition. A coil of platinum wire heated to a high temperature acquires the power of giving out light; yet on cooling, the platinum once more loses this property and is found to be in no way changed from the original metal, being chemically identical and no change in weight having taken place. Changes of this kind, in which form and properties only undergo modification, without any alteration in composition, are called *Physical changes*, and the study of this class of phenomena comes under the domain of Physical Science.

Chemical Change.—A second kind of change, however, is at work, in which the alteration affects not only the physical properties of the original mass, but also its composition. A fallen tree, exposed to air and moisture, gradually rots away and is converted into gases and soil. A candle burns, and the wax of which it is composed disappears. A metal dissolved in an acid loses its metallic properties and remains in solution in the liquid. A piece of magnesium wire, heated in contact with air, emits light, burns away, and at the end of the operation a white powder is left which is entirely different in form and properties from the metal magnesium. In all these cases a change of weight, as well as of properties and composition, has taken place; and if we collected and weighed the white powder formed during the combustion of the magnesium wire, it would be found to weigh more than the metal burnt. Changes of this class, in composition as well as properties, are called *Chemical changes*, and the study of the laws which govern and bring about such changes constitute the *Science of Chemistry*.

Conservation of Matter.—In Nature no such thing as loss or creation of matter occurs, although in many cases the products of the chemical changes taking place, being gaseous, escape our notice, as when a candle burns.

If, instead of allowing the candle to burn in the open air, it had been supported in a glass cylinder (A, Fig. 1) and the products of its combustion had been drawn by means of the aspirator bottle (L) through tubes (C) (C), containing small fragments of sodium hydroxide, which has the power of absorbing carbon dioxide and water vapour (the gaseous compounds formed by the combustion of the wax of the candle), it could be shown that the products formed weighed more than the wax consumed, by suspending the candle and absorption tubes to one end of a balance, when, instead of losing weight, as might have been expected, from the diminution in size of the candle, the candle and absorption

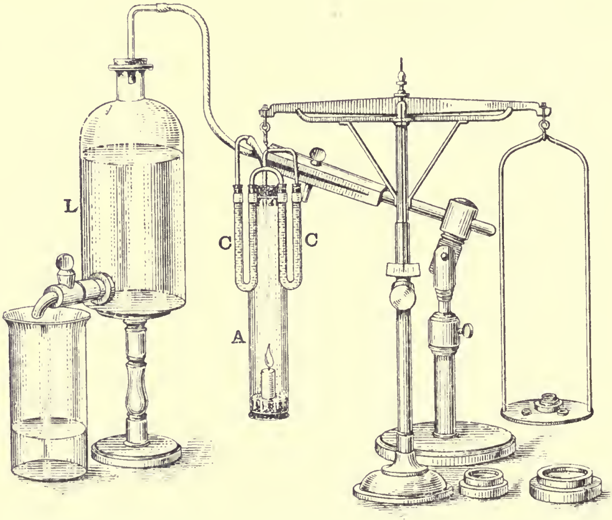


Fig. 1.—Candle on balance.

tubes are seen to increase in weight; this increment is due to the constituents of the wax having entered into chemical combination with one of the constituents of the air, the increase in weight shown by the balance being exactly equal to the loss of weight of the air.

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

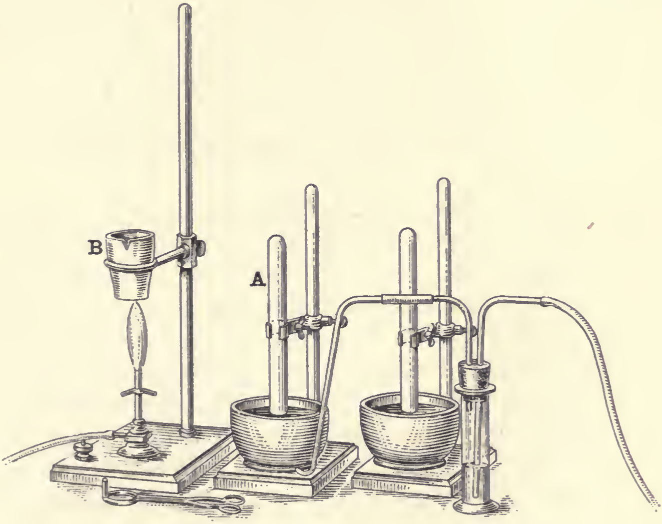


Fig. 2.—Oxygen and phosphorus in tubes.

which may be stated as follows—" *The mass of matter which takes part in any change, whether physical or chemical, remains unaltered.*"

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

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

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

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

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

The question now naturally arises: can we go on decomposing substances in this way to an unlimited extent? Further experiment shows that this is not the case. If mercury and oxygen are taken for experiments, it is found that they can be made to combine with other substances to form a large number of compounds, but by no means at present at our disposal can either be subdivided into anything but mercury and oxygen.

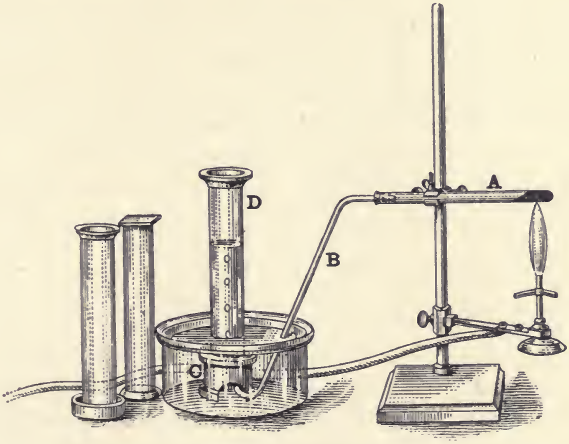


Fig. 3.—Heating mercuric oxide.

When, in this way, a substance resists further decomposition, it is called an *Element*, and at present about eighty-three such substances are known, and of these, as far as is known, all matter is built up.

Up to 1896 an element was usually defined as a substance which by no means at present at our disposal can be decomposed into anything simpler, but since that date a small class of bodies have been discovered which appear to be undergoing a sort of spontaneous change, and in view of these so-called "radioactive" elements, such as radium, actinium, uranium, polonium, and thorium, it is better to define the element as a substance, the molecule of which contains only one kind of matter.

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

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

The atomic weights of the elements vary so widely that a mere statement of the percentage composition of the crust of the earth given in percentages of weight gives a false idea of the relative quantity of the elements present; but if the most recent weight percentages be divided by the atomic weights of the elements to which they refer we obtain a truer idea of their relative importance in nature; Mellor gives such a table as follows:—

Oxygen	53·81	Calcium	1·40
Hydrogen	16·30	Iron	1·29
Silicon	15·87	Potassium	1·02
Aluminium	4·68	Carbon	0·27
Sodium	1·72	Titanium	0·16
Magnesium	1·61	Chlorine	0·11

It will be seen from this that only twelve of the eighty-three known elements exist in nature to the extent of more than a tenth of 1 per cent., and the enormous preponderance of oxygen is clearly brought out.

Elements are found combined as chemical compounds, or more rarely, exist free.

Mechanical Mixtures.—When in mechanical mixture the distinctive properties of the substances present are retained, although often modified by the properties of the other constituents; but in a chemical compound the properties of the original factors entirely disappear, and are merged in new characteristics distinctive of the compound formed.

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

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

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

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

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

Analysis and Synthesis.—We have seen that by chemical change complex substances may be resolved into simple bodies, and finally reduced to the condition of elements, whilst chemical change also enables elementary matter to be built up into compounds, and these processes can be utilised for revealing the composition of substances. If a body is taken and by chemical means broken up in such a way as to gain an insight into its composition, the process is termed *analysis*, whilst if we have an idea as to what the composition of the body is likely to be, it can often be verified by building up the compound from the elements it is expected to contain, a process which is called *synthesis*. For example, it can be proved that water contains hydrogen and oxygen by passing steam over iron heated to dull redness, when the oxygen remains combined with the iron, and the hydrogen may be collected in a free state. On the other hand, by passing a mixture of steam and chlorine through a hot porcelain tube the steam can be decomposed with the formation of hydrochloric acid and the liberation of oxygen, the two experiments taken together showing that water contains hydrogen and oxygen, this being an analytical method of arriving at the fact.

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

The Three States of Matter.—By matter is understood anything that has weight, and it may be either solid, liquid, or gaseous in its nature. These three states of matter are entirely dependent upon temperature. It so happens that at the ordinary air temperature zinc is a solid, water is a liquid, and carbon dioxide is a gas ; but if water is cooled down below 0° C. it becomes a solid, ice, whilst heated above its boiling point (100° C.) it is converted into gaseous steam. In the same way all substances which are not decomposed by heat can be obtained as solids, liquids, or gases.

If a bar of zinc at the ordinary air temperature is taken and its size determined, and then the bar is heated, it is found that the action of heat is to cause an increase in bulk, this increase proceeding at a definite rate until it is raised to the temperature of 423° C., when it becomes liquid. If now the liquid be further heated it will be found to still continue to expand until a temperature of 1040° C. is reached, when it boils like water and is converted into the gaseous state.

If the gas carbon dioxide is cooled down to near the freezing point of water and subjected to a pressure of 36 atmospheres (540 lbs. on the square inch), it is reduced to the liquid state, and in this condition can be kept in steel vessels of sufficient strength to resist the pressure necessary to keep it liquid. On allowing some of this liquid, however, to escape suddenly into a small brass box, made in two halves connected by bayonet joints and with an exit for the gas through hollow handles (Fig. 4), at ordinary atmospheric pressure, it is instantly converted into gas, and in the change from the liquid to the gaseous state takes up so much heat as to produce a degree of cold sufficiently intense to freeze some of the liquid escaping from the vessel into solid carbon dioxide, which is found as a white snow-like mass in the box.

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

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

In the same way when water is boiled it is converted into steam, the vapour so formed occupying about 1700 times the volume of the water taken. Roughly a cubic inch of water forms a cubic foot of steam. This enormous increase in volume may be explained in one of three ways: either the cubic inch of water is stretched under the influence of heat, like a piece of indiarubber, until it assumes the dimensions of the cubic foot; or the cubic inch of water is built up of an innumerable host of small particles which, when heated, undergo individual expansion, resulting in the enormously increased volume; or else this multitude of small particles do not themselves expand, but under the influence of heat tend to repel each other, and by spacing themselves further apart give the increase in volume.

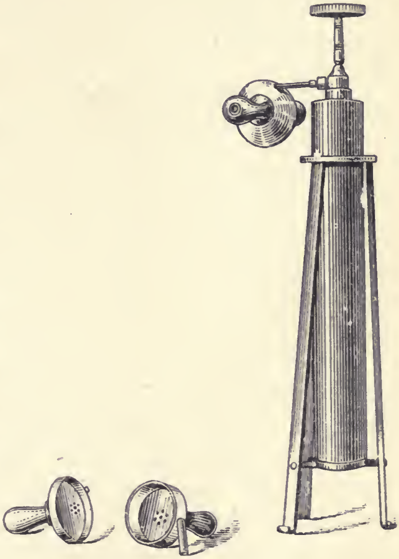


Fig. 4.—Production of solid carbon dioxide.

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

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

In the solid state, these particles, each of which has the same properties as the mass of which it is a part, are held together by the force of "cohesion," a force which varies with the nature of the substance; so that when a solid is heated, the particles tend to separate, but in different substances they do so to a different extent, as the stronger the force of cohesion existing between the particles, the greater is the work the heat has to do in separating them; at a certain temperature the particles are so far asunder that the force of cohesion is weakened, and the particles become free to move around each other, *i.e.* they assume the liquid state; continue the heating, the distances between the particles grow greater and greater until a point is reached at which cohesion exerts no influence, the particles move independently of each other, and we have the gaseous state.

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

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

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

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

Critical Temperature of Gases

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

When a gas that has been liquefied by pressure is again allowed to become gaseous, the change from the liquid to the gaseous state takes up and renders latent a large amount of heat, and in so doing can be made to cool bodies in contact with it to a very low temperature. For instance, the critical point of carbon dioxide being 31·9° C., the gas can readily be liquefied by pressure, and can be kept in the liquid state in a strong steel cylinder : if now the liquid be driven out into a vessel at atmospheric pressure, it is rapidly again converted into gas and lowers the temperature of bodies in contact with it to — 90° C. This is far below the critical point of the gas ethylene, so that if this gas is compressed to a sufficient extent in a cylinder cooled by boiling liquid carbon dioxide, the ethylene in turn becomes a liquid, which, when it boils at atmospheric pressure, gives a temperature of — 100° C., but if the conversion into the gaseous state is hastened by allowing it to gasify into a vacuum the temperature is lowered to — 140° C. At — 140° C. oxygen can be liquefied by pressure, and on allowing liquid oxygen to boil at reduced pressure a temperature of — 205° C. is reached, a point at which air liquefies by merely coming in contact with the cooled surface.

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

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

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

For this purpose it is necessary to maintain indefinitely the temperature at a few degrees below the freezing point rather than to obtain an excessively low temperature, and the processes employed may be grouped in three classes :—

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

The drawbacks to this system are its low efficiency, which makes the space occupied by the plant large as compared with refrigerating machines of the next class, whilst trouble is caused by the moisture in the air which freezing causes an accumulation of snow in the expansion cylinder; its great advantages are initial cheapness and the non-poisonous nature of the medium.

2. The second class of refrigerating machines depend for their action upon the alternate liquefaction and gasification of an easily condensable gas like ammonia, carbon dioxide, or sulphur dioxide. On a large scale the lowering of temperature caused by the evaporation of the liquefied gas is utilised to cool brine several degrees below the freezing point of water, the cold brine being then made to circulate through a system of pipes in the refrigerating chamber.

Of the three gases, ammonia is the most used, as on account of its high critical point (130° C.) it can be liquefied in any climate; but it has the drawbacks of attacking copper and its alloys, which cannot therefore be used in the fittings, and of being excessively poisonous if there is any large leakage; its pungent odour, however, leads to any leak being readily detected.

Carbon dioxide has the advantages that it is non-poisonous in the ordinary acceptance of the term, and has no action on any ordinary metal, but the extremely high pressure necessary for its liquefaction at ordinary temperatures necessitates very strong working parts and makes it difficult to prevent leakage, whilst in tropical climates its low critical temperature (31·9° C.) prevents liquefaction and lowers the efficiency of the plant.

Sulphur dioxide is not now used for anything but small plants, as, owing to the low pressure at which it liquefies, a large compressor would be needed, and considerations of space make ammonia preferable. It does not attack metals when anhydrous, but is highly poisonous.

3. The third class of machines depend upon the easy condensability of gaseous ammonia to the liquid state, and the fact that after the liquid has done the work of cooling during its gasification the gas is absorbed with enormous rapidity by cold water, and can be again driven out from this solution by heat.

In all large installations the second or "Compression" system is the one now employed, and the average commercial results are from 7 to 8 lbs. of mould ice per 1 lb. of coal used for power, whilst the yield of "plate" ice is rather higher.

CHAPTER II

THEORETICAL

Law of Constant Proportion.—Although the nature of many chemical substances has been known from very early times, little advance was possible in the study of the science until chemists introduced quantitative methods, and even then owing to necessarily crude apparatus, unsatisfactory measuring and weighing appliances, and impure materials, the results were often contradictory. Thus the very fundamental truth that every pure chemical substance is always composed of exactly the same elements in the same proportion was the subject of keen controversy for years, and it was only established finally by Proust in 1806.

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

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

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

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

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

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

It was for a long period thought that the atoms were the ultimate and indivisible form of matter ; that they were incapable of resolution into anything simpler. Researches during the last few years have shown, however, that the atoms of certain elements undergo spontaneous decomposition, and that by their disintegration and the re-association of the products entirely new elements result, which may themselves have only a transitory existence. In general such atomic disintegration is accompanied by radio-activity and enormous energies are involved. Radium, for example, gives rise to radio-active emanations and produces another element, helium. It is calculated that the heat energy liberated by the disintegration of 1 gram of radium is sufficient to raise 2,000,000,000 grams of water 1° C.; 1 gram of average coal would raise only 7000 grams of water through a like range.

This disintegration appears within our present means of detection to be confined to the elements with high atomic weight, the re-association of the parts giving rise to other elements of lower atomic weight; thus uranium (238·5 At. Wt.) gives ionium; this in turn gives radium (226·4 At. Wt.); radium (besides many forms of "emanation" of a radio-active kind) gives polonium, and the latter is believed to pass finally into lead (207·1 At. Wt.).

From the physical point Sir J. J. Thomson regards the atoms as built up of a large number of negatively electrified corpuscles held together by a positive electrical force equal in amount to the total negative charges of the corpuscles. He calculates that in the hydrogen atom there are 1700 such corpuscles, and this is the smallest number present in any atom, since hydrogen is the lightest substance known.

With the limitation that disintegration of one form of elementary atom may lead to the production of the atoms of other elements for the purpose of explaining chemical combination and chemical change the atoms may still be regarded as indivisible, and *the atom may be defined as the smallest portion of matter capable of entering into a chemical compound.*

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

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

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

2 vols. of hydrogen + 1 vol. of oxygen = 2 vols. of water (vapour).
2 vols. of carbon monoxide + 1 vol. of oxygen = 2 vols. of carbon dioxide.
1 vol. of hydrogen + 1 vol. of chlorine = 2 vols. of hydrochloric acid.

Whilst on decomposition—

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

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

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

It will be seen that nitrogen dioxide contains just twice as much oxygen by weight and by volume as nitrogen monoxide for the same weight and volume of nitrogen in each. In other words, when the number of atoms present has doubled, the volume has also doubled, hence there must be a very simple relationship between the volumes of gases and the number of atoms in these volumes.

The first conclusion arrived at was that in equal volumes of gases measured under the same conditions of temperature and pressure there were the same number of atoms, but it was soon realised that in many cases of chemical combination this would involve fractions of atoms taking part, which is in direct contradiction to the idea of the atom. Avogadro solved the difficulty by assuming that the smallest particles of matter existing as free entities in a gas were not simple atoms but small groups of atoms associated to form these individual particles which he termed *molecules.* Each individual molecule will possess all the properties characteristic of a mass of the same matter, be it gas, liquid, or solid.

Avogadro's hypothesis states that "Equal volumes of gases under the same conditions of temperature and pressure contain an equal number of molecules."

Complex Nature of Gaseous Molecules.—It is important to show that the molecules of most of the elementary gases contain *at least* two atoms, and the reasoning leading to this conclusion in the case of hydrogen and oxygen may be taken as an illustration. It can be shown experimentally that 2 volumes of hydrogen combine with 1 volume of oxygen to form 2 volumes of water (as gas), or—

Hydrogen	+	Hydrogen	+	Oxygen	=	Water
1 volume		1 volume		1 volume		2 volumes.

According to Avogadro these equal volumes contain the same number of molecules—it matters not what the actual number is, so that it may be assumed to be 1000 or any number, hence :—

Hydrogen	+	Hydrogen	+	Oxygen	=	Water
1000 mols.		1000 mols.		1000 mols.		2000 mols.

Each molecule of the water must contain 2 volumes of hydrogen and 1 volume of oxygen, otherwise it would not be water. In 2000 molecules of water there must then be 2000 *atoms* of oxygen, but we see that there are only 1000 oxygen *molecules,* therefore each oxygen molecule must contain 2 atoms. By a similar course of reasoning each hydrogen molecule contains 2 atoms.

The molecule then is an aggregate of the constituent atoms of the elements which go to form it—in the case of the elements the atoms are of the same kind ; in the case of compounds they are of different kinds. Any action which lends to the breaking down of the molecule with rearrangement of the atoms produces a chemical change.

The molecule is defined as the smallest particle of an element or compound which can exist in the free state, and which has the same composition as any larger mass of the substance.

The number of atoms in the molecule of a substance which is not chemically decomposed is largely a function of temperature, and since changes of temperature often result in change of physical state, from solid to the liquid, or liquid to the gaseous, the atomic complexity of the molecule of the same element or compound is probably much greater in the liquid condition than in the gaseous and still more complex in the solid. Thus, when in a state of vapour just above the boiling point, the molecule of sulphur contains 8 atoms, at 860° C. only 2 atoms. Water, again, above its boiling point contains 2 atoms of hydrogen and 1 atom of oxygen in the molecule, but the molecules in liquid water, whilst the ratio of the hydrogen to the oxygen atoms remains unchanged, contain simple multiples of the above number of atoms.

Influence of Temperature and Pressure on Gases.—It has long been known that all true gases behave identically in respect to their change in volume under the influence of varying pressure or temperature, quite irrespective of the composition of the gas, there is therefore some physical condition common to all gases, which is fully in agreement with Avogadro's hypothesis.

Boyle (1662) showed that the volume of any gas varies inversely to the pressure ; thus doubling the pressure halves the volume, or reducing the pressure by one half doubles the volume. Many gases obey this law almost exactly, but some show considerable deviation under high pressures. This is due to the pressure having brought the gas near to its point of liquefaction, when the molecules are no longer inert towards each other, but exercise a force of attraction which acts in the same direction as the pressure, so that near the point of liquefaction the decrease in volume is more rapid.

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

This temperature of $-273°$ C. is therefore taken as into *absolute zero*. A gas at 0° C. will therefore be at 273 on the absolute scale, or generally to arrive at the absolute temperature

273 must be added to each degree Centigrade. 10° C. will therefore equal 283 absolute, and $-10°$ C. will equal 263 absolute.

From a knowledge of these facts the volume of any gas under any conditions of temperature and pressure may be calculated. For change of temperature, let

$$\left.\begin{array}{ll} v & = \text{old volume} \\ v^1 & = \text{new volume} \\ t & = \text{old temperature} \\ t^1 & = \text{new temperature} \end{array}\right\} \text{ then } v^1 = \frac{v\,(273 + t^1).}{(273 + t)}$$

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

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

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

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

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

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

where—

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

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

A table which greatly facilitates such calculations will be found in the Appendix.

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

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

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

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

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

Atomic and Molecular Weight.—From the considerations which led Dalton to formulate the atomic theory it follows that the atom of every different element must have a definite weight, but it is impossible to ascertain this, and it is really immaterial ; all that is requisite is a knowledge of the relative weights of the atoms, for which purpose they must be all referred to that of one element chosen as a standard.

Hydrogen, being the lightest element known, was assumed to be unity, and all other atomic weights referred to this standard. In the large majority of cases the atomic weight of an element can be arrived at only by the study of a number of its compounds. Hydrogen, however, forms directly very few compounds with the elements generally, whilst the oxygen compounds are very numerous and easily prepared in a state of purity. Oxygen, therefore, is a much more convenient standard of reference, and is now universally agreed upon as the basis. Oxygen is actually 15·88 times as heavy as hydrogen, but a whole number being essential for the purpose, and the choice of the actual numerical value of the standard purely arbitrary, it is agreed to take oxygen $= 16$. On this basis hydrogen is 1·008.

Atomic and Molecular Weights from Density.—Assuming Avogadro's hypothesis to be correct then the weights of equal volumes of gases under the same conditions of temperature and pressure will be the relative weights of the individual molecules, and further, with elementary gases containing the same number of atoms to the molecule (which can be safely deduced from chemical behaviour, as already shown, and is confirmed by certain physical properties), this relative weight will likewise be the relative weight of the atoms themselves.

The specific gravity of a permanent gas or a volatile substance which can be converted into vapour may then be compared with that of some standard gas, assuming, in the case of hydrogen, that its value is unity, or in the case of oxygen a value of 16.

These relative specific gravities or *vapour densities* may be determined in the case of permanent gases by directly weighing a flask filled with the gas, and knowing, from the accurate determinations available, the weight which the same volume of hydrogen (or oxygen) would have under the same conditions, the comparison is at once made.

To determine the vapour density of a volatile liquid or solid, the method of Victor Meyer is most generally useful, an important point in its favour being that the temperature at which the substance is volatilised is of no importance to the result. All that is required is a constant temperature. The apparatus consists of a long glass tube (A) terminating at the bottom in a cylindrical bulb; near the top is a gas delivery tube (B), and attached to the top by a piece of wide indiarubber tubing is a small tube (C). The apparatus is set up as illustrated, the vapourising tube A being surrounded by the wider tube with a bulb at the bottom, the liquid in which boils at least several degrees above the vapourising point of the substance under examination. The side tube dips under water, and a graduated tube (E) is provided for collecting the air driven from the apparatus.

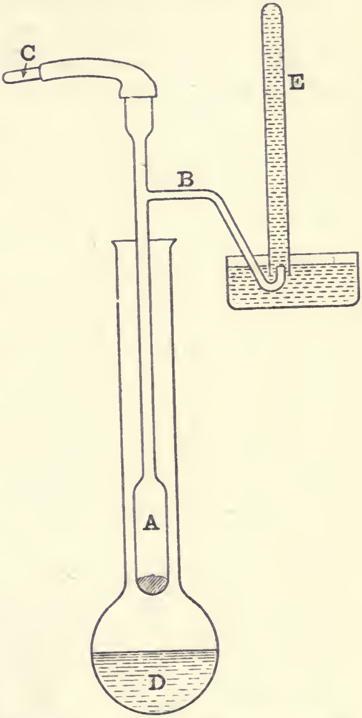


FIG 5.—Victor Meyer's determination of vapour density.

A known weight of the substance under examination is carried in a small bulb or tube slipped into the tube C, and the whole apparatus heated by boiling the liquid in D. When bubbles cease to escape from B the apparatus is at constant temperature. The measuring tube E is now brought over B, and C raised to shoot the bulb containing the substance down to the bottom of A; its fall being broken by some loose asbestos. The substance vapourises at once and displaces a volume of air proportional to the amount of the vapour, this volume of air being collected in E at the room temperature. By sinking E into a deep cylinder of water the volume of air collected is measured at atmospheric pressure and temperature, and when corrected to *dry* gas at 0° and 760 mm. pressure is obviously equal to the volume of vapour which would be set free from x grams of the substance, if this vapour could be cooled to standard conditions without condensation. The weight of the same volume of hydrogen (or oxygen) under these same conditions is easily arrived at, and hence the weight of the vapour under examination relative to that of the standard gas ascertained.

So far the comparison has been that of the relative weight of the molecule of the element or compound with that of the hydrogen or oxygen molecule. The molecule, however, is composed of atoms, and the molecular weight must necessarily be the sum of the relative weights of the atoms which go to form it. Since the molecule of hydrogen (or oxygen) has been shown to contain two atoms it follows that, for the sum of the atomic weights to equal the molecular weight, *the molecular weight must be twice the density.*

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

In the same way 2 grams of hydrogen occupy 2 (11·16) litres, or 22·32 litres, and this is taken as the imaginary molecule volume for gaseous elements and compounds, hence—

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

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

The molecular weight of any gas may therefore be defined as that weight of the gas in grams which will occupy 22·32 *litres at* 0° *C. and* 760 *mm. pressure.*

The above simple rules are of great service in making calculations involving gas volumes, for having written the correct equation for any reaction instead of putting in molecular weights, we can greatly simplify things by putting in molecular volumes (see p. 31).

Atomic Weight of Non-Volatile Elements.—Few of the elements can actually be gasified, therefore other methods than finding the density must be adopted. Many, however, give gaseous compounds or compounds easily gasified, and since the molecular weight is the sum of the atomic weights, by determining the composition and molecular weight of a number of these compounds it is possible to find the smallest weight of the particular element ever present in a molecule and this will be the atomic weight. Carbon, for example, is non-volatile except at the temperature of the electric arc, yet it forms numerous gaseous compounds, of which the following four with hydrogen may be selected, the composition being determined by analysis, and the molecular weight from the density—

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

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

Determination of Molecular Weight by other Methods.—The application of the method of vapour densities is confined obviously to such substances as are gaseous or may be converted readily into gases without decomposition, and hence is limited to a comparatively small number of substances. It is found, however, that a quantitative relationship exists between the amount of substance dissolved and its effect on the properties of the solvent in which it is held in solution.

It can be shown that in dilute solutions the molecules of a dissolved substance behave in exactly the same manner in relation to Boyle's Law and Charles' Law, as if they were gaseous molecules occupying a space equal in volume to that of the solvent, and hence Avogadro's hypothesis is equally applicable to dilute solutions. The liquid pressures (osmotic pressures) for solutions containing the same number of molecules in a given volume are the same, just as the gaseous pressure is the same when the number of molecules is identical, under the same conditions of temperature.

The measurement of these liquid pressures is difficult, but the influence which the dissolved substance also exerts on the raising of the boiling-point of the solvent (through lowering its vapour pressure) and the lowering of the freezing-point of the solvent, can be correlated strictly with the osmotic pressure. It is then true to state that, in dilute solutions, *an equal number of molecules of different substances when dissolved in a given volume of the same solvent raise the boiling-point equally, or lower the freezing-point equally:* conversely, the rise of boiling-point (or depression of freezing-point) is inversely proportional to the molecular weight of the dissolved substances. Measurements of the alteration in these physical properties are easily made, and afford a ready means of ascertaining the molecular weight of a large number of compounds: it may be compounds in water or other solvents, or one metal dissolved in another which acts as a solvent; the methods are of wide application.

The degree to which the boiling-point of a given solvent is raised or its freezing-point lowered by the molecular weight in grams of a substance of known composition for a given concentration of the solution is easily determined practically. From this fixed value for each solvent the unknown molecular weight of another substance can be found, for when the amount present in the solution produces exactly the same effect as by the gram molecule of the known substance, it is because the molecular weight in grams of the unknown substance is present.

Then, if A represents the rise in boiling-point, or depression in freezing-point, produced in a solution of 1 per cent. concentration, and M the molecular weight, $A M = \text{constant}$. This constant is characteristic for the particular solvent, and is known as the Molecular Elevation, in the case of boiling-point, and Molecular Depression, with freezing-points. For water, the elevation is 5·2 : the depression 19. For benzene, the elevation is 26·7 : the depression 53.

To determine the unknown molecular weight of a substance, a suitable solvent is selected so that concentrations between 1 and 10 per cent. can be attained, a series of determinations of the boiling-point (or freezing-point) for solutions of different concentrations made, and by exterpolation the effect with 1 per cent. concentration arrived at. The only unknown to the equation —$A M = \text{constant}$—is M.

An important point is that the above statements hold only for solutions which are non-conductors of electricity (non-electrolytes). Salts in solution which conduct electricity (electrolytes) give at great dilution multiples of the normal elevation or depression. It can be shown that this is due to dissociation, just as the vapour density determinations are abnormal with substances undergoing dissociation when heated.

Equivalents and Atomic Weights.—By the analysis of a compound it is only possible to find the ratio in which elements entering into it are present, and this ratio is said to be the equivalent of the elements in relation to each other. The true equivalent, which serves as a means of comparison between each and every element, can be obtained only when the results are all referred to some one element as the standard. One of the easiest ways of finding the equivalent is to analyse a number of oxygen compounds and, as previously mentioned, because of the much more general formation of oxygen compounds than of hydrogen compounds, the former has been universally agreed upon as the standard instead of hydrogen. The standard must, for convenience, be a whole number, and since, in water, oxygen is to hydrogen as 8 to 1 by weight, the equivalents of all elements are referred to oxygen as 8.

The equivalent bears a simple numerical relation to the Atomic Weight, but whilst the atomic weight must be fixed and unalterable for an element it is found that many elements may have more than one equivalent, which is evidently due to the same elements uniting in more than one proportion. Iron, for example, forms two oxides, having respectively the following composition :—

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

Their equivalents are therefore—

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

The atomic weight of iron must be some simple multiple of these equivalents, and this multiple may be arrived at by a determination of the specific heat of the metal.

Let the amount of heat required to raise a unit weight of water through 1° C. be taken as unity, then the amount of heat required to heat the same weight of other substances through 1° C. will be less than 1, and this fraction is called the *specific heat.*

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

$$\text{Atomic weight} \times \text{Specific heat} = \text{Constant (Atomic heat).}$$

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

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

This number is only approximately true, but it enables the atomic weight to be accurately determined, having first found the equivalent. Thus in the case of iron, the specific heat is found to be 0·1138, and $\frac{6\cdot4}{0\cdot1138} = 56\cdot2$. This is practically 2×28, and $3 \times 18\cdot66$, and hence 56 is taken as the atomic weight of iron.

Valency or Atomicity.—It has already been shown that an element may have more than one equivalent when compared with another, and since the atoms are indivisible in chemical reactions, this must be due to the number of atoms of a given element in different compounds of the same elements being liable to variation, or the combining power of the atoms of the same element is not constant. This combining power is known as the *valency* or *atomicity*, and the relative valency of different elements can be referred to some standard element which shows a minimum value, the most convenient being hydrogen. Hydrogen, for example, combines with chlorine, atom for atom, to form hydrochloric acid ; with oxygen, 2 atoms to 1 atom, to form water ; with nitrogen, 3 atoms to 1 atom, to form ammonia ; with carbon, 4 atoms to 1 atom, to form methane. The valency or atom-fixing power of these last three elements in relation to hydrogen is therefore 2, 3 and 4 respectively, which is expressed by terming them divalent, trivalent and quadrivalent.

The valency for the same element will vary with the other element or elements with which it is associated ; thus chlorine, bromine and iodine are all monovalent when combined with hydrogen ; amongst themselves they are multivalent ; for example, one atom of iodine combines with both three atoms of and five atoms of chlorine. Again, the conditions under which a reaction is carried out will influence the valency of two elements in relation to one another.

Symbols and Formulæ.—In order to express in a simple and concise manner the constitution of compounds and the chemical changes in which they are involved, a well-recognised system of symbols is in use, and knowing from analysis and molecular weight determinations the number of atoms in the molecule, the composition may be expressed by formulæ.

For the symbol the first letter of the name of the element may be selected, thus C represents carbon, but as there are other elements whose name commences with C, two letters must be selected—thus, Cl, for chlorine, Ca for calcium, Co for cobalt, Cu for copper, derived from its Latin name "cuprum." The symbol does not merely stand for an indefinite amount of the element, but invariably means also the atomic proportion by weight present. A complete list of symbols and atomic weights will be found in the Appendix.

A formula includes the symbols of all the elements entering into a compound and moreover indicates the actual number of atoms of each which are present. Thus sodium chloride is written NaCl, because the molecule contains an atom of sodium, or 23 parts by weight, combined with one atom of chlorine, or 35·5 parts by weight, to produce $23 + 35{\cdot}5 = 58{\cdot}5$ parts by weight of sodium chloride. When more than one atom of the same element occurs it would obviously be inconvenient to repeat the same symbol, so that a numeral placed after a symbol indicates the number of atoms of that element present, for example H_2SO_4, $KClO_3$.

In a large number of chemical compounds, groups of elements in well-defined proportions behave as single entities, that is, they pass into or out of combination with other elements as a whole. For example, all ammonium compounds contain the group (NH_4); sulphuric acid and all sulphates the group (SO_4). The number of these groups present is indicated by a number placed outside the bracket. Such groups are known as "*radicles,*" and chemical compounds are formed by the association of elements, or elements and radicles, or radicles alone, thus NaCl; $Na_2(SO_4)$; $(NH_4)_2SO_4$.

From what has been said on valency it will be seen that the number of atoms of each element (or radicles) of each kind will be dependent on the atom–fixing power of each. There are good grounds for stating that this is dependent upon overplus electrical charges in the atoms, or radicles, and that chemical combination is due to atoms with free positive charges (hydrogen and the metals) satisfying other elements or groups with free negative charges (non-metals, acid radicles, etc.). From theoretical considerations it should be possible to write a formula for any combination between a positively charged atom or radicle and a negative element or group if the valency is known. Expressed as electrical charges these must balance, so that for ferrous sulphate, the iron being divalent, and the (SO_4) radicle also divalent, the correct formulæ would be $Fe^{++}(SO_4)^{--}$, but it is customary to express this as the simple formula $FeSO_4$. Owing to the varying valency for the same element and to the fact that in many compounds there are unsatisfied electrical charges, giving unsaturated compounds, formulæ can only be correctly written to express the facts actually determined by practical methods.

Equations.—If the composition of the substances involved in a chemical reaction is known and also that of the resulting products, the change can be expressed by the use of symbols in the form of an equation. Thus sulphuric acid and zinc react, forming hydrogen gas and zinc sulphate, which may be expressed as follows :—

$$\begin{array}{ccccccc}
\text{Zinc.} & & \text{Sulphuric acid.} & & \text{Zinc sulphate.} & & \text{Hydrogen.} \\
Zn & + & H_2SO_4 & = & ZnSO_4 & + & H_2 \\
 & & \underbrace{2+32+64} & & \underbrace{65+32+64} & & \\
65 & + & 98 & = & 161 & + & 2 \\
\text{Parts by weight.} & & \text{Parts by weight.} & & \text{Parts by weight.} & & \text{Parts by weight.}
\end{array}$$

Reference has already been made (p. 25) to the fact that the atomic weight in grams of any elementary gas occupies 11·16 litres, and the molecular weight in grams of any gas, elementary or compound, 22·32 litres. Clearly, then, in the above equation, if grams are the units of weight, 65 grams of zinc will produce 2 grams of hydrogen, which at 0° C. and 760 mm. pressure will occupy 22·32 litres—enabling a simple calculation of the theoretical gas yield for any weight of zinc to be made. A further illustration of this important application of gaseous volumes in simplifying calculations may be given in the case of the decomposition of guncotton—

$$2C_6H_7O_2(NO_3)_3 = 9CO + 3CO_2 + 7H_2O + 3N_2$$
$$2[72+7+32+(14+48)_3] = 9(22{\cdot}32)+3(22{\cdot}32)+7(22{\cdot}32)+3(22{\cdot}32)$$
$$\text{or } 549 \text{ grams} = 491 \text{ litres of gaseous products.}$$

Since in any chemical change no loss of matter occurs and there is no change of mass, the weights of the bodies involved in any reaction must exactly equal the weights of the products of that reaction. It does not follow, however, that an equation in which the weights are arithmetically correct is also chemically correct, for in order to write a chemical reaction in this way, such a reaction must actually take place, and the composition of the resulting products must also be known. Further, it does not follow that, because an equation can be written, the reaction will take place. It is the invariable custom to put the formulæ of the reacting substance on the left and those for the products on the right, having the sign = between them ; this latter is better read as " produces " rather than as " equals."

Reversible Reactions and Equilibrium.—Many chemical reactions proceed in one direction under certain conditions and the reverse direction in others. Thus hydrogen passed over heated iron oxide reduces it, forming water and iron ; conversely steam passed over hot iron produces iron oxide and hydrogen. Such reactions may be conveniently written—

$$3Fe + 4H_2O \rightleftarrows Fe_3O_4 + H_2$$

Given these four bodies in a closed space at a given temperature, there being an unlimited quantity of iron, then the proportion of H_2O, Fe_3O_4 and H_2 will become constant when the reaction → proceeds at such a rate that the reaction ← just balances it, in other words, equilibrium is established. Increase the temperature and the reaction → accelerates, the reaction ← decreasing until again equilibrium is attained, when there will be a greater proportion of Fe_3O_4 and H_2.

Imagine now the temperature constant and a given ratio of H_2O, Fe_3O_4 and H_2 attained. If the hydrogen is removed the action ← is correspondingly diminished and → increased so that ultimately all the steam would be decomposed. Such equilibrum between two reactions is of great practical importance, and the conditions governing the direction of the reactions have to be carefully studied.

Empirical and Molecular Formulæ.—From the mere analysis of a compound only the relative number of atoms present in a given weight can be ascertained and not the actual number in the molecule. A formula which expresses in the simplest form the number of atoms present is an *empirical* one. For example, carbon forms with hydrogen two compounds, which on analysis give the following percentage composition :—

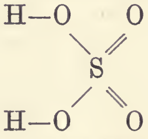
Carbon	92·3 per cent.
Hydrogen	7·7 ,,

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

On taking the vapour density of these compounds one is found to be 13 and the other 39 ; their molecular weights must be respectively 26 and 78. Consideration will show that in the first this is only possible when there are two atoms of carbon and two atoms of hydrogen in the molecule, since $[C_2=24 \text{ and } H_2=2]=26$, and the formula is therefore C_2H_2. In the second compound $72+6=78$, and the formula is C_6H_6. Such a formula is termed a *molecular formula,* and it signifies the actual number of atoms in the molecule.

Graphic and Constitutional Formulæ.—From the chemical behaviour and the valency of the constituent atoms in a compound formulæ can be written which express in a graphic manner the relative arrangement of the atoms in the molecule. A word of warning is necessary as to the interpretation of such formulæ, for they cannot represent the actual conditions existing in a molecule where the atoms are in constant motion, but such a conventional method of expressing the facts is of great service.

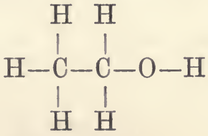
For each atom of hydrogen with which an element is capable of entering into combination a "dash" is attached to the symbol: thus, carbon is a tetrad, uniting with four atoms of hydrogen, which may be expressed $-\overset{|}{\underset{|}{C}}-$ or $C\equiv$. If such a formula for sulphuric acid (H_2SO_4)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



Such formulæ are termed "*graphic.*"

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

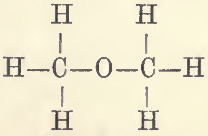
Graphic formulæ which express these differences may be written thus—



$$\begin{array}{ccccccccc} & & H & & H & & & & \\ & & | & & | & & & & \\ H & - & C & - & C & - & O & - & H \\ & & | & & | & & & & \\ & & H & & H & & & & \end{array}$$

Ethyl alcohol.

and



$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & | & & & & | & & \\ H & - & C & - & O & - & C & - & H \\ & & | & & & & | & & \\ & & H & & & & H & & \end{array}$$

Methyl ether.

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

$$CH_3.CH_2.OH \qquad \text{and} \qquad CH_3.O.CH_3$$

giving what is known as a *constitutional formula*.

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

Thermo-Chemistry.—When a chemical change takes place it is accompanied by the absorption or evolution of energy in some form or other, generally that of heat. The measurement of this heat is made in *Calories,* the calorie being defined as the amount of heat required to raise 1 kilogram of water 1° C. A smaller unit, the small calorie (written cal.), is one thousandth part of this, *i.e.* the heat required to raise 1 gram of water 1° C.

When a compound is formed from its elements heat is either evolved (*exothermic reaction*) or absorbed (*endothermic reaction*), and the *heat of formation* is the number of Calories involved when the molecular weight in grams of the compound is formed. Thus, in the following equations :—

$$\begin{array}{ccccccc} H_2 & + & O & = & H_2O\ (\text{gas}) & + & 58\ \text{Cals.} \\ \text{2 grams.} & & \text{16 grams.} & & \text{18 grams.} & & \\ C_2 & + & H_2 & = & C_2H_2 & - & 58\ \text{Cals.} \\ \text{24 grams.} & & \text{2 grams.} & & \text{26 grams.} & & \end{array}$$

when 18 grams of water are formed by the direct union of its elements 58 Calories are evolved ; when 26 grams of acetylene are similarly formed 58 Cals. have to be provided.

The *heat of decomposition* of a compound is equal to the heat of formation, but is of opposite sign. Thus to break down 18 grams of water into its elements 58 Cals., or the equivalent in some other form of energy, would have to be furnished. The acetylene, on the other hand, would, when decomposition was once initiated, evolve heat, and so decomposition would proceed through the gas without external assistance.

The heat generated by the reaction of substances one on the other is likewise constant for a given mass of the reacting bodies, and this is referred to as the *heat of reaction.* The heat involved in any reaction is independent of the mode in which the final result is arrived at, or the amount of heat evolved in any completed reaction is the same whether the final result is arrived at in one stage or by a succession of intermediate reactions, thus :—

$$\begin{array}{ccccccc} C & + & O_2 & = & CO_2 & + & 97{\cdot}6 \text{ Cals.} \\ \text{12 grams} & & \text{32 grams} & & \text{44 grams} & & \end{array}$$

$$\left.\begin{array}{ccccccc} C & + & O & = & CO & + & 29{\cdot}6 \text{ Cals.} \\ \text{12 grams} & & \text{16 grams} & & \text{28 grams} & & \\ CO & + & O & = & CO_2 & + & 68 \text{ Cals.} \\ \text{28 grams} & & \text{16 grams} & & \text{44 grams} & & \end{array}\right\} 97{\cdot}6$$

In all cases where consideration is given to the thermal changes accompanying chemical changes it is necessary also to specify the physical state of the substances involved ; in other words, since heat is expended in melting a solid or gasifying a liquid, which heat is again liberated on the liquid solidifying or the gas liquefying, the total amount of heat measured for the same reaction will vary if the product is in one case liquid and in another case gaseous. Similarly, when substances undergo solution in a solvent thermal changes are also noted. Illustrations of such reactions are given below :—

$$H_2 + O = H_2O \text{ (gas at } 100°) + 59{\cdot}4 \text{ Cals.}$$
$$H_2 + O = H_2O \text{ (liq. at } 100°) + 69 \text{ Cals.}$$
$$H_2 + O = H_2O \text{ (liq. at } 0°) + 71 \text{ Cals.}$$

The difference, $69 - 59{\cdot}4 = 9{\cdot}6$ Cals., represents the heat evolved when 18 grams of water vapour at 100° become liquid at the same temperature. On cooling to 0° further heat is given out, represented by $71 - 59{\cdot}4 = 11{\cdot}6$ Cals.

$$\begin{array}{ccccccccc} NaHO & + & HCl & = & NaCl & + & H_2O & + & 31 \text{ Cals.} \\ \text{Sodium} & & \text{Hydrochloric} & & \text{Sodium} & & \text{Water} & & \\ \text{hydroxide.} & & \text{acid.} & & \text{chloride.} & & & & \\ \text{(Solution.)} & & \text{(Gas.)} & & \text{(Solution.)} & & & & \end{array}$$

$$\begin{array}{ccccccccc} NaHO & + & HCl & = & NaCl & + & H_2O & + & 13{\cdot}7 \text{ Cals.} \\ \text{(Solution.)} & & \text{(Solution.)} & & \text{(Solution.)} & & & & \end{array}$$

The first of the above equations shows a higher heat evolution, because it includes the heat of solution of the HCl gas in water which equals $31 - 13{\cdot}7 = 17{\cdot}3$ Cals.

The heat evolved by the combustion of carbon, hydrocarbon gases, &c., with the production of carbon dioxide and water, is termed the *heat of combustion*. It follows that in such a fuel as charcoal the heat of combustion for 12 grams of carbon is also the heat of formation of 44 grams of carbon dioxide.

The character of the heat changes in any chemical reaction has a great influence on the properties of the products, and on the probability of a given reaction taking place. In general, reactions which result in heat evolution (exothermic) take place without external heating when once initiated, whilst endothermic reactions require assistance from outside the system. Exothermic substances are stable because as much heat must be imparted to the molecule to decompose it as was liberated in its formation. Endothermic substances are in general unstable, and hence are always liable to complete decomposition when once a change involving the liberation of heat at any point is set up. If the products of such a decomposition are gaseous, and at the same time there is considerable heat evolution, all the phenomena of explosion are noted. It does not follow that all explosives are endothermic substances. If the heat evolved during their formation is small (that is, they may be exothermic), and it is possible for a rearrangement of the constituent elements to form compounds, some of which are gaseous, with great evolution of heat, an explosive result will follow, the heat liberated by the secondary reactions being more than sufficient to carry on the primary reaction of decomposition. It is really the balance of the thermal reactions which will determine the matter.

CHAPTER III

HYDROGEN

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

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

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

Preparation.—The gas is most conveniently prepared for experimental purposes by acting upon dilute sulphuric acid with the metal zinc: for this purpose zinc, which has been granulated by pouring it into water whilst molten, thus increasing the surface, is placed in the two-necked bottle (Fig. 6), and water enough to cover the metal is then poured in, sulphuric acid being added a few drops at a time by means of the thistle funnel which passes, gas-tight, through a cork fitting the neck of the bottle, and terminates below the surface of the liquid. The addition of the acid causes an immediate evolution of gas, which is conducted by the leading tube below the surface of water in the pneumatic trough where it can be collected in cylinders by the displacement of water. The first portions of gas which escape must not be collected, being an explosive mixture of hydrogen and the air which originally filled the generating bottle.

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

$$\underset{\text{Zinc}}{Zn} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Zinc sulphate}}{ZnSO_4} + \underset{\text{Hydrogen}}{H_2}$$

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

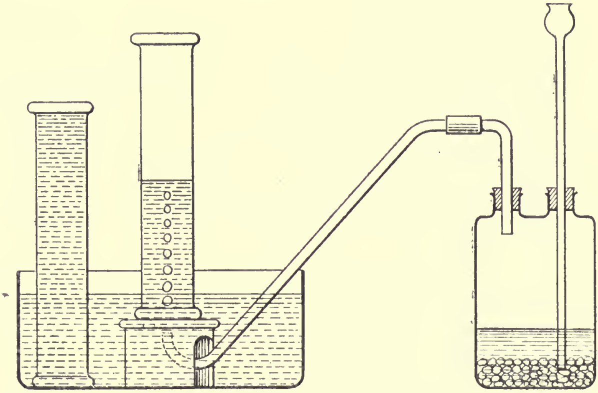


FIG. 6.—Preparation of hydrogen.

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

and when used on a commercial scale the triferric tetroxide can then be reduced to spongy iron once more by passing a stream of water gas (see Gaseous Fuels) over the red hot oxide.

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

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

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

$$\begin{array}{ccccccc} \text{Sodium} & & \text{Water} & & \text{Sodium hydroxide} & & \text{Hydrogen} \\ Na_2 & + & 2(H_2O) & = & 2(NaHO) & + & H_2 \end{array}$$

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

$$\begin{array}{ccccccc} \text{Potassium} & & \text{Water} & & \text{Potassium hydroxide} & & \text{Hydrogen} \\ K_2 & + & 2(H_2O) & = & 2(KHO) & + & H_2 \end{array}$$

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

$$\begin{array}{ccccccc} \text{Sodium hydroxide} & & \text{Sodium} & & \text{Sodium oxide} & & \text{Hydrogen} \\ 2(NaHO) & + & Na_2 & = & 2(Na_2O) & + & H_2 \end{array}$$

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

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

In burning it produces a greater heat than the same weight of any other known substance—1 lb. of hydrogen in combining with 8 lbs. of oxygen giving out sufficient heat to raise 34,462 lbs. of water 1° C., but as will be seen later, the enormous volume occupied by the pound of gas makes it by no means an effective fuel in the gaseous state. When, however, an intense temperature is required the combustion of hydrogen with oxygen in the oxy-hydrogen blowpipe enables a temperature of 2200° C. to be attained.

Up to the spring of 1895 hydrogen resisted all attempts to convert it into a liquid, but Professor Olszewski and Sir James Dewar have independently succeeded in liquefying it. At atmospheric pressures liquid hydrogen has a boiling point of —253°, and Dewar has reduced liquid hydrogen to the solid state by the cold produced by its own evaporation.

Hydrogen is the lightest body known, being 14·47 times lighter than air, hence up to the end of the nineteenth century it was taken as the standard with which the weight of all other gases were compared, and its atomic weight was called unity, but it having been shown that the ratio of weight between oxygen and hydrogen was not exactly as 16:1 but 16 : 1·008, it was considered more convenient to adopt oxygen = 16 as the standard on account of the larger number of compounds it forms with other elements and the atomic weight of hydrogen was altered to 1·008.

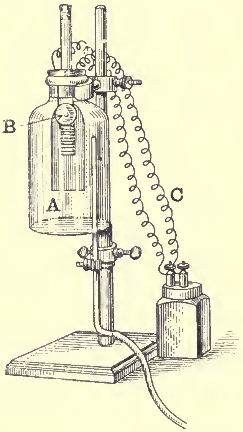


Fig. 7.—Electric bell in hydrogen.

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

This may be shown by mounting an electric bell (B, Fig. 7) in an open gas jar (A) and while it is ringing, passing in hydrogen gas by the tube (C) from a reservoir of compressed gas. Hydrogen, being so much lighter than air, will collect at the top of the jar and surround the bell, causing the sound to almost entirely disappear; and if now the supply of gas is cut off, and the cork of the exit tube be removed, the hydrogen will escape and the original intensity of the sound be restored.

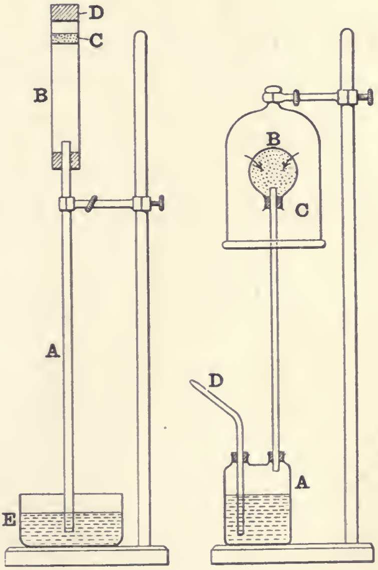
Temperature has an effect upon the solubility of gases; less being dissolved as the temperature rises, but until lately it was supposed that 100 volumes of water dissolved 1·93 volumes of hydrogen without reference to temperature; this, however, is a mistake, hydrogen behaving in the same way as other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

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

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

If a tube (A, Fig. 8) be connected with one of wider bore (B), which is closed an inch from the top by a porous plug of plaster of Paris (C) and closed above the plug by an india-rubber cork (D), diffusion through the plug may be shown by filling the tube with hydrogen, standing it in some coloured liquid (E) and removing the cork (D).

At once a rise of the liquid in the tube (A) takes place, showing that the hydrogen gas is diffusing out into the air faster than the air diffuses into the hydrogen, with the result that a reduction of pressure takes place in A and B, and water in



Figs. 8 and 9.—Diffusion of hydrogen.

consequence rises in the tube A. The same thing may be shown in the reverse way by the apparatus shown in Fig. 9. A two-necked bottle (A) is fitted with a tube ending in a porous earthenware vessel (B). Over this a bell jar (C) containing hydrogen gas is placed, and the hydrogen diffusing in faster than the air can diffuse out, causes an increase of pressure on the surface of the liquid in A, and drives some of it out from the jet (D).

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

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

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

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

A regular balloon corps is now attached to the army, and the hydrogen is carried compressed in steel cylinders on a waggon constructed for the purpose ; and the balloon when required is filled from these, and is sent up with a rope attached to it, so that when observations have been made of the enemy's whereabouts it can be again drawn down, emptied, and packed away. For ordinary purposes balloons are made of varnished silk ; but the leakage from this would be too great if hydrogen were used, and the military balloons are now all made of a double and sometimes treble thickness of gold-beater's skin, whilst in the large dirigible balloons thin india-rubber is often employed.

The hydrogen used for balloons has to be as pure as possible in order to obtain the highest lifting efficiency. Chemically pure hydrogen has a specific gravity of 0·070, which gives a buoyancy of 1203 grams per cubic meter, but moisture and the admixture of gaseous impurities, to which hydrogen is specially liable owing to diffusion, rapidly reduce this.

If the gas were made from a metal, such as zinc, and dilute sulphuric acid it could be obtained of fair purity, but this process has been abandoned at the Service factory owing to the gas often containing traces of acid, which act injuriously on the fabric and fittings of the balloon.

A process which has been employed in field plant is to act upon powdered silicon with a solution of sodium hydroxide—

$$\overset{\text{Silicon}}{\mathrm{Si}} + \overset{\text{Sodium hydroxide}}{4\mathrm{NaHO}} = \overset{\text{Sodium silicate}}{\mathrm{Na_4SiO_4}} + \overset{\text{Hydrogen}}{2\mathrm{H_2}}$$

This yields a very pure gas, but is expensive.

The action of aluminium on water or alkaline solutions has frequently been proposed. Under ordinary conditions aluminium does not act on water owing to a thin but very adherent film of oxide on the surface of the metal, but if a little mercury chloride is added to the water the oxide is reduced, and the mercury forms an amalgam with aluminium upon which the water acts, the generation of the gas being accelerated by the presence of an alkali.

The usual method, however, is to obtain the hydrogen by the electrolytic decomposition of water, to which an alkali has been added to make it a conductor; further details of the process will be found on p. 59. This is the method usually employed in this country, and electrolytic hydrogen having a lifting value of 71 pounds per 1000 cubic feet can be obtained. This enables a balloon of only 5000 cubic feet capacity to be used, which will lift the car containing an ordinary-sized man with the necessary apparatus, whilst the gas for filling it is contained in forty tubes weighing half a ton.

The latest process for making the gas is that devised by Linde, Frank and Caro, in which water gas (see Fuel) is produced by passing steam through a bed of incandescent carbon, and the mixture of impure carbon monoxide and hydrogen so formed is then subjected to pressure in a vessel cooled by liquid air, when the impurities being liquefied the hydrogen is left about 97 per cent. pure: this is then further purified, and hydrogen 99·2 per cent. pure is obtained, having a specific gravity of 0·079, and a buoyancy of 1190 grams per cubic meter.

It is claimed that by this process the pure gas can be made at a cost of 2*d*. per cubic meter (35·3 cubic feet).

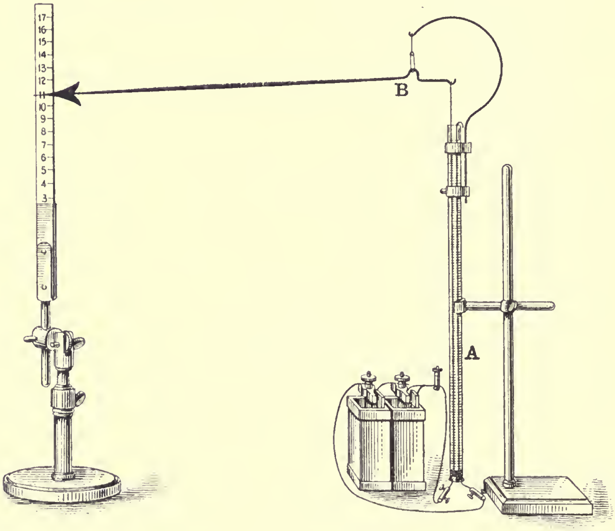


Fig. 10.—Palladium wire in dilute acid.

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

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

If a palladium wire, 2 ft. 6 in. long, be so arranged (Fig. 10) that it forms the negative pole in a galvanic circuit, with a large glass tube as a decomposing cell (A) and a platinum wire as the positive pole, on decomposing acidulated water hydrogen gas will be evolved on the surface of the palladium, and being occluded will cause an increase in length of the wire, which will be made visible by the lever arm (B).

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

CHAPTER IV

CHEMISTRY OF THE GALVANIC BATTERY

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

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

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

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

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

If the thermal conditions existing in the interior of the cell are examined, it is found that although heat is given off by the solution of zinc in sulphuric acid under ordinary conditions, yet, when the zinc is dissolved in contact with a copper plate and a galvanic current is produced, the generation of heat diminishes in the cell, although the zinc dissolves more rapidly, that is, the heat which is generated by the chemical action is converted into another form of energy, viz. electricity, and will again be reconverted into heat wherever resistance occurs.

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

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

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

The hydrogen acts in three ways in weakening the current: (1) being a non-conductor of electricity, the more hydrogen there is present, the more will the available surface of the copper or platinum be reduced in size, and therefore the smaller will be the acting surface; (2) the freshly liberated (nascent) hydrogen deposited on the surface of the copper being electro-positive to zinc, will set up a current in the reverse direction of the original one; (3) when much zinc sulphate is present in the solution, the nascent hydrogen tends to decompose it and a deposit of zinc is formed on the copper, so that we practically have two plates of zinc opposing each other instead of a plate of zinc and a plate of copper.

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

The theory of the solution of metals and polarisation is referred to on p. 58.

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

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

The current generated in a Daniell's cell is rarely as strong for the first few minutes as that generated by a single liquid cell, as the decomposition of the copper sulphate by the nascent hydrogen uses up a certain amount of chemical energy, and tends to create a current in the opposite direction, so that it is only the difference between the two forces that can be utilised as a current; the various forms of the Daniell cell are therefore used where a continuous but not very strong current is required.

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

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

Leclanché Cell.—In the "Leclanché" cell the copper plate is replaced by a block of dense carbon—the form used being that obtained from gas retorts, where the heat has caused some of the hydrocarbons present to be decomposed with deposition of carbon, the deposit being especially hard and dense; this carbon plate is surrounded with manganese dioxide (MnO_2), which is found native as the mineral dioxide "Pyrolusite," and this is rendered a better conductor of electricity, especially after it has been in use by mixing with it small pieces of carbon. The carbon plate, surrounded by the mixture of pyrolusite and carbon, is now placed in a porous vessel or bag made of porous material such as canvas or flannel, this standing in an outer cell containing a saturated solution of sal-ammoniac or ammonium chloride, in which the zinc plate is immersed.

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

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

The manganese dioxide gives up its oxygen so slowly that when short circuited for a time it acts almost like a single liquid cell, and the carbon is quickly polarised, whilst zinc oxy-chloride and a compound of zinc, chlorine, and ammonia, having the formula ZnC_2l2NH_3, are formed, which quickly weaken the current.

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

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

For Service use, the Leclanché is made up in sets of six cells, called " Ship's firing battery," which is used for firing the guns ; three-cell boat batteries are used for firing outrigger torpedoes, and ten-cell batteries are used for firing submarine mines and countermines.

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

In the Leclanché cell (Fig. 11) A is the carbon plate on to which is cast the lead connection and binding screw (B); D is the mixture of pyrolusite and carbon surrounding the carbon plate; and E the zinc plate immersed in the saturated ammonium chloride solution (F), the fearnought partition being replaced by a porous cell in older forms, but in the most recent patterns no cell is employed, the pyrolusite-carbon mixture blocks being fitted on the carbon rod.

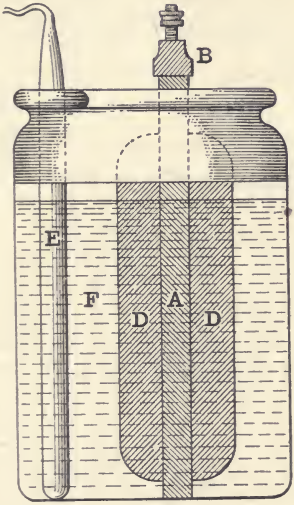


Fig. 11.—Leclanché cell.

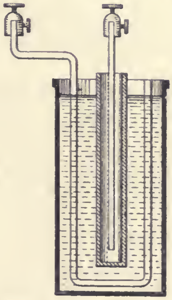


Fig. 12.—Grove cell.

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

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

A **U**-shaped zinc plate (Fig. 12) is immersed in dilute sulphuric acid contained in an ebonite or earthenware vessel, and inside the zinc is placed a porous earthenware pot containing strong nitric acid, in which is the platinum plate.

The zinc dissolves in the dilute sulphuric acid, forming zinc sulphate and hydrogen; and on the circuit being completed, the usual arrangement of the molecules takes place throughout the liquid, the molecule of hydrogen being liberated on the platinum plate, and in presence of the nitric acid which oxidises it forming water, whilst the acid is itself reduced with evolution of nitrous fumes. The reactions taking place may be represented as—

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

and

$$\begin{array}{ccccccc} \text{Hydrogen} & & \text{Nitric acid} & & \text{Water} & & \text{Nitrous acid} \\ H_2 & + & HNO_3 & = & H_2O & + & HNO_2 \end{array}$$

The nitrous acid becoming concentrated breaks up into—

$$\begin{array}{ccccc} \text{Nitrous acid} & & \text{Nitrogen trioxide} & & \text{Water} \\ 2(HNO_2) & = & N_2O_3 & + & H_2O \end{array}$$

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

$$\begin{array}{ccccc} \text{Nitrogen trioxide} & & \text{Oxygen} & & \text{Nitrogen tetroxide} \\ 2(N_2O_3) & + & O_2 & = & 4(NO_2) \end{array}$$

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

$$\begin{array}{ccccccc} \text{Nitric acid} & & \text{Hydrogen} & & \text{Water} & & \text{Nitrogen tetroxide} \\ 2(HNO_3) & + & H_2 & = & 2(H_2O) & + & 2NO_2 \end{array}$$

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

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

Bichromate Cell.—The Bichromate battery is a single liquid cell in which zinc is acted on by dilute sulphuric acid, and the hydrogen generated is oxidised to water by chromic acid, the negative element being formed by carbon plates.

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

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

$$\overset{\substack{\text{Potassium}\\\text{bichromate}}}{K_2Cr_2O_7} + \overset{\substack{\text{Sulphuric}\\\text{acid}}}{H_2SO_4} + \overset{\text{Water}}{H_2O} = \overset{\substack{\text{Chromic}\\\text{acid}}}{2(H_2CrO_4)} + \overset{\substack{\text{Potassium}\\\text{sulphate}}}{K_2SO_4}$$

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

$$\overset{\text{Zinc}}{Zn} + \overset{\text{Sulphuric acid}}{H_2SO_4} = \overset{\text{Zinc sulphate}}{ZnSO_4} + \overset{\text{Hydrogen}}{H_2}$$

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

$$\overset{\text{Chromic acid}}{2(H_2CrO_4)} + \overset{\text{Sulphuric acid}}{3(H_2SO_4)} + \overset{\text{Hydrogen}}{3H_2} = \overset{\text{Chromium sulphate}}{Cr_2(SO_4)_3} + \overset{\text{Water}}{8(H_2O)}$$

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

Secondary or Storage Cells.—By passing a galvanic current through water acidulated with a few drops of sulphuric acid the water can be decomposed, the oxygen being liberated at the pole at which the current enters the liquid, and the hydrogen at the pole at which it leaves, and so arranged that the gases are collected separately; if the battery is taken away and the wires connected with a galvanometer in circuit, the electrodes being in contact with the oxygen and hydrogen, the gases gradually recombine and a galvanic current will once more flow through the wires, but in an opposite direction to the direct current originally given by the battery; and such a source of electricity is called a gas battery.

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

In practice, the plates are made of cast lead in the form of grids, the holes being about ¼-inch square, and one plate has the holes filled with a paste of lead monoxide (PbO) and dilute sulphuric acid, whilst the other has the holes filled with red lead (Pb_3O_4); these plates are then placed in a vessel of dilute sulphuric acid and connected to a dynamo or other generator of electricity, and a current passed from the red lead (Pb_3O_4) plate to the lead monoxide (PbO) plate. The lead monoxide is reduced to spongy metallic lead, whilst the red lead is oxidised to lead peroxide.

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

$$\overset{\text{Lead}}{Pb} + \overset{\text{Lead peroxide}}{PbO_2} + \overset{\text{Sulphuric acid}}{2H_2SO_4} \rightleftarrows \overset{\text{Lead sulphate}}{2PbSO_4} + \overset{\text{Water}}{2H_2O}$$

Edison Nickel Cell.—The positive plate of this cell consists of a steel frame carrying a number of perforated steel tubes originally charged with nickel hydroxide $(NiOH)_2$, and flaked metallic nickel, the latter to ensure better contact. The negative plate is also of steel, and has perforated sides, the perforations being filled with iron oxide $Fe(HO)_3$. The electrolyte is a 21 per cent. solution of caustic potash, containing a little lithia.

After a short use the hydroxides in each plate become when charged $Ni(OH)_3$ and $Fe(OH)_2$: on discharging the nickelic hydroxide becomes nickelous hydroxide $Ni(OH)_2$, and the ferrous hydroxide becomes ferric hydroxide $Fe(OH)_3$.

One trouble likely to arise with the alkaline electrolyte is the formation of potassium carbonate on exposure to air.

These cells stand heavy overload, and may be short-circuited or charged in the reverse direction without permanent injury.

Electrolysis.—In all the primary cells mentioned it is found that the current generated flows from the metal which is acted upon, and which is called the positive metal, through the liquid of the cell to the metal unacted upon and called the negative metal, and then back to the positive metal by the wire connecting the plates outside the cell; and if we break the conducting wire the two ends are called poles, the negative pole being the end connected with the positive metal and the positive pole the one connected with the negative metal of the cell. If these two poles be now dipped into any solution which will conduct electricity, the current (if sufficiently powerful) in passing through the liquid will set up chemical decomposition.

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

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

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

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

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

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

Potassium sulphate

$$\underbrace{K_2SO_4}$$

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

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

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

I.

The solution is shown in a cell with porous partition down the centre, the liquid being coloured with red cabbage solution. No current is yet passing, and in the liquid are molecules of K_2SO_4 and free + K ions and − SO_4 ions.

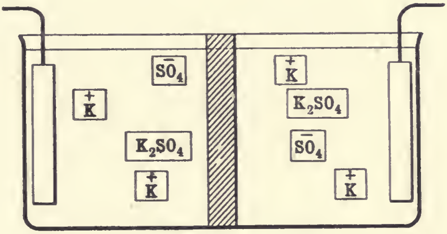


FIG. 13 I.—Electrolysis of potassium sulphate.

II.

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

III.

On reaching the cathode the + K ions are discharged, becoming atoms which can react as K itself does on water, liberating H at the kathode, and similarly the discharged SO_4 groups liberate O at the anode.

The general course of the solution of a metal is primarily due to its exerting a tendency to pass into solution (solution pressure) as positively charged ions. Let the zinc be in a solution in which dissociation into ions has to some extent occurred, say in very dilute hydrochloric acid, where normally the positive H and negative Cl ions exactly balance. With the passage of positively charged Zn ions into solution this balance is upset and the positive charges on the Zn ions result in a balance of negative electricity being produced in the zinc plate. This negatively charged plate attracts to its surface positively charged ions of Zn and H and further action ceases, in other words polarisation is set up.

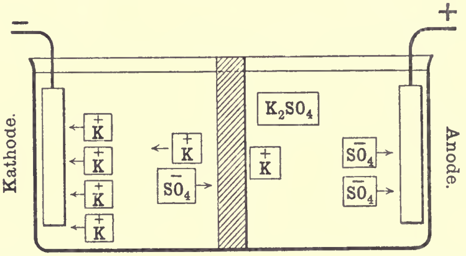


FIG. 13 II.—Electrolysis of potassium sulphate.

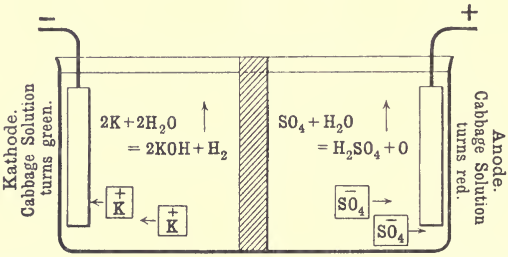


FIG. 13 III.—Electrolysis of potassium sulphate.

For further reaction to proceed, positive ions must be either removed from solution (depolarisation) or more negative ions must be set free. How lack of uniformity (impurity) contributes to this may be best seen by considering the action of zinc with a particle of carbon on its surface. The Zn is strongly electropositive to the carbon, positive zinc ions pass into solution, the zinc plate becoming negatively charged. The positive ions of zinc and hydrogen predominate over the negatively charged chlorine ions in the solution, but now there is a means of the balance adjusting itself. H ions yield their positive charge to the carbon particle, hydrogen gas (not in the ionic but in the molecular condition) escapes, but the carbon particle has become positively charged. Hence there exists the positively charged carbon particle in electrical contact with the negatively charged zinc, the zinc steadily passes into solution, that is, corrosion is rapid, and a continuous current results.

The Commercial Production of Hydrogen and Oxygen by Electrolysis.—We have seen that when a galvanic current is passed through water which has been rendered a conductor by the addition of an acid or the solution in it of a salt, oxygen is liberated at the anode and hydrogen at the kathode, and that when a demand arose for hydrogen of great purity for military ballooning this method of obtaining the gas was employed, whilst on the Continent it is largely used for making oxygen and hydrogen for autogenous soldering and other purposes.

In order to construct a commercially successful apparatus for doing this it is necessary to obtain the lowest possible internal resistance and to ensure the complete separation of the evolved gases. The former will be governed by the nature of the electrolyte, the surface of the electrodes and the distance they are apart, whilst the latter largely depends upon the nature of the diaphragm utilised to separate the two poles and which must be of such a nature as to allow a free circulation of the liquid, to offer the least resistance to the passage of the current and yet to prevent any passage of gas. Various forms of apparatus have been employed, and the Siemens plant may be taken as a type. In it the water is rendered a conductor by dissolving in it sodium hydroxide ($NaHO$), which allows the electrodes and tank to be made of iron and also ensures the absence of acid vapours in the gas, whilst the portion of diaphragm below the liquid is composed of iron gauze, which offers no resistance to the current and allows free circulation of the sodium hydroxide reformed from the sodium liberated at the kathode, but is found to satisfactorily prevent any passage of gas.

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

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

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

+
Aluminium
Chromium
Manganese
Zinc
Iron
Cobalt
Nickel
Tin
Lead
Bismuth
Copper
Mercury
Silver
Palladium
Platinum
Gold
—

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

Galvanic Action on Ships' Plates.—A great interest attaches to the electro-chemical behaviour of metals upon each other when exposed to the action of different electrolytes. The whole important question of the corrosion of metals appears to be dependent upon electrolytic action and its consideration in this aspect is deferred to the concluding chapter.

CHAPTER V

OXYGEN

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

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

Preparation.—It may be prepared—

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

$$\overset{\text{Mercuric oxide}}{2(\mathrm{HgO})} \quad = \quad \overset{\text{Mercury}}{2\mathrm{Hg}} \qquad \overset{\text{Oxygen}}{\mathrm{O_2}}$$

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

$$\overset{\text{Manganese dioxide}}{3(\mathrm{MnO_2})} \quad = \quad \overset{\text{Trimanganic tetroxide}}{\mathrm{Mn_3O_4}} \quad + \quad \overset{\text{Oxygen}}{\mathrm{O_2}}$$

Some oxides, like mercuric oxide, give off the whole of their oxygen on heating; others, of which the peroxide of manganese or manganese dioxide may be taken as a type, only give off a portion, whilst the members of a third class, like potassium or sodium oxide, are not broken up by heat.

3. By passing steam and chlorine through a hot porcelain tube, when the hydrogen and chlorine unite to form hydrochloric acid and oxygen is liberated. On collecting

the gases over water the hydrochloric acid is absorbed and only pure oxygen is left.

Steam		Chlorine		Hydrochloric acid		[Oxygen
$2(H_2O)$	$+$	$2Cl_2$	$=$	$4(HCl)$	$+$	O_2

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

Potassium chlorate		Potassium chloride		Oxygen
$2(KClO_3)$	$=$	$2(KCl)$	$+$	$3O_2$

This is the usual method adopted for its preparation.

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

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

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

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

It is upon this reaction that the process of Brin Frères, for the production of oxygen on a large scale, is based, Anhydrous barium oxide is placed in a series of retorts heated to 650° C., whilst air carefully freed from carbon dioxide is passed through them under a pressure of about 10 lbs.; the oxygen being absorbed by the barium oxide produces barium peroxide, the flow of air is then stopped and the pressure is taken off, and partial vacuum produced, when decomposition takes place, nearly pure oxygen being evolved.

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

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

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

The preparation of oxygen from water by electrolytic methods has already been dealt with.

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

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

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

Liquid Oxygen.—Oxygen can only be condensed to the liquid state by a combination of intense cold and pressure, a temperature of — 118° C. and a pressure of 50 atmospheres being required for its liquefaction.

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

Detection.—When free, oxygen can be detected—

(*a*) By its power of supporting combustion.
(*b*) By its forming a reddish-brown gas when brought in contact with the colourless gas nitrogen dioxide.
(*c*) By its being absorbed by potassium pyrogallate with formation of a deep brown compound.

OZONE.

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

Allotropes.—When elements change their physical properties and activity and yet remain unaltered in composition they are said to be "allotropes," or allotropic modifications, and this allotropism is due to a rearrangement of the particles of which the mass is built up. Thus ozone is said to be an allotropic modification of oxygen.

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

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

This may be effected in the apparatus shown in Fig. 14. An inner tube (A), closed at its lower end, is sealed near the upper end into a slightly larger tube (B), the latter being prolonged for some distance below (A) and terminating in a small manometer (D) partly filled with strong sulphuric acid suitably coloured. The tube B is furnished with a stopcock near its junction with the inner tube, and again just above the manometer. Surrounding a portion of these two tubes is a glass cylinder (C). Four platinum electrodes are provided (*p*).

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

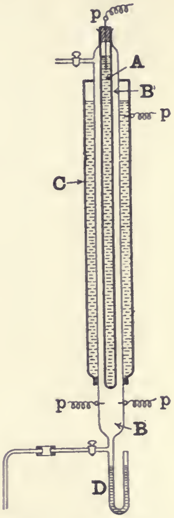


FIG. 14.—Ozone apparatus.

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

This is shown by half covering a freshly scraped stick of phosphorus with water, in the bottom of a large flask, the mouth of which is closed by a glass plate. The phosphorus slowly oxidises at the expense of some of the oxygen of the air, the products dissolving in the water, whilst a considerable amount of ozone is at the same time formed, and may be detected by the usual tests.

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

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

$$\overset{\text{Potassium iodide}}{2KI} + \overset{\text{Ozone}}{O_3} + \overset{\text{Water}}{H_2O} = \overset{\text{Potassium hydroxide}}{2KOH} + \overset{\text{Oxygen}}{O_2} + \overset{\text{Iodine}}{I_2}$$

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

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

On passing ozonised oxygen through a coil, cooled down to — 131° C. by surrounding it with boiling oxygen, ozone can be condensed to an intensely blue liquid having a boiling point of — 106° C.

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

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

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

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

Molecular Composition.—When oxygen is converted into ozone, at most one-fifth of the volume present, generally far less, is ozonised, and the formation of ozone is attended with a contraction of volume. This may readily be shown with the apparatus already described (p. 65). If oxygen is allowed to fill the space between the inner and outer tubes, on closing both taps and passing the silent discharge, in the course of a minute or so a considerable contraction will be observed from the movement of the acid in the manometer (D). If now the wires from the induction coil are connected to the two lower electrodes and sparks passed through the gas, the expansion due to the heating and consequent decomposition of the ozone may be demonstrated. Recent researches show that if pure oxygen is cooled to the temperature of liquid air, 99 per cent. of the gas can be converted into ozone. We have seen that the density of oxygen on the hydrogen scale is 16, and if 12 volumes of oxygen are taken and the brush discharge passed until contraction ceases, 11 volumes of mixed ozone and oxygen are left; on introducing some turpentine into this mixture all the ozone is absorbed, and 9 vols. of oxygen are left, so that 2 vols. of ozone were present and had been produced by 3 vols. of oxygen. Let the 12 vols. of oxygen weigh $12 \times 16 = 192$, then the 9 vols. left will $= 16 \times 9 = 144$, $192 - 144 = 48$, the weight of the 2 vols. of ozone formed, and therefore 1 vol. of ozone $= 24$, or one-third heavier than an equal vol. of oxygen.

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

$$\underset{\text{Mercury}}{Hg} + \underset{\text{2 vols. ozone}}{O_3} = \underset{\text{Mercuric oxide}}{HgO} + \underset{\text{2 vols. oxygen}}{O_2}$$

CHAPTER VI

OXIDES AND SALTS

The ordinary processes of combustion in which the oxygen of the air or oxygen gas alone is concerned are processes of oxidation and result in the production of oxides of the substances undergoing combustion. All the elements, with the exception of fluorine, combine with oxygen, and even fluorine forms some double salts containing oxygen, such as the oxy-fluoride of phosphorus. If the characters of the different oxides are examined, it is found that they admit of ready classification into three groups.

1. Acid-forming Oxides.—When sulphur, phosphorus, or carbon are burned in oxygen, the oxides formed are soluble in water forming *acids*, and these acid-forming oxides are sometimes called *anhydrides.*

$$\overset{\text{Sulphur}}{S} + \overset{\text{Oxygen}}{O_2} = \overset{\substack{\text{Sulphur dioxide or}\\\text{sulphurous anhydride}}}{SO_2}$$

$$\overset{\text{Phosphorus}}{4P} + \overset{\text{Oxygen}}{5O_2} = \overset{\substack{\text{Phosphorus pentoxide or}\\\text{phosphoric anhydride}}}{2(P_2O_5)}$$

$$\overset{\text{Carbon}}{C} + \overset{\text{Oxygen}}{O_2} = \overset{\substack{\text{Carbon dioxide or}\\\text{carbonic anhydride}}}{CO_2}$$

Combined with water they yield the corresponding acids—

$$\overset{\text{Sulphur dioxide}}{SO_2} + \overset{\text{Water}}{H_2O} = \overset{\text{Sulphurous acid}}{H_2SO_3}$$

$$\overset{\text{Phosphorus pentoxide}}{P_2O_5} + \overset{\text{Water}}{3H_2O} = \overset{\text{Phosphoric acid}}{2(H_3PO_4)}$$

$$\overset{\text{Carbon dioxide}}{CO_2} + \overset{\text{Water}}{H_2O} = \overset{\text{Carbonic acid}}{H_2CO_3}$$

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

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

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

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

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

The solution of a soluble basic oxide (the hydroxide) has exactly opposite properties to the solution of an acid oxide, for it turns red litmus blue, and, as is shown above, can exactly neutralise the solution of an acid-forming oxide (an acid).

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

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

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

3. Neutral Oxides.—Certain oxides exhibit neither acid-forming nor basic properties—in other words they are neutral oxides; but these must be regarded as somewhat exceptional: for example, water H_2O, and nitrogen monoxide and dioxide N_2O and NO.

Salts.—It has already been shown that the neutralisation of an acid by a basic oxide or hydroxide results in the production of a salt, and further, a salt has been described as resulting from the combination of a metallic radicle with an acid radicle.

Formation of salts—

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

$$\overset{\text{Sodium}}{Na} + \overset{\text{Chlorine}}{Cl} = \overset{\text{Sodium chloride}}{NaCl}$$

$$\overset{\text{Copper}}{Cu} + \overset{\text{Chlorine}}{Cl_2} = \overset{\text{Copper chloride}}{CuCl_2}$$

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

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

$$\overset{\text{Zinc}}{Zn} + \overset{\text{Sulphuric acid}}{H_2SO_4} = \overset{\text{Zinc sulphate}}{ZnSO_4} + \overset{\text{Hydrogen}}{H_2}$$

$$\overset{\text{Zinc}}{Zn} + \overset{\text{Hydrochloric acid}}{2HCl} = \overset{\text{Zinc chloride}}{ZnCl_2} + \overset{\text{Hydrogen}}{H_2}$$

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

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

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

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

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

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

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

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

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

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

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

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

$Hg++(OH-)(NO_3-)$	..	Basic mercuric nitrate.
$2(Pb++CO_3--).Pb++(OH-)_2$		Basic lead carbonate (white lead).

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

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

$$\overset{\text{Mercuric chloride}}{HgCl_2} + \overset{\text{Potassium iodide}}{2KI} = \overset{\substack{\text{Potassium}\\\text{chloride}}}{2KCl} + \overset{\substack{\text{Mercuric}\\\text{iodide}}}{HgI_2}$$

For any pair of salts such an equation can be written, but it does not follow that the chemical change indicated can really take place. The only general rule is, that when by such an interaction it is possible for an insoluble salt to result, then such reaction will always take place. The mercuric iodide above is insoluble, and therefore is precipitated. This simple rule is really the basis of all our methods of analysis in which reliance is placed upon the precipitation of definite compounds.

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

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

$$\overset{\text{Sodium nitrate}}{NaNO_3} + \overset{\text{Sulphuric acid}}{H_2SO_4} = \overset{\substack{\text{Sodium hydrogen}\\\text{sulphate}}}{NaHSO_4} + \overset{\substack{\text{Nitric}\\\text{acid}}}{HNO_3}$$

whilst, at a higher temperature, the hydrogen is totally replaced.

$$\overset{\substack{\text{Sodium hydrogen}\\\text{sulphate}}}{NaHSO_4} + \overset{\substack{\text{Sodium}\\\text{nitrate}}}{NaNO_3} = \overset{\substack{\text{Sodium}\\\text{sulphate}}}{Na_2SO_4} + \overset{\substack{\text{Nitric}\\\text{acid}}}{HNO_3}$$

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

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

$$\overset{\text{Calcium hydroxide}}{Ca(HO)_2} + \overset{\text{Ammonium chloride}}{2NH_4Cl} = \overset{\text{Calcium chloride}}{CaCl_2} + \overset{\text{Water}}{2H_2O} + \overset{\text{Ammonia}}{2NH_3}$$

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

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

Calcium combines with oxygen to form calcium ox*ide.*
Sodium combines with chlorine to form sodium chlor*ide.*
Lead combines with sulphur to form lead sulph*ide.*

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

An atom of lead forms with one atom of oxygen—lead *mon*oxide.

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

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

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

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

Ferrous chloride ($FeCl_2$) and ferric chloride ($FeCl_3$).
Mercurous iodide (HgI) and mercuric iodide (HgI_2).

To be systematic, the acids must be regarded as salts of hydrogen, hence H_2SO_4 is, strictly speaking, hydrogen sulphate, but by common usage the older system of nomenclature is general and leads to less confusion where the term acid is employed.

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

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

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

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

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

CLASSIFICATION OF THE ELEMENTS.

The division of the elements into non-metals and metals, based on their physical properties; metallic lustre, conduction of heat and electricity, etc., fails with certain elements which, although for other reasons are regarded as non-metals, yet physically resemble the metals. Chemists therefore base the classification on chemical properties, a metal being defined as an element forming at least one basic oxide.

For a more detailed and scientific method of classifying the elements the system based on the Periodic Law is universally adopted.

If the elements are arranged in the order of their atomic weights, it will be found that at certain regular intervals there is a recurrence in chemical and physical properties; in other words, *the properties of the elements are functions of their atomic weights.* If then the elements be tabulated in the order of their atomic weights, dividing them into periods where recurrence of properties are found, then they will be found arranged in well-defined families, the members of which exhibit close similarity in properties.

Taking the first fourteen elements, after hydrogen, for example, we shall have the following :—

Li = 7	Be = 9	B = 11	C = 12	N = 14	O = 16	F = 19
Na = 23	Mg = 24	Al = 27	Si = 28	P = 31	S = 32	Cl = 35·5

With these, there is a reappearance of properties at each *eighth* element, and, moreover, definite progression in properties as we pass horizontally along the elements. Lithium and sodium on the one hand, and fluorine and chlorine on the other, are strikingly similar. The former are strongly electro-positive ; the latter as strongly electro-negative. The valency of the elements in the first column is I. ; in the second, II. ; in the third, III. ; in the fourth, IV. ; in the fifth, III. ; in the sixth, II. ; in the seventh, I. ; a progressive increase and decrease. Such a group of elements is known as a *period.* It is not only in chemical properties that these regularities exist, but they extend also to the physical properties. The specific gravity of the solid elements increase to the middle of the period to a maximum and then decrease ; and the quotient obtained by dividing the atomic weight by the specific gravity of the liquid or solid element—termed the *atomic volume*—shows a decrease to the centre with higher values at either end, thus in the third period—

	Na	Mg	Al	Si	P (red)	S	Cl (liquid)
Specific gravity ..	0·97	1·75	2·67	2·49	2·14	2·06	1·33
At. volume ...	24	14	10	11	14	16	27

It is found that these functions are not confined to the elements, but are extended to their compounds also, and the character of the compounds formed by the elements in a series are identical in most respects.

In the next period which commences with potassium, it is found that the recurrence of similar properties does not occur until rubidium is reached, which is the eighteenth element in order, and here the period consists of 17 elements, so that this third period and the fourth succeeding it both form *large periods.* Closer examination of both these periods shows that they may be subdivided into two short periods of seven, because of similarity of properties, but three elements in the third, following strictly in the correct order of atomic weights (Fe, Co, Ni), and three elements in the fourth (Ru, Rb, Pd) are totally different, so they are respectively arranged in separate series.

The general arrangement of the elements on this system is shown in the Appendix. In considering the series it is found that the first members of the first row of a period are similar, thus in Series I. there is the well-defined family Li, Na, K, Rb, Cs, whilst the similarity in properties between the first members of the second row of a period is also well marked; thus again in Series I. the elements Cu, Ag, Au form a family. In order that the proper relationship may be apparent, elements forming a distinct family are arranged under each other, as shown, so that many series include two distinct groups.

It was found that if the elements were arranged strictly according to their atomic weights certain discrepancies occurred in the properties of elements which would fall in the same group. This might arise from two causes; inaccurate determination of the atomic weight, or the existence of an undiscovered element, in which case a gap would occur. Mendeléeff, who elaborated this Periodic arrangement, indicated certain elements, which, failing to comply with the requirements, should have different atomic weights to those accepted at the time, and re-determinations of these atomic weights proved the accuracy of his prediction. Further, he predicted exactly the properties, atomic weights, etc., of unknown elements which should occur to fill certain gaps, and in some cases these elements have been found, and fulfil in every detail their anticipated properties.

Clearly such a system of classification is of great value, in that it enables a control, within limits, of the atomic weights of known elements, and further is of advantage in pointing out the probable existence of hitherto undiscovered elements.

CHAPTER VII

COMBUSTION

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

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

The enunciation of these truths by the great French philosopher was one of the most important steps in the history of science; but with increase of knowledge it is found necessary to still further widen the views held with regard to combustion.

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

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

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

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

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

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

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

A tree left to rot upon the ground gradually disappears in the course of years, being mainly oxidised into gaseous products such as carbon dioxide and water vapour, and yet scarcely any evolution of heat is observed, although the same amount of heat is generated as if the tree had been cut into logs and burnt.

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

here in the capillaries the tissues of the body take the oxygen from the blood, replacing it by carbon dioxide, with the result that it again changes to purple, and in this condition returns by the veins to the heart and lungs, once more to give up carbon dioxide and take in a fresh supply of oxygen. The purple blood is called "venous," or the blood of the veins; the bright scarlet blood is called "arterial."

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

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

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

When the ignition point is below the ordinary temperature, as in the case of zinc methyl, the substance is said to be spontaneously inflammable, because it will take fire on coming in contact with air without the application of heat, whilst if the ignition point be above the ordinary temperature ignition has to be set up by raising the temperature to the necessary point.

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

The combination of nitrogen and oxygen is a good example of this latter class of phenomena, as, although they will combine at the temperature of the electric discharge, the combination does not emit sufficient heat to continue the combustion, and it is upon this that the safety of the atmosphere depends. The compounds of nitrogen and oxygen being all endothermic, energy, in the form of heat, must be continually supplied for their formation.

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

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

When the combustible substance has a great affinity for oxygen, and at the same time a low point of ignition, spontaneous combustion will take place with great ease. Indeed, in some cases, such as that of phosphorus, it is necessary to prevent the access of air to the body in order to avoid ignition taking place, and we also find that the finer the state of division of the substance the more readily will its spontaneous ignition take place, not because sub-dividing the body in any way lowers the point of ignition, but because the surface exposed to the oxidising action of the air is so much increased that the heat is generated with greater rapidity than it can be dissipated. If we take a piece of phosphorus and expose it to the action of the air, it almost directly commences to give off white fumes, and if the weather is warm it will in the course of a short space of time even ignite; in cold weather, however, it may be left until it has nearly all undergone slow oxidation without ignition. If, however, we dissolve it in carbon disulphide and pour some of this liquid upon a piece of blotting paper or linen, the carbon disulphide being highly volatile will all evaporate, and leave the phosphorus in such a fine state of division that it will at once spontaneously ignite.

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

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

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

Spontaneous Ignition of Charcoal.—Carbon is one of those substances which possess to an extraordinary degree the power of attracting and condensing gases upon their surface or within their pores, this power varying with the state of division of the particular form of carbon used. The charcoal obtained from dense forms of wood, such as box, exhibit this property to a high degree, one cubic inch of such charcoal absorbing, according to Saussure—

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

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

There are several very interesting points with regard to the spontaneous combustion of charcoal, which call for more attention than has yet been devoted to it. It is self-evident that the more porous a body is the greater amount of exposed surface will be available for the condensation of gases, and the great power which charcoal has of absorption is undoubtedly due to its great porosity. Now the temperature at which wood can be carbonised varies very considerably, and wood will begin to char, that is to say, will begin to be converted into charcoal at temperatures very little above that of boiling water, and in the manufacture of some kinds of gunpowder the charcoal is formed by heating with superheated steam.

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

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

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

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

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

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

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

Action of Pyrites.—Pyrites is found in coal in several different forms, sometimes as a dark powder, closely resembling coal itself, and in larger quantities in thin golden-looking layers in the cleavage of the coal, whilst sometimes it is found in masses and veins of considerable size. These masses, however, are very heavy, and are carefully picked out from the coal, and utilised in various manufactures. The yellow pyrites, and even the dark varieties when in the crystalline form, remain practically unaltered even after long exposure to moist air; but the amorphous and finely-divided portions will oxidise and effloresce with great rapidity, and it is during this oxidation that the heat is supposed to be generated.

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

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

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

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

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

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

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

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

Coal is a substance of purely vegetable origin, formed out of contact with air by long exposure to heat and pressure, from the woody fibre and resinous constituents of a vegetation which flourished long before the earth was inhabited by man. Coal, therefore, may be looked upon as a form of semi-charcoal, which, having been produced at a temperature lower than that of the charcoal burner's heap and under great pressure, is very dense, and still contains a quantity of these constituents which, in the ordinary burning, are driven off as wood naphtha, tar, etc., and these bodies consisting of compounds containing essentially carbon and hydrogen, together with a little oxygen and nitrogen, form the volatile matter and hydrocarbons of the coal. Coal also contains, besides these, certain mineral bodies which were present in the fibre and sap of the original wood, and these form the ash which is left behind on the coal being burnt. These mineral substances consist almost entirely of gypsum or sulphate of lime, silica, and alumina, together with some oxide of iron which gives the colour to the reddish-brown ash of many coals, and which has been formed by the decomposition of the pyrites in the original coal

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

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

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

It is well known that bituminous coals exposed to the air for any length of time rapidly lose their power of coking when carbonised, and also undergo considerable loss in calorific value, this action, which is called " weathering," being due to oxidation of the resinous constituents.

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

Actions leading to Ignition.—We can now trace the actions which culminate in ignition. As soon as the coal is brought to bank, absorption of oxygen commences, but, except under rare conditions, the coal does not heat to any great extent, as the exposed surface is comparatively small, and the size of the masses allows of the air having free access to all parts, so keeping down the temperature. After the coal has been screened, and the large pieces of pyrites picked out, it is put in trucks. Here it begins to get broken up, owing to the many joltings and shuntings, and so offers a larger surface to the action of the air. When it has arrived at the ship it is further broken up by being shot down the tips or shoots, and more harm is done at this than at any other period, for the coal is broken by reason of the distance it has to fall, and, as it has to bear the impact of every succeeding load falling upon it, it rapidly becomes slack, so that the under part of the shipload is a dense mass of small coal, which soon rises in temperature by reason of the large surface exposed to the air and the consequent absorption of oxygen. This sets up chemical combination between the oxygen absorbed by the coal and the hydrocarbons, and in some cases culminates in combustion.

Influence of Mass.—It is found that the mass of coal exercises a most important action in the liability to spontaneous combustion, as although with 500 tons of coal to the cargo the cases of spontaneous combustion amount to only about ¼ of a per cent., when the bulk is increased to 2000 tons cases of spontaneous combustion rise to 9 per cent., this being due to the fact that the larger the cargo the more non-conducting material will there be to keep in the heat, and also to the fact that the breaking up of the coal and the exposing fresh surfaces will of course increase with increase in mass; it is also found that coal cargoes sent to European ports rarely undergo spontaneous combustion, whilst the number of cases rises to a startling extent in shipments made to Asia, Africa, and America. This result is partly due to the length of time the cargo is in the vessel, the absorption and oxidation being a comparatively slow process, but the main cause is the increase of heat in the tropics, which causes the action to become more rapid; and if statistics had been taken, most of the ships would have been found to have developed active combustion somewhere about the neighbourhood of the Cape, the action fostered in the tropics having raised the temperature to the igniting point by that time.

Moisture has a most remarkable effect upon the spontaneous ignition of coal. The absorption of oxygen is at first retarded by external wetting, but after a time the presence of moisture accelerates the action of the absorbed oxygen upon the coal, and so causes a serious increase of heat. The researches of Cowper, Baker, Dixon, and others have so fully shown the important part which moisture plays in actions of this kind, that it is now recognised as a most important factor.

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

Professor Threlfall has advocated the wetting of coal cargoes as a preventative for spontaneous ignition, and if 15 per cent. or over of water were added to the cargo it would probably prove efficacious, but the increase in weight, or rather reduction in the amount of coal the ship could carry, would prove a serious drawback, whilst the addition of a smaller quantity of water or only partial treatment of the cargo would be an active danger, and a more practical method would be the displacement of all air in the cargo by an inert gas like carbon dioxide and sealing down of the hatches.

Spontaneous Ignition of Oily Rags.—Perhaps the commonest case of spontaneous combustion is to be found in the ignition of oily waste or greasy cotton rags. Nearly all vegetable and animal oils have the power of slowly absorbing oxygen, and in some of them this goes on with considerable rapidity, with conversion of the oil into a resin—a property which gives them the power of drying and causes a considerable rise of temperature.

A mass of oil, however, exposes only a very small surface to the oxidising influence of the air, but when such oil comes to be spread upon any non-conducting fabric, the oxidation is very rapid, and the non-conducting power of the fibre of the fabric prevents the rapid dispersion of the heat, with the result that even a small quantity of such oily substance will readily inflame.

There are plenty of well-authenticated cases in which even a handful of oily cotton waste, which has been used for polishing furniture, has ignited when thrown on one side, and caused most disastrous fires. Some years ago, Mr. Galletly read a most valuable paper before the Chemical Section of the British Association, in which he showed that the liability of oils to produce spontaneous combustion was in proportion to their tendency to dry. If a substance like cotton waste be rendered oily with anything except the mineral oils, it acquires the power of taking up oxygen from the air, and this gives rise to heat. The oxidation is slow at ordinary temperatures, and, accordingly, it may be some time before the increase of temperature becomes manifest; but when this point is reached the action proceeds with great rapidity, and the point of ignition is reached in a very short time, and then the mass bursts into flame. If the oily matter be placed in a warm position at first, spontaneous ignition may take place within a few hours, or even minutes. Galletly found that oily cotton at ordinary temperatures took some days to heat and ignite, whilst if placed in a chamber warmed to 130° to 170° F. (54° to 76° C.), the cotton, greasy with boiled linseed oil, ignited in 1 hour 15 minutes, and olive oil on cotton in five hours; and in a chamber heated to 180° to 200° F. (82° to 93° C.), olive oil on cotton ignited in two hours.

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

whilst if a few drops of a drying oil be allowed to fall on powdered charcoal or lamp-black, ignition is almost certain to follow in a few hours.

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

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

Again, potassium permanganate, a body rich in oxygen when mixed with strong sulphuric acid, has the power of giving oxygen to all substances which can take it up, and will even oxidise substances which do not combine with oxygen under ordinary conditions, whilst if glycerine be put on a pile of potassium permanganate, spontaneous ignition will take place in a few minutes.

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

CHAPTER VIII

WATER AND ITS PROPERTIES

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

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

Composition of Water by Volume.—The proportions of hydrogen and oxygen in water can be accurately determined by eudiometric synthesis. For this purpose we take a strong, accurately graduated glass tube (A, Fig. 15), open at one end and closed at the other, whilst through the closed end two platinum wires are fused, which terminate one-eighth of an inch apart inside the tube, and which can be connected with the poles of an induction coil (B) connected with the battery (C).

The tube is first filled with water, and is then inverted mouth downwards in a trough, also filled with water; hydrogen gas is then allowed to enter, and the volume it occupies is read off (say 100 volumes); oxygen is next passed in and the volume of mixed gases is noted (say 175). The tube is then pressed down upon a piece of flat india-rubber placed under the water, in order to prevent the sudden expansion due to heat (when combination takes place) blowing any of the gases out of the tube. An electric spark is now passed through the mixed gases by means of the platinum wires fused through the glass. A flash is seen to pass down the tube, showing that combination has taken place; and the water formed is deposited as dew on the sides of the tube and occupies only about $\frac{1}{2000}$ part of the bulk of the gases forming it. When the eudiometer is raised from the india-rubber pad the water rises in the tube and only 25 volumes of gas remain, and this is found to be pure oxygen.

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

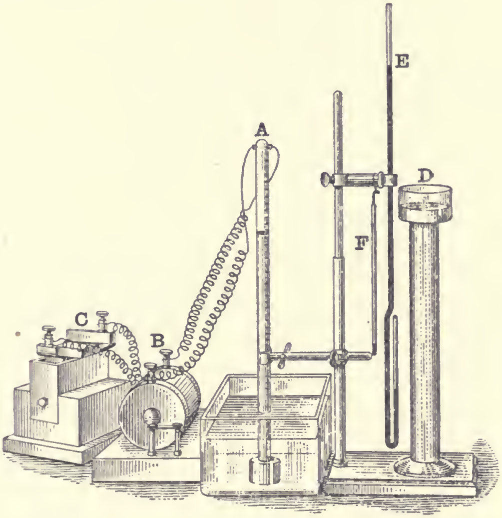


Fig. 15.—Composition of water by volume.

Thus we see that 100 volumes of hydrogen require exactly 50 volumes of oxygen for their complete combustion. In reading the quantities of gases contained in the eudiometer it is necessary to sink the tube in water until the level of the water inside the tube is the same as that on the outside, and this is done in the well (D).

Having thus proved that two volumes of hydrogen combine with one volume of oxygen to form water, we can repeat the experiment, using, however, a different shaped eudiometer and jacketing it with a glass tube through which the vapour of some liquid having a higher boiling point than water can be passed, so as to keep the water formed in the condition of steam (Fig. 16).

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

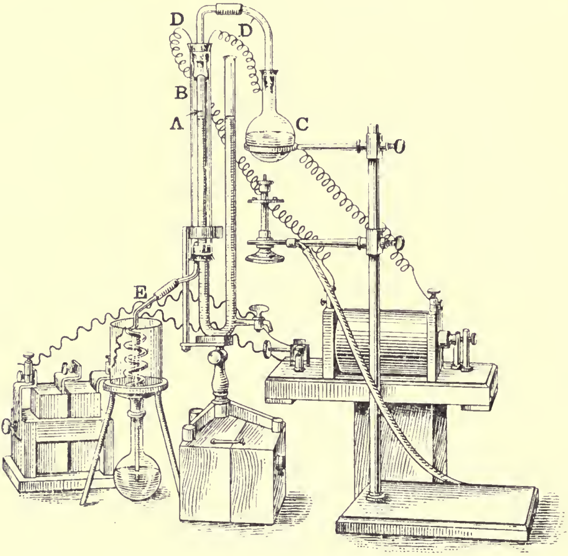


Fig. 16.—Combination of hydrogen and oxygen.

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

Composition by Weight.—Knowing that the atoms of oxygen are sixteen times heavier than the atoms of hydrogen, it would be easy to deduce the proportions by weight in which the two elements combine, and this can be also experimentally determined by passing hydrogen gas generated from zinc and dilute sulphuric acid in the generating bottle (A, Fig. 17), through the tube (B), which is filled with anhydrous calcium chloride, and which will absorb any moisture the gas may contain. The dried hydrogen now passes over heated oxide of copper in the tube (C), and reduces it to metallic copper, combining with the oxygen and forming steam, which passes on and condenses in the U tube (D), which is kept cool by standing in a vessel of water, whilst any moisture which escapes condensation is taken up by the chloride of calcium tube (E).

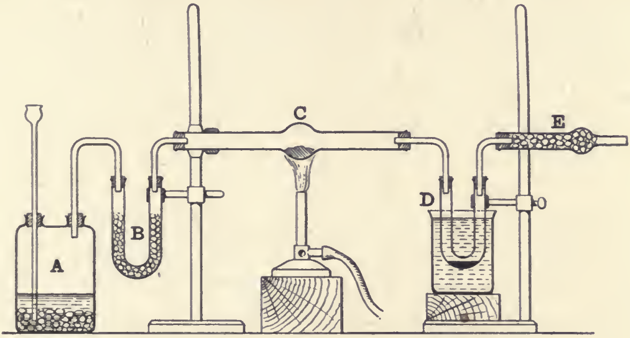


FIG. 17.—Hydrogen over copper oxide.

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

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

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

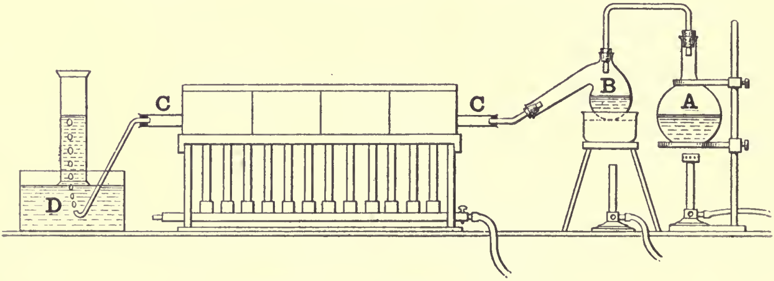


Fig. 18.—Steam and chlorine through tube.

This is best done by generating chlorine gas by gently warming a mixture of hydrochloric acid and black oxide of manganese in the flask (A, Fig. 18), and leading the liberated chlorine through water in the retort (B), which is kept just at the boiling point by a water bath; the chlorine so saturated with water vapour is then passed through a porcelain tube (C) heated to dull redness in the gas furnace—a larger heating surface being obtained by filling the tube with pieces of broken porcelain or glass. Under the influence of heat chlorine decomposes water vapour, and the resulting oxygen and hydrochloric acid, together with any chlorine or steam which may have been in excess, pass on; and if they are led into water in the pneumatic trough (D) and collected by displacement of water in the cylinder, the chlorine and hydrochloric acid, being soluble, will be absorbed by the water, any steam will be condensed, and nothing but oxygen will remain.

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

Water as a Solvent.—As a neutral solvent water is unsurpassed, and it dissolves all gases to a greater or less degree. If no chemical action takes place between the gas and the water the amount absorbed depends upon—(1) the nature of the gas; (2) the temperature of the water; and (3) the pressure under which the absorption is effected.

1. Some gases are much more soluble than others; a given volume of water at 0° C. will dissolve 1,149 times its own volume of ammonia gas, but only 0·019 of hydrogen.
2. The cooler the liquid the more gas will it dissolve.
3. The volume of the gas absorbed varies directly as the pressure; that is to say, at all pressures the water absorbs the same volume of gas, since the volume of the gas itself varies inversely as the pressure.

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

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

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

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

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

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

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

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

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

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

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

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

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

SPECIFIC HEATS OF SOLIDS AND LIQUIDS.

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

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

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

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

Another very important result that follows from the high specific heat of water and latent heat of liquefaction is that water only cools down slowly and so requires a long-continued low temperature for the production of ice, whilst the same factors slow down the melting of ice and snow, and so tend to prevent floods when the thaw sets in.

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

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

Bursting of Water-Pipes by Frost.—The sudden expansion due to the conversion of water into ice is a frequent cause of the bursting of water-pipes during severe frost. Pipes are left full of water and often under pressure, and when the water freezes, the sudden expansion bursts the pipe at its weakest point. The damage, however, is only discovered when the thaw comes, and the ice melting allows the outrush of the water. Leaden water-pipes are made perfectly cylindrical in order to give them the greatest carrying capacity; but if they were made oval instead of round, when the water froze it would by its expansion make the tube cylindrical, and so provide room for the surplus.

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

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

Boiling-Point.—Water boils when the tension of its vapour is equal to the superincumbent atmospheric pressure; therefore, at the top of a mountain, where the atmospheric pressure is less than at the sea-level, water boils below 100° C., but at the bottom of a deep mine, where the pressure of the atmosphere is greater, water has to be heated above 100° C. before it is converted into steam.

This may be shown by warming water to about 80° to 90° C. in a flask (A, Fig. 19) and attaching it to an air-pump; an empty bottle (B) and a long tube filled with calcium chloride (C) being interposed in order to condense and absorb water vapour and so prevent any reaching the air-pump. On giving a few strokes of the air-pump, the pressure is reduced on the surface of the water in the flask and the water boils briskly. This principle is applied in the sugar-maker's vacuum pan, in which water is boiled off from the saccharine syrup at temperatures far below the boiling-point in air ; and also in " Papin's digestors," where, by increasing the pressure, the boiling-point is raised.

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

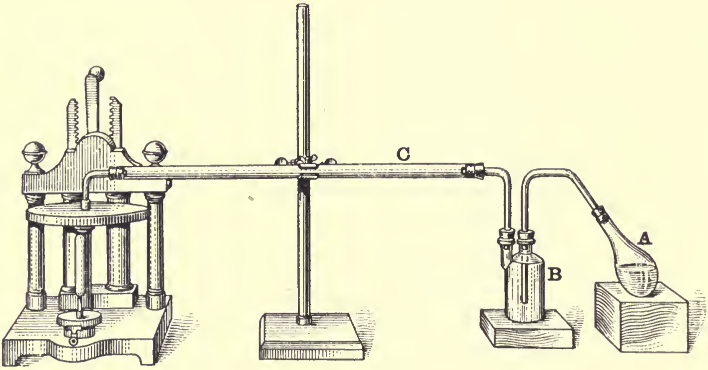


Fig. 19.—Water boiling under reduced pressure.

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

Spheroidal State.—When water is thrown upon a heated silver dish it is seen to assume a spheroidal form and does not boil, although the plate or dish is heated very far above its ordinary boiling-point. If the dish be now allowed to cool, at a certain point the water suddenly bursts into violent ebullition and is converted into steam. This spheroidal form is due to the generation of a cushion of steam between the water and the heated surface which prevents the water coming in contact with it, so that it only slowly evaporates away ; but on allowing the temperature to fall, a point is reached when the heat is no longer sufficient to rapidly generate the steam.

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

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

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

The fact, however, that even at ordinary temperatures water above the mercury column causes a depression, shows that it has a certain tendency to volatilise, and it is this power which causes it to evaporate at all temperatures. When water boiled and was converted into steam, we saw that a large amount of heat was rendered latent, *i.e.* disappeared as sensible heat, because it was doing the work of keeping the particles of water in a state of vapour ; and, no matter how low the temperature may be at which water is converted into vapour, it takes up and renders heat latent.

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

The Circulation of Water.—It is evident that as evaporation is dependent on the tension of the aqueous vapour, and as this increases with the temperature, the warmer it is the more rapid will evaporation be, so that in tropical climates water vaporizes with great rapidity from the surface of the sea, and the water vapour being lighter than air forms an ascending current, and fresh air from the north and south is drawn in to take its place; whilst in order to replace these supplies the ascending air divides and forms upper currents which flow back from the equator overhead in the opposite direction to that which the lower currents are taking. If the earth were stationary these currents would flow due north and south, but the earth revolves on its axis once in the twenty-four hours, and as the circumference of the globe is 24,900 miles at the equator, it is evident that anything relatively stationary there is moving with the earth at more than 1000 miles an hour, and although the air nearest the earth moves with the earth, still there is a certain amount of friction which deflects these currents from due north and south, and gives them a north or south-easterly direction.

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

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

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

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

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

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

In the magnesium limestone districts, about 20 per cent. penetrates; in the new red sandstone, 25 per cent.; in the chalk, 42 per cent.; and in the loose tertiary sand, 90 to 96 per cent. Sinking into the ground, the water comes in close contact with considerable quantities of carbon dioxide generated from the decaying vegetable matter in the subsoil, and it absorbs a considerable quantity of this gas, forming with it carbonic acid, and then penetrates more or less deeply into the ground, dissolving anything it can take up, either by its own solvent properties or by the solvent power of the carbonic acid, formed by the solution of carbon dioxide in the passage of the rain through the air and top-soil. The carbonic acid so present in the water causes it to be fresh and sparkling, and where there is a deficiency of carbonic acid, as is the case in waters from some sandy soils, there the water is flat and unpalatable.

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

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

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

In falling from the clouds, the rain performs the important function of washing the air and collecting the ammonia and nitric acid necessary for plant life, and brings them down to the plants in the condition in which they can be most readily assimilated ; whilst in its passage from the springs to the ocean it washes away those waste products of animal life which, if they were allowed to remain, would breed pestilence and, if the free flow of the rain and spring water be interrupted, stagnant pools and swamps, breeding disease and exhaling malaria, are the result.

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

HYDROGEN DIOXIDE.

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

It is neutral to test papers and bleaches litmus solution.

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

Barium percarbonate is first formed, and breaks up in contact with water into normal barium carbonate and hydrogen peroxide, the completed reaction being—

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

The carbon dioxide is generated from marble and hydrochloric acid in the bottle (A, Fig. 20), and is washed by being made to bubble through water in the wash bottle (B), which frees it from any traces of acid which might be mechanically brought over by the gas, and it is then passed through the barium dioxide suspended in water in the cylinder (C). The barium carbonate formed gradually settles down to the bottom of the cylinder, and the dilute solution of hydrogen dioxide can then be concentrated by evaporation over sulphuric acid in vacuo.

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

$$\overset{\text{Silver}}{Ag} + \overset{\text{Hydrogen dioxide}}{2(H_2O_2)} = \overset{\text{Silver}}{Ag} + \overset{\text{Water}}{2(H_2O)} + \overset{\text{Oxygen}}{O_2}$$

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

$$\overset{\text{Sulphurous acid}}{H_2SO_3} + \overset{\text{Hydrogen dioxide}}{H_2O_2} = \overset{\text{Sulphuric acid}}{H_2SO_4} + \overset{\text{Water}}{H_2O}$$

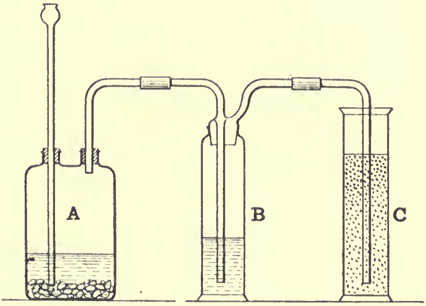


Fig. 20.—Preparation of hydrogen dioxide.

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

$$\overset{\text{Silver oxide}}{Ag_2O} + \overset{\text{Hydrogen dioxide}}{H_2O_2} = \overset{\text{Silver}}{Ag} + \overset{\text{Water}}{H_2O} + \overset{\text{Oxygen}}{O_2}$$

$$\overset{\text{Manganese dioxide}}{MnO_2} + \overset{\text{Hydrogen dioxide}}{H_2O_2} = \overset{\text{Manganese oxide}}{MnO} + \overset{\text{Water}}{H_2O} + \overset{\text{Oxygen}}{O_2}$$

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

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

CHAPTER IX

THE IMPURITIES IN WATER

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

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

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

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

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

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

$$\overset{\substack{\text{Calcium}\\ \text{bicarbonate}}}{CaCO_3.H_2CO_3} + \overset{\substack{\text{Calcium}\\ \text{hydroxide}}}{Ca(HO)_2} = \overset{\substack{\text{Calcium}\\ \text{carbonate}}}{2CaCO_3} + \overset{\text{Water}}{2H_2O}$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The part played by the rivers of the world in changing the face of the globe may be imagined from the fact that in suspended matter alone the Amazon discharges into the sea over 950 million tons of solids per annum, and it has been estimated that the suspended matter annually discharged into the sea by the Mississippi is equal to 4000 million cubic feet of clay, and that the quantity thus conveyed into the Bay of Bengal by the Ganges and Brahmapootra amounts to ten times as much.

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

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

SALTS IN SPRING, RIVER, AND SEA WATER.

In grains per gallon.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Of the processes which combine chemical with mechanical action, the "Porter-Clark" process may be taken as a type. In this system "milk of lime" (p. 113) is mixed, by means of agitators, with the water to be purified, and by combining with the carbonic acid in the water, causes a deposition of the calcium carbonate as a very fine powder—the separation of the finely divided carbonate also mechanically removing a large portion of the organic matter—and the water is then clarified by forcing it through a filter press in which frames covered by stretched canvas or other filtering media retain the solid particles.

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

At a later date filtering material, such as various forms of carbon, spongy iron, and other media were introduced, animal charcoal being the most popular, but as early as 1878, it was pointed out by the Royal Commission on River Pollution, that it had the serious drawback, that when water which had been filtered through it was allowed to stand, minute organisms, both animal and vegetable, made their appearance in the water and rendered it not only unfit to drink but actually offensive. Whilst if the animal charcoal has not been burnt at a sufficiently high temperature, which is rarely done, as it means a certain loss of carbon, some of the nitrogenised organic matter of the bone remains and becomes a breeding-place for myriads of minute organisms which find their way into the water. Also, fresh organic matter like the white of an egg (albumen), which has not yet entered into putrefactive change, passes through animal charcoal almost unacted upon.

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

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

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

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

Fig. 21 shows a section of a single cell tap filter of the Pasteur-Chamberland type, in which (A), the cylinder of unglazed porcelain, is closed at the top, whilst the bottom is provided with an external flange and open nozzle. Surrounding the cylinder is a metal tube (B) sufficiently large in bore to leave a space between it and the sides and top of the porcelain tube. The upper end of this jacket is soldered to the water tap, whilst the lower end can be clamped tightly to the flange of the porcelain tube by the screw cap (c).

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

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

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

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

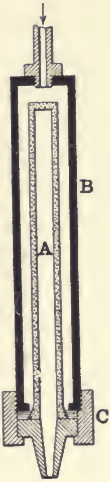


Fig. 21.—Pasteur-Chamberland filter.

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

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

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

CHAPTER X

BOILER INCRUSTATION

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

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

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

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

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

Salts in Solution in River and Sea Water, Grains per Gallon.

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

In the older forms of marine boilers, working at comparatively low pressures, sea water was almost universally employed ; but with the introduction of high-pressure tubular boilers the amount of deposit formed was so serious, and the difficulty of removing the incrustation from between the tubes so great, that it became almost imperative to discontinue the use of the sea water, and to rather accept the expense of supplying the boilers with distilled water than risk the burning and destruction of the tubes and plates in inaccessible portions, where the deposit had to be allowed to collect until the time could be spared for a complete clean out and refit.

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

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

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

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

The presence of calcium sulphate exercises a very marked influence upon the condition and physical properties of the incrustation, as, under the conditions in which it is formed in a boiler, it separates in a crystalline form, and binds the deposit into a hard mass, an action which is also aided by the presence of magnesium hydroxide.

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

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

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

Calcium Sulphate is to the marine engineer the most important constituent of boiler incrustation, and its separation as a deposit from water is dependent upon a totally different class of phenomena to those which bring about the precipitation of calcium carbonate. Calcium sulphate is dissolved in water by the solvent power of the water itself, and not through the agency of carbon dioxide, and therefore merely boiling water at ordinary pressure does not suffice to cause its deposition, and for this reason it forms, together with soluble magnesium salts, the "permanent hardness" of fresh water.

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

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

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

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

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

(1) Deposition of basic magnesium carbonate.

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

(3) Deposition of the calcium sulphate.

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

SALINE CONSTITUENTS PER CENT.

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

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

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

If sea water be boiled merely under atmospheric conditions, it would be quite possible, by taking care that its density does not rise above a certain point (1·09), to prevent the deposition of the calcium sulphate ; but any such regulation of the density is rendered abortive by the fact that pressure, and consequent raising of the boiling-point, acts upon the calcium sulphate in solution in exactly the same way as concentration and increased temperature, so that in the older forms of boiler, working even at a comparatively low pressure, most of the sulphate was deposited, whilst in the high pressure boilers now in use, if the water contains the smallest trace of calcium sulphate, it will be deposited ; and as any deposit formed amongst the tubes in such a boiler cannot easily be got at, it is practically impossible to use sea water in them, so that they are supplied with the water from the condenser augmented by distilled water made in special distilling plant. The question has been raised as to whether, if sea water were mixed with distilled water so as to greatly reduce its density, it would deposit the calcium sulphate ; but experiment shows that, even if sea water is mixed with many hundred times its bulk of distilled water, the minute trace present is deposited under pressure when the temperature approaches 140° C. So that when, through a breakdown in the distilling apparatus, sea water has to be used with the condenser water in even very small quantities, a slight scale is sure to be formed. When a saline solution containing calcium sulphate is heated under pressure or concentrated until calcium sulphate begins to separate, the sulphate will continue to precipitate even after the liquid has cooled down or the pressure has been removed ; and, finally, when calcium sulphate has separated at a high temperature or pressure from sea water, even though the water has only the ordinary density (1·027), the rate at which the sulphate will re-dissolve is so extremely slow that its consideration may be neglected.

These two last properties are due to the form which in the calcium sulphate separates from sea water under pressure. Calcium sulphate occurs in Nature as gypsum, in which each molecule of calcium sulphate is combined with two molecules of water of crystallisation ; when calcium sulphate is deposited from sea water in a boiler it comes down in small crystals containing two molecules of calcium sulphate to one of water ; whilst, after deposition in the boiler and in contact with the heated plates and tubes, it undergoes a further change of crystalline form, loses water, and becomes " anhydrite," which is pure calcium sulphate free from water of crystallisation, and it is this change in crystalline form which binds deposits containing it into such a hard mass.

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

$$\overset{\text{Magnesium chloride}}{MgCl_2} + \overset{\text{Water}}{2(H_2O)} = \overset{\text{Magnesium hydroxide}}{Mg(HO)_2} + \overset{\text{Hydrochloric acid}}{2(HCl)}$$

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

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

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

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

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

When distilled water only is used, a slight coating is formed, practically consisting only of organic matter, whilst if at any time through a breakdown in the distilling apparatus sea water is mixed with the distilled water, a thin and very hard scale of calcium sulphate is formed. An incrustation of this character gave on analysis—

Calcium sulphate	90·84
Magnesium hydroxide	0·75
Sodium chloride	1·41
Silica	0·85
Copper carbonate	1·11
Oxides of iron and alumina	0·24
Organic matter	2·96
Moisture	1·84
	100·00

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

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

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

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

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

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

If the engines of a vessel are in good condition, she will approximately require 1 ton of water per 1000 horse-power per twenty-four hours to make up the volume of the condenser water to the amount required for the boilers, so that even supposing the engines not to be in good order, and considerable waste to take place, twenty tons per diem would be an outside allowance for even very large vessels.

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

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

$$\underset{\text{Calcium sulphate}}{CaSO_4} + \underset{\text{Sodium carbonate}}{Na_2CO_3} = \underset{\text{Calcium carbonate}}{CaCO_3} + \underset{\text{Sodium sulphate}}{Na_2SO_4}$$

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

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

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

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

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

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

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

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

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

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

The cause of this is that the steam brings over some of the lubricants from the cylinders, and the greasy steam being condensed and the water returned to the boiler, takes the oil with it in finely divided particles. Having thus entered the boiler, the minute globules of oil, if in great quantity, coalesce to form an oily scum on the surface of the water, or, if present in smaller quantities, remain as separate drops; but show no tendency to sink, as, their specific gravity being 0·889, they are lighter than the water, and the difference in gravity is probably even greater at the temperature existing in the boiler.

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

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

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

CHAPTER XI

CARBON AND SOME OF ITS COMPOUNDS WITH HYDROGEN

CARBON exists in several allotropic forms ; in the free state it is found as the diamond and as graphite, substances which although they are physically dissimilar, yet can be proved to be chemically identical. That they are both pure carbon is proved by the fact that when equal weights of the diamond and graphite are burnt in oxygen gas, in each case the same weight of carbon dioxide, and nothing else, is produced, whilst if a diamond be heated in the electric arc it swells up and is converted into a black mass resembling graphite.

The diamond occurs in well-defined crystals and has a specific gravity of 3·5. It is one of the hardest substances known, and is used for cutting glass and polishing other precious stones. Graphite, on the other hand, is so soft that when drawn across a piece of paper some rubs off and leaves a mark, and on account of this property it is used as the core of pencils. It has a specific gravity of 2·2, and, unlike the diamond, is a good conductor of electricity.

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

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

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

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

This power of absorption varies with different gases; at ordinary temperatures a cubic inch of freshly prepared cocoanut charcoal will absorb 170 cubic inches of ammonia gas, but only 17 of oxygen. The oxygen absorbed from the air by fresh charcoal is in a highly active condition, and for a certain space of time can be utilised for the destruction of oxidisable gases, but after being kept for a long time, the oxygen by contact with the carbon gradually becomes converted into carbon dioxide. Finely powdered charcoal sprinkled over decomposing animal matter absorbs the gases evolved, and oxidises them by virtue of the condensed oxygen in its pores, and for this reason it is largely used in the construction of sewer traps, and also in respirators.

ABSORPTION OF GASES BY CHARCOAL (HUNTER).

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

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

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

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

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

Twelve parts by weight of carbon will unite with four parts by weight of hydrogen, and when these elements are united in this proportion, the body formed is incapable of combining with chlorine or any other element of the same kind, the constituents having formed what is termed a *saturated compound;* but the compound may exchange the whole or part of its hydrogen for other elements.

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

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

Besides this series there are many others in which the ratio of hydrogen to the carbon is not so high, and which can therefore unite directly with some other elements, and for this reason are called *unsaturated hydrocarbons.*

As examples of these series may be cited—

The Ethylene series having the ratio C_nH_{2n}.
The Acetylene series having the ratio C_nH_{2n-2}.
The Benzene series having the ratio C_nH_{2n-6}.

In the paraffin series the lower members are gaseous, whilst as the molecule becomes more complex they assume the liquid state and become less volatile and more viscid as the series is ascended, the higher members being crystalline solids.

The first member of each of the above series may be taken as illustrating the general chemical behaviour of the whole of the members of the series.

Methane or Marsh Gas.—CH_4 is the first member of the C_nH_{2n+2} series, and is formed in Nature by the slow decay of vegetable matter out of direct contact with air; for instance, the vegetable deposits under water in marshes and pools give off this gas in abundance, and it is also one of the products of the conversion of woody fibre into coal.

Preparation.—Methane has been obtained by the direct union of carbon and hydrogen, but is generally prepared for laboratory purposes by heating a mixture of sodium acetate and sodium hydroxide, when—

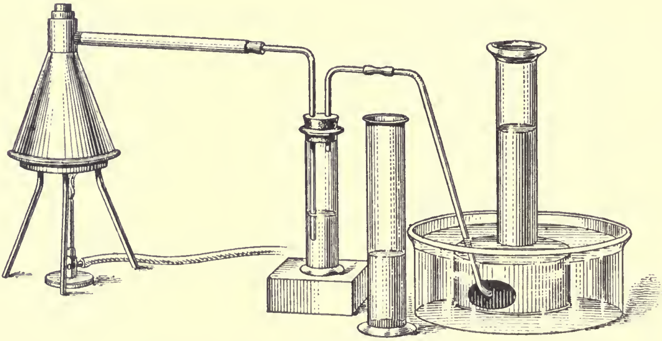


Fig. 22.—Preparation of methane.

$$\underset{\text{Sodium acetate}}{NaC_2H_3O_2} + \underset{\text{Sodium hydroxide}}{NaHO} = \underset{\text{Sodium carbonate}}{Na_2CO_3} + \underset{\text{Methane}}{CH_4}$$

The sodium hydroxide is, in order to facilitate the operation, mixed with quicklime, which, however, takes no part in the decomposition. The heat required to effect decomposition is considerable, and it is therefore found necessary to conduct the operation in a metal generator (Fig. 22); or, if a glass flask is to be used, to protect it by coating it with fire clay, otherwise it would soften at the temperature necessary to cause the evolution of the gas.

Properties.—Methane is a colourless, odourless, tasteless gas, with no distinctive poisonous action. It does not support combustion, but burns with a slightly luminous flame, forming carbon dioxide and water vapour. It is only slightly soluble in water, 100 volumes at 0° C. absorbing about 5·4 of the gas. Until lately it was supposed to be a permanent gas, *i.e.* not reducible to the liquid state, but it has been liquefied by a combination of great pressure and cold; the liquid boils at —155° C.

Coal has the power of occluding methane and again evolving it if the pressure be reduced or the temperature increased. This may occur in coal mines and also in the coal bunkers of a ship. In some cases 100 grains (6·48 grams) of coal will give off as much as 200 cubic centimeters of gas, which on analysis proves approximate to—

Methane	89·61
Nitrogen	9·61
Carbon dioxide	0·23
Oxygen	0·56
	100·00

Methane Explosions.—In the coal bunkers of a ship this liberation of the occluded gases will take place when a sudden fall in the barometer occurs, and also when the vessel passes into regions of increased temperature. In order to prevent accumulation of the liberated gases the coal bunkers should be adequately ventilated, otherwise serious explosions may ensue, many vessels having been lost from this cause.

Methane, when mixed with ten times its volume of air, or twice its volume of oxygen, forms a mixture which explodes with great violence on application of a light, yielding carbon dioxide and water vapour—

$$\underset{\text{Methane}}{CH_4} + \underset{\text{Oxygen}}{2O_2} = \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Water}}{2(H_2O)}$$

and in coal mines not only is methane present occluded in the coal itself, and ready to issue into the workings when a fall of the barometer takes place, but also during the formation of coal under pressure great quantities of methane are generated; and this often is found accumulated under high pressure in the coal seams, discharging itself with considerable violence into the mines from the fissures made in hewing out the coal. The gas issuing from the fissure would burn quietly if a light were applied to it, since methane is not explosive unless mixed with air ; but when the gas escapes into the mine and mixes with air it forms an explosive mixture as soon as the proportion of gas amounts to one-eighteenth of the volume of the air, and the most explosive mixture consists of one volume of methane and ten volumes of air. The explosive mixture of methane and air is called *fire-damp ;* and the gases resulting from the explosion—carbon dioxide, water vapour, and nitrogen—are called *choke-damp*, and this often is as fatal in its effect as the explosion itself.

Safety Lamps.—The mixture of oxygen and methane requires a fixed temperature to ignite it, and unless this temperature be reached explosion cannot result. If a piece of wire gauze is held over a gas jet, the gas may be ignited above it without the flame passing through and igniting the gas on the under side ; the metallic wires composing the wire gauze conducting the heat away so rapidly that the temperature of the gas on the lower side does not rise to the point of ignition.

This simple principle was utilised by Sir Humphry Davy in the construction of the safety lamp for miners. It consists of an oil lamp entirely surrounded with fine wire gauze, through which the air can enter and through which the products of combustion can pass out, but no flame can pass from the inside to the outside of the gauze, even if the explosive gases burn in the interior of the lamp, unless the wire gauze is heated to the ignition point of the methane.

In Fig. 23, three forms of safety lamps are shown ; (1) is the old form first used and entirely surrounded with wire gauze, which, however, gave so feeble an illumination that the wire gauze immediately surrounding the flame was replaced by a glass cylinder (No. 2), and until 1887 this was the best form in use ; it has been shown, however, that although the flame, when burning under ordinary conditions, cannot pass through the gauze, yet a sudden disturbance of the air, such as is caused by the blasting of coal in the mine, will sometimes jerk the flame by a sudden impulse through the gauze, and so communicate with the explosive mixture outside. To do away with this risk a form of lamp has been introduced in which the wire gauze cylinder is entirely surrounded by a shield of iron plate (No. 3), which prevents the direct impact of the air upon the gauze, and greatly increases the value of the lamp.

It would greatly decrease the risk of explosion in coal bunkers and in coaling vessels, if when a light is required, only such lamps were used, and employment of a naked flame never allowed, as besides the gas present, it has been shown that the presence of fine dust of coal in the air of the bunkers very much increases the liability to explosion.

When methane or marsh gas is passed through a tube heated to bright redness it can eventually be decomposed entirely into carbon, which is deposited, and hydrogen which passes on, the same decomposition taking place when a series of electric sparks is passed through the gas, and the hydrogen liberated occupies double the volume of the methane decomposed—

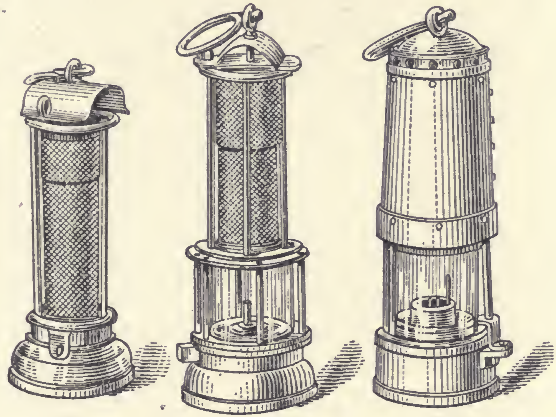


FIG. 23.—Safety lamps.

$$\underset{\text{2 vols.}}{CH_4} = C + \underset{\text{4 vols.}}{2H_2}$$

As we have seen, methane is CH_4, and contains 1 carbon atom combined with 4 of hydrogen. Each member of the group gradually rises by an atom of carbon and 2 atoms of hydrogen at a time, so that its next member is ethane, C_2H_6, and so on to C_4H_{10}, these bodies being gaseous. The next member of the group is pentane, which is a liquid so excessively volatile that unless it be kept in well corked-up cans, very little of it will be left in the can after an hour's exposure on a warm day.

With pentane this series of hydrocarbons becomes liquid, and gradually, with increase in the number of carbon atoms, gets more and more viscid, with a higher and higher boiling point, until at about the fifteenth member of the group one arrives at substances which, although still liquid, are so viscid that the fifteenth member is that jelly-like substance known under the name of vaseline. For another five members they are still slightly viscid, and above the twentieth member of the group begin the real solids, a mixture of which constitutes paraffin wax.

OLEFINES (C_nH_{2n}).

The first member of this series is *ethylene* or olefiant gas (C_2H_4) which exists in small quantities in the gases evolved during the dry distillation of many organic bodies. It is prepared by acting upon alcohol with sulphuric acid, when the alcohol is dehydrated and olefiant gas liberated.

$$\overset{\text{Alcohol}}{C_2H_6O} + \overset{\text{Sulphuric acid}}{H_2SO_4} = \overset{\substack{\text{Sulphuric acid}\\ \text{and water}}}{H_2O,H_2SO_4} + \overset{\text{Ethylene}}{C_2H_4}$$

In preparing the gas one volume of alcohol and four volumes of strong sulphuric acid are mixed with sand, to prevent frothing, and are then heated, care being taken to avoid too high a temperature, which would cause the evolution of sulphur dioxide.

Ethylene or olefiant gas consists of two atoms of carbon combined with four of hydrogen; it is a colourless gas with a slightly sweetish taste; it can be condensed to a liquid by pressure at a temperature of — 100° and burns in air with a luminous smoky flame. When mixed with three times its own volume of oxygen it forms a highly explosive mixture, which if ignited combines, forming carbon dioxide and water.

$$\overset{\text{Ethlyene}}{C_2H_4} + \overset{\text{Oxygen}}{3(O_2)} = \overset{\text{Carbon dioxide}}{2(CO_2)} + \overset{\text{Water}}{2(H_2O)}$$

It used to be called olefiant gas because when mixed with its own volume of chlorine it forms an oily liquid. The members of this series can combine with other elements directly, hence these hydrocarbons are "*unsaturated.*"

$$\overset{\text{Ethlyene}}{C_2H_4} + \overset{\text{Bromine}}{Br_2} = \overset{\text{Ethylene dibromide}}{C_2H_4Br_2}$$

Like methane, it can be decomposed by passing a series of electric sparks through it, and also by heat, which breaks it up in three stages, dependent upon the temperature employed.

Ethylene is one of the constituents of coal gas, which owes some of its illuminating power to its presence.

Acetylene (C_2H_2).—This gas is the first member of the C_nH_{2n-2} series. It is a colourless gas with a garlic-like odour as usually prepared, but with very little smell when quite pure. Water dissolves its own volume of the gas and under a pressure of 21·5 atmospheres at 0° C. the gas is liquefied. It is endothermic and can be detonated into carbon and hydrogen by firing a small charge of mercuric fulminate in it.

It has the formula C_2H_2 and can be most easily prepared by acting upon calcium carbide with water—

Calcium carbide		Water		Acetylene		Calcium hydroxide
CaC_2	+	$2H_2O$	=	C_2H_2	+	$Ca(OH)_2$

Mixed with air it forms an explosive mixture over a very wide range, any mixture containing from 3 to 82 per cent. of acetylene being explosive.

When burnt in a small flat flame it gives a very high illuminating value and is widely used where coal gas is not available. Used with oxygen in a suitable form of blowpipe, an intensely hot flame is produced, which is largely utilised for cutting steel. The thickest armour plate is readily cut by this method and with great economy of cost and time.

Attempts have been made to use it in the liquid state as a source of power and light, but this has proved too dangerous as the liquid alone is liable to detonation, but the gas is very soluble in acetone, and if porous material in a steel cylinder be saturated with acetone and acetylene be then compressed into it, a very large volume of the gas can be taken up, and under these conditions is free from any danger. In this form it is much used for lighting trains, omnibuses, motor cars, yachts, buoys and also for autogenous soldering.

It is formed by the action of heat on hydrocarbons as an intermediary product in their decomposition, and is itself decomposed by heat into its constituents with liberation of the heat taken up during its formation.

Benzene (C_6H_6) is the first member of the C_nH_{2n-6} series of hydrocarbons. It is a colourless liquid having a specific gravity of 0·899. Below 5° C. it forms a white solid, and cooling mixtures containing it to a low temperature is frequently used for its purification. It boils at 80·5° C. and yields a vapour having a distinctive but not unpleasant odour, and as several other hydrocarbons of this series have a similar smell, it was often called the *aromatic series.*

It can be obtained pure by heating benzoic acid with calcium hydroxide—

$$\overset{\text{Benzoic acid}}{C_7H_6O_2} + \overset{\text{Calcium hydroxide}}{Ca(HO)_2} = \overset{\text{Calcium carbonate}}{CaCO_3} + \overset{\text{Water}}{H_2O} + \overset{\text{Benzene}}{C_6H_6}$$

It is present in coal tar, which is the commercial source from which it is usually obtained, but perhaps the most interesting method of forming it is by heating acetylene when three molecules of the latter combine together to form benzene.

$$\overset{\text{Acetylene}}{3C_2H_2} = \overset{\text{Benzene}}{C_6H_6}$$

It will be seen that acetylene and benzene contain the same elements in the same proportions by weight, and are therefore *isomeric.*

Coal Gas.—The compounds of hydrogen and carbon we have taken as types all play an important part in products of the destructive distillation of coal for the production of coal gas.

Bituminous coal rich in hydrogen, is heated out of contact with air in fireclay retorts which may be set in a horizontal, sloping or vertical position, and the products of distillation are then led off by a tube from the mouth of the retort. In the case of horizontal or sloping retorts this tube, after ascending above the level of the bench of retorts, bends over and descends into a cylindrical tube, which is about half full of tar; and into this the delivery tube from the retort just dips, the tar closing the mouth of it gas-tight. This main collecting tube runs horizontally over the whole of the front of the bench of retorts, and they all discharge into it by means of their delivery tubes, each of which is sealed off by the tar, kept at a constant level by means of an overflow siphon at the end of the collecting tube, which is called the hydraulic main.

Each retort is fitted at the end which projects from the furnace with a mouth-piece and lid, which can be removed to allow of the coke being withdrawn and the fresh charge of coal inserted, and the vertical pipes which lead up to the hydraulic main start from the top of the mouth-piece. The reason why these pipes are sealed by dipping under the surface of the liquid in the hydraulic main is that the gas from the other retorts cannot escape down the pipe, as would be the case if they simply opened into the main, and this enables any of the retorts to be opened for recharging, whilst the others are still giving off gas, and also prevents leakage from the whole bench of retorts should one accidentally crack. A large quantity of volatile products escapes as vapour with the gas into the hydraulic main, where much condenses as tar and ammoniacal liquor (consisting of ammonia, carbonate and sulphide of ammonium, etc., in solution), and these run off through the overflow siphon to the tar well, where they are collected. The gas passes down from the hydraulic main to the condensers, which cool down the gas as it passes through them and cause a further deposition of tar, ammoniacal liquor, and any easily condensable hydrocarbon which may be present. After leaving the condensers the gas next passes through the scrubbers, which consist of towers built of iron plate and filled with coke, or brushwood, over which water or diluted ammoniacal liquor is sprayed and trickles down, meeting the gas which is made to pass up them. The alkaline liquor absorbs some of the sulphuretted hydrogen and carbon disulphide present in the gas, and also removes the last traces of tar and ammonia, and the gas still containing some sulphuretted hydrogen, carbon disulphide and carbon dioxide, passes on to the purifiers.

Purification.—It is important to get rid of these impurities, as carbon dioxide when present even in small quantities affects the illuminating power of the gas to a serious extent, whilst carbon disulphide and sulphuretted hydrogen on combustion produce sulphur dioxide, which in contact with air and condensing moisture becomes oxidised to sulphuric acid, and this is credited with having a detrimental effect upon the furniture and drapery of rooms.

The gas first comes to the dry lime purifiers, where it passes over trays or through grids on which is placed slaked lime, and this absorbs the carbon dioxide, sulphuretted hydrogen, and a good deal of the carbon disulphide, forming calcium carbonate and sulphide, whilst cyanides are also found in the spent lime. To remove the last of the impurities the gas is now passed through other purifiers containing hydrated ferric oxide or else a mixture of sulphate of iron, sawdust, and slaked lime, which combining with the last trace of sulphuretted hydrogen keeps it back, whilst the gas passes on to the gasometer and thence to the mains.

The spent lime from the purifiers is difficult to get rid of, and as it gives off sulphuretted hydrogen in contact with air, its removal creates a nuisance in the neighbourhood of the works, and for this reason lime purification for sulphur compounds has been largely given up and iron purification used to remove the sulphuretted hydrogen.

Bituminous coal may be looked upon as containing the residues left after geological ages of the vegetable tissues and resinous constituents of a prehistoric vegetation, and consists of carbon and peaty compounds containing oxygen luted together by resinous bodies and hydrocarbons formed from them.

On submitting a complex substance of this character to destructive distillation, it will be found that the yield and quality of the products will vary very considerably with the temperature existing in the retorts, with the size of the charge of coal used, with its distribution in the retort, with the length of time the distillation has been going on, and with an infinity of other factors of a more or less complex nature. The products will, however, in their main characteristics remain the same. They may be divided into: (*a*) Solids, such as the coke and retort carbon; (*b*) liquids, consisting of the tar and ammoniacal liquor; and (*c*) gases, consisting of the unpurified coal gas.

Carbon Residue.—The chief solid residue, coke, is not pure carbon, as it contains the mineral non-volatile constituents which remain behind as ash when the original coal is burnt, and which, to a considerable extent, existed in the sap that filled the cells in the vegetation from which the coal was found, and it also contains a certain amount of volatile matter which the heat of carbonisation has failed to drive out. The retort carbon formed as a dense deposit on the crown of the retort by the action of the high temperature upon the hydrocarbons is, however, carbon in a very pure form; and, on account of its density, it is largely used for electrical purposes.

Tar.—The liquid products of the destructive distillation of coal are tar and ammoniacal liquor. Tar derived from ordinary bituminous coal is a black, somewhat viscid liquid, varying in specific gravity from 1·06 to 1·2. This is dependent upon the temperature to which the tar vapour has been exposed during distillation, low temperatures giving much tar of low specific gravity (1·06 to 1·1) whilst at the high temperatures used in large gasworks, the tar is less in quantity, contains quantities of soot, and has a specific gravity of 1·2.

The ultimate composition of tar is approximately as follows :—

Carbon	77·53
Hydrogen	6·33
Nitrogen	1·03
Sulphur	0·61
Oxygen	14·50
	100·00

These elements in tar are built up into about 140 different compounds, traces of which can be identified ; but for all practical purposes we may take the following as being the chief constituents—

	Neutral hydrocarbons.	Boiling point, °C.	Formulæ.	Sp. Gr.
Liquid	Benzene	80	C_6H_6	0·88
	Toluene	110	C_7H_8	0·87
	Xylene	142	C_8H_{10}	0·87
	Isocumene	170	C_9H_{12}	0·85
Solid	Naphthalene	217	$C_{10}H_8$	—
	Anthracene	360	$C_{14}H_{10}$	—
	Chrysene	—	$C_{18}H_{12}$	—
	Pyrene	—	$C_{16}H_{10}$	—
	Alkaline products.	Boiling point, °C.	Formulæ.	Sp. gr.
	Ammonia	—	NH_3	—
	Aniline	182·5	C_6H_7N	1·02
	Picoline	130	C_6H_7N	0·96
	Quinoline	239	C_9H_7N	1·08
	Pyridine	117	C_5H_5N	—
	Acids.			
	Carbolic acid	180	C_6H_6O	1·07
	Cresylic ,,	—	C_7H_8O	—
	Rosolic ,,	—	$C_{19}H_{14}O_2$	—
	Brunolic ,,	—	—	—
	Acetic .,	118	$C_2H_4O_2$	1·06
	Free carbon.			

In roughly considering the proportions in which the main constituents occur in coal tar, we can still further simplify the composition, and look upon it as containing benzene, naphtha, naphthalene, anthracene, carbolic acid, and pitch ; and if this tar be carefully re-distilled, it can be separated into the constituents which distil over at various temperatures.

First, light oils pass over, from which benzene and its homologues can be obtained ; then heavy tar oil, from which carbolic acid is made ; and finally anthracene oil, from which a substance called anthracene can be separated, pitch being left. The benzene obtained is the source from which aniline is prepared ; and it is from aniline that most of the coal-tar colours are derived.

When benzene is acted upon with strong nitric acid, *nitro-benzene* [$C_6H_5(NO_2)$] is formed. On treating this with dilute sulphuric acid and zinc dust, or acetic acid and iron filings, hydrogen is evolved, and in its nascent state attacks the nitro-benzene and removes its oxygen—leaving behind the compound of carbon, hydrogen, and nitrogen called *aniline* [$C_6H_5(NH_2)$]. It is from aniline that the brilliant colours, mauve, magenta, and other purples and reds, are produced by acting upon it with oxidising agents ; and from it can also be obtained the beautiful series of aniline yellows, blues, and violet.

The naphthalene used in the albo-carbon system of enriching gas is prepared from the second portion of the distillates, and this portion is also rich in phenols and cresols. The second distillate is again distilled ; and the residue left becomes semi-solid, owing to the separation of naphthalene, which on standing collects and cakes on the top of the oil. This is then removed, and pressed by hydraulic power in a hot press, each plate of which contains a steam pipe to heat it. The crude naphthalene so obtained is then distilled ; but it still contains a number of impurities, which would cause it to turn yellow. To get rid of these, it is melted, and forced by steam pressure into a steam-jacketed cylinder, where it is washed in dilute alkali to get rid of the phenol, and four times with strong sulphuric acid to remove sulphonates, meta-naphthalene, etc. It is then water-washed free from acid. These washings take about seventy-two hours. The naphthalene now undergoes a final distillation, after which it is melted in steam-jacketed coppers, and is ladled out and cast into sticks in an apparatus of the same construction as the old-fashioned candle-machines ; these sticks being afterwards cut into the smaller pieces used in the lamp reservoirs.

Gas Liquor.—The second liquid product of the destructive distillation of coal is the ammoniacal gas liquor, which consists of water partly condensed from the hot gas, and partly added to wash the gas in the scrubbers. It contains, as its principal constituents, ammonia, partly combined with carbonic acid and sulphuretted hydrogen to form compounds which are decomposed on boiling, with evolution of ammonia gas, and partly combined with stronger acids to form compounds which require to be acted upon by a strong alkali before the ammonia contained in them can be liberated. The ammonia in the first class of compounds is technically spoken of as "free"; that present in the latter as "fixed." The following analysis will give an idea of the relative quantities in which these compounds exist in the liquor:—

		Grammes per litre.
Free.	Ammonium sulphide	3·03
	Ammonium carbonate	39·16
Fixed.	Ammonium chloride	14·23
	Ammonium thiocyanate	1·80
	Ammonium sulphate	0·19
	Ammonium thiosulphate	2·80
	Ammonium ferrocyanide	0·41

From a scientific point of view, the term "free" is absolutely incorrect; and in using it, the fact must be clearly borne in mind that in this case it merely stands for ammonia which can be liberated on simply boiling the liquor.

Composition of Coal Gas.—The gas which is obtained by the destructive distillation of coal, and which we employ as our chief illuminant, is not a definite compound, but a mechanical mixture of several gases, some of which are reduced to the lowest limit, in order to develop as fully as possible the light-giving properties of the most important constituents of the gas.

The following analysis gives a fair idea of the composition of an average sample of gas made from coal and without enrichment—

Hydrogen	52·22
Unsaturated hydrocarbons	3·47
Saturated hydrocarbons	34·76
Carbon monoxide	4·23
Carbon dioxide	0·60
Nitrogen	4·23
Oxygen	0·49
	100·00

These constituents may be divided into three classes:—(*a*) light-yielding hydrocarbons; (*b*) combustible diluents; and (*c*) impurities.

The hydrocarbons, upon which the luminosity of the flame entirely depends, are divided in the analyses into two groups—saturated and unsaturated—according to their behaviour with a solution of bromine in potassium bromide, which has the power of absorbing those termed "unsaturated," but not affecting in diffused daylight the gaseous members of the saturated series of hydrocarbons; and they may be separated in the same way by concentrated sulphuric acid, which has an absorbent effect on the one class, and not on the other.

The chief unsaturated hydrocarbons present in coal gas are—

Ethylene	C_2H_4
Butylene	C_4H_8
Acetylene	C_2H_2
Benzene	C_6H_6
Naphthalene	$C_{10}H_8$

Whilst the saturated hydrocarbons consist chiefly of—

Methane	CH_4
Ethane	C_2H_6

The light-giving power of coal gas is undoubtedly entirely due to the hydrocarbons; and the idea held up to sixteen years ago was that the illuminating value depended upon the amount of ethylene present. This, however, is manifestly incorrect, as, if it were true, 4 per cent. of ethylene mixed with 96 per cent. of a combustible diluent such as hydrogen should give a 16 to 17 candle gas, whereas a mixture of 10 per cent. of ethylene and 90 per cent. of hydrogen is devoid of luminosity. In 1876, Berthelot came to the conclusion that the illuminating value of the Paris coal gas was almost entirely due to benzene vapour. But here, again, another mistaken idea arose, owing to a faulty method of estimating the benzene; and there is no doubt but that methane is certainly one of the most important of the hydrocarbons present, when the gas is burnt in such a way as to evolve from it the proper illuminating power, while the benzene vapour, small as the quantity is, comes next in importance, and the ethylene last. It is the combined action of the hydrocarbons which gives the effect; not any one of them acting alone.

Flame.—The use of coal gas for illuminating and heating purposes necessitates the consideration of the structure and properties of flame.

When a solid which is incapable of being volatilised burns under ordinary conditions, no flame is produced, but when a volatile solid, a vapour or a gas undergoes combustion in air, flame is formed.

Flame may therefore be looked upon as the combustion of gaseous matter, and as combustion is merely extremely vigorous chemical combination, it is manifest that if the gases only come in contact during combustion, the flame can only exist where the two gases meet.

If a jet of hydrogen be ignited in air, the conical flame which is produced consists of a hollow sheath of burning gas, surrounding an inner core of unburnt hydrogen, and flames formed by a simple gas which burns without decomposition and only forms one product from its combustion, all have this simple structure, the sheath of flame being produced where the combining gases meet.

The fact that such a flame is hollow can be at once proved by inserting a tube into the inner cone, when some of the unburnt gas will pass through it and can be burnt at the other end.

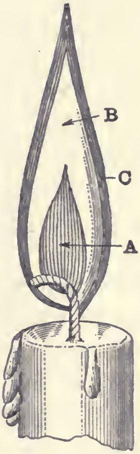


Fig. 24.—Diagram of candle flame.

Compound gases, which undergo decomposition during combustion, or gaseous mixtures give flames with a rather more complex structure, and it is usual to describe the flame of coal gas or of a candle as consisting of three zones. The first of these is the inner non-luminous cone (A, Fig. 24), in which no combustion is taking place, but where some very important chemical changes are going on, the second (B) is the zone of luminosity, upon which the light-giving power of the flame depends, whilst the third is a thin non-luminous envelope which entirely surrounds the flame, and which is clearly seen if a small piece of card be held in front of the flame so as to shield the eye from the light emitted by it and only to leave the edge visible. This latter zone may be again divided into two parts, a small blue portion at the base of the flame and the envelope of the upper part of the flame.

The Actions in a Candle Flame.—When a candle is lighted, the burning wick melts the wax or material of the candle in contact with it, and then by capillarity sucks up the liquid, and the heat of the burning wick in the first instance, and afterwards the heat of the flame, convert the hydrocarbons into a mixture of gases and vapours of much the same character as a rich coal gas.

In each case, therefore, the gases flowing from the wick or the jet contain unsaturated hydrocarbons, methane and hydrogen as their chief constituents.

These gases when ignited burn, but the lighter they are the more rapidly will they diffuse and so reach the outside of the flame; the result of this is that the hydrogen and the methane are the first to burn, and the heavier hydrocarbons flowing upwards between the walls of flame become highly heated and largely converted into a mixture of acetylene and hydrogen.

Taking ethylene as the type of the unsaturated hydrocarbons present in the gas, the change would be represented by—

$$\begin{array}{ccccc} \text{Ethylene} & & \text{Acetylene} & & \text{Methane} \\ 3(C_2H_4) & = & 2(C_2H_2) & + & 2(CH_4) \end{array}$$

and near the edges of the inner non-luminous zone 80 per cent. of the unsaturated hydrocarbons present are found to be acetylene. The temperature of the flame rapidly rises the higher the point, and at the spot where the luminosity of the flame commences the temperature is over 1,000° C., and this causes sudden and extremely rapid decomposition of the acetylene into its constituents—

$$\begin{array}{ccccc} \text{Acetylene} & & \text{Hydrogen} & & \text{Carbon} \\ C_2H_2 & = & H_2 & + & C_2 \end{array}$$

Acetylene being an endothermic compound, at the moment of decomposition heat is liberated, and having no time to dissipate itself amongst the other gases present, heats up the carbon particles to a temperature far higher than the average temperature of the flame, causing them to become incandescent and so rendering the flame luminous, the incandescence of these solid carbon particles being further aided by the temperature of the flame and by their own combustion, partly by the oxygen of the air and partly by the action of water vapour and carbon dioxide upon them—

$$(a)\quad \overset{\text{Carbon}}{C} + \overset{\text{Oxygen}}{O} = \overset{\text{Carbon monoxide}}{CO}$$

$$(b)\quad \overset{\text{Carbon}}{C} + \overset{\text{Water vapour}}{H_2O} = \overset{\text{Carbon monoxide}}{CO} + \overset{\text{Hydrogen}}{H_2}$$

$$(c)\quad \overset{\text{Carbon}}{C} + \overset{\text{Carbon dioxide}}{CO_2} = \overset{\text{Carbon monoxide}}{2CO}$$

and it is the combustion of the carbon monoxide and hydrogen which gives the outer non-luminous envelope to the flame.

The small blue portion of the outer envelope at the base of the flame is caused by the rapid inrush of air, the nitrogen so diluting the hydrocarbon molecules at that point that they are burnt up without being first decomposed, and there being therefore no separation of carbon there is no luminosity, and the same blue colour may be observed when a gas flame is rendered non-luminous by dilution with nitrogen or carbon dioxide.

This explanation holds good for all luminous hydrocarbon flames, but the combustion of many other substances emits light, such as phosphorus, magnesium, zinc and arsenic, but in these cases the products of combustion are solid, and in the finely divided condition in which they are formed are rendered incandescent, and in the case of phosphorus and arsenic are again volatilised by the heat of their own formation.

Flames which can only contain gaseous matter can be rendered incandescent if a sufficiently high temperature can be obtained; for instance, if hydrogen be burnt in an atmosphere of oxygen under a pressure of several atmospheres, light is developed, but the temperature of such a flame is many times hotter than an ordinary hydrogen flame burning in oxygen, as pressure acts on flame in the same way as on a gas, and at a pressure of several atmospheres, several times the amount of hydrogen and oxygen would be consumed, as would be the case under ordinary conditions of temperature and pressure.

The luminosity of flame may therefore be stated to be due either to the presence of incandescent solid particles, or at a far higher temperature to incandescent gases.

Bunsen Flames.—If air be supplied to the interior of a flame it loses its luminosity, an effect due partly to the oxygen so supplied causing complete combustion of the carbon, and partly also to the diluting influence of the other constituent of air, nitrogen.

It is upon this principle that the Bunsen burner is constructed.

Gas is brought through the tube (A, Fig. 25) under the ordinary pressure, and is discharged from a small orifice into a metal chamber, which has holes at the side open to the air, and into which is screwed a vertical tube (C) which is immediately over the orifice from which the gas is issuing. The gas rushes upwards and impinges on the side of the tube (C), diminishing the pressure at the sides of the chamber (B) by its uprush, and so the air is drawn in through the holes at the side, the mixture of air and gas passing together up the tube and being burnt at the top. That the non-luminosity of the flame is due to the air introduced can be proved by closing the air holes with the fingers, when the ordinary luminous gas flame is at once obtained. The Bunsen flame is smaller and more compact than the flame given by the same amount of gas burning without admixture of air.

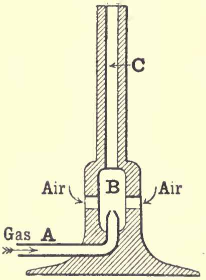


Fig. 25.—Diagram of Bunsen burner.

Oxidising and Reducing Flames.—In the Bunsen flame, and also in a blow-pipe flame obtained by blowing air through an ordinary flame, the different parts have different chemical functions.

If a piece of metallic copper be held just beyond the extreme tip of the flame (B, Fig. 26), it will quickly become coated with black copper oxide, because the flame will have used up all the oxygen it requires for its own combustion, and the great heat generated will make any oxidisable metal combine with the oxygen of the air present; for this reason the outer is called the *oxidising flame*. If, however, the copper oxide so formed is held in the inner zone of the flame at (A), there combustion is not complete, and the unburnt hydrocarbons or carbon monoxide will attack the metallic oxide and take from it its oxygen, forming carbon dioxide, at the same time reducing the copper oxide to metallic copper; hence the inner zone is called the *reducing flame*.

In the complete combustion of any of the hydrocarbons, carbon dioxide and water vapour are the products formed.

The Incandescent Mantle.—The discovery by Dr. Auer von

Welsbach in 1885 of the method of making the incandescent gas mantle, and the use of the oxides of thorium and cerium for its composition, discovered in 1892, gave a method of developing light from coal gas which has so far surpassed any other way of burning it that the old forms of burner are now but little used. This system consists of consuming the gas in an atmospheric or Bunsen burner, so as to obtain a non-luminous but very hot flame, and then utilising this to raise to incandescence a mantle made of—

Thorium oxide	99
Cerium oxide	1
	100

a mixture having a far higher power of light emissivity than carbon particles.

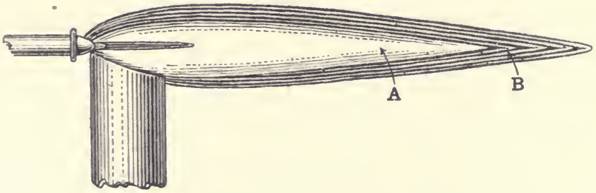


Fig. 26.—Diagram of blowpipe flame.

The mantles are made by saturating a cotton fabric with a solution of the nitrates of the two metals mixed in the right proportions. The fabrics are then shaped and dried and are burnt in a Bunsen flame, the organic matter of the original fabric burning away and the nitrates being converted into oxides which retain the shape of the original structure. The oxide mantle is then shaped and hardened in a blowpipe flame and is rendered sufficiently strong for handling and distribution by dipping it in a solution of collodion. When fixed on the burner the collodion is burnt off, and the mantle of oxides, which just fits the outer zone of the Bunsen flame, is heated to high incandescence and emits ten times the light that the same amount of gas burnt in flat flame burner would have given.

The Standard of Light to which the illuminating power of gases is compared is that emitted by a sperm candle burning

120 grains per hour, but irregularities in burning have led to the adoption of a lamp burning pentane vapour (C_5H_{12}) as the standard for comparison, the results, however, being still expressed in terms of the standard candle.

CHAPTER XII

THE OXIDES OF CARBON

Carbon, when burnt in a free supply of air or in oxygen, forms carbon dioxide (CO_2), unless the combustion be checked or a large excess of red-hot carbon be present, in which case a second oxide—carbon monoxide (CO) is formed.

Carbon dioxide (CO_2) occurs free in the air and is also present in many mineral waters, and is frequently found in wells and old mine shafts, and being irrespirable, often proves fatal to workmen who descend them without first taking the precaution of ascertaining its absence.

Carbon dioxide is found combined with various bases as carbonates, which are very plentiful in Nature, whole chains of hills being formed of calcium carbonate or chalk.

Preparation.—When carbon is burnt in oxygen gas, the oxygen is converted into carbon dioxide, which occupies the same volume as the oxygen used in its formation.

$$\underset{C}{\text{Carbon}} \quad + \quad \underset{O_2}{\text{Oxygen, 2 vols.}} \quad = \quad \underset{CO_2}{\text{Carbon dioxide, 2 vols.}}$$

This may be shown by burning carbon in oxygen confined over mercury in the apparatus (Fig. 27).

A bulb tube is closed by a glass stopper (B) through which pass a small deflagrating spoon (D) and a thick copper wire (E); these are joined by a piece of thin platinum wire, which is coiled round a small lump of charcoal in the spoon (D).

The bulb having been filled with oxygen, the stopper is closed, and the height of the mercury at (F) having been noted, a current from a battery is passed through the connections (CC), and heats the thin platinum wire to redness, igniting the charcoal, which burns in the oxygen forming carbon dioxide. The heat generated by the combustion expands the gas and depresses the mercury, but on allowing the gas and apparatus to cool down to its original temperature, the mercury again rises to the point (F), showing that no change in volume has taken place.

The most convenient way of preparing it is to act upon calcium carbonate with a strong acid, which expels the carbon dioxide and unites with the calcium, at the same time forming water.

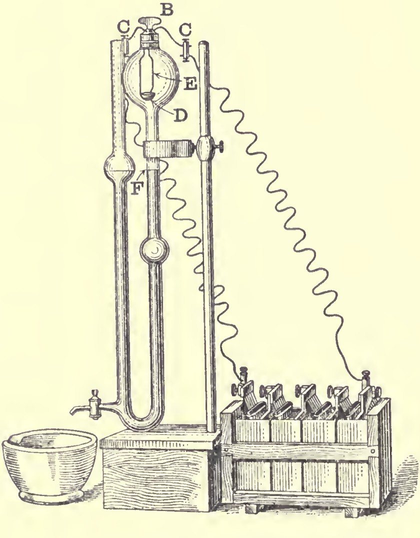


Fig. 27.—Carbon burning in oxygen.

Calcium carbonate		Hydrochloric acid		Calcium chloride		Water		Carbon dioxide
$CaCO_3$	+	$2(HCl)$	=	$CaCl_2$	+	H_2O	+	CO_2

This is most conveniently done by taking a dense form of calcium carbonate, either limestone or marble (which, as well as chalk, are all the same composition but formed under different circumstances) in order to avoid frothing which would follow if the less dense substance (chalk) had been used, and after breaking into small pieces, placing it in a two-necked bottle (see Fig. 6, p. 38), the calcium carbonate is now covered with water and hydrochloric acid is poured down the thistle funnel; carbon dioxide escapes in abundance and is conducted by the leading tube under water in the pneumatic trough, where it can be collected by displacement of water.

Properties.—Carbon dioxide is a colourless, odourless gas which will not burn or support ordinary combustion; it has a slight acid taste and reaction. Carbon dioxide is twenty-two times as heavy as hydrogen, and may be poured from one vessel to another like water. It does not burn or support combustion in the ordinary sense of the word, but the metal potassium when heated will burn in it, decomposing it, and forming potassium oxide, at the same time depositing carbon.

$$\overset{\text{Carbon dioxide}}{\mathrm{CO_2}} + \overset{\text{Potassium}}{\mathrm{4K}} = \overset{\text{Potassium oxide}}{\mathrm{2(K_2O)}} + \overset{\text{Carbon}}{\mathrm{C}}$$

And the potassium oxide so formed at once combines with the excess of carbon dioxide present, forming potassium carbonate.

$$\overset{\text{Potassium oxide}}{\mathrm{K_2O}} + \overset{\text{Carbon dioxide}}{\mathrm{CO_2}} = \overset{\text{Potassium carbonate}}{\mathrm{K_2CO_3}}$$

In most of its properties it resembles nitrogen, but can be distinguished from it by giving a white precipitate with lime water, with which it combines, forming calcium carbonate, and as this is practically insoluble, it is thrown down as a precipitate.

$$\overset{\substack{\text{Lime water or}\\ \text{calcium hydroxide}}}{\mathrm{CaH_2O_2}} + \overset{\text{Carbon dioxide}}{\mathrm{CO_2}} = \overset{\substack{\text{White precipitate of}\\ \text{calcium carbonate}}}{\mathrm{CaCO_3}} + \overset{\text{Water}}{\mathrm{H_2O}}$$

Carbon dioxide is completely absorbed by sodium or potassium hydroxide, whether in solution or when the solid is moistened. The carbon dioxide unites with the alkaline hydroxide forming a carbonate and liberating water.

$$\overset{\text{Potassium hydroxide}}{\mathrm{2(KHO)}} + \overset{\text{Carbon dioxide}}{\mathrm{CO_2}} = \overset{\text{Potassium carbonate}}{\mathrm{K_2CO_3}} + \overset{\text{Water}}{\mathrm{H_2O}}$$

a reaction frequently used to separate carbon dioxide from other gases not absorbed by the alkaline hydroxide.

Carbonic Acid.—Carbon dioxide in presence of water or moisture has faint acid properties, but does not completely neutralise the alkalies, and when added to a solution of blue litmus turns it claret red; but the original blue colour can be restored by boiling which drives off the carbon dioxide; other acids, like sulphuric or nitric, give with blue litmus a bright red, which is permanent on boiling.

The solution of carbon dioxide in water is supposed to contain the hydrogen salt H_2CO_3, carbonic acid, from which the class of salts called carbonates is produced by replacement of the hydrogen by metals, but the acid has never been isolated.

It forms two classes of salts—normal carbonates, in which both atoms of hydrogen are replaced by metals, as—

$$\overset{\text{Sodium hydroxide}}{2(NaHO)} + \overset{\text{Carbonic acid}}{H_2CO_3} = \overset{\text{Sodium carbonate}}{Na_2CO_3} + \overset{\text{Water}}{2(H_2O)}$$

and acid carbonates, or bicarbonates as they are often called, in which only half the hydrogen present is replaced—

$$\overset{\text{Sodium hydroxide}}{NaHO} + \overset{\text{Carbonic acid}}{H_2CO_3} = \overset{\text{Sodium bicarbonate}}{NaHCO_3} + \overset{\text{Water}}{H_2O}$$

Nearly all spring waters contain the gas carbon dioxide dissolved in them in greater or less quantity; and many of the properties of spring water, such as temporary hardness, are due to its presence, the carbon dioxide in solution forming an unstable acid called carbonic acid, which is able to dissolve many substances, such as chalk (calcium carbonate), magnesium carbonate, and ferrous carbonate, which the water alone is unable to do, or at any rate only to a small extent. The carbon dioxide so present is obtained by the water partly from the subsoil through which it has filtered, and to a much larger extent from subterranean sources. It is well known that caverns, deep wells, mines, etc., nearly always contain large quantities of this gas, and also that it issues in large quantities from fissures in the ground in various parts of the globe; and as it is always present in underground strata, it is evident that water permeating these strata will become charged with as much of this gas as it can take up.

Water, under ordinary conditions of temperature and pressure, dissolves its own volume of the gas—that is to say, at 15° C., and with the barometer standing at 30 inches (760 mm.) a pint of water will dissolve a pint of the gas; but a change either in the temperature of the water or in the pressure of the atmosphere, will be accompanied by a change in the quantity of gas dissolved, so that if the water were cooled down to 0° C., the pint of water, instead of dissolving one pint of the gas, would dissolve nearly one and three-quarter pints. Any increase of the atmospheric pressure, shown by a rise in the barometer, would also cause an increased absorption of the gas, and if the water be then brought to its initial temperature of 15° C., or if the extra pressure were removed from its surface, the amount of carbon dioxide over and above the pint it can dissolve under those conditions once more escapes and causes the water to effervesce.

In the case of many springs which rise from considerable depths, the water has come in contact with carbon dioxide under increased pressure, the gas being confined in subterranean caverns through which the water passes; and such springs, on reaching the outer air, give off once more the excess of gas which they have taken up, the pressure being reduced to ordinary atmospheric pressure. Such waters sparkle and effervesce, and being very pleasant to the palate were much sought after as table waters; but, from the rarity of the springs and the paucity of the supply, waters of this kind, such as the natural seltzer water, commanded a high price, and attempts were made to manufacture them artificially.

Aërated Waters.—The machines in use for saturating water with carbon dioxide are numerous, but the principle in nearly all is the same.

Carbon dioxide is generated by acting upon some carbonate, generally carbonate of lime in the form of whiting, with dilute sulphuric acid, and the gas so generated is led into a gasometer, after having been washed by passing through water. Liquid carbon dioxide is now largely employed by mineral water manufacturers. It is obtained from the vats in which malt liquors are fermented, whence it is drawn off, compressed and sent into the market in steel cylinders. The gasometer is connected with a gun-metal pump, which also is connected with a reservoir containing pure water, in which about one ounce of bicarbonate of soda has been dissolved to every gallon of water; this solution and the carbon dioxide are forced together by means of a pump into a very strong condenser lined with tin, and in which the gas and liquid are agitated together by means of revolving arms fixed on a spindle and driven at high speed, and it is in this condenser that the water becomes highly impregnated with the gas under pressure.

The liquid is then drawn off, corked and wired down whilst still under pressure, and so long as the cork fits airtight into the bottle the pressure will be maintained, but the moment the cork is taken out the liquid is brought back to ordinary atmospheric pressure, and the excess of gas escapes.

The main points to be attended to in making a highly aërated water are to drive all air out of the apparatus before the manufacture commences, and to maintain a regular, but not too high pressure in the condenser chamber.

The earliest forms of aërated waters were made by mixing together in the bottle two solutions which would act upon each other and generate carbon dioxide in the liquid itself; the great drawback to this is that the salts so introduced have an effect upon the system, which, except in special cases, it is well to avoid.

In sparkling wines and the old-fashioned ginger beer, carbon dioxide is generated in the bottle by fermentation of the liquid present, and this gas as it escapes into the space above the liquid creates a greater and greater pressure, and assists its own solution.

In the various forms of gasogenes used for making effervescing drinks in the house, a mixture (usually consisting of tartaric acid and bicarbonate of soda) is introduced into the lower portion of a glass apparatus, and generates carbon dioxide, which passing up through a tube develops pressure, and saturates water in the upper part of the arrangement.

Liquid Carbon Dioxide.—Carbon dioxide can be condensed to a liquid by cold or by a pressure of 36 atmospheres at 0° C., and if the liquid carbon dioxide is allowed to assume the gaseous state, by letting some of the liquid escape into the air in the manner described, the cold produced by the sudden transition from the liquid to the gas is so intense that some of the liquid is frozen into the solid form, and produces a snow-like substance which blisters the hands when pressed upon the skin and has a temperature below — 78° C.

By placing the solid carbon dioxide in contact with mercury and adding a little ether, the cold produced is so intense that the mercury is frozen, and it is possible to attain a temperature of — 101° C. by this method.

CARBON MONOXIDE.

Preparation.—When carbon dioxide is passed over red-hot charcoal, the dioxide gives up one half its oxygen to the carbon, and forms twice its own volume of carbon monoxide.

$$\begin{array}{ccccc} \text{Carbon dioxide, 2 vols.} & & \text{Carbon} & & \text{Carbon monoxide 4 vols.} \\ CO_2 & + & C & = & 2(CO) \end{array}$$

The pure gas may be made by heating formic acid with sulphuric acid, the decomposition being of the same character as with oxalic acid, but carbon monoxide only is evolved—

$$\begin{array}{ccccc} \text{Formic acid} & & \text{Water} & & \text{Carbon monoxide} \\ \left\{\begin{matrix} H \\ COOH \end{matrix}\right. & = & H_2O & + & CO \end{array}$$

It may also be prepared by acting upon oxalic acid with sulphuric acid, oxalic acid consisting of hydrogen, carbon, and oxygen in the proportions necessary to form water, carbon dioxide, and carbon monoxide. When this is heated with sulphuric acid, the elements of water are taken up by the acid, and carbon dioxide and monoxide are set free; these mixed gases are now led through sodium hydroxide, which absorbs the carbon dioxide, forming sodium carbonate and water, and the carbon monoxide passes on free.

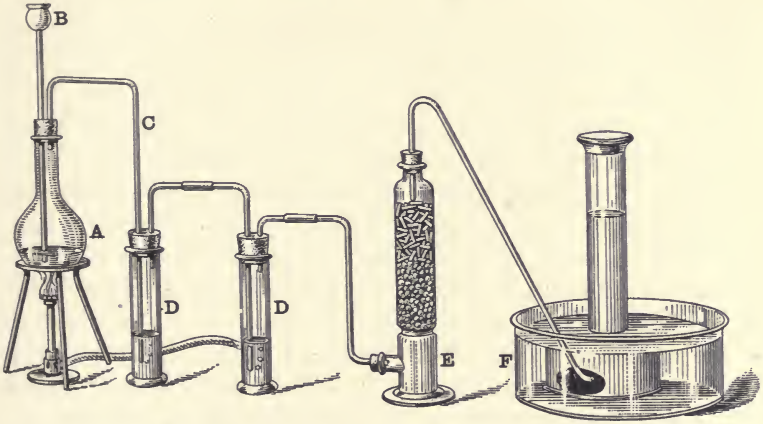


Fig. 28.—Preparation of carbon monoxide.

The operation is carried on in an apparatus such as is shown at Fig. 28.

The mixture of oxalic and sulphuric acids is heated in the flask (A), fitted with a safety funnel (B), and the mixed carbon monoxide and dioxide pass by means of the leading tube (C) through a solution of sodium hydroxide in the wash bottles (DD);

this absorbs some of the carbon dioxide, the remainder being got rid of in the absorption tower (E), which is filled with glass marbles, on the top of which are sticks of moistened sodium hydroxide; the purified carbon monoxide then passes on and is collected over water in the pneumatic trough (F). The action may be represented by the equations—

$$\begin{array}{ccccccc} \text{Oxalic acid} & & \text{Water} & & \text{Carbon dioxide} & & \text{Carbon monoxide} \\ \left\{\begin{array}{l}\text{COOH}\\ \text{COOH}\end{array}\right. & = & H_2O & + & CO_2 & + & CO \end{array}$$

The mixed gases then pass through the sodium hydroxide solution when—

$$\begin{array}{ccccccccccc} \begin{array}{c}\text{Carbon}\\ \text{monoxide}\end{array} & & \begin{array}{c}\text{Carbon}\\ \text{dioxide}\end{array} & & \begin{array}{c}\text{Sodium}\\ \text{hydroxide}\end{array} & & \begin{array}{c}\text{Sodium}\\ \text{carbonate}\end{array} & & \text{Water} & & \begin{array}{c}\text{Carbon}\\ \text{monoxide}\end{array} \\ CO & + & CO_2 & + & 2(NaHO) & = & Na_2CO_3 & + & H_2O & + & CO \end{array}$$

Carbon monoxide (CO) is a colourless, tasteless gas, highly poisonous and very little soluble in water; it does not support combustion but burns with a pale blue flame, taking up another atom of oxygen and becoming carbon dioxide. The blue flame of carbon monoxide may often be seen at the top of a clear coke fire, and its formation may be explained in the following way: At the bottom of the fire the fuel is in contact with excess of air drawn through it by the up-draught of the chimney, and here the fuel burns to water and carbon dioxide; carbon dioxide passing up through the red-hot coke, becomes reduced to carbon monoxide, and this in time coming in contact with more air at the top of the fire, burns with its characteristic pale blue flame, again forming carbon dioxide, which, with the water vapour and nitrogen of the air, pass up the chimney.

Carbon monoxide has a powerful reducing action, and will take oxygen from several of the metallic oxides under the influence of heat, forming carbon dioxide, and leaving the metal free, an action which is utilised in metallurgical processes.

Carbon monoxide forms metallic compounds, as for example, iron carbonyl, $Fe(CO)_5$, and nickel carbonyl, $Ni(CO)_4$. These substances are liquid at ordinary temperatures, but can be easily volatilised, and are broken up at a higher temperature, depositing the metal, a process utilised by Mond in the production of nickel.

It may be distinguished from carbon dioxide by burning with a blue flame, and not affecting lime water until combustion has converted it into carbon dioxide.

Carbon monoxide mixed with nitrogen is made commercially by passing air through a column of incandescent carbon in the form of coke or anthracite, when the carbon dioxide formed where the air enters becomes reduced to the monoxide in its passage over more incandescent carbon and the mixture of 30 per cent. carbon monoxide with the residual nitrogen of the air and other impurities which results is known as air-coke gas or producer gas, and is largely employed as a fuel (see p. 198).

Poisonous Properties.—The gas has such powerful poisonous properties, that less than 1 per cent. of it in air renders the air fatal to breathe, and many fatal accidents have arisen from its being formed during checked combustion, as when metallic surfaces cooled on one side by water are exposed to a gas flame, as is found in some forms of "water heaters"; also by the imperfect combustion taking place in kilns, in slow combustion stoves, and in charcoal pans.

The gas acts as a poison by forming a compound with the hæmoglobin of the blood and preventing it from carrying out its natural function of taking up oxygen during respiration and carrying it to the capillaries of the body.

A man who has been affected by carbon monoxide should be treated in the same way as for drowning, artificial respiration and the application of oxygen as a rule soon restoring consciousness

CHAPTER XIII

FUEL

Heat is not only an essential for life and comfort, but is also the form of energy from which we generate mechanical force for nearly all industrial purposes, and those substances which by their combustion in air liberate heat energy, and are sufficiently abundant to be widely used, are generally classed as fuel. In these bodies carbon and hydrogen play the most important part, and by their combustion to carbon dioxide and water generate the heat of combination in such a form as to be applicable to all the uses for which it is required.

In Nature wood, peat, coal, and petroleum are found in enormous quantities, and so widely distributed that they can be obtained everywhere, whilst further investigation shows that they have all been formed by the growth of vegetation, and that whilst wood and peat are still being produced, coal and petroleum are relics of a by-gone past, formed from the growths of the carboniferous and tertiary periods of the world's formation.

All the ordinary forms of plant in which the green pigment, known as "chlorophyll," is present owe their growth to energy derived from the sun, under which the chlorophyll contained in the small glands of the plant absorbs carbon dioxide and water vapour from the atmosphere, whilst more moisture and traces of mineral salts are drawn in by the roots. Once absorbed, the carbon dioxide and water vapour under the influence of the chlorophyll commence a marvellous series of changes, which result in the formation of the first solid product, the starch granules, and also sugars, which afterwards become practically the food of the plant, and are incorporated as the cellulose or woody fibre of which the solid portion chiefly consists, the completed reaction being of some such nature as that expressed by the equation—

$$\left.\overset{\text{Carbon dioxide}}{6CO_2} + \overset{\text{Water vapour}}{5H_2O}\right\} + \text{Sun's energy} = \left\{\overset{\text{Cellulose}}{C_6H_{10}O_5} + \overset{\text{Oxygen}}{6O_2}\right.$$

The chemical actions which resulted in the formation of the celluloses and other bodies that go to form the vegetation have required an expenditure of energy which, in the primary decomposition of the carbon dioxide and water vapour, can be expressed in terms of the heat necessary to raise a unit weight of water one degree.

A unit weight of carbon in burning to carbon dioxide raises 8,140 units of water 1° C., or 14,647 units of water 1° F. The former are spoken of as "calories," and the latter as "British thermal units," these terms being generally abbreviated to "cals." and "B. Th. U." respectively.

In the same way a unit weight of hydrogen in burning to form water develops 34,500 calories, or 62,100 British thermal units, and in order to again decompose the carbon dioxide and water so as to liberate the unit weight of carbon and of hydrogen, and to render them available for other combinations, just as much energy, expressed in heat units, will be absorbed. As in the growth of the plant, this energy has been derived from the sun, and has been partially rendered latent in the cellulose and other closely allied bodies; when we burn these compounds so as again to convert the carbon and hydrogen to carbon dioxide and water vapour, once more the stored energy is set free in the form of heat and is rendered available for heating purposes.

The natural forms of fuel in many cases can be converted into gases in order to facilitate their application as fuel for special purposes, and so yield the gaseous fuels.

The heating value of a fuel, solid, liquid or gaseous, may be arrived at by one of two methods—

1. By analysis of the fuel and calculation of its calorific value from that of its individual constituents.

2. By direct determination in a calorimeter.

Calculation of Calorific Values.—The heat generated during the combustion in oxygen of different elements and compounds was first determined by Andrews, and later by Favre and Silbermann, Thomsen and others. Some small discrepancies exist between the values obtained by these observers, which must have an influence on the calculated results, but figures derived from determinations in some form of bomb calorimeter must be accepted in preference to those obtained by older methods. The results are generally expressed in *calories*, that is, the number of grams of water raised in temperature 1° C. at the point of maximum density by the combustion of 1 gram of the substance. Amongst engineers the Fahrenheit scale is employed and the *British Thermal Unit* (B.Th.U.) is the number of pounds of water raised 1° F. by the combustion of 1 lb. of the substance. If results are expressed in calories, then the B.Th.U. corresponding will be $\frac{212-32}{100} = \frac{9}{5}$.

When water is one of the products of combustion, it is clear that the available heat will depend upon whether this water escapes as steam (as under a boiler) or is condensed to the liquid form, as in most calorimeter determinations. In practice it is usual to assume that the water formed is always condensed, but allowance can readily be made for its escape as steam by taking the latent heat of steam into account.

HEATS OF COMBUSTION.

Combustible	Products of combustion	Calories per gram
Hydrogen	Water (condensed)	34,500
Carbon	Carbon dioxide	8,140
Carbon monoxide	,,	2,490
Methane (CH_4)	Carbon dioxide and water	13,240
Ethylene (C_2H_4)	,, ,,	11,900

When a fuel consists of carbon and hydrogen only, it is considered sufficiently accurate in practical working to determine its composition, and then to multiply the carbon present by 8,140, and the hydrogen by 34,500, the sum of the numbers so obtained being taken as representing the calorific value of it as a fuel ; for instance, on analysing methane we find that it has a percentage composition of—

Carbon	75
Hydrogen	25
	100

and—

$$\frac{(75 \times 8{,}140) + (25 \times 34{,}500)}{100} = 14{,}730.$$

14,730 would therefore be taken as the calculated calorific value of methane.

This value, however, is far higher than the figure obtained by direct determination, and this is due to the heat of formation of the compound being neglected in the calculation.

It has been seen that when a chemical compound is formed heat is either absorbed or given out, and when the compound is again decomposed during combustion, as much heat reappears or is absorbed as was the case during its formation, and to make the calculation of calorific value correct, this must be allowed for.

The heat of formation of the molecule of methane (CH_4) is $+20{,}414$ thermal units, and our value for methane so corrected would be $14{,}730 - \frac{20{,}414}{16}$, or 13,450 thermal units, a number much more nearly approaching that obtained by actual experiment, namely 13,240.

The calculation become rather more complicated when the fuel already contains a certain amount of oxygen existing in combination, for those elements being already partially oxidised can only yield a portion of their total heating value; further, if moisture be present, a certain amount of the heat will be used up in vapourising this.

Since in an ordinary analysis the oxygen and nitrogen are usually determined by difference and the amount of nitrogen in coal approximates closely to 1 per cent., the oxygen present will be $[(O + N) - 1]$, and this oxygen is always assumed to be wholly combined with the hydrogen, which requires eight times its weight. A formula suitable for coal, therefore, is—

$$\frac{1}{100}\left[8{,}140\ C + 34{,}500\left(H - \frac{(O+N)-1}{8}\right) - \left(600 H_2O\right)\right]$$

the latter term making a sufficiently close approximation to the loss of heat in vapourising the water present in the coal from ordinary temperatures.

An example of the use of such a formula may be cited. A sample of coal gave on analysis :—$C = 76{\cdot}71 : H = 4{\cdot}67 : H_2O = 1{\cdot}94 : O + N = 7{\cdot}46$ per cent., then—

$$\frac{1}{100}\left[\left(8{,}140 \times 76{\cdot}71\right) + \left\{34{,}500 \times \left(4{\cdot}67 - \frac{7{\cdot}46 - 1}{8}\right)\right\} - \left(600 \times 1{\cdot}94\right)\right]$$
$$= 7564 \text{ calories per gram}$$

whilst the actual determination in a bomb calorimeter gave 7,527 calories.

The results expressed in calories or B.Th.U. serves for a comparison between different fuels, but to the engineer the evaporative duty of the coal is the important factor, and this is usually stated as "lbs. of water at 100° C. (or 212° F.) converted into steam at 100° C. (or 212° F.)," therefore by dividing the calories (or B.Th.U.) by the latent heat of steam on either the centigrade or Fahrenheit scale, the number of units of water evaporated per unit of fuel is obtained, whether these units be grams or pounds.

Thus, in the example given—

$$\frac{7564}{536\cdot5}\text{ cals.} = 14\cdot1 \text{ grams from and at } 100^\circ \text{ C.}$$

or in B.Th.U.—

$$\frac{13{,}615}{965\cdot7} = 14\cdot1 \text{ lbs. from and at } 100^\circ \text{ C.}$$[1]

Calculated heating and evaporative values are open to certain objections. In the first place there is the difference in heating value given by different observers for the same combustible. Again, the process of analysis requires expert skill in order to obtain accurate results, and any errors become largely multiplied in the calculation. As already pointed out, heat is required to break down most forms of chemical combination, and as to the amount of heat used up in this way we have no actual knowledge in reference to most fuels, but recent researches show that coal is slightly endothermic and that any heat required to break it down may be practically disregarded. Close agreement is obtained between calculated and determined values with a large number of coals which contain a low percentage of oxygen, but directly the oxygen in the coal rises above 10 per cent. the calculated value becomes lower than that given by direct determination in the bomb, and therefore a doubt is cast upon calculated values generally.

Calorimeters.—The most satisfactory method of determining the calorific value of a fuel is undoubtedly by direct measurement of the heat evolved during combustion in a calorimeter.

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[1] In the Service and Mercantile Marine the Fahrenheit scale is still retained and the evaporative value is mostly calculated from the percentage composition by the formula—

$$0\cdot15\left\{C + 4\cdot28\left(H - \frac{O}{8}\right)\right\} = \text{lbs. from and at } 212^\circ.$$

Hydrogen has approximately 4·28 times the heating value of carbon, which in the above formula is taken at Favre and Silbermann's number—14,540 B.Th.U., then $\frac{14{,}540}{966 \times 100} = 0\cdot15.$

In all forms of calorimeter the principle relied on is to burn the fuel to be tested in a vessel entirely surrounded by water and to calculate its heating power from the increase in temperature of the water.

Many forms of calorimeter have been devised, but they may be classified into the following types :—

1. Where combustion of the fuel is effected by admixture with a solid oxidising agent, as is done in the Lewis Thompson, Parr, or Wild calorimeters.
2. Combustion with oxygen at constant pressure.
    - (*a*) Where the temperature of the escaping gases is undetermined, as in the William Thomson calorimeter.
    - (*b*) Where the temperature of the escaping gases is under control, as in the Fischer calorimeter.
3. Combustion with oxygen at constant volume, as in the Mahler bomb.

Of these various types of calorimeter undoubtedly the best and most accurate is the Mahler bomb, the chief drawback to it being the expense of the apparatus, whilst the least accurate and most used is the Lewis Thompson, which has gained popularity amongst engineers owing to its ease of manipulation.

In *Mahler's Calorimeter* the combustion of the material takes place in a closed bomb or cylinder of steel in oxygen under a pressure of 25 atmospheres. The bomb is of the shape shown at (B), Fig. 29, and is coated internally with a thin lining of porcelain in order to resist the corrosive action of the trace of nitric acid formed during combustion. The cover of the bomb screws down on to a lead washer placed in a groove on the rim, thus ensuring a tight joint. A tube on the cover serves for the admission of the oxygen, and is fitted with a screw-down conical valve. Through the cover also passes an insulated rod, to the lower end of which a platinum rod is attached by means of a clamp (E). Attached to the cover and in electrical contact with it is a second platinum rod, to which is clamped yet a third platinum rod carrying the platinum capsule (C), in which is placed the substance to be burnt. The two ends of the platinum rods can be connected by a fine iron or platinum wire, which is caused to rest on the combustible material.

The bomb is placed in the calorimeter vessel (D), which contains about 2·25 litres of water, the volume of water being capable of thorough agitation by means of the vanes on the frame (S), worked by the lever (L) through the rod (K), on which a spiral thread is cut, thus causing the vanes to have a circular motion. The standard carrying the agitator is also fitted with a small clamp for the thermometer (T), graduated to read to the hundredths of a degree.

In actual working the charge of combustible is weighed into the platinum capsule, which is then clamped on to its rod, and a fine iron wire is attached to the platinum rods so that it rests on the charge. The cover is then screwed down firmly on to the bomb,

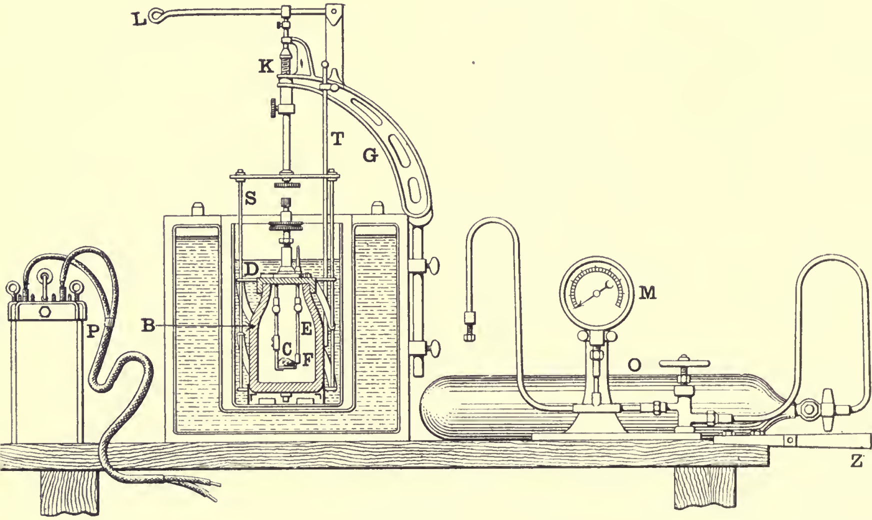


FIG. 29.—Mahler bomb calorimeter.

a wrench being applied to the cover whilst the bomb is held in its special clamp (Z). The connecting tube from the oxygen cylinder is attached to the tube in the cover of the bomb, and oxygen is slowly admitted from the cylinder until the pressure gauge shows 25 atmospheres. The valve is then screwed down, and the oxygen tube removed. The bomb is placed in the calorimeter, which has previously been filled with the required amount of water, and the water is thoroughly stirred to obtain a uniform temperature. Observations of the thermometer are taken at frequent intervals for a few minutes to determine the rate of change of the temperature of the water, and the charge is ignited by touching the insulated rod in the cover and any part of the bomb with the two wires from a battery. The agitator is kept at work during the whole time, and the temperature of the water is taken at regular intervals until it reaches a maximum and then falls regularly, and then for another five minutes to ascertain the rate of cooling. The bomb is now removed from the water, the valve opened, and the cover unscrewed. The interior is rinsed out with distilled water to collect any acid that is formed during combustion.

The result is then calculated from the observed rise in temperature of the water, which is corrected for radiation; the weight of the water-equivalent of the bomb, appendages, and gas being added to the weight of the water originally taken.

Lewis Thompson's Calorimeter.—In this instrument the fuel to be tested is burnt by combined oxygen in a small metal diving bell, under the surface of a known weight of water, and the calorific value is then determined by the increase in temperature of the water.

These instruments are graduated for use with the Fahrenheit thermometer, and on this scale the latent of steam heat is 966, that is to say, the amount of heat rendered latent in converting a pound of water at 212° F. into steam at the same temperature would raise 966 lbs. of water 1° F. It is clear, then, that if a unit weight of fuel is burnt under the surface of 966 unit weights of water, and if all the heat is imparted to the water and raises it one degree, the same amount of heat would have converted a unit weight of water at 212° F. into steam at the same temperature. In practice, two grams of the fuel in a finely divided condition are taken, and having been mixed with eleven times the weight (22 grams) of a finely powdered mixture of chlorate of potash and nitrate of potash (three of the former to one of the latter)—which is to supply the oxygen for its combustion—the mixture is then pressed a little at a time into a small brass crucible. When the mixture is all introduced, a small fuse, made of cotton soaked in nitrate of potash, is placed in a cavity in the top of the mixture, and the crucible is then fixed by means of a brass plate with clutch springs in the mouth of the diving bell or chamber; having first ignited the fuse, the whole arrangement is plunged under the surface of $966 \times 2 = 1{,}932$ cc. of water of known temperature. The fuse ignites the mixture, and the fuel burns at the expense of the combined oxygen present in the chlorate and nitrate of potash, whilst the products of combustion escaping through small holes in the bottom of the chamber pass up through the water, and are supposed in this way to be cooled. When the combustion is complete the water is admitted to the chamber by opening a tap in the tube connected with it, when the water rushes in and cools the crucible. After having well agitated the water by raising and lowering the whole apparatus several times so as to obtain a uniform temperature, the apparatus is withdrawn and the thermometer again inserted, and the rise of temperature observed. Ten per cent. is now added to the number so obtained to make up for loss of heat absorbed by the apparatus, radiation, etc., and the total is looked upon as giving the number of unit weights of water which a unit weight of the fuel would evaporate. For instance—

Temperature of water before combustion = 62° F.
,, ,, after ,, = 75° F.
Rise in temperature 13
10 per cent. 1·3
Evaporating power = 14·3

As a gram of the fuel will evaporate 14·3 grams or cc. of water, therefore one pound will evaporate 14·3 lbs. The objections to this form of calorimeter are that the fuel is never completely consumed, particles of unburnt carbon being ejected from the crucible during combustion; that the products escape too rapidly through the water to be properly cooled and that the apparatus is very liable to loss of heat by radiation.

In the Parr and Roland Wild calorimeters sodium peroxide is used as the solid oxidising agent, and the products of combustion —carbon dioxide and water—being absorbed by the sodium oxide left, no gas escapes, but allowances have to be made for the heat evolved in these reactions.

The calorific value of a fuel is very different from its calorific intensity, which is entirely dependent upon the rate of burning. It must be remembered that a pound of wood, when completely converted into carbon dioxide and water vapour, will, during the process of conversion, give out a certain quantity of heat; and that the same amount of heat will be given out, whether the wood rots away by slow combustion, is burnt in an open grate, or in a furnace urged on by a blast of air. In each case the total amount of heat given out is the same, but the intensity in each case is very different. The shorter the space of time in which the complete combustion of the wood takes place, the greater will be the intensity of the heat.

It must also be remembered that besides having to vapourise moisture, the combustion of the fuel has also to raise the carbon dioxide (formed by the burning carbon) and the residual nitrogen of the air used to a high temperature; and this must be allowed for in any calculation which is to express at all fairly the heat available for other purposes.

Wood.—In wood, the main constituent, cellulose, is common to all species, the chief differences being in the density and constituents of the sap.

As a fuel, the value of wood varies with the amount of moisture it contains and the ash, which is made up chiefly of the mineral constituents of the sap.

The moisture in wood varies with many circumstances, such as the season of the year at which it was cut down, the species of tree, and the way in which it has been kept between the time of cutting and burning. When wood is cut in the spring, say during April, it will often contain nearly 10 per cent. more water than the same species of timber cut in the winter. For instance—

Wood.	Cut in January. Water.	Cut in April. Water.
Ash	28·8	38·6
Sycamore	33·7	40·3
Horse chestnut	40·2	47·1
White fir	52·7	61·0

It also varies in quantity according to the species of tree, the average quantity of moisture present being shown in the following table :—

Water contained in 100 parts of fresh-cut wood :—

Hornbeam	18·6
Willow	26·0
Sycamore	27·0
Ash	28·7
Birch	30·8
Oak	34·7
Horse chestnut	38·2
Pine	39·7
Elm	44·5
Larch	48·6
Poplar	51·8

A certain amount of this moisture can be got rid of by exposing the wood to air and at the same time protecting it from rain, but under favourable circumstances, and after a year's exposure, air-dried wood will still contain about 20 per cent. of moisture, whilst after several years keeping in a warm room it will often retain 17 per cent. of moisture.

For all practical purposes, therefore, wood will, under favourable circumstances, only contain 80 per cent. of solid matter, whilst the large amount of heat absorbed in heating and evaporating the water present is a serious drawback to its employment as a fuel. The ash left on burning wood varies from ½ to 5 per cent., and an excess of ash, as it is incombustible, must be looked upon as diminishing the value of fuels for heating purposes.

The amount of combined oxygen present in any fuel seriously detracts from its value, as its presence means that some of the combustible constituents of the fuel are already combined with oxygen, and are no longer available for generating heat.

The calorific value of various kinds of air-dried wood are given in the following table :—

	Calories.	B.Th.U.
Ash	4,711	8,480
Beech	4,774	8,591
Birch	4,771	8,586
Elm	4,728	8,510
Fir	5,035	9,063
Oak	4,620	8,316
Pine	5,085	9,153

Wood when heated out of contact with air yields a variety of volatile products and leaves a residue of charcoal. This charcoal is not pure carbon ; it always contains oxygen, hydrogen, and a small quantity of nitrogen, in addition to the mineral constituents or ash of the wood, but the moisture and a large percentage of the combined oxygen having been got rid of, the charcoal is bulk for bulk a much more valuable fuel than wood, so that in cases where great local heat is required, it is preferable to convert the wood into charcoal before using.

Charcoal which is to be used as fuel is nearly always prepared in most countries in charcoal heaps, in which the combustion of some of the wood subjects the remainder to destructive distillation, air being as far as possible excluded by coating the heap with clay or loam. During the partial burning of the heap, some moisture is distilled off as water, whilst the combined oxygen and most of the hydrogen escape, partly combined together and partly combined with carbon as tar, naphtha and other hydrocarbons, which distil out of the heap and are lost. In foreign countries, however, wood is frequently subjected to destructive distillation almost entirely for the sake of the tar (Stockholm tar) and pyroligneous acid which are evolved, and in order to collect these substances, the carbonisation is carried on in closed vessels. When the charcoal is to be used for the manufacture of gunpowder, it must be prepared with great care, and at a low temperature; superheated steam being often employed as the source of heat. The rate at which the carbonisation takes place has a great effect upon the yield of charcoal obtained. With rapid heating there is a considerable loss, not more than from 17 to 20 per cent. by weight of charcoal being obtained, whilst, with careful heating, as much as 25 per cent. of the weight of wood taken remains as charcoal.

As a fuel, charcoal has about double the calorific value of air-dried wood, yielding 8,137 calories, or 14,646 British Thermal Units.

Peat.—Another kind of fuel much employed for domestic purposes in certain parts of the world is peat, which is composed of vegetable matter, generally mosses of the character of sphagnum, which, growing from above and dying away from below, has under the combined agency of time and checked decay been converted into the spongy, brownish-black substance found in the peat bogs. This peat is cut out in long square blocks, and is piled up, exposed to air until dry. The relative heating power of dense air-dried peat is about the same as that of wood and half that of coal.

Peat has attracted a considerable amount of attention of late, as it contains from 1 to 3 per cent. of nitrogen, which, if the peat is gasified in a producer (see p. 199), can be recovered as sulphate of ammonia, and the producer gas used for power production.

The fact that has always militated against the use of peat as a fuel is that as obtained from the bog it contains 80 to 90 per cent. of water, most of which is held as a slime in the cells and on the surface of the peat fibre, and cannot be got rid of by mechanical means. It has now been found by Ekenberg that if heated under pressure to 150° C. this slime is hydrolysed, and the water can then be squeezed out mechanically, and, after further drying, the residue briquetted to form an excellent fuel. The calorific value of peat depends entirely upon the amount of water that can be got rid of, and may be given as—

Peat	Calories	B.Th.U.
30 per cent. water	3,000	5,400
20 ,, ,, ...	4,000	7,200
10 ,, ,, ...	5,000	9,000
5 ,, ,, ...	5,500	9,900

In composition, peat occupies a position intermediate between wood and coal, and the formation of peat is considered by many to be a stage in the great natural process by which woody fibre is converted into the most valuable of our fuels—coal.

Coal is now ascertained to be of entirely vegetable origin, and is the remains of a vegetation which covered the land long before it was inhabited by man (see p. 87). This vegetation has undergone partial decomposition, and has been covered by accumulations of clay and sand; the pressure of these deep, overlying strata has prevented the evolution of gas, and has destroyed most traces of vegetable structure, and has given to the pit coal its close and compact form; but ample proof of its origin is to be found in the strata immediately above the coal seams, which abound in the fossil remains of upwards of 500 different kinds of mosses and ferns, whilst in the layer immediately below the seam fossil roots are found in abundance.

The three principal varieties of coal are lignite, bituminous coal, and anthracite, the lignite or brown coal being the least carbonised, showing indications of organised structure, and containing considerable proportions of hydrogen and oxygen; whilst anthracite is the most carbonised, and often contains little else than carbon and the mineral matter or ash.

When moist vegetable matter undergoes fermentation and decay, carbon dioxide and methane are the gaseous compounds which escape, and it is easily conceivable that the final action taking place during long ages, aided by pressure and the internal heat of the earth, is the conversion of woody fibre into carbon in the dense form known to us as graphite; whilst intermediate steps in the decomposition give bodies of the nature of peat, lignite, bituminous coal, and anthracite. The complete reaction could be represented by the equation—

$$\underset{\text{Woody fibre}}{2(C_6H_{10}O_5)} = \underset{\text{Carbon dioxide}}{5(CO_2)} + \underset{\text{Methane}}{5(CH_4)} + \underset{\text{Carbon}}{2C}$$

which is supported by the fact that these two gases are always found in the coal seams. The theory that bituminous coal is a "younger coal" than anthracite is not, however, borne out by the fact that in the eastern part of Wales the coal is of a bituminous nature, gradually shading away into the anthracite found in the western portion of the Principality, as it is extremely unlikely that there is any very great difference in the age of the different parts of the Welsh coalfield.

The gradual conversion of woody fibre into peat, coal, and graphite, is illustrated by the following table, in which, to show the gradual elimination of hydrogen and oxygen, the carbon is kept as a constant number :—

	Carbon	Hydrogen	Oxygen
Wood	100	12·18	88·07
Peat	100	9·85	55·67
Lignite	100	8·37	42·42
Bituminous coal	100	6·12	21·23
Anthracite (Wales)	100	4·75	5·28
,, (Pennsylvania)	100	2·84	1·74
Graphite	100	0·00	0·00

Lignite is found in the Tertiary formations, and is not looked upon as a true coal, whilst the coals of the carboniferous period are roughly classified according to their composition and behaviour when heated into bituminous, semi-bituminous, and anthracite coal.

The amount of hydrogen present in a fuel exercises an important influence upon the way in which it burns, as hydrogen is expelled at a fairly low temperature in combination with some of the carbon as hydrocarbon gases which are inflammable at a moderate temperature ; the burning gas surrounds the fuel and continues to heat it, whilst the escape of the gas leaves the remaining and less inflammable carbon in a porous condition, which is favourable to carrying on the combustion. Flame is burning gas, and therefore the nearer to pure carbon that the fuel approaches the less the amount of flame produced by its combustion, because the smaller will be the quantity of inflammable gas evolved.

Lignite contains more hydrogen and oxygen than any other variety of coal, and is for this reason more easily ignited and burns with more flame than any of the others, but has the lowest heating value ; the next in this respect are the bituminous coals, such as the Silkstone and Wallsend, whilst the harder forms of anthracite are difficult to ignite, and when lit can be kept burning only by a strong draught, thus rendering them unfit for use in ordinary grates.

The tarry products formed from bituminous coals when heated cause them to cake together, and this property enables the dust to be used for firing if certain precautions be taken.

Service requirements necessitate the use of a coal which shall combine high evaporative power with the minimum production of smoke, ash, and caking, and as Welsh steam-coal best fulfils these needs, little else is used in the Navy.

An idea of the average composition of water-free coals may be obtained from the table—

—	Carbon.	Hydrogen.	Oxygen.	Sulphur.	Ash.	Calorific value.	
						Calories.	B.Th.U.
Lignite—Bovey Down	66·76	5·59	22·81	2·09	2·75	7098	12,758
Bituminous—							
Derbyshire	79·68	4·94	11·69	1·44	4·88	8120	14,616
Lancashire	77·90	5·32	10·83	1·24	3·77	8113	14,602
Newcastle	88·12	5·31	7·04	1·43	4·91	8446	15,203
Steam coal or semi-bituminous coal—							
Welsh	88·03	4·11	2·94	0·79	3·22	8340	15,021
Anthracite	91·65	3·02	2·43	0·49	1·43	8677	15,619

Coke.—During the destructive distillation of coal for the production of coal gas a residue of carbonaceous matter called coke is left behind. This "gas coke" is largely used as a fuel, but is neither hard enough or sufficiently pure for metallurgical work. At the collieries mining coals of the bituminous class, which yield on carbonisation the best coke, there is produced a large quantity of small coal and dust of but little commercial value, and this, after washing to free it from as much pyrites as possible, is carbonised in bulk in coke ovens.

In the process of making coal gas the carbonisation is of a small bulk of coal for six or eight hours, but in the coke oven the large mass of coal is heated to the highest attainable temperature for a much longer period with the result that a hard, dense coke of much greater purity called "metallurgical coke" is obtained, and forms the fuel mostly used in the blast furnaces for the recovery of iron from its ores. The modern forms of coke oven are all designed to recover the tar and ammonia given off during the destructive distillation of the coal, whilst the gas is used for heating the ovens, and any surplus is employed either for local lighting or for the generation of power in the gas-engine. In the north of England, however, the old form of coke oven, called from its shape the "beehive oven," in which the products are burnt to waste, is still the kind most used, as with many bituminous north-country coals so much swelling takes place during coking as to give trouble with closed ovens.

The calorific value of coke is about the same as of coal, but where local intensity of heat is required the absence of volatile matter renders it superior.

	Calories	B.Th.U.
Oven coke	8,020	14,436
Gas coke	7,900	14,226

LIQUID FUEL.

Ease in handling and high calorific value have during the last thirty years attracted a large amount of attention to the use of certain grades of mineral oil as a substitute for coal, and although the limitations placed upon its use by cost and supply would always prevent its general adoption in countries where coal is cheap, there are certain directions in which its use gives such great advantages that cost becomes a secondary consideration. In England the only forms of liquid fuel that could be locally produced are certain fractions of the shale oil obtained by distillation of the Scotch shales, and tar oil obtained from the residuals of the gas-works and coke ovens. The chief liquid fuel, however, and the one that gives the best results in practice, is the residue left after distilling off the more volatile fractions of mineral oil or petroleum.

Mineral oil occurs in enormous deposits contained in porous sand and limestone beds in various parts of the United States, which at the present moment supplies over 60 per cent. of the world's output, in the Caucasian and Caspian districts of Russia, in Mexico, Canada, India, the West Indies, the Dutch East Indies, Australia, New Zealand, Peru, and Africa.

All forms of mineral oil as they leave the oil wells are mixtures of hydrocarbons which, however, vary a good deal in composition according to the part of the world from which they are obtained.

In the American oil fields natural gas occurs, and methane, the simplest member of the C_nH_{2n+2} or paraffin group, is the chief constituent, and in the oil from these fields liquid members of the group are practically all of them represented.

With oil from the Russian fields, on the other hand, are found hydrocarbons of a different character, belonging to a curious class of bodies called naphthenes. These bodies are isomeric with ethylene, and are allied to the benzene hydrocarbons (C_nH_{2n-6}), which, with additional hydrogen, yield hydrocarbons of the C_nH_{2n} type. They are not, however, unsaturated hydrocarbons, and this difference in the composition of these bodies, although it has but little effect on their action during combustion when used as a fuel, makes a very great difference in their chemical properties, and the alterations which can be brought about in them by heat and other processes.

Theories of Origin.—There are several theories to account for the formation of petroleum. One class of theorists insists upon its vegetable origin, declaring that it is the result of distillations from such fossilised vegetation as coal. Another and perhaps a larger class argues that it has been formed from animal remains, whilst a third party is perfectly clear in its views as to these hydrocarbons having been formed by the action of water or steam under considerable pressure upon metallic carbides. Carbides are substances formed by the combination of metals and carbon. There is one carbide perfectly well known—calcium carbide—and by the action of water it yields acetylene. In the same way as water and calcium carbide give acetylene, so water and some of the carbides of the rarer earths will give hydrocarbons of exactly the same composition as many of the hydrocarbons found in the mineral oils.

All practical evidence, however, goes to show that mineral oil has been formed in the strata in which it is found from low forms of marine life and weed which flourished during the carboniferous and Tertiary ages, and the differences which exist in the composition of the oil are due to whether the animal or vegetable source of the oil predominated. This theory is further confirmed by brine and salt deposits always being found in the strata containing the oil.

Advantages of Liquid Fuel.—With land boilers the use of oil has great advantages, but for use on board ships the advantages are greater still. One of the worst jobs on board ship is coaling.

All the coal has to be got into the bunkers, meaning an enormous amount of extremely hard labour, everything on the ship is made filthy by the coal dust, necessitating cleaning and polishing up afterwards. As regards the advantages of oil in this direction, there can be no reasonable doubt. Taking the oil in from big storage tanks alongside the wharf, it can either be run by gravity into the portions of the ship which are reserved for storage, or it can be pumped in, and instead of having the coal bunkers, as one is obliged to for coal, above the level of the stoke-hold, the storage tanks for the paraffin, or whatever liquid fuel it may be, may be in practically the ballast tanks, and as the oil is used it can be replaced by water. That gives an enormous increase in capacity to the vessel. If it be a ship of the Mercantile Marine, it gives a large amount of cargo room, which means, of course, greater earning power for the ship ; if it be a man-of-war, it does more—it gives the power of storing a much larger amount of energy in the same space as coal would have occupied.

Liquid fuel is far in advance of coal as a steam-raising agent, as will be seen later. In point of fact, it is found that one ton of oil is about equal to 1·5 of coal, and the result is that for the same weight an amount of fuel can be carried which will give a very much greater radius of action, and this at the present time in the Navy is of the very greatest possible importance. Again, in the feeding of the oil to the furnaces, instead of needing a very large number of stokers for trimming the coal in the bunkers and keeping up the fires, the use of oil reduces that number to about one-fourth, whilst there being no ash, cinder and clinker to clear out of the furnaces and throw overboard, another economy in labour is effected.

These factors have led to the introduction of liquid fuel in nearly all the navies of the world, but as the total supply would at present be a mere fraction of that needed if it were burnt alone, it is mostly used as an adjunct to coal when full power is required.

It is manifest that crude petroleum, being a mixture of many hydrocarbons, will have so low a flash-point that its use as a fuel would be attended with danger on land, and would certainly never be permissible afloat, and it is from such residues as are left after the distillation of the more volatile portions and the lamp oil that the chief source of liquid fuel must be sought.

Flash Point.—The flash point of an oil is the temperature at which it begins to give off inflammable vapours in an enclosed space, and for liquid fuel the Admiralty have decided that it shall not be below 200° F.; in the Mercantile Marine and German Navy the flash point is fixed at 150° F.

This means that as the crude oil comes from the well it has to undergo a process of distillation, the most volatile fraction supplying the motor spirit, whilst the next fraction of the distillate is lamp oil, after which the residue is fitted for use as fuel.

The Combustion of Liquid Fuel.—Many ways have been tried to obtain the maximum of evaporative efficiency with the minimum of smoke in the combustion of liquid fuel, but the method now universally adopted is to convert the oil into a fine spray or mist by means of a suitable injector and to burn the so-called "atomised" fuel as a flare in the furnace and combustion chamber of the boiler.

The spraying or atomising of the oil may be attained in three ways, each of which has its special advantages and drawbacks, so the choice of the system to adopt will largely depend upon the conditions that have to be fulfilled. The three systems of injection and spraying are—

(1) Injection or spraying by steam.
(2) ,, ,, by placing the oil under pressure.
(3) ,, ,, by compressed air.

1. Steam Injection.—By far the best known and most used of the burners are those in which the oil is pulverised by steam, a method that was first used by Messrs. Aydon, Wise, and Field in 1865–7, the general principle being that the oil is led down to the injector by gravity, and there meets a steam jet which drives it out from the nozzle of the injector with high velocity and in a fine state of division, whilst the outrush of the steam and oil is usually made to suck in air around the jet to aid the combustion in the furnace.

Of these burners, perhaps at the present time the best known are those of the Holden type, and it is a form of these that is employed in the highly successful installations of liquid fuel that Mr. Holden has fitted up, and which have shown themselves to be of a most satisfactory character. One form of the injector or burner is that used on locomotives, which is made to serve the double purpose of injecting the fuel and also maintaining the vacuum necessary for the brakes. In a second pattern, however, arranged for marine work, valves are designed to supply the oil in two portions to the steam injector, in order that if a change from half speed to full speed, or *vice versa*, be desired, the supply of fuel can be arranged without any alteration in the steam consumption. At the mouth of the burner an ingenious arrangement of a steam ring performs the important function of allowing jets of steam at various angles to catch the oil spray as it leaves the burner and to more evenly distribute it through the furnace, the steam ring also serving to draw in air for the primary combustion.

Another form of steam pulverising burner largely used in practice is that designed by Messrs. Rusden and Eeles, which is the burner employed on the vessels of the Shell Transport Company. This excellent burner has shown itself very successful in working, and in it oil, after having been heated by a steam jacket, is sprayed out by the steam, and as the burner is so made as to allow of separate adjustments of the steam and oil jets, the consumption of the fuel can be nicely adjusted to the work which it has to do.

The burner used by Messrs. Armstrong, Whitworth & Co. is that designed by Mr. E. L. Orde. In this burner highly superheated steam is employed, 600° F. being the temperature at which it probably works best, and the steam is so arranged as to sweep out and spray the oil with a very high velocity, thus inducing a current of heated air together with the jet of steam and oil, this being found to help the combustion.

2. **Pressure Injection.**—The system of direct pulverisation by pressure was very successfully carried out by Körting, and has been employed on the Hamburg-American Line and in many German steamers. The Körting injector is shown in Fig. 30, and in using it the oil is heated to a temperature of 130° C., and is then forced into the injector under an air pressure of 50 lbs. on the square inch. In the injector the oil flows into a chamber feeding the jet, and into this jet is fitted a spindle carrying a spiral screw. The oil at a pressure of 50 lbs. is forced down this spiral, and acquires a centrifugal action which sprays it out of the jet in a very finely divided condition.

Another form of burner, the action of which also is merely dependent upon the pressure, is the Swensson, in which the oil under pressure is heated in a steam jacketed tube, and is then forced out from a fine jet on to the point of a V-shaped metal cutter, which has the effect of pulverising it into a very fine spray.

The most successful burner of this type is one designed by Kermode, in which the swirling motion given to the spray in Körting's burner is much accentuated, and forms a cone of mist, the apex of which is at the burner mouth.

In this burner, shown in Fig. 31, the oil fuel enters the burner through the channel marked (A) in Fig. 31, and passes between the outer wall of the burner marked (D), and the inner cylinder marked (B), which abuts against the cap-nut (E). The end of the cylinder (B) is an exact fit in the outer casing (D) where it abuts against the nut (E), and in this end of (B) a number of grooves are cut parallel to the centre line of the burner, while there are similar grooves in the end of the part (B) at right angles to the axis of the burner. These grooves are shown at (H) in Fig. 31, and it will be seen that they are tangential to the cone end of the spindle (C), which serves to contract, or enlarge, the opening through the cap-nut (E). The movement of (C) is indicated on the graduated wheel (F).

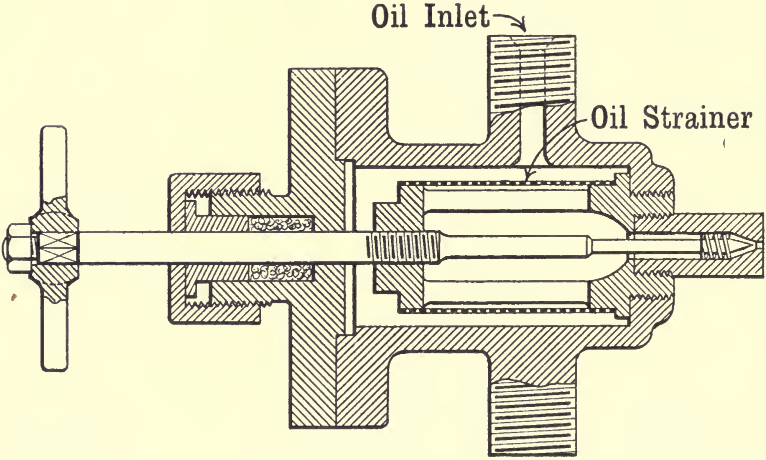


FIG. 30.—Körting injector.

By means of this arrangement the oil fuel is pulverised very completely by being forced through a restricted opening with a rotary motion, which is given to it by the tangential grooves in the face of the plug (B), and it is distributed in the form of a cone by means of the reaction or deflection which is set up by the oil impinging on the cone end of the spindle (C). The fixed pointer marked (G) serves to indicate the degree to which the wheel (F) has been rotated, either to increase or diminish the opening through the nut (E).

3. **Air Injection.**—The third type of injector depends upon the principle of atomising the oil by compressed air in the same way as steam is used in the first type; indeed, some burners are so constructed that either can be employed, and where a very intense heat is needed they have proved highly successful, and are employed for glass melting, welding, and many other processes of the same kind.

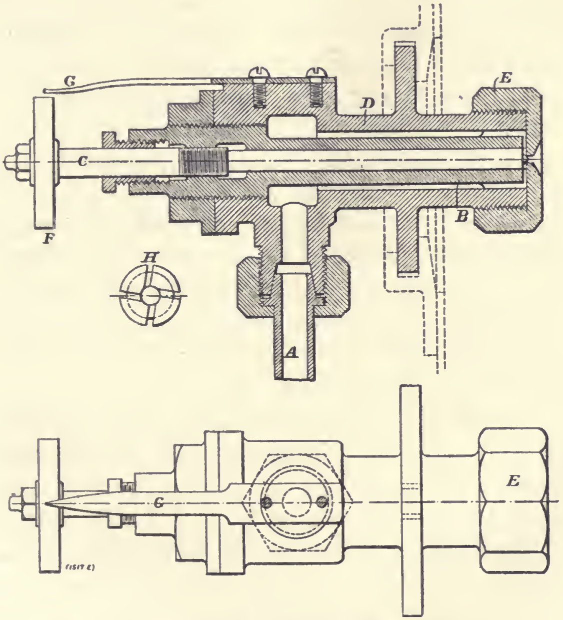


Fig. 31.—Kermode's pressure jet burner.

Although there have been many other forms of burner employed, these types may be taken as fairly covering the most successful methods of bringing the oil into a sufficiently finely divided condition to allow of rapid and complete combustion.

The method now employed in the Service consists of direct pulverisation by pressure, as, if steam is used for injection, 0·2 lb. of steam per I.H.P. per hour is required, which could not be obtained at full power without extra boilers.

When the liquid fuel has been disintegrated by the injectors or vapourised, in most cases it is brought in contact either with a layer of fuel or brickwork near the mouth of the furnace, and in some cases, as in the Körting system adopted by the Hamburg-American Line, the furnaces are bricked right round. Under these conditions the brickwork can be made to fulfil two requirements : in the first place it gets heated to a very high temperature, and serves to ignite the oil vapour and air coming into the furnace, and in the next place if the oil jet is made to dash straight against it, it serves to disintegrate and gasify it, prevents the burning oil and flame being driven too rapidly through the furnace, and saves the plates from the direct impact of the flame. For these latter purposes also various forms of brick baffle are frequently employed.

In burning oils there is always a risk that there may be present small particles of solid matter which may choke the injector, and also water, the latter being present when the oil has been stored in the double bottoms and ballast tanks of the vessel, and also in crude oil. It has been found that the presence of drops of water in the oil is apt to extinguish the flame at the injector nozzle, and if that were to take place, and the finely-divided oil spray or oil gas were to get into the furnace mixed with air in any large quantity it would give rise to an explosion.

Use of Settling Tanks.—In order to get rid of solid particles and water, the oil is pumped into settling tanks, fitted with a steam coil, which can be used to raise its temperature, the necessity of this being found in the fact that the specific gravity of the oil generally used as a fuel is only a little below that of water, and that therefore the separation would be very slow, but when slightly warmed the oil expands at a much greater rate than the water, and the separation, therefore, takes place with much greater rapidity.

The coefficient of expansion of water at about 15° C. is 0·00015 for a rise of 1 degree in temperature, whilst the coefficient of expansion for the oil is about 0·00085.

In some systems two settling tanks are employed, each capable of containing twelve hours' supply, and the one which is out of use, after standing twelve hours, has the water drawn off from the bottom, whilst the oil is pumped out through a wire gauze filter. In other forms of settling tanks, a filtering cage of wire gauze is employed, which is kept by a float near the surface of the oil, whilst a steam coil is used as before to aid the separation.

In most installations the oil is heated before it reaches the burner to about 150° to 180° F. in a steam-heater, the oil passing through a nest of tubes and steam being admitted to the outer casing and circulating round them, the condensed water being drawn off through an outlet at the bottom of the casing. The temperature must not be allowed to rise above 180° F., as the oil gives off vapour above 200° F., which might cause a break in the column and cause trouble at the burner. In all systems the oil should pass through wire-gauze filters before reaching the burners, and in many cases a filter is placed between the pressure pump and the heater.

In every system the great necessity is to obtain an ample supply of air for the complete combustion of the fuel, and to so arrange the supply as to ensure the mixing of the air with the sprayed oil, and the great advantage of such burners as the Kermode is that the swirling motion given to the oil mist ensures the air being dragged into the burning cloud to complete the combustion. When forced draught is used, the air is admitted to each spray through separate air inlets brought several inches in front of the burner nozzle, so that air is fed in all round the spray. The rate of combustion can be arranged in several ways, such as the number of burners, their size, the pressure at which they are worked, and the degree to which the value of the burner is opened.

Heat Value of Fuel Oils.—The fuel oils differ but little in the ratio of carbon and hydrogen present, and the following table gives the ultimate composition of the chief available fuel oils, showing the Texas oil to be a little the best :—

FUEL OILS.

(Orde.)

	Carbon.	Hydrogen.	Oxygen, etc.	B.Th.U.
Borneo ..	87·8	10·78	1·24	18,831
Texas ..	85·6	11·03	3·31	19,242
Caucasus ..	84·9	13·96	1·25	18,611
Burmah ..	86·4	12·10	1·50	18,864

Taking a good sample of liquid fuel, its theoretical evaporative efficiency would work out at about 20 lbs. of water, whilst the best steam coal will work out at about 15, a gain of only 33 per cent. In practice the evaporative power to be obtained from oil averages 15 as against 10 obtained with steam coal in the same boiler, a gain of 50 per cent.

In practical work such oils as the blast furnace and heavy tar oils, owing to their chemical nature and the difficulty of decomposing them, give lower evaporative results than the petroleum oil. The general run of these differences may be seen from the following table, giving the practical results obtained with the same boiler :—

LIQUID FUELS.

Description.	Specific Gravity.	Flash point.	Calorific value by bomb.		Actual evaporative power in practice, from and at 212° F.
			Calories.	B.Th.U.	
American Residuum	0·886	350	10,904	19,627	15·0
Russian Ostatki ..	0·956	308	10,800	19,440	14·8
Texas	0·945	244	10,700	19,242	14·79
Burmah	0·920	230	10,480	18,864	14·5
Barbadoes	0·958	210	9,899	17,718	14·2
Borneo	0·936	285	10,461	18,831	14·0
Shale oil	0·875	288	10,120	18,217	13·8
Blast furnace oil ..	0·979	206	8,933	16,080	12·0
Heavy tar oil ..	1·084	218	8,916	16,050	12·0

The best results obtainable with this type of boiler fired with coal would have been an evaporative duty of between 9 and 10 lbs. of water from and at 212° F., when using the best Welsh steam coal.

For Service use the limitation of the supply of liquid fuel has led to its being fitted as an adjunct to coal, and not as the sole fuel, as it has been realised that until its supply in large quantities is placed upon a more reliable basis than at present, it would be incurring a grave risk to fit a large battleship for burning liquid fuel only, although with smaller vessels, such as destroyers, it is permissible to do so. As an auxiliary to coal, it has very great advantages, as with a fleet manœuvring at half speed it gives the power of suddenly increasing to full steam by the mere turning on of the oil supply to the injectors, and it is with this object in view that all the newer English, German, and French battleships and cruisers have been fitted either for burning coal alone, or a mixture of coal and oil.

So far we have considered liquid fuel only from the point of view of steam raising, but the internal combustion engine has made such rapid strides during the last fifteen years, and engines using heavy oil are giving such good results, that the question must now be considered from this point of view.

Liquid Fuel for use in the Internal Combustion Engine.—These engines fall naturally into two main groups: (1) those using a combustible gas or vapour, which passes into the cylinder mixed with the necessary air for its combustion, and is there exploded by means of a spark or other device, and (2) those using heavy oil, which is injected or sprayed into the cylinder, and, being gasified by heat, is then exploded or burnt with air.

The first class contains all the petrol motors and gas engines, whilst the second class is best known from the Diesel engine, of which so much is expected.

It has been seen that crude petroleum as it is obtained from the well may be looked upon as a mixture of all the saturated hydrocarbons from the first liquid member, pentane, C_5H_{12}, up to solid paraffin wax, whilst the natural gas that accompanies the oil contains most of the gaseous members of the series, methane, CH_4, being its chief constituent. The distillation of the crude oil to obtain from it the fractions used under the trade names of petrol, kerosene, Solar distillate, lubricating oil, fuel oil, vaseline, paraffin wax, etc., takes place generally at refineries on the oil-fields, and further purification is often carried out afterwards.

When distilled, the first fraction that comes over up to about 50° to 60° C. is generally known as petroleum ether, has a specific gravity of 0·650 to 0·680, and is used in dry cleaning as a grease solvent, and for use in aeroplane motors; it consists chiefly of pentane, C_5H_{12}, with small quantities of higher and lower members of the group. The second fraction consists of "petrol," and contains pentane, hexane, C_6H_{14}, heptane C_7H_{16}, and now that the demand for petrol is so great even traces of octane C_8H_{18}.

Petrol.—Petrol has a specific gravity of 0·680 to 0·740, a flash-point below ordinary temperature, and is so volatile that air readily takes up the vapour, the mixture containing between the limits of 2 and 5 per cent. of the vapour being explosive, whilst the maximum explosive result is obtained from a mixture of 2·6 per cent. of petrol vapour and 97·4 per cent. of air, and it is this property which gives it its value in the internal combustion engine, and also gives rise to the dangers that attend its use.

One of the greatest dangers attending the use of petrol is the ease with which it evaporates, and the fact that the vapour being more than four times the weight of air diffuses only slowly and creeps along the floor for considerable distances. A pint of petrol poured upon a level surface will cover eighty square feet with an inflammable layer of vapour, which, if it comes in contact at any point with a flame, will ignite over the whole space.

Fortunately the igniting point of the mixture of petrol vapour and air is over 1000° C., so that it requires a dense spark to cause ignition, whilst cigarette ends, cigars, or pipes at their highest temperature fail to ignite it, unless there is actual flame.

The motor industry has grown with such rapidity that the demand for petrol is increasing at a rate which threatens a serious rise in price, and substitutes for it are being eagerly sought.

Benzol (benzene), C_6H_6, which is obtained from the light oil distilled from tar, answers perfectly well, and is 10 per cent. stronger than petrol, but the supply is so limited that any large demand would quickly make it dearer than petrol; also the exhaust from the cylinders after explosion is unpleasant, and in cold weather a little difficulty is sometimes found in starting.

Many experiments are also being made on the use of kerosene, or lighting oil, to fit it for use with motor engines, and it is found that with properly constructed carburettors, if the engines are started and kept running until thoroughly heated with petrol, kerosene of a specific gravity of 0·8 can then be turned on and used for steady running, but it has not the flexibility in use that is needed for great variations in speed.

There is no doubt that if the demand for a fuel for motor engines continues to increase at the present rate, the supply of petrol will become a serious question, as many crude oils contain only a small fraction, and although America, Burma, Sumatra and other oil-fields supply very large quantities, the whole civilised world is using it.

Alcohol, C_2H_6O.—There is no doubt but that at some future time the restrictions placed by Government upon the manufacture of alcohol will have to be relaxed in order to allow it to take its proper place in the generation of energy. It is only by the growing of starch-producing vegetation and its fermentation into alcohol that the sun's energy can be regenerated rapidly in a form available for the production of power, and as the coal and oil supplies become exhausted it will be the only fuel to take their place, and the motor engine can be adapted easily to use it in the place of petrol.

Alcohol that is to be used for commercial purposes is allowed free of duty if it is denatured, *i.e.* mixed with something sufficiently foul in smell and taste to prevent its being drunk, and in England this is done by mixing 10 per cent. of wood naphtha with the alcohol. The mixture is called methylated spirit, and has a calorific value of 6,200 calories, or 11,160 B.Th.U., whilst petrol is 11,624 calories or 20,913 B.Th.U., so that if calorific value alone governed the value of a fuel for motor purposes, alcohol would be only half the value of petrol. In practice, however, the percentage of the thermal value that can be converted into power depends upon many other factors, and the use of alcohol enables a higher compression to be used, a cool cycle in the engine, a moderate volume of air and a greatly increased range over which the mixture is explosive, these factors practically resulting in making alcohol nearly as effective a fuel as petrol.

In a trial of the relative values of the two forms of fuel made in two 8-H.P. engines the results obtained were—

Alcohol,	373·5 grams	per brake	horse-power hour
Petrol,	340 ,,	,,	,,

whilst with its use most of the dangers attending the use of petrol would disappear.

Heavy Oil Engines.—This term is applied to internal combustion engines using as a fuel oil having a specific gravity of from 0·8 upwards, and in which, instead of carburetting air with the inflammable vapour before its introduction to the explosion cylinder, as is done in light oil engines, the heavy oil is vapourised at a high temperature, generally in the cylinder itself. If a kerosene oil be distilled in a retort, it is found that the temperature gradually rises as the lighter portions distil until eventually a residue of carbon is left in the retort, although probably the oil itself was all distilled at a temperature below 300° C. This is due to decompositions taking place in the oil itself, which tend to form lighter and heavier hydrocarbons, but if air or dry steam be passed through the distilling oil these are prevented, and the whole distils over at 300° C., or slightly above. It is upon this fact that the possibility of using a heavy oil in the engine cylinder depends, as if the oil is injected as a spray into air in the cylinder, the heat of the walls and the heat of compression cause complete volatilisation of the minute oil particles in presence of excess of air.

In the Diesel engine the outstanding features are that compression is carried to the point when the heat evolved is sufficient to ignite the mixture of oil vapour and air, and that the action partakes more of the nature of a burning than of an explosion. The successful adoption of the Diesel engine in sea-going vessels, such as the *Vulcanus* and *Selandia*, and more recently in the destroyer *Hardy*, has attracted much attention to the system, which it is claimed works perfectly well with a very wide range of oils, the only proviso being that the percentage of hydrogen in the oil, upon which the temperature of ignition largely depends, must be sufficiently high to ensure easy liberation of inflammable gases. In the fuel oils obtained from crude petroleum the percentage of hydrogen is from 10 to 14, and such oils work perfectly, but with tar oils, in which the hydrogen generally is under 7 per cent., a pre-injection of 3 to 5 per cent. of petroleum oil into the cylinder is necessary to ensure ignition.

GASEOUS FUEL.

The ease of application and the many advantages presented under certain conditions by the use of gaseous fuel in various manufacturing processes have led to considerable attention being paid to the subject, and ever since the discovery of water gas by Fontana in 1780, engineers have busily attempted to perfect methods for its economical production.

Under the head of gaseous fuel may be comprised—

(1) Coal gas and coke oven gas, made by the destructive distillation of coal.
(2) Water gas, made by passing steam through incandescent carbon.
(3) Producer gas, made by the passage of air through incandescent carbon.
(4) Semi-water gas and suction plant gas, made by passing mixtures of steam and air through incandescent carbon.

Coal Gas.—The manufacture of coal gas has been fully described (pp. 144, 145), and its composition given; its heating value varies with the temperature of carbonisation of the coal, and also the kind of coal used. London gas has a heating value of 135 calories gross, or 540 B.Th.U. per cubic foot, and nearly all coal gas now varies between 500 and 650 B.Th.U.

Coal gas is year by year rapidly increasing in favour for power purposes and as a fuel for domestic purposes, such as heating and cooking, the only drawback being the cost of gas as compared with coal as a fuel. When used for such purposes the gas is burnt mixed with air in atmospheric burners, and during complete combustion a very high temperature is attained. Modern gas-stoves have been so greatly improved in their efficiency that their practical use is but little more expensive than for the same amount of heat developed from coal fires, and the economy of being able to turn on the gas just when required, and to turn it off when the desired effect has been produced, when taken in conjunction with the saving of labour and absence of dirt and smoke, considerably decreases the margin in favour of coal.

Coke Oven Gas is in composition much the same as coal gas, but contains a slightly lower percentage of illuminating hydrocarbons. It is used to a limited extent in the colliery districts where metallurgical coke is produced, and has a heating value of 500 B.Th.U. per cubic foot.

When used in the gas engine both coal gas and coke oven gas will develop one brake-horse-power-hour for the consumption of about 17 cubic feet.

Water Gas.—Water gas depends for its formation upon the fact that at high temperatures carbon has a greater affinity for oxygen than hydrogen has, and that when steam and carbon (in any of its amorphous forms) are heated to such temperatures, the steam is decomposed with liberation of hydrogen and either carbon monoxide or dioxide, the oxide formed being to a great extent dependent on temperature, which itself is largely governed by the quantities of steam and carbon interacting.

The action may be represented as follows :—

$$\overset{\text{Carbon}}{C} + \overset{\text{Steam}}{H_2O} = \overset{\text{Carbon monoxide}}{CO} + \overset{\text{Hydrogen}}{H_2}$$

or—

$$\overset{\text{Carbon}}{C} + \overset{\text{Steam}}{2(H_2O)} = \overset{\text{Carbon dioxide}}{CO_2} + \overset{\text{Hydrogen}}{2(H_2)}$$

The effect of temperature on the proportions of the two oxides of carbon is shown in the following table :—

Temperature	Per cent. of steam decomposed	Hydrogen	Carbon monoxide	Carbon dioxide
674° C.	8·8	65·2	4·9	29·8
1010° C.	94·0	48·8	49·7	1·5
1125° C.	99·4	50·9	48·5	0·6

and the value of the gas as a fuel depends on keeping the proportion of carbon dioxide as low as is possible.

An average sample of water gas made with coke as the fuel would contain—

	Per cent.
Hydrogen	48·31
Carbon monoxide	35·93
Carbon dioxide	4·25
Nitrogen	8·75
Methane	1·05
Sulphuretted hydrogen	1·20
Oxygen	0·51
	100·00

The ideal condition to attain in the decomposition is—

$$\underset{\text{Carbon}}{C} + \underset{\text{Steam}}{H_2O} = \underset{\text{Carbon monoxide}}{CO} + \underset{\text{Hydrogen}}{H_2}$$

But in order to obtain this a large amount of heat is used up.

A unit weight of hydrogen in burning to water gives out 34,500 calories, and as 2 units burn to form 18 of water, the heat evolved during its production will be 34,500 × 2 = 69,000 calories; when the 18 units weight of water is again decomposed, this amount of heat will be again absorbed. In this case, however, the water has had to be converted into steam, and so contains an amount of heat equal to the latent heat of steam plus the heat used to raise it to the boiling point. It has been seen that the latent heat of steam is 536 calories per unit of water, and to allow for the heat necessary to bring it up to the boiling point, this is generally called 600. In the present case we are dealing with 18 units of water as steam, so the heat present in it will be 600 × 18 = 10,800 calories, and the extra heat used up in decomposing the 18 units weight of water will be 69,000 — 10,800 = 58,200 calories.

The water having been decomposed, the oxygen of it is available to burn the 12 units of carbon to carbon monoxide, and as in doing this one unit of carbon emits 2,489 calories, the 12 will yield 2,489 × 12 = 29,868 calories. If this be deducted from the previous heat deficit, we have—

$$\begin{array}{r} -\ 58{,}200 \\ +\ 29{,}868 \\ \hline -\ 28{,}332 \end{array}$$

or a shortage of 28,332 for the 12 units of carbon, or 2,361 for one. If the units be taken as pounds, we see now that 1 lb. of carbon in decomposing 1·5 lb. of steam to hydrogen and carbon monoxide uses up 2,361 calories. In order to supply this heat attempts were made to use heated retorts of the kind employed in coal gas manufacture, but it was found that the low conductivity of the fire-clay prevented the heat being poured into the charge with sufficient rapidity to keep up the temperature, and the method was adopted of making the water gas in a cupola furnace, in which was placed the coke, and after ignition this was blown up to the required temperature by an air blast; the blower was then cut off and steam injected, making the water gas, until the temperature fell to a point when carbon dioxide began to be formed in quantity, the operations of blowing and steaming then being repeated. In the early forms of water gas generator a deep bed of fuel was used, and the result of the "blow" was to form carbon monoxide. It has been shown that 2,361 calories are needed for 1 lb. of carbon to decompose 1·5 lbs. of steam, and as 1 lb. of carbon by its combustion to carbon monoxide gives 2,489 calories, theoretically it should be possible by burning one-half the coke to carbon monoxide to convert the other half into water gas, but in practice the loss of heat in the products and by radiation reduces the proportion of carbon converted into water gas to about 30 per cent.

In the new forms of water gas generator the fuel bed is kept of a constant depth and the air blast increased to burn the carbon to carbon dioxide, and under these conditions 1 lb. of carbon gives 8,140 calories instead of the 2,489 calories given in forming the monoxide, and this brought about such an economy that now nearly double the volume of water gas can be made per pound of coke than was possible before.

Water gas has a thermal value of about 290 B.Th.U. per cubic foot (72·5 cals.), and forms an effective fuel in many metallurgical operations; it is largely used for welding and other engineering work.

It is also used as the basis of an illuminating gas, by mixing with it the gases formed by the decomposition of various grades of oil; these gases being rich in hydrocarbons endow it with illuminating power, and the mixture is generally known as carburetted water gas.

The various forms of generator employed for the manufacture of carburetted water gas are very numerous, but the only one used in this country is that originally devised by Lowe. In this apparatus the coke is heated to incandescence by an air blast in a generator lined with fire-brick; and the producer gas thus formed passes on to the superheaters—more air being admitted to ensure its combustion. By this means the superheater is raised to a high temperature. When the fuel and superheater are sufficiently hot, the air blast is cut off, and steam blown through the generator, forming water gas, which meets the enriching oil at the top of the first superheater, called the carburettor, and then passes on to the fixing chambers, where the hydrocarbons are rendered permanent gases. The chief advantage of this apparatus is that a low temperature can be used for fixing, owing to the large amount of surface for superheating, which to a great extent does away with deposition of carbon.

Producer Gas or Air Coke Gas is identical with the gas made during the "blow" with a deep bed of fuel in the early water gas processes; it is a mixture of carbon monoxide and nitrogen, having the theoretical composition—

Carbon monoxide	34·3
Nitrogen	65·7
	100·0

and is the least efficient of the gaseous fuels. It is formed by passing air through a column of heated coke, when the carbon at the lower surface of the column burns to carbon dioxide, combining with the oxygen of the air; and the carbon dioxide, by contact with the heated carbon over which it has to pass, is then reduced to carbon monoxide—

$$\underset{\text{Carbon}}{C} + \underset{\text{Air}}{2(N_4 + O)} = \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Nitrogen}}{4(N_2)}$$

and—

$$\underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Carbon}}{C} = \underset{\text{Carbon monoxide}}{2(CO)}$$

the carbon monoxide and residual nitrogen from the air forming the "generator gas."

So that the final reaction is—

$$\underset{24}{2C} + O_2 = \underset{56}{2CO}$$

and if 24 lbs. of carbon yield 56 lbs. of carbon monoxide, 1 gives 2·3̇. When 1 lb. of carbon burns to carbon monoxide 2,490 calories are given out, and this takes place in the producer. The gas which is given off contains 2·3̇ lbs. of carbon monoxide, and this, on afterwards burning to carbon dioxide, would evolve 2,435 × 2·3̇ cals. = 5,673·5 cals., so that in round numbers one-third of the carbon has been burnt to gasify the remaining two-thirds, so that only 66·6̇ per cent. of the heat of the fuel is available.

When, however, the producer gas is used hot, a further economy is obtained, and Siemens revolutionised many manufacturing processes when he introduced the idea of gaseous fuel of this kind in conjunction with regeneration.

In such a process the air supplied to the producer to make carbon monoxide is spoken of as primary air, whilst that supplied to burn the carbon monoxide in the furnace is called secondary air, and in the Siemens' furnace the hot products of combustion were made to heat up chambers full of chequer brickwork, through which the secondary air supply was afterwards passed to heat it before entering the furnace to combine with the carbon monoxide.

The calorific value of the air-coke gas is only 72 B.Th.U. per cubic foot, but it is a very effective form of fuel for glass melting, the heating of gas retorts, brick burning, pottery kilns, and many processes of this character, in which, used hot in connection with a Siemens' regenerative furnace, it gives splendid results.

Siemens Gas.—This only differs from generator gas in that small coal or slack is used as the fuel instead of coke, with the result that the gas contains a small proportion of gaseous hydrocarbons which increase its thermal value.

Mixed Fuel Gas.—In the formation of generator or producer gas heat is evolved by the processes taking place in the generator, whilst in the making of water gas a very large amount of heat is absorbed, so that the temperature of decomposition has to be attained and kept up either by exterior heating, as used in the retort processes of making water gas, or by blowing up the fuel to incandescence by an air blast, as practised in all the successful water gas processes. A large number of gas generators are now made in which air and steam are simultaneously passed through the incandescent fuel in such proportions that the formation of producer gas by the partial combustion of the carbon by atmospheric oxygen shall raise the temperature in the same ratio that the decomposition of the steam by the red-hot carbon into water gas lowers it, the result being a uniform temperature in the generator, and the production of a gas which is practically a mixture of producer gas with water gas, and which has a higher thermal efficiency than the producer gas alone, and answers well in gas engine practice.

Producers for making these mixed gases are known by the names of their inventors, and the Wilson, Dowson, Dawson, and Duff processes are all of this character. Mond gas, however, differs from these in as much as by using an excess of steam in the generator the temperature of the fuel is kept low, and a large proportion of the carbon monoxide is converted into dioxide, this, however, being accompanied by an increase in the volume of hydrogen produced, and the low temperature favouring the formation of ammonia from the nitrogen in the slack used as fuel yields a valuable by-product.

Blast furnace gas consists of the gases which until lately were blown to waste from the mouth of the blast furnace during the reduction of iron from its ores, and which has a composition not very different from that of producer gas.

The composition, thermal values, etc., of the various gaseous fuels are given in the following table :—

Constituents	Blast furnace gas	Producer gas	Siemens gas	Dowson gas	Mond gas	Water gas	Coal gas
Carbon monoxide ..	27·11	29·0	22·6	25·07	11·0	40·08	5·6
Carbon dioxide ..	8·62	4·0	4·4	6·57	16·0	4·80	1·3
Hydrogen	1·34	2·5	7·8	18·73	29·0	51·89	52·1
Methane	0·00	0·0	1·5	0·64	2·0	0·10	34·6*
Nitrogen	61·23	64·5	63·7	48·98	42·0	3·13	3·0
Combustible ..	28·45	31·5	31·9	44·44	42·0	92·0	96·7
Non-combustible ..	71·55	68·5	68·1	55·56	58·0	8·0	4·3
Thermal value in B.Th.U.	70	72	125	148	154	290	540
Volume of gas needed to give I.B.H.P. in gas engine	—	—	120	80	80	31	17
Fuel used	coke	coke	slack	anthracite	slack	coke	coal
Cubic feet per ton of fuel	—	200,000	190,000	170,000	160,000	70,000	10,000

* Contains also 3·4 per cent. of unsaturated hydrocarbons.

The great value of gaseous fuel, however, is now the creation of power by means of the gas engine, which has practically revolutionised the generation of power. When the gas engine was first introduced it was entirely with a view to using it with coal gas, and the only drawback was the price of the gas, but in large cities where space was cramped the gas engine made rapid headway, owing to its convenience, cleanliness, and the advantage of being able to dispense with furnaces and boilers for the generation of steam. The expense, however, greatly militated against the use of engines of 20 H.P. and upwards. It was then found that even gases so poor in calorific value as the mixed producer and water gas gave excellent results, and since then the gas engine has grown with such rapidity that it is now made up to 2000 H.P., whilst its use is so extended that in Germany steam as a motive power for stationary work is looked upon as practically dead.

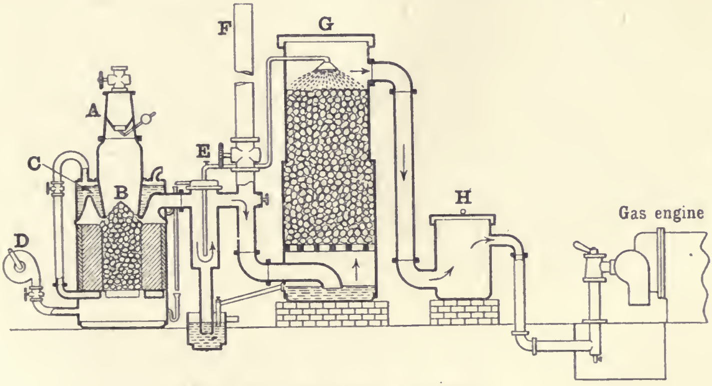


FIG. 32.—Suction gas plant.

A. Fuel hopper.
B. Generator.
C. Vapouriser.
D. Starting fan.
E. Separator.
F. Waste gas pipe.
G. Coke scrubber with water spray.
H. Gas expansion box.

Suction Plant.—A type of gas generator known as a suction gas plant is now being made which does away with all the paraphernalia of blowers, boilers, and gasometers needed for the earlier forms of fuel gas generators.

In this form of apparatus the stroke of the gas engine draws air and steam through a bed of incandescent fuel and so converts it into gas, which is then purified by passage through a washer, condenser, and scrubber before entering the engine cylinder. The fact that in such a plant the whole of the apparatus is never above the ordinary atmospheric pressure renders it far safer and far more convenient to use than the old forms of apparatus in which the pressures were obtained by means of fans or blowers for driving the air into the generator, which of course always leads to a tendency to leakage.

Marine Gas Engines.—The latest developments in the gas engine have been in the direction of trying to adapt it for marine purposes, and Capitaine, who played a leading part in developing the oil motor, has been working at the marine gas engine for the past twenty-five years. Although at first there seems little or no chance of success, marine suction gas plants and engines are now *un fait accompli* for small powers, and the possibility of manufacturing marine engines on this principle from 25 to 1000 H.P. has been entirely demonstrated.

The floor space occupied by the suction generator and engine for the larger powers may be taken as half a square foot per H.P., which compares favourably with the space taken up in vessels of the Mercantile Marine using steam power, although of course considerably above that possible in the Service or fast liners. The superficial area of engine and boiler space in various vessels is shown in the following table :—

Ship	s.s. Deutschland	s.s. König Wilhelm der Grosse	H.M.S. King Alfred	s.s. Celtic	s.s. Duke of Cornwall	H.M.S. Juno	s.s. Indian
Total I.H.P.	38,900	30,000	30,000	13,000	5520	9830	2120
Highest mean speed in knots	23·51	22·79	23·00	16·00	19·75	20·00	10·75
Superficial area of engine and boiler space per I.H.P. square feet	0·425	0·42	0·346	0·96	0·405	0·44	0·949
Total weight machinery in tons	5670	4460	2575	2975	612	904	455
I.H.P. per ton of machinery	6·35	6·71	11·65	4·37	9·02	10·88	4·66

The following table shows the approximate overall efficiency (boilers and engines, or producers and engines) under ordinary conditions. Higher efficiencies, and therefore lower fuel consumptions, are frequently attained under test conditions at full load, but would not be maintained in everyday practice under variable load, etc.

CONSUMPTION OF FUEL AT FULL LOAD UNDER RUNNING CONDITIONS.

—	Overall efficiency per cent.	Coal. lbs.	Oil. lbs.	Coal gas. cu. ft.	Producer gas. cu. ft.	Blast furnace gas. cu. ft.
STEAM ENGINES.						
Small non-condensing reciprocating	5	4·5	—	—	—	—
Large, multiple expansion condensing ..	6–7	3–4	2–2·5	—	—	—
Over type, superheat, condensing and small turbine sets	12–15	1·4–1·7	0·9–1·1	—	—	—
Large turbine sets ..	15	1·4	0·9	—	—	—
INTERNAL COMBUSTION.						
Ordinary oil engines and petrol motors	15	—	0·8–1·0	—	—	—
Pressure gas producers	20	0·9–1·1	—	—	90	140
Suction gas producers ..	22	0·85–1·0	—	—	—	—
Large gas engines on gas supplied	25	—	—	17	75	115
Diesel engine	30	—	0·45	—	—	—
,, ,, (on test) ..	38	—	0.36	—	—	—

CHAPTER XIV

NITROGEN AND ITS COMPOUNDS

Nitrogen.—This gas was first discovered by Rutherford in 1772, and its properties were afterwards fully examined by Scheele and Lavoisier, the latter giving it the name "azote," from its inability to support life; the name "nitrogen" being given to it at a much later date, to denote that it was one of the principal ingredients of potassium nitrate or nitre.

Nitrogen constitutes 79·1 per cent. by volume, and 76·9 per cent. by weight of the atmosphere; and also occurs in nitric acid and metallic nitrates, as well as in ammonia and in animal and vegetable organisms.

Preparation.—It can be prepared from air by taking away the oxygen, and this can be conveniently effected by burning some phosphorus in a jar of air standing over water. The phosphorus combines with the oxygen of the air, forming white fumes of phosphorus pentoxide, which dissolve in the water, leaving fairly pure nitrogen gas behind.

$$\overset{\text{Phosphorus}}{P_2} \quad + \quad \overset{\text{Air}}{5(N_4+O)} \quad = \quad \overset{\substack{\text{Phosphorus}\\ \text{pentoxide}}}{P_2O_5} \quad + \quad \overset{\text{Nitrogen}}{10N_2}$$

Air may also be passed over copper turnings heated to redness, when the copper takes up the oxygen, forming copper oxide, and nitrogen passes on free, but the gas is not pure nitrogen, containing notable quantities of argon and other gases.

If it is required perfectly pure it is made from a compound called ammonium nitrite, which, when heated, breaks up into water and nitrogen.

$$\overset{\text{Ammonium nitrite}}{NH_4NO_2} \quad = \quad \overset{\text{Water}}{2(H_2O)} \quad + \quad \overset{\text{Nitrogen}}{N_2}$$

Instead of using ammonium nitrite direct, it is more convenient to heat together saturated solutions of potassium nitrite and ammonium chloride, which interact with the formation of ammonium nitrite and potassium chloride, the former salt then decomposing to nitrogen and water.

$$\overset{\text{Potassium nitrite}}{KNO_2} + \overset{\text{Ammonium chloride}}{NH_4Cl} = \overset{\text{Potassium chloride}}{KCl} + \overset{\text{Water}}{2(H_2O)} + \overset{\text{Nitrogen}}{N_2}$$

If a stream of chlorine gas, generated by the action of hydrochloric acid on black oxide of manganese, be led through a saturated solution of ammonia, nitrogen is liberated, and the hydrochloric acid produced unites with some of the ammonia to form ammonium chloride.

$$\overset{\text{Ammonia}}{8(NH_3)} + \overset{\text{Chlorine}}{3Cl_2} = \overset{\text{Ammonium chloride}}{6(NH_4Cl)} + \overset{\text{Nitrogen}}{N_2}$$

When nitrogen is prepared in this way, it is important to keep the ammonia in excess, for if chlorine were to predominate, it would react upon the ammonium chloride, and form a highly explosive combination of chlorine and nitrogen called nitrogen trichloride.

The gas can be collected over water as it is very sparingly soluble, 100 volumes of water only dissolving 1·5 volumes of the gas at ordinary temperatures.

Properties.—Nitrogen in the free state is an inert gas, and is characterised by its inability to burn or to support combustion, and generally by its disinclination to combine directly with other elements.

It is a colourless, tasteless and odourless gas, which will not support life.

It is evident that it has no poisonous properties, as our atmosphere contains so large a proportion of the gas.

Although so inert in its relations towards most substances, it combines with the elements tungsten and titanium with great energy, converting them into nitrides and causing them to become incandescent when they are thrown in a finely-divided state into a jar of the gas, and it also forms compounds with boron, silicon and magnesium termed "nitrides." Many of these are strongly magnetic, the manganese nitride being nearly as strongly so as iron itself.

Ammonia.—Nitrogen cannot be readily made to unite directly with hydrogen, but by indirect means an important compound of 14 parts by weight of nitrogen and 3 of hydrogen can be obtained, viz. ammonia gas.

In Nature ammonia is chiefly produced during the spontaneous decomposition of nitrogenised organic matter, such as animal excreta, and the name ammonia was given it because the Arabs first prepared it from camel's dung, near the temple of Jupiter Ammon in the Libyan desert. Ammonia is found during the manufacture of coal gas as one of the by-products, and is obtained in combination with hydrochloric acid as sal ammoniac or ammonium chloride, and it is from this salt that we can most conveniently obtain the gas. If we mix together powdered ammonium chloride and quicklime and gently heat the mixture, ammonia gas is given off, and calcium chloride and water are formed.

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

Properties.—Ammonia gas so prepared cannot be collected over water on account of its great solubility, water dissolving 1,149 times its own volume of the gas at normal temperature and pressure. It is best collected over mercury, but being much lighter than air can also be collected by upward displacement in the same way as hydrogen.

Ammonia gas is readily recognised by its pungent odour and strong alkaline reaction, turning yellow turmeric paper brown, and red litmus paper blue. The test papers which have been acted upon, however, soon regain their original colour when exposed to air, as the ammonia rapidly volatilises, hence it is sometimes called a "volatile alkali." The gas does not support combustion, nor does it burn in the ordinary sense of the word; but if it be ignited in oxygen, it readily burns with a non-luminous flame forming water and liberating nitrogen; and a mixture of ammonia and oxygen will explode when a light is applied to it, the products of the explosion also being nitrogen and water.

$$\underset{\text{Ammonia}}{4(NH_3)} + \underset{\text{Oxygen}}{3O_2} = \underset{\text{Nitrogen}}{2N_2} + \underset{\text{Water}}{6(H_2O)}$$

When ammonia gas comes in contact with hydrochloric acid gas, dense white fumes of ammonium chloride are formed.

Ammonia gas can be liquefied by a pressure of about seven atmospheres, and this liquid if cooled below −75° freezes to a transparent solid.

Ammonia is used in large quantities in various forms of refrigerating machinery (p. 12).

Composition.—If ammonia gas be passed through a red-hot tube, or if electric sparks be passed through it for some time, its volume is doubled, and on analysis is found to consist of a mixture of one volume of nitrogen and three of hydrogen, hence the formula NH_3 is given to the gas. 22·32 litres of the gas at normal temperature and pressure are found to weigh 17 grams, hence its density as compared with hydrogen is $\frac{17}{2}$ or 8·5.

Ammonia acts as a strong base, being able to neutralise the strongest acids, forming with them salts analogous in composition to the salts formed by potassium or sodium.

Ammonia		Hydrochloric acid		Ammonium chloride
NH_3	+	HCl	=	NH_4Cl
Ammonia		Nitric acid		Ammonium nitrate
NH_3	+	HNO_3	=	NH_4NO_3
Ammonia		Sulphuric acid		Ammonium sulphate
$2(NH_3)$	+	H_2SO_4	=	$(NH_4)_2SO_4$

If these ammonium salts are contrasted with the corresponding potassium or sodium salts, it will be seen that in them the metal potassium (K) or sodium (Na) is replaced by the group (NH_4)—

Chlorides	Sulphates	Nitrates
$NaCl$	Na_2SO_4	$NaNO_3$
KCl	K_2SO_4	KNO_3
NH_4Cl	$(NH_4)_2SO_4$	NH_4NO_3

So strong is the analogy between them that this group (NH_4) is often looked upon as a metal, and is called ammonium, its salts being called ammonium salts.

Great interest centres in the ammonium salts on account of their great manurial value, and their chief commercial source is the small quantity of nitrogen always present in coal, peat, and other fuels formed from vegetable matter. On converting these substances into gaseous fuel in producers (see p. 198) a certain proportion of the combined nitrogen is liberated as ammonia gas, which can be absorbed and converted into ammonium sulphate by washing with dilute sulphuric acid. In making "Mond Gas" from coal slack, about 50 to 60 pounds of ammonium sulphate can be obtained from a ton of slack, whilst in the manufacture of coal gas and metallurgical coke on an average 23 pounds of ammonium sulphate are obtained per ton of coal carbonised.

Ammonia is now being made in Germany from the nitrogen of the air, by liquefying air by the Linde process, allowing the nitrogen to boil off and passing it over heated calcium carbide when calcium cyanamide, $CaCN_2$, is formed and this on treatment with hot water evolves ammonia.

$$\begin{array}{ccccccc} \text{Calcium cyanamide} & & & & \text{Calcium carbonate} & & \text{Ammonia} \\ CaCN_2 & + & 3H_2O & = & CaCO_3 & + & 2NH_3 \end{array}$$

The calcium cyanamide is also used as a manure.

Ammonium Amalgam.—If a strong solution of ammonia is electrolysed, the negative pole being in contact with some mercury in the bottom of the cell, and the positive above it in the liquid, the mercury swells up into a bulky buttery mass, which still retains its metallic appearance, and on allowing this to stand it evolves ammonia gas and hydrogen, and once more contracts to its original volume. This experiment was considered by Berzelius to show that ammonium (NH_4) was liberated at the negative pole and formed an amalgam with the mercury, but all attempts to isolate the ammonium have so far failed.

Another way of forming this "ammonium amalgam" is to put some freshly prepared sodium amalgam into a saturated solution of ammonium chloride, when sodium is replaced by ammonium, and the amalgam at once swells up to many times its former bulk, forming a spongy substance lighter than water, whilst sodium chloride passes into solution.

Ammonium compounds may be recognised by their giving off ammonia gas when heated with a strong alkali such as sodium hydroxide, the gas evolved being identified by its pungent odour, and by its forming white fumes with hydrochloric acid gas.

Strong solutions of these salts also give a yellow crystalline precipitate with a solution of platinum chloride, and a white crystalline precipitate with a saturated solution of sodium hydrogen tartrate.

Oxides of Nitrogen.—When through a mixture of oxygen and nitrogen a series of electric sparks is passed for some time, a gradual combination of the two gases takes place, and reddish-brown fumes form in the vessel.

Since the combination always involves strongly endothermic reactions, it only progresses during the actual passage of the sparks. The process is extensively utilised for the production of nitrates (p. 218). By indirect methods oxygen and nitrogen can be obtained in combination in five distinct proportions, as—

Nitrogen monoxide	N_2O
Nitrogen dioxide	NO
Nitrogen trioxide	N_2O_3
Nitrogen tetroxide	NO_2 or N_2O_4
Nitrogen pentoxide	N_2O_5

Whilst from the action of an electric discharge on moist nitrogen dioxide and oxygen, a nitrogen hexoxide is suspected to exist.

The higher oxides liberate iodine from salts such as potassium iodide, a property on which the Abel Heat Test is based.

Nitrogen Monoxide.—Nitrogen monoxide, nitrous oxide, or "laughing gas," is prepared by heating ammonium nitrate, the salt formed when nitric acid is neutralised with ammonia, and this breaks up into nitrogen monoxide and water.

$$\underset{\text{Ammonium nitrate}}{NH_4NO_3} = \underset{\text{Nitrogen monoxide}}{N_2O} + \underset{\text{Water}}{2(H_2O)}$$

Properties.—The gas is best collected over hot water or water saturated with salt, as cold water dissolves more than two-thirds its own volume of the gas. It is colourless and odourless, but has a sweetish taste; when inhaled it produces a kind of intoxication, hence its name; it is also used as an anæsthetic in slight operations. It can be condensed to a liquid at a pressure of 30 atmospheres, or if cooled down to − 88° C.

The gas will not burn; but if a combustible be burning with vigour, nitrogen monoxide will support its combustion nearly as freely as oxygen, the heat of the burning body tending to decompose the gas and liberate oxygen, which then supports the combustion. If feebly burning sulphur be plunged into the gas, it is extinguished because the heat is not sufficient to effect decomposition; but if the sulphur be burning strongly, then it continues to burn in the gas with increased brilliancy.

When carbon is burnt in nitrogen monoxide, more heat is evolved than when it is burnt in oxygen, showing that the decomposition of the monoxide is attended with liberation of heat, and it is therefore called an " endothermic " compound.

Nitrogen monoxide can easily be distinguished from oxygen by shaking it up with water, which absorbs the former, but would not appreciably diminish the bulk of oxygen, and also by bringing it in contact with nitrogen dioxide, which forms red fumes with oxygen but none with the monoxide.

Composition.—Potassium or sodium heated in the gas burns with formation of potassium or sodium oxide, and the residual nitrogen is found to occupy the same volume as the nitrogen monoxide used ; and as its molecular weight is forty-four, it is evident that the molecule contains two atoms of nitrogen to one of oxygen, and its formula therefore is N_2O.

Nitrogen Dioxide (NO) or nitric oxide is a colourless gas obtained by acting upon metallic copper with nitric acid. The reaction which takes place may be represented by the equation—

$$\overset{\text{Copper}}{3Cu} + \overset{\text{Nitric acid}}{8(HNO_3)} = \overset{\text{Copper nitrate}}{3[Cu(NO_3)_2]} + \overset{\text{Water}}{4(H_2O)} + \overset{\text{Nitrogen dioxide}}{2(NO)}$$

Properties.—In contact with oxygen, nitrogen dioxide instantly forms red fumes of the higher oxides ; it is insoluble in water, does not burn, and only supports the combustion of bodies which burn with high intensity.

It will extinguish a burning splint of wood or burning sulphur, but phosphorus when strongly burning is able to decompose it, and burns with increased brilliancy.

It is the most stable of the oxides of nitrogen, a low red heat not sufficing to break it up ; it may be slowly decomposed into its constituents by a series of electric sparks. Nitrogen dioxide is readily absorbed by solutions of ferrous salts, forming a dark brown compound, which is decomposed by heat. When potassium or sodium is burnt in the gas, the oxygen is absorbed, and the residual nitrogen is found to occupy one-half the volume of the original gas. The molecular weight of the gas is thirty, and it is therefore built up of one atom of nitrogen = 14, and one atom of oxygen = 16, and its formula is NO.

Nitrogen Trioxide (N_2O_3).—When nitric acid of a specific gravity of 1·34 acts upon starch or arsenic trioxide, a reddish-brown gas is evolved, which led to it being regarded as nitrogen trioxide. On passing the gas through tubes surrounded by a freezing mixture, it condenses at about −21° to a bluish liquid.

There has been much controversy as to the existence of N_2O_3 as a definite chemical substance, the vapour density of the gas as prepared by the above method agreeing with that of a mixture of equal volumes of NO and NO_2. There seems little doubt but that at low temperatures it can exist as a definite compound in the liquid condition, but with slight rise of temperature it dissociates into a mixture of nitrogen dioxide and tetroxide.

Nitrogen trioxide may be looked upon as the anhydride of *nitrous acid.*

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

Nitrogen Tetroxide.—When nitrogen dioxide comes in contact with free oxygen it combines with it to form another reddish-brown gas, nitrogen tetroxide, which contains an atom more oxygen than the dioxide, and at low temperatures has the composition N_2O_4; but this undergoes complete dissociation at 140° C. into $2(NO_2)$, and NO_2 is therefore generally adopted as its molecular formula. At ordinary temperatures the gas will consist of a mixture of N_2O_4 molecules with NO_2 molecules.

The gas can be obtained by heating lead nitrate, which breaks up into lead oxide, oxygen and nitrogen tetroxide.

Lead nitrate		Lead oxide		Nitrogen tetroxide		Oxygen
$2[Pb(NO_3)_2]$	=	$2(PbO)$	+	$4(NO)_2$	+	O_2

Properties.—Nitrogen tetroxide forms colourless crystals at −10° C., and these fuse to a colourless liquid which soon assumes a yellow colour, the tint increasing with the temperature up to 22° C., when the liquid is converted into a reddish-brown vapour which continues to deepen in colour, until at 40° C. it is nearly black, and this leads to the conclusion that N_2O_4 is nearly colourless whilst NO_2 is very dark brown.

In ice cold water nitrogen tetroxide dissolves with formation of nitrous and nitric acids—

Nitrogen tetroxide		Water		Nitrous acid		Nitric acid
$2(NO_2)$	+	H_2O	=	HNO_2	+	HNO_3

In water at ordinary temperatures it dissolves forming liquids which are blue, green, or orange, according to the amount of the gas dissolved.

The gas (NO_2) may be heated to low redness without undergoing any actual decomposition.

Vigorously burning phosphorus and charcoal decompose it and burn with great energy, whilst potassium inflames spontaneously in the vapour and burns with a red flame.

Nitrogen Pentoxide.—The highest oxide of nitrogen—nitrogen pentoxide $(N_2O)_5$—was discovered in 1849 by Deville, who prepared it by acting upon fused silver nitrate with dry chlorine.

Silver nitrate		Chlorine		Nitrogen pentoxide		Silver chloride		Oxygen
$4(AgNO_3)$	$+$	$2Cl_2$	$=$	$2(N_2O_5)$	$+$	$4(AgCl)$	$+$	O_2

It is a colourless solid, and forms prismatic crystals which have no colour below 15° C., but become dark yellow above that temperature, and melt at 30° C. to a light yellow liquid. Between 40° and 50° C. the liquid decomposes into nitrogen tetroxide and oxygen, and if rapidly heated explodes. When brought in contact with water it combines with it, with great evolution of heat, forming nitric acid—

Nitrogen pentoxide		Water		Nitric acid
N_2O_5	$+$	H_2O	$=$	$2(HNO_3)$

The reverse process, removal of the elements of water from strong nitric acid by the action of phosphorus pentoxide yields nitrogen pentoxide.

Nitric Acid.—On an experimental scale nitric acid can be easily made from one of the more commonly occurring nitrates, such as potassium nitrate (saltpetre) or sodium nitrate (Chili saltpetre) by heating with concentrated sulphuric acid. Equal weights of dry potassium nitrate and concentrated sulphuric acid are mixed in the retort (Fig. 33), and gently heated, when nitric acid escapes as a vapour, and is condensed to a yellowish liquid in the receiver, which is kept cool by water dripping upon it.

Under these conditions, and at a temperature to which a glass retort can be safely subjected, the reaction is represented by the equation—

Potassium nitrate		Sulphuric acid		Acid potassium sulphate		Nitric acid
KNO_3	$+$	H_2SO_4	$=$	$KHSO_4$	$+$	HNO_3

That is to say, one-half of the hydrogen present in the sulphuric acid is replaced by the metal potassium, whilst the hydrogen combines with the nitric acid radicle to form nitric acid. Nitric acid, when pure, is colourless; but some is decomposed by heat into nitrogen tetroxide, the ruddy fumes of which may be noticed in the retort, and which, dissolving in the condensed acid, colour it yellow.

When a higher temperature than that obtainable in a glass vessel is employed, the whole of the hydrogen of the sulphuric acid is replaced, hence half the amount of sulphuric acid is required for the preparation of the same quantity of nitric acid.

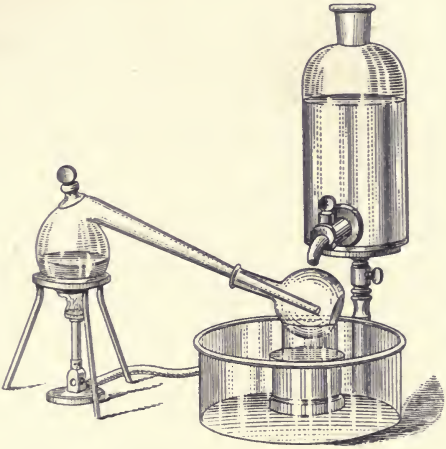


FIG. 33.—Preparation for nitric acid.

Potassium nitrate		Sulphuric acid		Potassium sulphate		Nitric acid
$2KNO_3$	$+$	H_2SO_4	$=$	K_2SO_4	$+$	$2HNO_3$

This is of importance in the commercial production of the acid, and since sodium nitrate gives a greater yield of nitric acid for the same weight of salt than does potassium nitrate, and is moreover considerably cheaper, the former is always employed on the manufacturing scale.

Manufacture of Nitric Acid.—On the large scale the action between the nitre and sulphuric acid is carried on in cast iron vessels, in order that a higher temperature may be attained. It is possible to get the whole of the sodium nitrate converted into sodium sulphate by employing a little over half its weight in sulphuric acid, but there are two objections to this. In the first place the residue is solid and not easily removed from the retort, and in the second the higher temperature leads to the decomposition of the acid produced, increasing the amount of nitrogen tetroxide present. Usually therefore about equal weights of nitre and acid are employed, so that a liquid mixture of sodium sulphate and bisulphate results, which may easily be run off whilst still fused.

The purity of the acid produced largely depends on the freedom from impurity of the Chili saltpetre employed, sodium chloride being the chief one, leading to contamination of the acid by chlorine. The strength of the product mainly depends on that of the sulphuric acid used, and on the moisture present in the nitre. For nitric acid to be used in the production of explosives the nitre is usually dried, the sulphuric acid employed being quite concentrated.

For the weaker acids the retort is generally cylindrical, its length being from 5 to 6 feet with a diameter of 2½ to 3 feet. It is provided with either stone or cast iron ends which can be luted in, each end having a hole at the upper portion, one of which serves for charging and the other as an exit for the vapours.

For the manufacture of strong acid to be used in the production of explosives, retorts of the type shown in Fig. 34 are employed. The retort (A) is provided with a collar into which the lid portion can be luted, this latter having a charging hole (C) through which the nitre is introduced, and the cover of this has another small hole (C) through which the acid can be charged. An outlet for the vapours is shown at (D) and the discharge pipe for the residual products at (E). The most convenient condensing arrangement is that devised by Guttmann, which consists of a slightly inclined main, 4 inches internal diameter (GG) made up of sections divided by a partition, each section carrying two sockets, into which the vertical condensing tubes (FF) are fitted, these being slightly over four feet in length. Each section of the main connects with the adjacent sections by means of a syphon tube. The acid as it condenses flows through these tubes, which being full of liquid, seal it so far as the passage of vapours is concerned, and then passes into the receiver (H). Any uncondensed vapours are absorbed in a suitable tower. The whole of the condensing apparatus is of glazed earthenware.

Properties.—Pure nitric acid is colourless, but as ordinarily obtained has a yellow colour due to the presence of nitrogen oxides, nitrous acid, etc. It has a specific gravity of 1·53. It is a most powerful oxidising agent, oxidising such elements as sulphur, phosphorus and iodine into the corresponding sulphuric, phosphoric and iodic acids. The strongest acid attacks many organic substances, such as turpentine, with such vigour that they are inflamed.

Its action on metals is of importance, in most cases it results in the formation of the nitrate, but hydrogen is not evolved, this being apparently due to the reduction of the excess of acid by the nascent hydrogen, with the evolution of oxides of nitrogen.

The strength of the acid and the presence of the salts produced have a great influence in determining the particular oxides of nitrogen evolved.

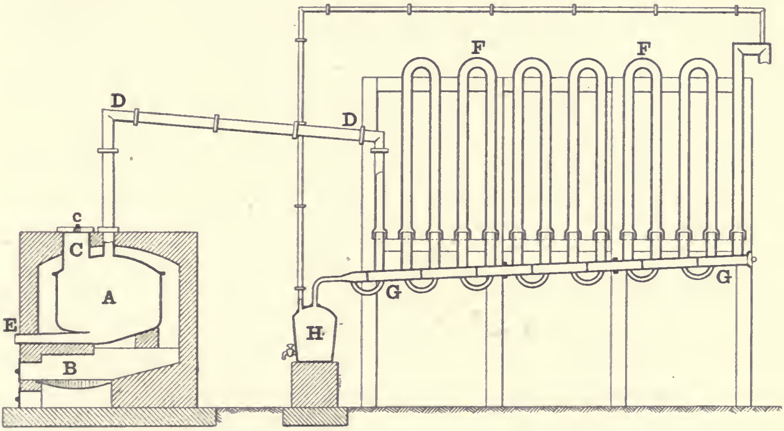


Fig. 34.—Manufacture of nitric acid.

One of the most important actions of nitric acid is that in which it replaces other elements in such substances as glycerin, cellulose, etc., producing bodies which are largely used as explosives. Commercially the most important salts of nitric acid are potassium nitrate or saltpetre (KNO_3) and sodium nitrate ($NaNO_3$).

Nitrates.—Saltpetre occurs in Nature as a deposit in certain parts of India, and large quantities are obtained from Bengal and Oude, where it is extracted from the earth by treating it with water, and, after filtering, allowing the solution to evaporate in shallow pans, the crystals so obtained being exported under the name of "grough" saltpetre, which, however, is far from pure, the usual composition being about—

Potassium nitrate	93·95
Sodium sulphate	3·21
Sodium chloride	0·85
Sand	0·25
Water	1·74

If this saltpetre be heated to 335° C. it melts, and can be cast into cakes, which on breaking exhibit a crystalline fracture, which varies in appearance with the amount of impurity present, a property which at one time was used to roughly indicate the value of any sample of the salt, and was called the "refraction" of the nitre. The term is to a certain extent still retained to indicate the amount of impurity present, and the sample of nitre, of which an analysis is given above, would be quoted as having "6 per cent. refraction."

This "grough" saltpetre has to be very carefully purified for use in the manufacture of gunpowder, which is done by recrystallising it. 100 grams of water will at 100° C. dissolve 200 grams of saltpetre, whilst at 21° C. it will dissolve only 30 grams; if therefore a saturated solution of saltpetre is made in boiling water and is then allowed to cool down, $\frac{17}{20}$ths of the dissolved salt will crystallise out, and the impurities present being not much more soluble in hot water than in cold, will remain in solution.

Saltpetre for Gunpowder.—Indian saltpetre, purified as above, is the best for the manufacture of powder, but a considerable portion of the saltpetre is obtained from sodium nitrate, found in Chili and Peru in large deposits and called "Chili saltpetre." Sodium nitrate itself could not be used instead of saltpetre as an ingredient of gunpowder in climates containing much water vapour in the air, as it is hygroscopic—that is, it has the power of attracting and absorbing moisture, which would cause the disintegration of the powder; but in hot, dry climates it is often used for making rough and blasting powders. Sodium nitrate can, however, be easily converted into potassium nitrate by double decomposition with boiling concentrated solution of potassium chloride, which forms potassium nitrate and sodium chloride, these two salts being separated by crystallisation.

$$\overset{\text{Sodium nitrate}}{NaNO_3} + \overset{\text{Potassium chloride}}{KCl} = \overset{\text{Potassium nitrate}}{KNO_3} + \overset{\text{Sodium chloride}}{NaCl}$$

This reaction is due to the fact that sodium chloride is far less soluble in hot water than potassium nitrate.

	100 parts of Boiling water dissolve	100 parts of Cold water dissolve
Sodium nitrate	218	50
Potassium nitrate	200	30
Sodium chloride	37	36
Potassium chloride	53	33

So that when a hot concentrated solution of sodium nitrate is taken and potassium chloride added to it little by little, sodium chloride forms and crystallises out, being removed from the solution by perforated ladles, whilst the mixture of salts remaining behind is roughly separated by crystallising, and then purifying in the same way as the "grough saltpetre." The potassium chloride used in this process is obtained from the great mines at Stassfurth, in Saxony, and also from the vegetable refuse left after the manufacture of sugar from beetroot.

The deposits of saltpetre in India and elsewhere are due to the decomposition of animal refuse containing carbon, hydrogen, nitrogen and oxygen, which, during processes of decay, become chiefly converted into ammonia and carbon dioxide, and the ammonia by a process of oxidation in the porous soil, aided by a certain form of "mycoderm," becomes converted into nitric acid, which combines with the potassium which is to be found in all fertile soils and forms saltpetre.

The Fixation of Atmospheric Nitrogen.—Growing plants can only obtain the nitrogen they need direct from the air to a very limited extent, but when the nitrogen is in the form of ammonia or nitrates they easily assimilate it and the yield of grain, etc., is enormously increased. The increase in the world's population demands a constantly augmented supply of wheat, and to satisfy this demand chemical manures such as ammonia salts and nitrates are used in very large quantities.

The great deposits of Chili saltpetre (sodium nitrate) have, up to recently, supplied the required quantity, but these are now showing signs of exhaustion, and several processes have been devised for making nitrates from the air.

One of the most successful of these is that devised by Birkeland

and Eyde, which may be taken as typical of the method usually employed.

When an electric discharge is passed through air traces of oxides of nitrogen are formed and the amount produced depends upon the temperature obtained, so that although at 1300° C. only 0·37 per cent. of nitrogen dioxide is found, at 3000° C. the amount rises to 4·5 per cent.

If, however, the nitrogen dioxide remains in the heated zone it is again decomposed. So that to obtain it in any large quantity it must be removed and cooled as quickly as possible. In the Birkeland and Eyde system the electrodes consist of copper tubes through which water flows to cool them, whilst in order to spread the arc as much as possible, an electro magnet is placed at right angles to them to deflect the flame into a disc-like form some six feet in diameter. This arrangement is enclosed in a chamber lined with fire-brick, and the air is driven past both sides of the disc of flame and quickly withdrawn.

About 1 to 1·5 per cent. of nitrogen dioxide is thus formed in the air and instantly combines with more oxygen to form nitrogen tetroxide—

$$\underset{\text{Nitrogen dioxide}}{2NO} + \underset{\text{Oxygen}}{O_2} = \underset{\text{Nitrogen tetroxide}}{2NO_2}$$

The gases then pass through absorption towers in which they meet water, when the nitrogen tetroxide dissolves and forms nitric and nitrous acids, which are neutralised by lime, forming calcium compounds which are recovered by evaporation and sold as fertilisers.

Tests for Nitrates.—When nitric acid is added to metallic copper a colourless gas is given off which instantly becomes ruddy brown on coming in contact with the air, and this reaction constitutes a test for the acid. If, however, the nitrate is present as a salt, it is necessary to liberate the acid by warming with excess of sulphuric acid.

When the nitrate is present only in very small traces a still more delicate test is necessary.

An equal bulk of strong sulphuric acid is added to the solution supposed to contain the nitrate. The mixture is then cooled and a solution of ferrous sulphate is carefully poured on to the surface of the mixture, and if a nitrate be present a brown ring forms at the junction of the two liquids.

CHAPTER XV

THE ATMOSPHERE AND VENTILATION

The air in which we live and breathe is essentially a mixture of the two elementary gases, nitrogen and oxygen, containing also small quantities of carbon dioxide, water vapour, argon, and ammonia, which are always present—and have special functions to perform with regard to the economy of Nature—and it is also charged with all the gaseous impurities formed both naturally and artificially on the earth's surface.

Extent of the Atmosphere.—The atmosphere forms a gaseous layer surrounding the earth, and, according to calculations made by Wollaston, based upon the duration of twilight, it extends about forty-five miles above the surface of the earth; whilst other observers, basing their calculations upon purely mathematical data, urge that there is no such limit, and that the atmosphere extends through space. It is well-known, however, that the density of the atmosphere rapidly diminishes as we ascend from the earth's surface, and that at an elevation of three-and-a-half miles its density is reduced to one-half that at the sea level.

Weight of Air.—The fact that the air has weight, and is therefore exerting a pressure upon all objects, was not proved until the middle of the seventeenth century, when Torricelli, in trying to find an explanation of the fact that a pump would only raise water a little over thirty-three feet, discovered that if water were enclosed in a tube which dipped into a reservoir of water open to the air, and if there were a perfect vacuum in the upper portions of the tube, the water would stand at a height of thirty-three feet; whereas, under the same conditions, mercury only stood at a height of thirty inches. On determining the relative weights of mercury and water, he at once found that if he employed tubes of equal diameter, the column of mercury thirty inches in height weighed the same as the column of water thirty-three feet in height; and from this he concluded that there must be some natural sustaining force of which this weight of mercury or water was a measure, and after searching for a cause, he finally came to the conclusion that it must be the pressure of the atmosphere which was balancing the columns of liquids; a conclusion which was verified by Blaise Pascal, in 1648, taking Torricelli's tubes up a high mountain, when he found that as he ascended and the amount of atmosphere above his instruments decreased, so the height of the liquid columns was diminished.

If a large glass **U** tube is taken, each arm of which is thirty-three inches long and open at each end, and if into this mercury be poured, the mercury will stand level in each arm of the tube (A, Fig. 35), but if now one end is closed and is then completely filled with mercury, on replacing the tube in position, the mercury will only fall in the tube until the difference between the levels of the mercury is thirty inches (B, Fig. 35), that is to say, the pressure of the atmosphere on the surface of the mercury in the open tube is able to balance a column of thirty inches of mercury in the closed arm of the tube with no air above it. The vacuum left in the closed arm of the tube is called after its discoverer the "Torricellian vacuum."

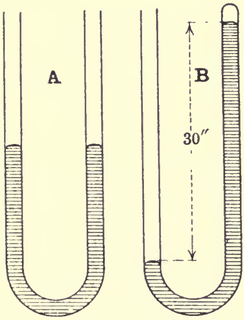


Fig. 35.—Barometer tubes.

The Barometer.—Torricelli's tube was afterwards named by Boyle the "Barometer," and it is the instrument in general use for measuring the pressure of the atmosphere; if in the experiment with the **U** tube, a tube had been chosen having a sectional area of one square inch, the atmospheric pressure on the square inch of mercury exposed would have been equal to the weight of the column of mercury supported, *i.e.* thirty cubic inches, and this amount weighs 15 lbs., so that the pressure of the atmosphere is said to be 15 lbs. on the square inch.

The effect upon the height of the mercurial barometer exerted by the pressure of the air can easily be shown by placing a barometer tube under the receiver of an air pump, when each stroke of the pump will cause a corresponding fall in the column of mercury.

29·96 inches is equivalent to 760 millimetres, which is taken as the normal height of the barometric column in all scientific work, whilst the pressure exerted by the atmosphere would be expressed in the metrical system as 1·03296 kilograms on a square centimetre.

The pressure of 15 lbs. on the square inch is taken as the pressure of one atmosphere, and pressures are often expressed in this way; if, for instance, the pressure of steam in a boiler was equal to 60 lbs., it would be said to exert a pressure of four atmospheres.

If, taking 15 lbs. on the square inch, the pressure exerted on any extended surface be calculated, it is found to be very considerable, an ordinary sized man sustaining a pressure of nearly sixteen tons on the surface of his body. This pressure, however, is so counterbalanced that he is perfectly unaware of its existence.

If water be boiled for some time in a circular tin bottle, the escaping steam drives all air out of the vessel, and being itself at the same pressure as the atmosphere balances it; if, however, the tin be corked air-tight whilst still full of steam, and cold water is thrown over the vessel, the steam is condensed, and the vessel being unable to withstand the external pressure of the atmosphere is at once crushed.

Air is 14·47 times the weight of the same volume of hydrogen.

Air a Mechanical Mixture.—Air is not a chemical compound, but a mechanical mixture of the two elements, oxygen and nitrogen.

The percentage composition of air is—

	By weight	By volume
Nitrogen	76·9	79·1
Oxygen	23·1	20·9

or roughly, four volumes of nitrogen to each volume of oxygen.

During the years 1774–75 oxygen gas was discovered independently by Priestley in England and Scheele in Sweden, and three years later the great French chemist Lavoisier discovered and pointed out the functions of oxygen and the part played by it in all cases of combustion in air—a discovery which is by many considered to be the birth of modern Chemistry.

It has been shown (p. 6) that a mechanical mixture retains the properties of the substances forming it, and we have in it the component parts merely lying side by side in a state of physical mixture; in a chemical compound, on the other hand, we have all the properties of its components merged, and new properties developed which are characteristic of the compound formed.

The reasons for considering air to be a mixture and not a compound are as follows:—

1. If oxygen and nitrogen are mixed together in the proportions in which they occur in air, there is no elevation of temperature or alteration in volume, and yet the mixture has all the properties of air.
2. The relative quantities of the two gases present are not those of their combining weights, nor of any simple multiples of these weights.
3. When air is shaken up with a small quantity of water some of it is dissolved, and if this dissolved air be expelled from the water by boiling, it is found to consist of oxygen and nitrogen, in the proportions of 1 to 1·87 and not 1 to 4. Now had air been a chemical compound it would have dissolved as a whole, and on being expelled from solution the oxygen and nitrogen would still be in the original proportion of 1 to 4.
4. The proportions in which the two gases occur occasionally vary slightly.
5. Nitric oxide forms ruddy fumes in contact with air, showing that the oxygen present is uncombined.

Analysis of Air.—The volumetric composition of air is best determined by means of the eudiometer, the same method being employed as in the volumetric synthesis of water, the only difference being, that instead of experimenting with pure oxygen air is used, and having passed up excess of hydrogen, the mixture is exploded and the diminution of volume noted. Now two volumes of hydrogen combine with exactly one volume of oxygen to form water; hence, one-third of the observed diminution in volume must represent the oxygen which has disappeared and therefore the volume of oxygen in the air taken.

The amount of oxygen by weight in air is determined by passing a known volume of purified air slowly over red-hot copper turnings in a hard glass tube; the copper takes all the oxygen from the air, forming copper oxide, and by carefully weighing the tube of copper before and after the experiment, the increase in weight—due to the oxygen in the volume of air taken—is determined.

Argon.—Cavendish, who was the first to carefully analyse air, found that atmospheric nitrogen contained a minute trace of something which appeared more inert than nitrogen itself; and Lord Rayleigh, whilst determining the density of nitrogen, found that when that gas was obtained from air it had a slightly higher density than when prepared by chemical means.

This was found to be due to the trace of inert gas noticed by Cavendish, and this having been isolated by Lord Rayleigh and Sir William Ramsay, was found to be a new element to which the name "Argon" has been given.

Preparation.—Argon is found in the atmosphere to the extent of 0·9 per cent. by volume or 0·2 per cent. by weight. It is obtained by passing air over red-hot copper, in order to remove the oxygen, and then through a long series of tubes containing red-hot magnesium, which absorbs the nitrogen. After repeating the latter portion of the process several times the argon is obtained by itself.

Other methods are to add some oxygen to the air and to pass induction sparks through the mixture for a very long period over potassium hydroxide, which absorbs the oxides of nitrogen produced, the process being continued till all the nitrogen has disappeared. The excess of oxygen can then be absorbed by phosphorus, heated copper, or pyrogallate of potassium, when the argon is left.

Another method for obtaining it is to heat air with a mixture of magnesium, sodium, and freshly ignited lime; calcium is formed in a finely divided condition, and both the oxygen and nitrogen are absorbed, the argon remaining behind.

The gas occurs in small quantities in solution in some mineral waters and rare minerals.

Properties.—Argon is a colourless gas, having a specific gravity of 19·9 and a molecular weight of 40. The molecule consists of only one atom; the atomic weight therefore is also 40. By cooling it with boiling oxygen under a pressure of 50 atmospheres it has been condensed to a liquid. It is so inert in all its characteristics that no compounds of argon have been prepared, and there is no doubt now that it is an element.

Traces of four other rare gases have also been discovered in air by Sir William Ramsay—helium, neon, crypton, and xenon. These bodies all display characteristic lines in their spectra and, like argon, their molecule consists of only one atom.

Functions of the Constituents.—Air being a mechanical mixture and having the properties of its constituents, it is at once evident that oxygen is the great supporter of life, and combustion, whilst the function of the nitrogen is to dilute it and keep its action within the proper limits. This fact having been established by Priestley and Lavoisier, it was imagined that the great secret of health had been discovered, and that air was wholesome in proportion to the amount of oxygen it contained ; but of late years this theory has been exploded by the fact that the variation in the percentage of oxygen in good and bad air is very slight. In a long series of analyses made by Angus Smith of samples of air, the extreme variations are 20·99 per cent. in a sample of air from the Scotch moors, and 20·63 per cent. in air collected in the gallery of a London theatre towards the close of the performance.

Minor Constituents of Air.—Besides oxygen and nitrogen, there are three other important gaseous bodies present in air—water vapour, carbon dioxide, and ammonia—which have distinct parts to play in natural processes, and must not therefore be looked upon as impurities until the amount exceeds a certain limit.

AVERAGE COMPOSITION OF THE ATMOSPHERE.

Oxygen	20·61
Nitrogen	77·95
Carbon dioxide	0·04
Aqueous vapour	1·40
Nitric acid Ammonia }	traces
	100·00

Functions of the Minor Constituents.—Ammonia is present in very small traces, but is of great importance to vegetable life, as it is from this gas that plants obtain a large proportion of the nitrogen which they require to form their seeds and fruit. It is evident that ammonia could not be present in large quantities in the air unnoticed, on account of its pungent odour ; but small as are the traces present its great solubility enables every shower that falls to collect it from the air, and bring it down to the vegetation which needs it.

Water vapour is present in varying quantities dependent chiefly upon the temperature. The warmer the air the more water it can hold in suspension as vapour; when warm air is cooled by coming in contact with colder layers of air, it cannot any longer hold so much moisture, and deposits the surplus as rain. In the night time, while the surface of the ground is receiving no heat from the sun, it is constantly losing heat by radiation, and on a clear night soon becomes colder than the air above it, the lower strata of air being cooled by contact with it, so causing a condensation of moisture in the form of dew.

Water vapour in the air has an enormous influence upon our comfort and health. The human body is largely composed of water, and if the air becomes too dry, evaporation from the skin and lungs is increased, causing great discomfort.

The aqueous vapour in the atmosphere also plays an important part in warming the air, as the vapour contains a large amount of latent heat which is given up to the air during condensation, besides which its presence retards the passage of heat rays through the air and so raises the atmospheric temperature.

Withdrawal of Oxygen.—When animals or human beings breathe, the life supporting principle of the air is exchanged for carbon dioxide, which by this process is continually being poured into the atmosphere, and this gas is also formed during all processes of combustion, whether they be rapid, as when wood is burnt in a fire, or slow, as when vegetable matter rots away. It is also produced by processes of fermentation, and escapes in quantities into the atmosphere from the earth, from natural sources.

It must be remembered that during most processes which give rise to carbon dioxide, oxygen is being absorbed, and it has been computed that this takes place at the rate of over three-and-a-half million tons per diem. It has, however, been shown by the researches of Fruchot, Schultze, and others, that in the open air the percentage of carbon dioxide varies but little, the average amount being four volumes in 10,000 of air—this quantity decreasing after rain and increasing during frost and fog and at night time, but again diminishing after sunrise; it is therefore evident that there is some natural agency at work which tends to neutralise the effects of animal life and decay, and it is found that vegetable life plays an important part in this process of purification, although the vastness of the atmosphere is the chief cause of the constant proportions of its constituents.

Action of Vegetable Life.—If the leaves of any form of vegetation be examined, they will be found to be covered with minute funnel-shaped pores which are in connection with small cells containing a green matter called "chlorophyll," which gives the colour to vegetation (see also p. 166).

Under the influence of the sun's rays the growing plant absorbs carbon dioxide from the air through the pores in the leaves, and it is then decomposed by the chlorophyll, the carbon being mostly assimilated together with water by the plant to form its woody fibre and so carry on its growth, whilst the oxygen is once more returned to the air, tending to keep the percentage of oxygen constant.

Diffusion.—This wonderful process would, however, be of little use by itself, as in large towns and manufacturing districts where enormous amounts of carbon dioxide are formed, there is, as a rule, but little vegetation and still less sunshine, so that the gas would accumulate and seriously impair the purity of the air were it not that the winds and air currents, aided by the diffusion of gases, tend to mix all the constituents of the atmosphere evenly together, and where sunshine and vegetation exist, there the carbon dioxide is decomposed, and the oxygen once more spread throughout the air by these methods, a practically constant proportion being thus maintained.

Were it not for the action of gaseous diffusion and wind the constituents of the atmosphere would arrange themselves in layers according to their densities, and life would be an impossibility.

Organic Matter.—It has already been shown that a process of slow combustion is taking place in the animal system, and this leads to the formation of carbon dioxide and water. It is computed that the ordinary adult exhales nearly a pint of water in twenty-four hours. If water produced in this way be allowed to stand for a few days, or even hours, it will putrefy and become offensive, showing that besides water there is present organic matter. It is this organic matter which is accompanied by the germs of disease, and is one of another class of impurities which are to be found in the atmosphere, and which are purely local and have local causes, and which perhaps affect health more than anything else.

True Impurities.—These are—First, suspended solids, which are found floating in the air as dust ; partly mineral substances which induce certain diseases from the merely mechanical effect of local irritation; and partly organic bodies, such as the germs of infusoria, fungi, etc., which have come into great prominence during the last few years from the investigations of Schrœder, Davaine, and Pasteur, and which at the present moment are the favourite explanation of the spread of many kinds of disease.

Secondly, suspended liquids, such as the fog formed by partly condensed water vapour, which, by keeping down the smoke and solid impurities, irritate and affect respiratory organs and eyes; and thirdly, gases, such as sulphur dioxide and sulphuretted hydrogen in volcanic districts, hydrochloric acid and chlorine in manufacturing districts, and marsh gas or methane on bog lands, these gases having a greater effect on vegetation than on human beings.

Ventilation.—It will be obvious that the removal of oxygen from the air in a closed space and its replacement by carbon dioxide and other accompanying impurities in the breath, quickly vitiate the air, rendering imperative some system of ventilation by which the air can be efficiently changed.

It has usually been regarded that the amount of carbon dioxide permissible in the air of a dwelling-room shall not exceed six parts in 10,000, the normal amount in free open air being four parts. Distinction must be drawn between this gas produced by animal life and by processes such as combustion, the latter, volume for volume, being comparatively innocuous. Views with regard to ventilation are at the present time undergoing considerable change, as Dr. Haldane has shown that the effect of carbon dioxide and organic matter on health has in the past been overrated, whilst Dr. Leonard Hill points out that cool air not too highly charged with moisture and kept in constant motion is far more important to health than chemical purity.

In ventilation, attention should be paid to the following points: (1) The air which enters should be pure; (2) Its movement should be imperceptible, otherwise it causes what we call a draught and sensation of chill; (3) The incoming air must be evenly distributed through the room, so that every part shall be undergoing change; (4) The air should be removed so quickly that there is no risk of the same air being breathed more than once.

The means by which air is set in motion for purposes of ventilation may be natural or artificial; in nature, the causes at work are, diffusion, wind, and the differences in weight between unequally heated masses of air. Air diffuses with great rapidity through chinks and openings due to bad carpentry, and also through bricks and walls built of porous materials. The amount of purification effected by diffusion is, however, insufficient.

Wind acts as a powerful ventilating agent. If it can pass freely through a room with open doors and windows at a rate of two miles an hour, which is almost imperceptible if the room is 20 feet wide, it will change the air of the room 528 times in one hour. Air is called " still " when in reality it is moving a mile or a mile-and-a-half per hour. The average movement of air in England is six to eight miles per hour.

It will be seen that the methods employed in heating and lighting a house not only play an important part in deteriorating the quality of air by removing oxygen and giving back to the air carbon dioxide, but they also may be made important factors in the ventilation, owing to the tendency to upward movement produced in the foul air by rise of temperature and moisture formed during combustion; and one of the most ordinary forms of ventilation consists in making openings near the top of the room, leading either into the flue or into the open air, whilst corresponding openings are arranged near the floor for the admission of fresh air.

The open fire, inefficient as it undoubtedly is from a heating point of view, provides an excellent system of removal of impure air from a room—often the only method in an ordinary dwelling. Slow combustion stoves do not withdraw anything approaching this amount of air per unit of effective heat generated, and it is clear that systems of heating by hot water or steam radiators do not directly contribute to ventilation.

Ventilation of Ships.—In the ventilation of ships it must be remembered that the possibility of diffusion through the wall space is entirely eliminated, and that it is therefore necessary to pay all the more attention to artificial ventilation, a subject which has received but scant attention in the Navy, owing to the structural difficulties which have to be contended with, and which do not exist in the fast ocean steamers and Mercantile Marine.

In the older boiler and furnace arrangements, burning with natural draught, the stokeholds and engine rooms were practically open, whilst the other portions of the ship were in connection by means of air tubes and canvas cowls, which, whilst the vessel was in motion, kept up a constant air supply. With the introduction of forced draught, however, a change had to be made, as it was not considered desirable to feed the draught directly to the fire-boxes, as is done in most of the fast liners, but to make the stokehold as air-tight as possible, and to feed air into it by means of fans, so as to make it an air reservoir, with practically the only outlet through the furnace; this arrangement was considered necessary, in order that when the vessel was not required to go full speed, natural draughts could be used by opening up traps over the stokehold, whilst, when great speed was required, the stokehold was battened down, and the pressure of air obtained by the use of the fans.

The great objection to this is that the outlet for the air is at the bottom of the stokehold, whilst the hot foul air accumulates above, and being under pressure may leak out into other portions of the vessel, heating and vitiating the air.

The objection which exists to making any openings in the steel deck, which can possibly be avoided, renders any definite statement on ventilation of war ships very difficult, but it is desirable that some more efficient system than that at present adopted should be employed in the newer types of war ship.

The bellmouth canvas cowls when properly set and when the ship is going at full speed act in driving air into the ventilation trunks between deck, but when the ship is at rest, unless a high wind is blowing, they are perfectly inactive, and in bad weather have to be closed in order to prevent water finding its way down, besides which, even when they are acting, no provision is made for removing the vitiated air.

In some of the big liners cowls are replaced by water-tight down draughts, which supply an abundant quantity of air to all parts of the vessel, whilst self-acting air pump ventilators extract the vitiated and heated air from every part of the ship.

CHAPTER XVI

EXPLOSIVES—GUNPOWDER

Effect of Time on Intensity in Combustion.—It can readily be proved that when organic substances containing hydrogen undergo decay, some of the hydrogen present unites with the oxygen of the air to form water, and the heat generated by the combination is spread over so long a period that at no one moment of time is it perceptible to the senses. If, however, hydrogen gas is confined under pressure in a gas holder, and allowed to escape through a jet into the air, on being ignited it burns with an intensely hot flame. In this case, as much hydrogen is converted into water in the course of a minute as would have been formed in some years by the process of slow combustion, and the increase in calorific intensity obtained is due solely to the increased rate of combustion, the total thermal value of the hydrogen being the same, whether it is burnt by a slow process taking years, or rapidly in a minute. If now the same volume of hydrogen be mixed with sufficient air to supply it with the oxygen required to convert it into water, and if a light be applied to the mixture, the molecules of hydrogen being side by side with the oxygen necessary for their conversion into water, combustion takes place with enormous rapidity, and the intense heat generated expands the vapour formed to such an extent that an explosion results.

It is, therefore, evident that explosion may be looked upon as intensely rapid chemical action giving rise to gases or vapours which, being largely expanded at the moment of their formation by the heat developed during the action, occupy an enormously larger volume than the original substance.

There is no line of demarcation between ordinary combustion and explosion, it depends entirely upon the rate at which the chemical action proceeds. If it takes place slowly the products can move the air and make way for themselves, but if enclosed in a containing envelope, the pressure bursts the walls and explosion results: the ignition of a small pile of gunpowder gives rapid combustion, but if confined, explosion. When, however, the chemical action becomes so rapid that there is no time for the products to displace or drive back the air, then explosion is produced without confinement.

Effect of Temperature.—Rapidity of combustion, by increasing the calorific intensity, expands the products of combustion, if they be gaseous, to an enormous extent at the moment of their formation, and as the effect of explosion is dependent upon the sudden generation of a large volume of gas from as small a volume as possible of original matter, the amount of heat generated during explosion is an important factor in the value of an explosive.

Requirements for an Explosive.—In an effective explosive these two essentials must be combined, and a solid or liquid occupying a small bulk must contain within itself the constituents necessary for building up a large volume of gas, whilst the change in condition must take place infinitely rapidly and generate so much heat that the volume of the gaseous products is again largely increased by expansion.

Effect of Initial Space.—The smaller the space into which the original explosive can be packed the greater will be the effect produced; a mixture of air and hydrogen explodes, but the explosion is much more violent if the same quantity of hydrogen is mixed with pure oxygen instead of air, as the retarding influence of the nitrogen is removed, and the mixture occupies less than one-half of the space occupied by the air and hydrogen.

The explosion of a mixture of hydrogen and oxygen produces a pressure of 240 pounds on the square inch, which is very small as compared with gunpowder, which gives on explosion a pressure of forty-two tons on the square inch, this being due to the fact that the ingredients of the powder are solid, and therefore occupy the minimum amount of space; if the mixture of hydrogen and oxygen were compressed to the same density as gunpowder, it would develop on firing a pressure of over 300 tons on the square inch.

Oxidising Agents.—Oxygen in the gaseous form could not be used in explosives, as it would occupy too large a space, but there are certain compounds rich in oxygen, which hold it in such feeble combination and are so ready to give it up to bodies capable of being oxidised, that they can be used as a form of compressed oxygen, and by their decomposition they supply to the combustibles present in the explosive the oxygen necessary to convert them into large volumes of gases.

In the older forms of explosive like gunpowder, these oxygenating bodies were mechanically mixed with the substance to be burned, but in most modern explosives compounds are utilised in which a combustible base is combined with an acid radicle containing the necessary oxygen, so that both being in the same molecule, a rearrangement of the atoms is all that is needed to give explosion.

In nearly all cases of chemical decomposition heat is absorbed, and the compounds which behave so are called "exothermic," because in their formation heat was given out, but the oxidising compounds used in some of the explosives are exceptions to this law, and during decomposition evolve heat which helps the action, these compounds being called "endothermic."

Importance of Fine Division.—It is of great importance that the combustible and the supporter of combustion in an explosive mixture should be in as fine a state of division as possible and well mixed, so that at the moment of explosion, each molecule of combustible shall find itself side by side with the molecules with which it is to combine, and that as little inactive material as possible should be present. The important effect of these conditions may be shown by taking four small pieces of phosphorus of equal size, and placing one on a saucer, when it will enter into slow combustion with the oxygen of the air, and if the day be warm the temperature may rise to the point necessary for rapid combustion; but if not, many hours will have elapsed before the action is complete and the last of the phosphorus oxidised. The second piece can now be ignited in a deflagrating spoon and immersed in a bell jar of air, when it will burn away in a few minutes with evolution of heat and light; whilst if the third piece be now in the same way ignited and plunged into a jar of pure oxygen, it will burn away still more rapidly, and the increase in calorific intensity is shown by the bright light produced.

If now the fourth piece of phosphorus be dissolved in a few drops of carbon disulphide, and this solution be poured upon a small heap of powdered potassium chlorate, placed on a piece of blotting paper supported on the ring of a retort stand, the disulphide will evaporate and will leave the phosphorus in a very finely divided condition on the surface of the chlorate, a violent explosion at once ensuing, caused by the spontaneous ignition of some of the finely divided phosphorus, which causes the chlorate to decompose and give up its oxygen. This is an "endothermic" decomposition, and the heat so generated, together with the heat produced by the combination of the phosphorus and oxygen, gives on account of the rapidity of the action, great calorific intensity, with enormous expansion and consequent violence of explosion.

The intense rapidity of combustion was in this case due to the fineness of division of the phosphorus, and to the small bulk into which the oxygen was compressed, the chlorate necessary to burn the phosphorus only occupying roughly $\frac{1}{600}$th the volume of oxygen necessary, or $\frac{1}{3000}$th the volume of air.

Classification of Explosives.—The explosives in use may be classified into mixtures and compounds, the former class containing the combustible and the oxygen-supplying substance in the condition of intimate mechanical mixture, whilst the latter class consists of organic compounds, containing oxygen loosely held in combination by nitrogen, the oxygen on any disturbance of the molecular structure of the compound entering into new combinations with the carbon and hydrogen already present in the molecule. In some of the new explosives these two classes are combined, and the gas-generating power of the second class is augmented by the admixture of highly oxidising substances, which tend to render the combustion more complete, and so increase the amount of heat generated.

Gunpowder, which was the most important and most commonly used of the explosives, is an example of the first class, being an intimate mixture of potassium nitrate or saltpetre (which supplies the oxygen), sulphur and charcoal. English black Service powder had the average composition—

Potassium nitrate	75
Charcoal	15
Sulphur	10
	100

Although in some of the slow-burning prismatic powders the percentages of potassium nitrate and charcoal were increased, and less sulphur used, the black Service powders of various foreign Governments approximated closely to this composition.

Gunpowder as a propellant has been entirely superseded in the Service by smokeless powders, but it is still used for certain kinds of demolition work, as priming for charges of smokeless powder, as fuses and igniters. In other directions, however, such as for mining, it is still largely used, and it has played so important a part in the history of the world, and illustrates so perfectly the conditions necessary for the work that explosives for Service purposes have to perform, that it is necessary to fully consider its manufacture and action if only as an introduction to the modern explosives.

Historical.—Discovered and used long before the Christian era, gunpowder has undergone but few changes in composition, and it is remarkable that these changes have been restricted to comparatively short periods ; the first of which may be taken as comprising the fifteenth century, whilst the second and most important has occurred during the past thirty years.

Discovery of Gunpowder.—Invented according to tradition by the Chinese, and rediscovered, probably independently, by Roger Bacon in 1267, and by Berthold Schwartz in 1320, there is ample proof of its being used for warlike purposes at the battle of Crecy in 1346, but it was not until the last years of the fourteenth century that any improvement was made in the proportions in which the ingredients were present. Up to that time, the carbon, sulphur, and saltpetre had been blended in practically equal proportions, but at the end of the fourteenth century a gradual increase in the quantity of saltpetre used began to be observable, and the writings of the Italian Sartaglia show us that before 1537 the proportions of the ingredients had been improved until they closely approximated to the composition of the ordinary powders of the last century.

Potassium nitrate, nitre or saltpetre (KNO_3) is the ingredient in powder which supplies the oxygen necessary for the combustion of the carbon.

Changes in Form of Powder.—Simultaneously with improvements in the composition of the powder attempts were made to improve its mechanical condition, and undoubtedly the most important of these consisted in converting the finely powdered and mixed constituents, which were known by the name of meal powder, into grains which would be more convenient for handling, and which, at the same time, by opposing less resistance to the passage of the flame between the particles, increased to a great extent the rapidity of its combustion.

The earliest attempt in this direction was to sprinkle the meal powder with a spray of water, which caused the fine meal to collect into small spherical masses. These were afterwards gathered together and dried, but the ease with which such grains crumbled into fine powder again prevented any important increase in the rate of combustion being attained, and it was not until the idea was adopted of compressing the meal powder into dense hard cakes, and then again breaking these up into grains of the required size, that any great advance in this direction was made.

These improvements having been effected, the importance of mixing the ingredients in such a way that the maximum intimacy of admixture should be attained, began to attract attention, and the perfection in this direction which was reached in the manufacture of English powder shows in marked contrast to the powders used in some Eastern countries. The most important era in the history of powder is undoubtedly to be found in the improvements and alterations made during the last fifty years.

The Growth of Guns.—The causes which led to these alterations were to be found in the new forms of guns which were introduced soon after the close of the Crimean War. With the changes from the short smooth-bore cannon to the long-rifled ordnance of to-day, a corresponding alteration became necessary in the rapidity with which the powder developed its propulsive force, as the sudden impulse which the grain powders employed at that time gave to the projectile in the guns then in use, would have developed strains of a dangerous character in the breech of some of the modern forms of artillery, and at the same time would have given an extremely low muzzle velocity to the projectile.

With the introduction of rifled ordnance, a change came over the science of gunnery, and an enormous increase in the size of the guns and in the charge of powder used followed. During the Crimean War, the largest guns used were the 68-pounder smooth-bore guns, weighing 112 cwt. and using a charge of 18 lbs. of powder, whilst at the bombardment of Alexandria, the smallest gun used was a 6½-ton one, using a charge of 30 lbs. of powder, and the old 110-ton guns required a charge of 960 lbs. of powder, and it is evident that the form of the powder had to be modified to keep pace with such radical alteration in the conditions under which it was to be used.

Desired Action of Charge.—It is required of a perfect powder that when the charge is fired in the breech of the gun, the combustion shall commence comparatively slowly so as to gradually overcome the *vis inertiæ* of the projectile without throwing too great a strain on the gun, and that, as the projectile passes up the bore of the gun, the combustion shall increase in rapidity so as to supply gas more and more rapidly to increase the momentum of the shot which should leave the muzzle of the gun with the maximum velocity. In the old-fashioned grain powders this was never secured, and such powders could not have been used in the modern long-bore guns, as the rapidity with which they burnt threw an enormous strain upon the breech, and would have given the maximum velocity to the projectile before it was half way up the bore of the gun, leaving friction to reduce the velocity to a considerable extent before the muzzle was reached.

Methods of Retarding Burning.—The rate at which the combustion of gunpowder takes place, and at which therefore the pressure is developed, can be modified in various ways by mechanical means. As has already been seen, the rate can be diminished by burning the powder in the form of meal, but such a method would be inadmissible in practice, as the density of the mixture is very low, and the charge would occupy too large a space.

The combustion might also be retarded by reducing the intimacy with which the ingredients are mixed, but this again would be a bad and unscientific method to adopt.

The elimination of these two methods practically reduces the mechanical means for modifying the rapidity of the burning of the powder to three.

1. Varying the size and form of the grains of powder.
2. Varying the density of the powder.
3. Varying the surface-coating of each individual grain or mass, so as to retard or accelerate the ignition.

The English Committee of 1857 was strongly of opinion that it was not right to modify the proportions in which the ingredients existed in gunpowder until they had exhausted all other devices for reducing the rate of burning, as an alteration in the proportion would sacrifice a certain amount of the total explosive force developed by a given weight of powder, and as the result of their labours, the first methods employed were of a purely mechanical nature.

Increase in Size of Grains.—The first step was to increase the size of the grains used for cannon powder at that time, and the larger grain powder gave fairly good results with the first modified forms of guns then introduced, but as the guns and charges increased in size, this powder in burning became too violent, and the next step was to produce a powder in which the grains should be uniform in shape and size.

This was done by compressing the meal powder into small moulds, so as to obtain small cylindrical pellets of about three-quarters of an inch in diameter, and three-eighths of an inch in height, with indentations at each end in order to increase the surface.

The manufacture of this powder was, however, somewhat costly, and in order to facilitate the manufacture, a powder less regular in size than the pellet powder was produced by compressing the meal powder into cakes, and then cutting these cakes into small cubes of about five-eighths of an inch, and from these small cubes the charges of powder in the guns were built up, and later on experiments were made by increasing the size of these cubes until a large pebble powder, consisting of cubes of one-and-a-half inches, was arrived at.

With all these forms of powder, however, maximum rapidity of burning and evolution of gas takes place at first, owing to the ignition spreading over the whole surface of the cubes, and instead of the gas coming off with more and more rapidity as the space in the gun became larger, the evolution rapidly diminished with the decrease of surface caused by the burning away of the powder.

Built up Charges.—In order to avoid this defect as far as possible, built up charges were resorted to, and it was General Rodman, of the American Service, who first tried to overcome this difficulty by building up the charge of solid slabs perforated with holes, so as to expose the minimum surface of powder at the commencement of combustion, whilst the enlarging holes produced a greater and greater surface of powder as the space behind the projectile increased.

This idea has been revived, but large perforated cakes are always liable to break, and it was found far better to build up the charge of hexagonal prisms with a central core moulded in them.

Prism Powder.—It was in accordance with this idea that the black prism was first made, and the increase in rapidity in combustion is due to the enlargement of the core and subsequent exposure of a larger surface, and to the fact that as the walls of the prism grow thin they break up across the lines of least resistance (A A′, Fig. 36), converting the powder during the last moments of its existence into what is practically a R.L.G. powder, thus giving enormously rapid combustion, due to the exposure of a large number of fresh faces.

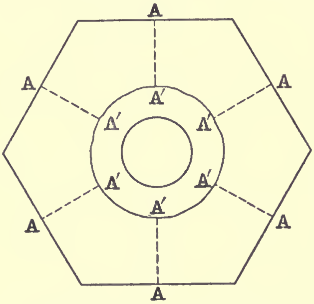


Fig. 36.—Prism powder.

That this is really the case was shown by a prism being occasionally blown out with the projectile and extinguished by the sudden rush through the air, when it was seen to have been partly consumed and broken up in this way.

Side by side with these advances in the mechanical tempering of the combustion, other advances equally great in the manufacture were being made. It was realised that in order to obtain uniformity of results, absolute uniformity of ingredients, mixing, incorporation, pressure, density and degree of dryness, as well as uniformity in size, must be attained, and new methods were introduced into the process of manufacture with this object in view, great attention being also paid to the "finishing" of the powder prisms and the blending together of various batches of powder which presented any variation in their ballistic properties.

With the continued growth, however, in the size of the guns employed, other changes became necessary, as even when using the black prism powder for built up charges the pressure given began to throw too severe a strain upon the breech of the gun, even when the cartridges were made up in such a way as to leave air spaces at the seat of the charge, in order to relieve as far as possible the initial pressure.

Changes in Composition.—In order to secure further modifications in the pressure developed, it soon became manifest that chemical alterations in the composition of the powder would be necessary. Sir Frederick Abel and Sir Andrew Noble had already made researches which conclusively showed that advantages might be secured in powder to be used in heavy guns by increasing the proportion of carbon and reducing the quantity of sulphur present, when Mr. Heidmann and Mr. Duttenhofer almost simultaneously produced a prismatic powder, in which the saltpetre was increased in quantity, the sulphur reduced, and low burnt charcoal in larger proportion was employed. This powder, which received the name of "Cocoa powder," from the brown colour imparted to it by the semi-charred woody fibre, gave a considerably lower initial strain and a much longer sustained action when used in large guns.

In the powders not only did the change in the proportions of the ingredients effect a considerable alteration in their point of ignition and rate of combustion, but the introduction of charcoal produced at a comparatively low temperature also brought into play other important considerations.

Where it is important to retain a certain proportion of moisture in powder, low burnt charcoal is of the greatest value, and the straw carbonised by superheated steam, which was used in the cocoa powder, played a most important part in imparting to the densely pressed prisms sufficient hygroscopic power to enable them to hold the necessary percentage of moisture.

The introduction of the cocoa powder was a great advance, but with the heaviest guns it became necessary to obtain even slower combustion, and by slight modifications in composition, the Service powders known as S.B.C. and E.X.E. prism were introduced.

The E.X.E. prism was distinguished by its slate colour and by a groove moulded round the core, whilst the S.B.C. prism was recognisable by its brown colour and by a circular indentation round the core.

Saltpetre for Powder.—In making Service powders all the saltpetre used is obtained from native or grough saltpetre, found as a deposit in certain parts of India and carefully purified by recrystallisation before use (see p. 216).

It is especially important that no trace of chloride should be left in the saltpetre, as both sodium and potassium chlorides tend to reduce the power and rapidity of explosion of the powder, and would also cause the grains to crumble.

Saltpetre crystallises in long grooved six-sided prisms; when heated it fuses at 335° C., and on continuing the application of heat it commences to decompose. At a red heat this decomposition consists of the evolution of one-third the oxygen contained in the salt and the formation of potassium nitrite.

$$\begin{array}{ccccc} \text{Potassium nitrate} & & \text{Potassium nitrite} & & \text{Oxygen} \\ 2(KNO_3) & = & 2(KNO_2) & + & O_2 \end{array}$$

When dried and finely powdered saltpetre is thrown upon red-hot charcoal, the carbon undergoes rapid combustion at the expense of the oxygen of the nitrate, and in the same way when powdered carbon is thrown upon fused potassium nitrate, violent combustion takes place, the reaction probably being—

$$\begin{array}{ccccccccc} \text{Potassium} & & & & \text{Potassium} & & \text{Carbon} & & \\ \text{nitrate} & & \text{Carbon} & & \text{carbonate} & & \text{dioxide} & & \text{Nitrogen} \\ 4(KNO_3) & + & C_5 & = & 2(K_2CO_3) & + & 3(CO_2) & + & 2N_2 \end{array}$$

One part (by volume) of solid potassium nitrate contains as much oxygen as 3000 times its own bulk of air, and it is this fact which renders it so valuable in gunpowder, in which it may be looked upon as being a store of condensed oxygen to be used for the combustion of the carbon.

Charcoal for Powder.—The carbon used in gunpowder consists of charcoal prepared with great care from various vegetable tissues, the nature of which depends upon the character of the powder in which it is to be used. Great care has to be taken in regulating the temperature at which the substances are carbonised, as if a high temperature is employed a very dense charcoal is obtained, which, as it is not easily combustible, is not so good for use in powder as a charcoal made at a lower temperature. The reason of this is that woody fibre consists mainly of cellulose ($C_6H_{10}O_5$), and the higher the temperature employed the greater the percentage of oxygen and hydrogen eliminated, and with the elimination of the hydrogen the inflammability is decreased.

Effect of Temperature on Composition.—The difference in composition of the charcoal formed at various temperatures is strikingly shown by the following table :—

PERCENTAGE COMPOSITION OF CHARCOAL.

Temperature	Carbon	Hydrogen	Oxygen	Ash
270° C.	71·0	4·60	23·00	1·40
363°	80·1	3·71	14·55	1·64
476°	85·8	3·13	9·47	1·60
519°	86·2	3·11	9·11	1·58

Woods Used.—In the Government Powder Factory the following woods were the ones mostly used :—

Powder	Wood	Time of burning (hours)
M.G.$_1$, R.F.G. ..	Dogwood	4
R.F.G.$_2$		8
R.L.G.$_2$	Alder and willow	3½
R.L.G.$_4$, P. ...		4
P$_2$		6
Prism (black) ..		4
S.B.C. (slow burning cocoa prism)	Straw	

The temperature of carbonisation varied between 360° C. and 520° C., whilst the rapidity with which the maximum temperature was reached also had an important influence on the quality of the charcoal formed, the quicker the heating the higher being the percentage of carbon obtained.

Low-burnt Charcoal.—Charcoal which has been carbonised at temperatures below 260° C. has a brown colour and is highly inflammable, and although the large percentage of oxygen left in it reduces its calorific value (see Fuel), yet where it was important to retain a certain portion of moisture in the powder, as in the case of the E.X.E. and S.B.C. prism powders, in which a given quantity of moisture was almost as important an ingredient as the sulphur, then the hygroscopic properties of the lightly burnt charcoal are of great value in the closely pressed prisms. Some of the brown charcoals were carbonised in retorts heated by superheated steam instead of directly by fire.

Sulphur.—The sulphur used in powder manufacture is native sulphur purified by re-distillation, and on testing should not leave more than 0·25 per cent. of residue when burnt, and when boiled with water should not render it perceptibly acid, although a very faint reddening of litmus is not considered sufficient ground for rejecting a sample.

Sulphur in gunpowder has several important functions to perform ; in the first place, it lowers the point of ignition by itself inflaming at a temperature of 250° C., and by its combustion quickly raising the temperature to the fusing-point of the saltpetre, 335° C., which, but for the presence of the sulphur, would determine the point of ignition of the powder. The action of sulphur in lowering the ignition point of powder is very much the same as the part it plays on a match ; being itself easily ignited it burns, and by its combustion raises the other ingredients of the powder to the requisite temperature.

The effect which sulphur has in increasing the rate of combustion may be shown by making two trains of equal length, one of ordinary small grain powder, and the other of the same powder from which sulphur has been abstracted by treating it with carbon disulphide, and if these be simultaneously fired it will be found that the one containing sulphur will not have burnt through more than half its length in the same time.

Manufacture of Gunpowder.—The saltpetre is not ground before use, but the charcoal is ground in an enclosed mill until it will pass through a 32-mesh sieve, and the ingredients are then ready for the manufacture of the powder ; the first three processes entailed are the same for all kinds of powder ; they are—

1. Mixing the ingredients.
2. Incorporating or milling them.
3. Breaking up the mill cake.

The ingredients of the powder are first accurately weighed out, allowance being made for the moisture present in the refined saltpetre, and are then mixed in charges of from fifty to sixty pounds in a revolving gun-metal drum, which contains arms moving in an opposite direction to the drum itself : the mixture is next passed through a coarse copper sieve to make sure that no foreign solid material is present, and is then called *green charge*. This is now taken to the incorporating mill, which consists of two iron or stone edge runners, weighing from three to four tons, which revolve on a bed made of the same material as the runners themselves and having a sloping rim (Fig. 37A). The runners are worked by machinery from below, and make seven to eight revolutions per minute.

Milling.—The green charge is placed on the bed of the mill, and is moistened with a very small quantity of distilled water to prevent any of the charge flying about as dust and also to aid the incorporation, and is milled for from three to eight hours, according to the nature of the powder.

The incorporating mills are in a long building containing six mills, each of which is shut off from the next by a partition, whilst over each mill is an iron cistern, connected by a lever arm to a large wooden shutter which is exactly over the bed of the mill. Explosion of the charge would raise the shutter and deluge the mill by upsetting the tank; all the tanks work on one shaft, so that the upsetting of one would drown the charges in all the mills.

Mill Cake.—The "*mill cake,*" as the charge is now called, is perfectly uniform in appearance and should contain from 1 to 3 per cent. of moisture if it is to be used for small grain powders, and 3 to 6 for the larger kinds. It is next conveyed to the breaking down machine, where the mill cake is placed in a hopper, and is carried by an endless band to the top of the machine and then falls between a pair of grooved rollers, and afterwards between plain rollers which break it into what is termed "*meal.*"

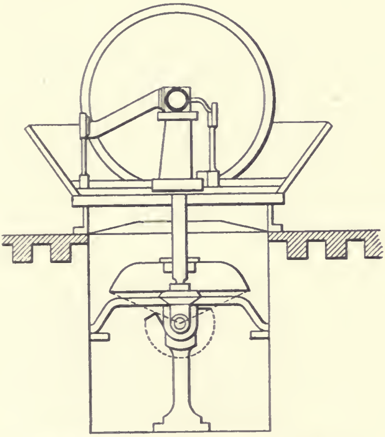


FIG. 37A.—Incorporating mill for powder (elevation).

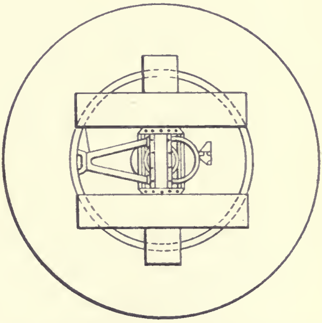


FIG. 37B.—Powder incorporating mill (plan).

Press Cake.—In making all the small arm and R.L.G. powders this meal was packed in layers in the press box, and subjected to a pressure of about seventy tons on the square foot for about a quarter of an hour, which rendered it excessively hard and compact, and as far as its composition goes, it is now gunpowder; but in order to regulate its rate of combustion it must be granulated to the required size, which is done in a machine much resembling the breaking down machine.

Granulating.—Here the "*press cake*" has to pass through successive pairs of grooved gun-metal rollers, which break it up into grains, and from which it falls into sieves which are continually vibrating, and are fixed at an angle below the rollers. The grains are thus sorted into the various sizes required, and are shot out into boxes placed to receive them.

Dusting.—Powders made with "dogwood" charcoal are very dusty, and when they leave the granulating machine are passed through an inclined wooden framed cylinder covered with 20-mesh copper gauze and making about forty revolutions per minute, the dust passing through the gauze, and the grains passing out at the lower end.

Glazing.—The powder now goes to the glazing drums in which it is placed in charges of about 900 lbs. at a time, and the drums are driven at about twelve revolutions per minute, for from one-and-a-half to ten hours, according to the kind of powder; this imparts by mere friction a fine glaze to the surface of the smaller grained powders, but with the larger powders it is necessary to add a small quantity of graphite.

Drying, Finishing and Blending.—The glazed powder is now put in a drying room heated by steam pipes, and through which a constant stream of air is passing to remove excess of moisture, and then is "finished" by a second glazing in a horizontal "reel," which rotates at high speed. The finished powders are finally blended, *i.e.* several batches being mixed together so as to give as uniform a quality of powder as possible, and are then ready for use.

Pebble Powder.—In making pebble powders the press cake was made of particular thicknesses, $\frac{5}{8}$ and $1\frac{1}{2}$ inch respectively, and the press cake then cut into cubes of the required size, which were glazed, stoved, finished, and blended as before.

Manufacture of Prism Powder.—The processes employed in making the prism powder were the same as used for the black grain powder, with the exception that the granulated press cake, instead of being glazed, was compressed in a hydraulic press into regular six-sided prisms.

Great attention was paid to the stoving of the later forms of prism powder—E.X.E. and S.B.C.—as the amount of moisture in them had an important bearing upon their rate of explosion, and they were dried first for twenty-four hours at 32° C., and then for twelve hours at 60° C., which left them with from 1·7 to 2·2 per cent. of moisture, this being the normal amount which these powders retained under ordinary atmospheric conditions.

Proofing and Blending.—A day's production at the Royal Government Factory represented about 100 barrels, or 10,000 lbs. of powder, and it was essential that this large quantity should be as nearly as possible uniform in itself, so that when fired in charges the results, both as to muzzle velocity and pressure, should only vary within extremely narrow limits.

The 10,000 lbs. of powder, however, are made in many machines, and it is manifest that not only atmospheric conditions, but also slight differences in the methods of work employed by the different men tending the machines, will make considerable differences in the batches turned out by each machine, and, if unadjusted, the batches of powder would of necessity give irregular results when used in guns.

In order to overcome this the batches of powder were blended, that is to say, the results obtained by firing a charge or charges from each batch were carefully noted, and the prisms from each batch then mixed in such proportions as to give uniformity in the results obtained from the whole output.

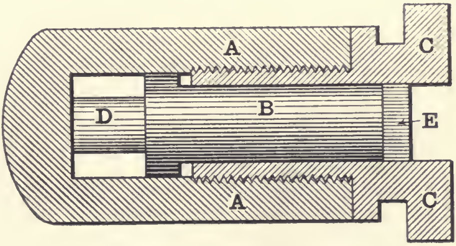


FIG. 38.—Crusher gauge.

Crusher Gauge.—The pressure exerted in the breech of a gun during the explosion is measured by a contrivance called a "crusher gauge" (Fig. 38), which consists of a steel cylinder into which a collar screws gas-tight, and carries a steel piston also rendered air-tight by a gas check.

A small cylindrical piece of copper (D), which has been compressed to a known density by exposing it to a hydraulic pressure of twelve tons, and which is 0·5 of an inch in length, is placed in the bottom of the steel cylinder; the piston is then put in its place and the collar screwed up, the gas check fitted and the crusher gauge placed in the base of the cartridge, the solid end of the cylinder being against the breech of the gun and the gas check towards the projectile. On firing the gun the gauge is subjected to the full pressure developed by the explosion of the powder, which forces the steel piston down the copper cylinder and compresses it. The crusher gauge having no powder behind it, is left after the explosion in the breech of the gun, and is opened, the length of the copper being accurately measured on a micrometer scale, the amount of compression indicating the pressure in the breech of the gun. Used in this way, the crusher gauge gives very reliable results, but it has been shown that when inserted in the wall of the gun, certain waves of pressure and difficulties of adjustment occasionally interfere with the results obtained.

The Chronograph.—The muzzle velocity of the shot is determined by means of the chronograph, which is diagrammatically illustrated in Fig. 39. Two screens are arranged, one about 120 feet from the muzzle of the gun, and the second 120 feet beyond the first. These screens consist of wooden frames strung with fine copper wire, the disruption of a single strand of which is sufficient to break the flow of the galvanic current. In the Boulengé chronograph, a current from a battery of eight Bunsen cells flows through these wires and back to the instrument house, where the wire from each frame is coiled round a separate soft iron core, and converts it into an electro-magnet, each of which attracts and holds a rod of iron. The electro-magnet in connection with the second frame is fixed at a lower level than the electro-magnet connected with the first, and carries a short rod (A) with a weight at the bottom, whilst the first magnet is at a much higher level, and carries a longer rod. The current being allowed to pass through both electro-magnets, the rods are suspended in position. By pressing a key (F) both circuits can be simultaneously broken, with the result that both the rods are liberated and drop down guide tubes; the short rod strikes a catch (C) and causes a knife edge to be brought against the longer falling iron (B) and to make a nick in it. When both rods are liberated simultaneously, this nick is at the point (D). The current is again allowed to pass, and the rods hung on the electro-magnets, and the gun containing the charge, the power of which is to be tested, is fired, the projectile passing through the screens 1 and 2 and breaking the current by cutting the wires. Under these conditions the long rod (B) is liberated a fraction of a second sooner than the rod (A), the result being that the nick from the knife blade is now at the point (E) instead of at (D), as in the previous case. By now measuring the distance between (E) and (D), and knowing the length of time to which this is equivalent, allowance being made for time taken in liberating knife, catch, etc., the interval of time which elapses whilst the projectile passes between screens 1 and 2 can be calculated, and being corrected for distance of screen 1 from muzzle, gives the muzzle velocity of the projectile.

Each batch of powder made was tested in this way, and the batches were then blended according to the results they had given, so as to obtain a powder best suited to the work required of it.

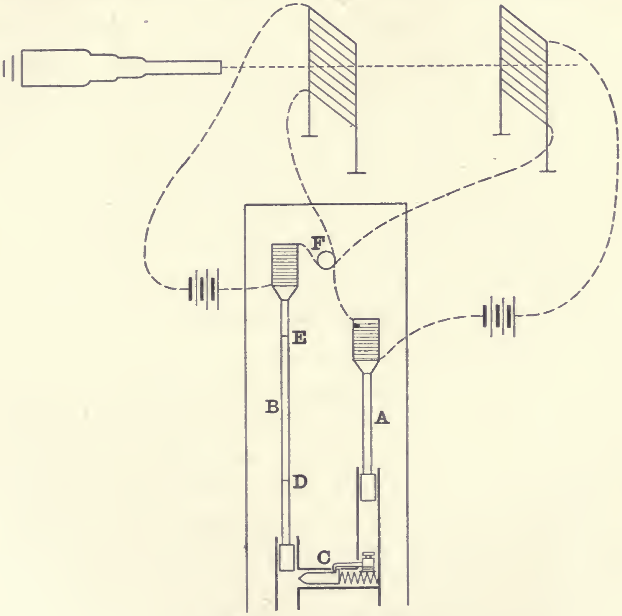


FIG. 39.—Chronograph.

The best proof that can be adduced to show that the pressure gauge, when used in this way in the breech of the gun, gives reliable results is that an expert operator can, from the pressure recorded, predict within a few feet per second what the muzzle velocity as recorded by the chronograph will be.

Influences affecting Burning.—The way in which powder burns is influenced to a great extent by the conditions under which it is ignited; if some powder is placed in a cylinder and touched with a hot wire it catches fire, and burns with a "puff," but if the powder is heated in a test tube at a certain temperature it explodes. In the one case the combustion spreads from grain to grain, whilst in the second case the whole mass is heated to a high temperature, and the increase of rapidity in burning is manifested by explosion.

Variation in pressure has a considerable influence upon the rate at which powder will burn, as under low pressures the flame from the powder escapes so rapidly that its power of passing on the combustion from grain to grain becomes seriously impaired. If some powder is placed on a watch glass under the exhausted receiver of an air pump, and is then heated by a thin platinum wire in connection with a voltaic battery, the grains of powder in contact with the wire will fuse and burn, but the remainder of the powder will not be ignited; on now allowing air to enter and again heating the wire the powder at once inflames.

The retarding effect of a low barometric pressure on powder fuses is well known; a fuse arranged to burn for thirty seconds will be retarded in its combustion one second for each inch the mercury of a barometer falls.

The Chemical Reactions when Powder Burns.—The chemical reactions taking place during the combustion of gunpowder are, in the first place, fairly simple, the oxygen of the potassium nitrate converting the carbon into carbon monoxide (CO) and carbon dioxide (CO_2), whilst the nitrogen is liberated; the potassium unites partly with carbon dioxide and oxygen to form potassium carbonate (K_2CO_3), and partly with sulphur and oxygen to form potassium sulphate (K_2SO_4), and the following might be taken as the simplest equation representing this principal reaction :—

$$\overset{\substack{\text{Potassium}\\\text{nitrate}}}{4KNO_3} + \overset{\text{Charcoal}}{4C} + \overset{\text{Sulphur}}{S} =$$

$$\overset{\substack{\text{Potassium}\\\text{carbonate}}}{K_2CO_3} + \overset{\substack{\text{Potassium}\\\text{sulphate}}}{K_2SO_4} + \overset{\substack{\text{Carbon}\\\text{dioxide}}}{2CO_2} + \overset{\substack{\text{Carbon}\\\text{monoxide}}}{CO} + \overset{\text{Nitrogen}}{2N_2}$$

but this equation does not even approximately represent the proportions in which the ingredients are present in powder, the ordinary Service powders having the molecular proportion

$16KNO_3 + 21C + 6S$, whilst the products of combustion vary with every change in the methods of burning, also with the pressure under which the combustion takes place. Probably also the size of the charge used exercises an influence on the products.

Moreover, the powder contains moisture and the carbon contains hydrogen and oxygen condensed in its pores, and the hydrogen from both these sources plays an important part in the reactions taking place in the breech of a gun, so that to represent the chemical changes taking place by an equation with any degree of accuracy is an absolute impossibility.

The Researches of Debus.—Dr. Debus has shown that it is probable from the work of Bunsen and Schischkoff, Linck, Karolyi, Noble and Abel, that during the combustion of gunpowder in the breech of a gun two distinct stages may be traced.

The first reaction is a process of oxidation occupying a very short space of time and constituting the explosion, during which, as in the previous equation, potassium sulphate, potassium carbonate, carbon dioxide, and traces of carbon monoxide, together with nitrogen, are formed. The proportions in which the original ingredients are present, and the proportions of the resulting products show that the equation must be taken as—

$$\begin{gathered}16KNO_3 + 13C + 5S = \\ 3K_2CO_3 + 5K_2SO_4 + 9CO_2 + CO + 8N_2\end{gathered}$$

Some of the carbon and sulphur are left unacted upon, and these in the second stage of the action, which goes on whilst the products of the first stage are under great pressure and at a very high temperature, partly reduce the potassium carbonate and potassium sulphate, with formation of more carbon dioxide and potassium disulphide according to the equation—

$$\begin{aligned}4K_2CO_3 + 7S &= K_2SO_4 + 3K_2S_2 + 4CO_2 \\ 4K_2SO_4 + 7C &= 2K_2CO_3 + 2K_2S_2 + 5CO_2\end{aligned}$$

During the combustion of the powder also a small quantity of the sulphur present unites with the metal of the gun, and some also with both the hydrogen occluded by the charcoal and that liberated by the decomposition of the moisture present in the powder, giving small traces of sulphuretted hydrogen gas. Deducting an atom of sulphur from the equation in order to allow for this secondary action, it is found that the final combustion of the ordinary Service powder can be approximately represented by the equation—

$$\overset{\text{Potassium nitrate}}{16KNO_3} + \overset{\text{Charcoal}}{21C} + \overset{\text{Sulphur}}{5S} = \overset{\text{Potassium carbonate}}{5K_2CO_3} +$$

$$\overset{\text{Potassium sulphate}}{K_2SO_4} + \overset{\text{Potassium disulphide}}{2K_2S_2} + \overset{\text{Carbon dioxide}}{13CO_2} + \overset{\text{Carbon monoxide}}{3CO} + \overset{\text{Nitrogen}}{8N_2}$$

Using this equation, the volume of gas generated by one gramme of the powder can be readily calculated.

				Grammes
Saltpetre	$16KNO_3$	=	16×101 =	1616
Carbon	$21C$	=	21×12 =	252
Sulphur	$5S$	=	5×32 =	160
				2028

The gaseous products of the combustion are—

		Litres		Cubic centimetres
Carbon dioxide ..	$13CO_2$ =	13(22·32)	=	290,680
Carbon monoxide ..	$3CO$ =	3(22·32)	=	67,080
Nitrogen	$8N_2$ =	8(22·32)	=	178,880
				536,640

2,028 grammes of powder therefore yield, according to this equation, 536,640 cubic centimetres of gas, measured at 0° C. and 760 mm. pressure, or one gramme of the powder yields 264·6 c.c. of gas. The mean of the results experimentally obtained by Captain Noble and Sir Frederick Abel for Pebble R.L.G. and F.G. powders is, under these conditions, 263·74 c.c. of gas, a quantity which, considering the risk of experimental error and slight unavoidable inaccuracies, agrees wonderfully closely with the calculated result.

The volume of the gas being measured at 0° C. and 760 mm. pressure, it is evident that at the moment of explosion the high temperature attained will expand it to an enormously larger volume.

Heat of Combustion.—Noble and Abel found, as the mean of a number of experiments, that one gramme of powder during combustion gave off enough heat to raise 714·5 grammes of water from 0° C. to 1° C., that is, gave out 714·5 thermal units, whilst Dr. Debus calculated that the heat generated by the reactions between the saltpetre, sulphur, and charcoal in one gramme of English Service powder is 660 thermal units, but the difference would be much smaller if the amount of heat produced by the action of the sulphur upon the iron of the apparatus were known and could be subtracted from the experimental number.

CHAPTER XVII

EXPLOSIVES—GUN-COTTON AND NITRO-GLYCERIN

Gun-cotton and nitro-glycerin differ from gunpowder in being chemical compounds, which contain within their own molecules atoms of carbon and hydrogen which can be oxidised, and oxygen which can be rendered available for this purpose, the action being prevented in the compound by the presence of the element nitrogen, which, loosely holding the oxygen, prevents any re-arrangement of the atomic constituents of the molecule until such time as heat or a sudden jar causes a redistribution of the atoms with evolution of gaseous products.

It is manifest that in an explosive chemical compound, there being only one action to convert the solid into gas, the combustion must of necessity be more rapid than in a mechanical mixture, in which there has first to take place a breaking up of saltpetre in order to render available the oxygen, and then a combination of that with the combustibles present to evolve the gaseous products.

History.—It was in 1832 that Braconnot, in France, observed that by acting with nitric acid upon starch he could convert it into an easily combustible body, to which he gave the name of xyloidin, whilst some six years later Pelouze noticed that when some fabrics, or unsized paper, were soaked in this highly corrosive acid they underwent but little change in appearance, but had increased in weight by nearly 80 per cent., and that after all the acid had been washed out from the substance, they manifested a most extraordinary increase in the rapidity with which they were able to burn, and there is no doubt that Pelouze in this observation laid the foundation of the discovery of what is now one of our most important explosives.

It was, however, not until seven years later that the re-discovery of this interesting substance by Schönbein, in 1845, attracted much attention, and it was his proposal to use cotton wool which had been soaked in a mixture of the strongest nitric acid with sulphuric acid, and then washed and dried, as a substitute for gunpowder that drew general attention to the use of nitrated compounds as explosives. The process which Schönbein employed he kept secret, and in August, 1846, Böttger found how to prepare this substance, and they together submitted their discovery to the German Federation, but did not make it generally public. In 1847, however, several others discovered the method of preparation, and the manufacture of gun-cotton became general.

At this time the European Powers fully realised the advantages offered by a powder which would evolve little or no smoke in its combustion, and when the discovery was made that cotton wool treated by nitric acid had the power of burning with enormous rapidity and without the formation of solid residue, Schönbein conceived that it could with great advantage be utilised as a smokeless explosive, but neither he nor any of the chemists of that period were able to make it answer their expectations in this direction, and although nearly every European Power commenced experiments with it, it took thirty-five years to bring it within the range of practical utility in guns.

Experiments were at once instituted on a large scale and its manufacture carried on in England and also on the Continent, but in 1847 a very serious explosion occurred at the works in which it was manufactured by Messrs. Hall, at Faversham, whilst a year later an even more serious explosion took place in the gun-cotton factory at Bouchet, near Paris. As no reason could be assigned for these and other similar explosions, gun-cotton was looked upon as too dangerous an explosive for ordinary use and its manufacture was discontinued; a result which was further borne out by the decisions of committees, which reported against gun-cotton as an explosive for use in guns. In Austria, however, General von Lenk continued to experiment upon the causes which had led to the previous disasters and failures, and he succeeded in showing that if the gun-cotton were entirely freed from every trace of the acids used in its manufacture, it could be stored and kept with perfect safety, and it is also to the same officer that we owe many experimental facts connected with this substance.

The apparent success of the experiments in Austria attracted attention once more to the subject, and in 1862, the British

Association appointed a committee to ascertain all that was known, and to inquire into the possibility of applying gun-cotton to warlike purposes. Much valuable information was obtained by this committee, with which Sir Frederick Abel was associated, and it was he who first introduced the improved processes of manufacture until recently employed in the Government factory.

Action of Nitric Acid on Organic Compounds.—When an organic body is nitrated, *i.e.* acted upon by strong nitric acid to form a compound containing the nitrogen and oxygen radicle (NO_2), the compound so formed may be either—

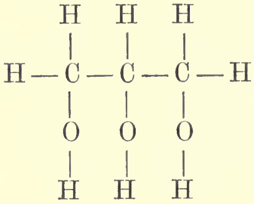
(1) A nitric derivative, or
(2) A nitro-substitution compound.

The difference between these two classes of bodies is that when a nitric derivative is acted upon by a reducing agent, the original compound is wholly or in part reformed, whilst with a nitro-substitution product no reproduction of the original compound is possible.

Nitro-cellulose and nitro-glycerin are nitric derivatives, and by the action of reducing agents upon them cellulose and glycerin can be again reproduced, whilst picric acid is a nitro-substitution product, and cannot be decomposed so as to reproduce the carbolic acid from which it was formed by nitration.

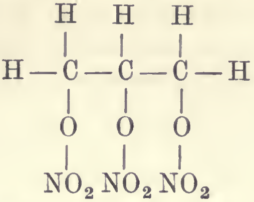
The chemical difference between these two classes of compounds is due to their structural formation ; in a nitro-substitution product the nitrogen and oxygen introduced are linked directly to the carbon atoms, whilst in a nitric derivative the nitrogen and oxygen derived from the nitric acid are linked to the carbon through the intermediary of an oxygen atom.

For instance, if glycerin is considered as an example, its molecular arrangement may be structurally shown as follows :—



$$\begin{array}{ccccccccc} & & H & & H & & H & & \\ & & \vert & & \vert & & \vert & & \\ H & - & C & - & C & - & C & - & H \\ & & \vert & & \vert & & \vert & & \\ & & O & & O & & O & & \\ & & \vert & & \vert & & \vert & & \\ & & H & & H & & H & & \end{array}$$

Upon acting on this with the strongest nitric acid the hydrogen atoms attached to the oxygen of the original compound are replaced by the nitrogen and oxygen radicle, nitryl, (NO_2), and we obtain nitro-glycerin.



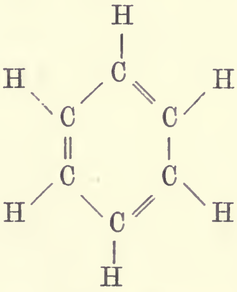
$$\begin{array}{ccccccc} & & H & & H & & H & \\ & & | & & | & & | & \\ H & - & C & - & C & - & C & - & H \\ & & | & & | & & | & \\ & & O & & O & & O & \\ & & | & & | & & | & \\ & & NO_2 & & NO_2 & & NO_2 & \end{array}$$

By acting upon this with reducing agents glycerin can again be obtained and this is typical of a nitric derivative. The reaction of an alkaline hydroxide is to produce salts of acids derived from the same series of compounds as the glycerin, but glycerin is not itself actually obtained, thus—

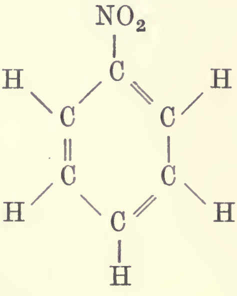
$$\overset{\text{Nitro-glycerin}}{C_3H_5(NO_3)_3} + \overset{\text{Potassium hydroxide}}{5KOH} =$$

$$\overset{\text{Potassium nitrate}}{KNO_3} + \overset{\text{Potassium nitrite}}{2KNO_2} + \overset{\text{Potassium acetate}}{CH_3.COOK} + \overset{\text{Potassium formate}}{H.COOK} + \overset{\text{Water}}{3H_2O}$$

On the other hand, if we take benzene, C_6H_6, it has a structural formula



Upon acting on this with nitric acid the hydrogen attached to one of the carbon atoms is replaced by nitryl, and nitro-benzene is produced,



By acting on this with reducing agents the benzene is not reproduced, so that it is a nitro-substitution product.

We may look upon nitric acid as having been formed from water by the replacement of one atom of hydrogen by the radicle (NO_2), so that its structural formula would be $HONO_2$.

Cellulose.—In the same way cotton is one of the purest forms of cellulose or woody fibre ($C_6H_{10}O_5$), which is one of a class of organic compounds called "alcohols," in which one of the atoms of hydrogen in water has been replaced by some group consisting of hydrogen and carbon, or carbon, hydrogen and oxygen, so that its formula might be expressed as $C_6H_7O_2(HO)_3$. When a small portion of cotton is acted upon by the strongest nitric acid, the hydrogen of the group HO in the cellulose is replaced by the NO_2 group from the nitric acid with the simultaneous formation of water.

$$\underset{\text{Cellulose}}{C_6H_7O_2(HO)_3} + \underset{\text{Nitric acid}}{3(HNO_3)} = \underset{\text{Gun-cotton}}{(C_6H_7O_2)O_3(NO_2)_3} + \underset{\text{Water}}{3(H_2O)}$$

If gun-cotton were made on a large scale in this manner, the water formed during the action would dilute the nitric acid and would give rise to an inferior kind of gun-cotton called collodion cotton, in which only two-thirds of the HO groups contained in the cellulose would have the hydrogen replaced by NO_2.

$$\underset{\text{Cellulose}}{C_6H_7O_2(HO)_3} + \underset{\text{Nitric acid}}{2(HNO_3)} = \underset{\text{Collodion cotton}}{(C_6H_7O_2)(HO)O_2(NO_2)_2} + \underset{\text{Water}}{2(H_2O)}$$

In order to prevent this dilution taking place, the strongest nitric acid is mixed with two and a half times its own volume of strong sulphuric acid, which, having a strong affinity for water, absorbs it as fast as it is formed, and so maintains the nitric acid at its original strength.

Accepting the formula $(C_6H_7O_2)O_3(NO_2)_3$ as representing gun-cotton, it is seen that the group (NO_2) is the oxidising portion of the molecule, just as in gunpowder the NO_2 contained in the potassium nitrate (KNO_2O) supplied the oxygen necessary for the combustion of the charcoal and sulphur.

Taking the formula of the molecule of cellulose as $C_6H_7O_2(HO)_3$, it is clear that three forms of nitro-cellulose would be possible—

Mono-nitro-cellulose ..	$(C_6H_7O_2)(HO)_2O(NO_2)$
Di-nitro-cellulose	$(C_6H_7O_2)(HO)O_2(NO_2)_2$
Tri-nitro-cellulose	$(C_6H_7O_2)O_3(NO_2)_3$

and the proportions of nitrogen in these would be 7·34, 11·13 and 14·14 per cent. respectively. The researches of Eder and Vieille, however, show several forms of nitro-cellulose in which the percentages of nitrogen lie between those necessary for the di- and tri-nitro compounds, and it is probable, therefore, that although $C_6H_{10}O_5$ is the simplest formula that will represent the proportions of the elements in cellulose, yet that the true molecular composition is some multiple of it.

Manufacture.—In the ordinary method employed until lately for the manufacture of gun-cotton, which is known as the "Abel" process, the best white cotton waste only is used, and is supplied free from all grease and dirt, which has been previously extracted by boiling it with dilute alkaline solutions: this is important, as, if any greasy or resinous substances remained in the cotton, they would form compounds with the acids employed, which would be liable to cause decomposition.

The cotton is first picked over by hand, all foreign substances being removed, and it is then passed through the "teasing machine," in which rollers bearing iron teeth rotate and tear up any knots or lumps which exist in the waste; after this it is passed through the "cutting machine," which chops it into pieces not exceeding two inches in length. If any moisture were present in the waste, it would cause evolution of heat on dipping it in the acids; the cotton is therefore dried by passing it through a chamber heated to about 83° C., in which the cotton placed on endless bands travels backwards and forwards for about twenty minutes; it is then weighed up into lots of 1 lb. 5½ oz., called a charge, and is placed in an air-tight box, to keep it dry until it has cooled down and is ready for dipping.

Acids Used.—The mixture of acids consists of one part by weight of nitric acid of specific gravity 1·52 to three parts by weight or 2·45 by volume of sulphuric acid of specific gravity 1·84. These are forced by compressed air in the right proportions into a mixing tank fitted with a lid, through an opening in which they can be thoroughly mixed by means of jets of air under pressure. Mixing the acids is attended by evolution of a considerable amount of heat, and the mixture is allowed to stand until thoroughly cool, when it is run into a dipping-pan, a small cast-iron tank, holding about 220 lbs. of the mixed acids, and surrounded on the outside by running water, in order to guard against rise of temperature during the formation of the gun-cotton, which would tend to increase the percentage of collodion cotton present in the finished product.

Nitration.—The charge of dry cotton is now taken from its tin, and is stirred as quickly as possible into the mixed acids, in which it is allowed to remain five or six minutes; it is then lifted on to a perforated shelf at one end of the dipping-pan, and the large excess of acids squeezed out by a plate worked by a lever. The 1 lb. 5½ oz. of cotton, which has absorbed 14 lbs. of acids, is now transferred to an earthenware pot fitted with a cover, the pot being placed in running water to prevent any rise in temperature, and the charge remains under these conditions for upwards of twenty-four hours, when the excess of acids present completes the conversion of the cotton. In some works the charge of cotton is put into an aluminium pan which is dipped in the acid mixture, and the pan with its contents is then put in the stream of water to soak for two hours, the large excess of acid completing the action in the shorter time.

Washing.—The next step is to get rid of the free acids which are still present in quantity. To do this the contents of six pots are transferred to a centrifugal machine consisting of a perforated iron cylinder made to rotate at a rate of 1,200 revolutions per minute, about 10 lbs. of acids being in this way separated from each charge of cotton.

The converted cotton is next placed in a cistern of water, where it is kept continually stirred in running water until it no longer tastes acid to the tongue. The gun-cotton is now again wrung out in a centrifugal machine, and is then boiled in several changes of water in wooden tanks heated by steam coils. At Waltham Abbey the total boiling time was 72 hours; at the conclusion the gun-cotton was practically free from acid.

The gun-cotton is next reduced to pulp in a machine of the same construction as a paper-maker's "hollander," in which the fibre suspended in water is made to pass continually between a bed-plate and a roller, both being armed with knives, and after being pulped for five hours, is brought to a very fine state of division and then passed through a pipe into the "poaching machine." This is another large oval tank in which paddle wheels keep the pulp constantly agitated with a large volume of fresh water, which owing to the fine state of division of the pulp, thoroughly washes every portion of it. After six hours in the poacher, samples of the pulp are tested, and if the requirements of the test are satisfied, enough lime water, whiting, and caustic soda—sodium hydroxide—are mixed with it to leave between one and two per cent. of free alkali in the finished gun-cotton. The pulp is now drawn up by means of a vacuum pump into an iron reservoir called the "stuff chest," in which revolving arms keep the pulp from settling, and from which measured quantities can be run off into moulds, the bottoms being made of a very fine wire gauze, that allows the water to pass through but keeps back the fine pulp, the filtration being aided by the action of a partial vacuum maintained below the moulds.

Casting.—When most of the water has been in this way separated, hydraulic pressure of about 34 lbs. on the square inch is brought to bear upon the semi-solid pulp, which expels a large proportion of the remaining water, and renders the blocks sufficiently hard to bear careful handling. The moulded gun-cotton is now taken to the "press-house," where it is subjected to hydraulic pressure of about six tons on the square inch, which reduces it to one-third of its original bulk, making it so hard that it does not perceptibly yield to the pressure of the finger, and when dry will just sink in water.

"Displacement" Process.—Important alterations in the manufacture have been in use at Waltham Abbey since 1905. Nitration is now performed in shallow earthenware pans, having a pipe at the bottom which serves for either an inlet or outlet, this being covered by two perforated plates. Four pans form a "set" for charging purposes. 650 lbs. of nitrating acid, having the following composition, are forced up into each pan from below, the temperature of the acid being 10° C. to 15° C.

Sulphuric Acid	70·5	per cent.
Nitric Acid	21·0	,,
Nitrous Acid	0·6	,,
Water	7·9	,,
	100·0	

A charge of 20 lbs. of dried cotton is then immersed in the mixture.

The general construction of the nitrating-pan is shown in Fig. 40. The charge of cotton having been all put in and pressed down by an aluminium tool into the acid, a perforated plate (F) made in four sections is then fitted over it and a stream of water from the distributor is led by means of an indiarubber tube on to the surface of the plate. The water is at 5° C. to 10° C., and is run on in a thin layer which seals the holes in the plate but does not mix with the acid owing to its superior specific gravity, and merely serves to prevent the escape of any acid fumes.

The pans are covered by aluminium fume hoods connected with down-draught flues, and these are kept on whilst the cotton, which is introduced through an opening, is being put into the acid ; but as soon as the layer of water has been floated over the plate the hoods are removed to a fresh set of pans.

After two and a half hours the nitration is completed, and water is run on to the upper plate whilst the acid cock (H) is opened to allow the acid to drain off at the same rate. The strong acid is run back to the store tanks and is there made up again to the proper strength by the addition of Nordhausen sulphuric acid and strong nitric acid. The acid and water mixtures which follow are collected separately, and treated to recover the nitric and sulphuric acids. Water is allowed to run through the nitrated cotton charge until it ceases to give any very acid reaction, and the charge is then ready for the subsequent boilings, no centrifugal wringing being required. The boiling periods are, 2 of 12 hours, 5 of 4 hours, 3 of 2 hours ; in all 50 hours as against 72 for the Abel process. The rest of the purification is the same as in the Abel process. The yield of nitrated cotton by the Abel process is 159 per cent. of the cotton treated, whilst by the displacement process it is 170 per cent.

Great economy in acid, labour and time results, and the product obtained is more uniform and staple.

Precautions.—During the process of manufacturing gun-cotton, every precaution is taken to prevent any great rise of temperature during the period when the cotton is in contact with free acid, which would lead to decomposition of the gun-cotton with evolution of large quantities of red fumes—oxides of nitrogen—and the formation of oxalic acid and other products, whilst even a small rise in temperature increases the proportion of collodion cotton present, and so detracts from the value of the finished product.

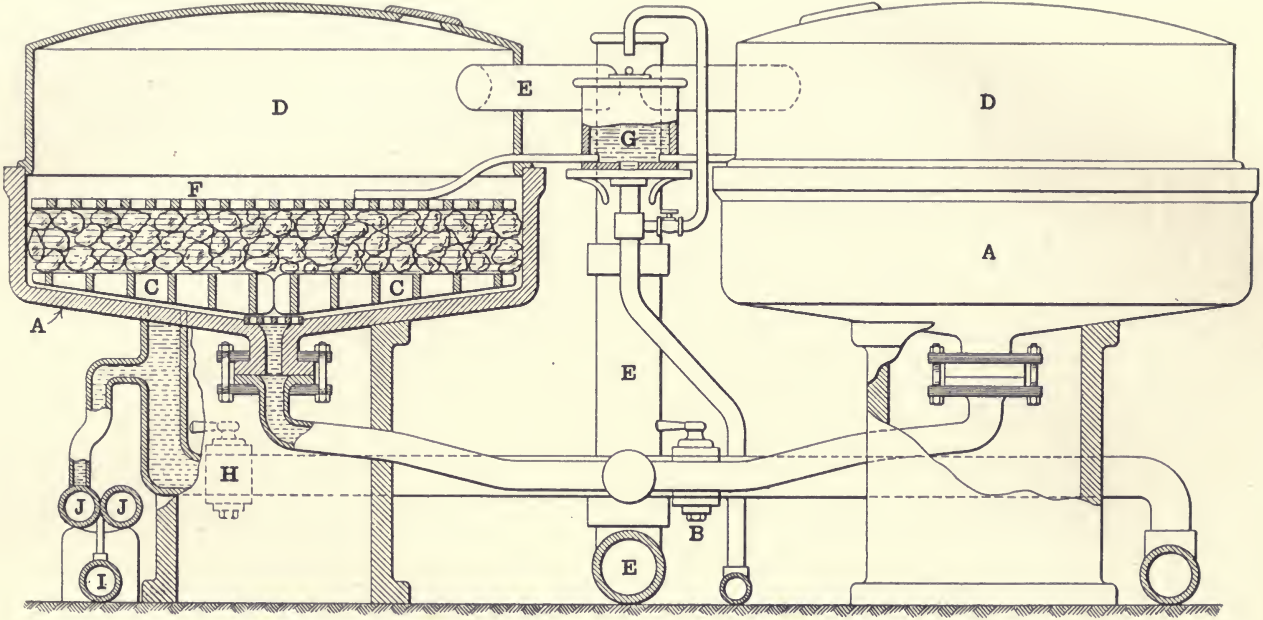


FIG. 40.—Displacement process for gun-cotton.

A. Earthenware nitrating pans.
B. Acid inlet cock.
C. Perforated earthenware plates.
D. Aluminium fume hoods.
E. Fume pipe.
F. Perforated earthenware plates on top.
G. Water distributor.
H. Outlet cock.
I. Waste water pipe.
J. Waste acid pipes.

In the second stage of the manufacture—from the removal of the superfluous acid in the centrifugal wringing machine to the moulding of the blocks—the object of all the operations is to free the converted fibre thoroughly from every trace of free acid, as it has been conclusively proved that it was to a great extent owing to the retention of free acid that the explosions which attended the early manufacture of gun-cotton were due.

Cotton when examined under the microscope is seen to consist of minute tubes, which during immersion in the mixed acids become filled with them, and the last traces cannot be removed by any ordinary rinsing process such as was at first considered sufficient. It has been proved that imperfectly purified gun-cotton contains sulphuric acid compounds with cellulose, similar in type to the nitro-celluloses, and that these are the most potent factor in bringing about decomposition. When such impure gun-cotton is packed in cases chemical action is maintained by the traces of acid present, the heat generated being confined to the centre of the mass by the non-conducting properties of the cotton surrounding it ; the action increases very rapidly with the rise of temperature, and a point is soon reached at which the gun-cotton becomes ignited.

The liability to spontaneous decomposition is much increased when cotton which has not been thoroughly cleaned, or which contains any fatty or resinous matter, is used, and also by the presence of a large proportion of collodion cotton, which is not so stable as the completely nitrated product.

This latter cause undoubtedly was a source of danger in the gun-cotton first manufactured. This was not left long enough in contact with the acids, so that the complete conversion of the whole of the cotton had not taken place, and some less stable products were present.

Testing the Finished Gun-cotton.—It is first tested for alkalinity ; the amount of free alkali present should not be more than 2 per cent. or less than 0·5 per cent.

Stability.—The finished gun-cotton is submitted to the Abel test, which is fully described later (p. 291). All water is pressed from the material, which is then placed in an oven at 40° C. for fifteen minutes, and after exposure to the air for four hours is ready for the test. The only modification in the actual test is that the test paper is kept in the upper part of the tube until a ring of moisture is seen just above the bath, when the test-paper is lowered to the normal position.

Another method, first devised by Professor Will, consists of determining the rate of evolution of oxides of nitrogen when the gun-cotton is heated to 135° C.

In carrying out Will's test, the weight of the nitrogen from a unit weight of gun-cotton in a unit time, expressed in milligrams, is a characteristic constant of the decomposition, and the result so obtained, when applied to gun-cotton, gives a valuable indication of its stability. This test was undoubtedly the most valuable addition made up to that period for the determination of the condition of nitro-cellulose, and the ample verification it received in the course of many hundreds of tests made at Waltham Abbey, in which it afforded information as to the condition of nitro-cellulose which other tests failed to give, led to modifications being made in it by Dr. Robertson, and in its improved form it has been of the greatest possible service.

In carrying out this test 3·5 grams of the sample containing about 3 per cent. of moisture are packed into a tube, provided with a glass spiral, heated in an oil bath to a temperature of 135° C.; a uniform current of pure carbon dioxide is passed through the heated sample, and washes the oxides of nitrogen out with it. The mixed gases are then passed through a heated tube containing metallic copper, which reduces the nitrogen oxides with formation of oxide of copper and liberation of nitrogen, which is measured after absorption of the carbon dioxide in sodium hydroxide.

The apparatus employed is illustrated in Fig. 41.

The properly made and purified gun-cotton is always undergoing slow intrinsic decomposition, the rate of which decomposition is readily accelerated by rise in temperature, so that no matter how pure the gun-cotton may be, there will always arrive a period at which active decomposition will be reached, this being a point when it would be dangerous to further store it, and the great value of the Will test is in showing when this point has been reached, and also the presence of impurities in the gun-cotton which would normally tend to accelerate this decomposition, *i.e.* the presence of less stable forms of nitro-compounds.

The impurities in gun-cotton are mostly due to traces of cotton seed, particles of wood and small pieces of metal in the waste itself, lime salts, minute traces of oxides of iron and alumina, and silica from the wash waters, and of these the ligneous bodies, *i.e.* the woody particles from the cotton seed, etc., are the most dangerous, as when nitrated they form compounds of far less stability than the true trinitro-cellulose, and the rapid evolution of nitrogen in the early stages of the Will test makes the presence of these at once apparent.

Nitrogen.—The determination of nitrogen in the gun-cotton depends upon the fact that when nitro-cellulose is treated with sulphuric acid in the presence of mercury it is decomposed with the formation of nitrogen dioxide which can be measured and the percentage of nitrogen calculated, the operation being carried out in a Bunté nitrometer.

Lower Nitro Compounds.—The percentage of collodion cotton present is next determined by treating a carefully weighed sample of the gun-cotton for some hours with a mixture of alcohol and ether, which dissolves the collodion cotton but not the fully nitrated product. When fifty grains of the gun-cotton are treated in this way for three hours, with frequent shaking, with four ounces of a mixture of two parts by volume of ether and one volume of alcohol, the loss of weight, due to collodion cotton dissolved out from it, should be very small.

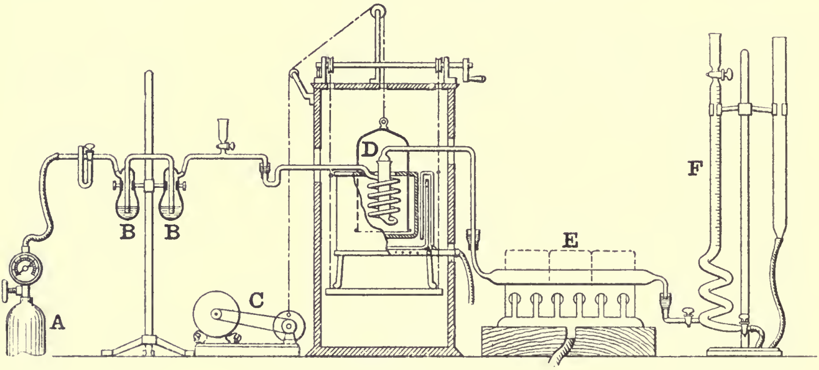


Fig. 41.—Will test apparatus.

A. CO_2 cylinder.
B. Sulphuric acid washers.
C. Motor for stirring gear.
D. Decomposition tube in oil bath.
E. Furnace for copper tube.
F. CO_2 absorption tubes.

Unconverted cotton can be detected by treating the gun-cotton with acetic ether, which dissolves the converted but not the unconverted cotton fibre.

Properties.—Gun-cotton differs very widely from gunpowder in its properties, requiring a much lower temperature for its ignition, as gunpowder has to be heated to a temperature of at least 250° C., whilst the ignition point of highly purified dry gun-cotton is about 185° C. Many commercial samples ignite at about 150° C. Gun-cotton can be fired by striking it with a steel hammer on an anvil. The explosion, however, is confined to the portion struck, but it is very difficult to ignite powder in this way.

The rate at which gun-cotton burns is dependent upon the mode of its ignition, and the conditions under which it is placed. A piece of loose gun-cotton, placed on the hand, and touched with a hot glass rod, burns away so rapidly that the skin is not scorched or burned. For the same reason, a piece of gun-cotton can be fired upon a small pile of gunpowder without igniting the powder, and grains of powder can indeed be wrapped up in gun-cotton and the gun-cotton ignited without the powder being burnt.

Rapid as this combustion is, however, it occupies an appreciable time, as may be seen by igniting a train of loose gun-cotton, which takes several seconds to burn a few feet, giving at the same time a large flame. If gun-cotton be confined at the moment of ignition this flame is forced back into the mass, and by rapidly heating it brings it to the point at which combustion passes into explosion. Prior to 1868, when gun-cotton was required for destructive purposes, it was always confined in strong cases, but in that year Mr. E. O. Brown, of Woolwich, discovered that when a detonating fuse was exploded in contact with compressed gun-cotton, the unconfined mass at once exploded with enormous violence, and this discovery of the possibility of detonating gun-cotton marks the second great stage in the history of the substance.

Detonation.—The fact that certain unstable compounds could be caused to undergo instantaneous decomposition by the sympathetic vibration set up in them by a sharp explosion, either in contact with or close to them, had been previously known, and Nobel had exploded nitro-glycerin by detonation some years previously, but another new and most important fact was discovered, namely, that gun-cotton, when wet, and containing 15 to 29 per cent. of water, could be detonated, and gave even better results than when dry, provided that a small portion of dry gun-cotton was placed in contact with the detonating fuse, the explosion of this portion ensuring the detonation of the wet mass.

The great importance of this discovery is seen when one considers that the sudden conversion of the solid mass into gaseous constituents endows gun-cotton, when exploded in this way, with an enormous destructive power, which is as great when the explosive is free as when it is confined, and that although it can be detonated when wet, in this condition it is not inflammable. A hole may be bored through a block of wet gun-cotton with a red-hot iron without inflaming it, a fact which renders it the safest of explosives, as it can be stored wet in closed vessels and dried as it is required for use, or even used wet with a small primer of dried gun-cotton.

Wet Gun-cotton.—The non-explosive properties of wet gun-cotton, under all ordinary conditions, were demonstrated by the Government Committee of 1871, who constructed two small magazines, and in one placed a securely-fastened tank, containing 2,240 lbs. of gun-cotton in discs, whilst in the second magazine the same amount was packed in eighty closed boxes, 28 lbs. in each; in both cases the gun-cotton contained about thirty parts of water to 100 of dry material. The remaining space in the magazines was now filled with shavings and other inflammable material, which was fired. In two hours the entire contents had burnt away, but without the slightest sign of explosion, although the heat generated was very great, as was shown by the distortion of iron bars upon which the cases had rested.

If dry compressed gun-cotton is ignited by touching it with a hot rod, it burns away with a fierce flame, but without explosion, but if larger quantities were ignited in this way, the portions first burning would quickly heat up other parts of the mass to the temperature at which combustion becomes explosively rapid, and as soon as this point was reached detonation of the whole mass would take place.

Action of Detonation.—The great increase in effect gained by detonating such explosives as gun-cotton arises from the enormous increase in rapidity of explosion. A train of ordinary gun-cotton fired by a hot rod takes several seconds to burn a distance of a few feet, but if a train of compressed gun-cotton be fired by detonation, the explosion would travel at the rate of 200 miles a minute. When gun-cotton is fired by touching it with a red-hot rod, its combustion occupies an appreciable time, and the gaseous products evolved have time to find space for themselves in the surrounding air. If, however, detonation be employed, the conversion of the solid into an enormously increased volume of gas takes place instantaneously, and the atmospheric pressure forms just as good a "tamping" for the gun-cotton as the strong metal cases which were employed before the principle of detonation was recognised.

In order to detonate gun-cotton, fuses charged with mercuric fulminate are generally employed.

Theory of Detonation.—Several theories have been brought forward to explain the phenomenon of detonation, the first being that the vibrations caused by the detonator are able to set up similar waves in the body detonated, and that these vibrations start a sympathetic decomposition, and determine its instantaneous resolution into the products of explosion.

Abel.—When a particular note is sounded on a violin, the string of a second similar instrument will spontaneously vibrate and emit the same note, and the same synchronism of vibrations in the detonator and explosive are—according to Sir Frederick Abel's theory of detonation—the cause of the explosion.

The facts which most strongly support this view are that the detonators which will cause explosion of one compound must be varied to fit them for producing a similar result with a different explosive, and also that the detonation of a small disc of gun-cotton at one end of a tube three feet long will produce detonation of a similar disc at the other end of the tube, although if the discs are in the open air, they must be placed within half-an-inch of each other for detonation to take place.

Berthelot.—This theory assumes that the vibrations are transmitted through and by the explosive, but Berthelot contends that the explosive substance does not detonate because it transmits the movement, but because it stops it, and transforms its mechanical force into calorific energy capable of suddenly raising the temperature of the substance to a degree at which its decomposition is effected, this in turn giving rise to the reproduction of a similar shock.

This vibratory movement Berthelot regards as a complex movement of a chemical and physical order when it is going on in the explosive, whereas it is purely physical when being transmitted through a substance like air whose nature is not changed by the wave, but on impact with the explosive body the wave is propagated by reason of a series of similar shocks incessantly reproduced in the explosive material, and which, as they continue, regenerate the energy throughout the wave and propagate the action with increasing velocity.

When, however, the shock has to be transmitted through air, the propagation is effected solely by reason of the last shock communicated to the air by the explosive, and which being no longer regenerated rapidly weakens by distance.

If Berthelot's theory be correct, the increase in velocity during detonation ought to admit of measurement by means of Noble's chronoscope, and experiments made by Sir Frederick Abel showed that when 170 cylinders of compressed gun-cotton were placed end to end and detonated from one end of the series, the rate of detonation for the first six feet was 17,466 feet per second, and for the last six feet 17,738 feet per second, an observed increase which might well come within the limit of experimental error. It is probable, however, that no matter how closely the cylinders are placed together, the break in the continuity of the compressed cotton must tend to check the rapidity of propagation, and would therefore invalidate the results.

If a heavy ball be allowed to fall through the air from a height under the influence of gravity, the fall becomes more and more rapid as the distance from starting point increases, but if the ball be allowed to roll down a long flight of steps, the total vertical fall being equal to that of the previous case, each step breaking the fall, the increase in rapidity observed on the last step is but small.

Threlfall's Theory.—Threlfall has also investigated the phenomenon of detonation, and concludes that the shock of explosion is transmitted in one of three ways—

1. By the rush of the products of explosion ;
2. By undulations of the medium ;
3. By vortex ring motion ;

the action being transmitted in slow explosions by 1 + 2, whilst 3 comes into play with fulminates and nitro-glycerin.

Products of Combustion.—When gun-cotton is fired under ordinary atmospheric pressure, the products of combustion are found to be carbon dioxide, carbon monoxide, methane, nitric acid, nitrogen, water vapour, and sometimes traces of cyanogen and hydrocyanic acid ; but as the rapidity of explosion and the pressure increase, so the products become less complex. When detonated the gaseous products of the decomposition are—

	Dry gun-cotton	Wet gun-cotton
Carbon dioxide	24·24	32·14
Carbon monoxide	40·50	27·12
Hydrogen	20·20	26·74
Nitrogen	14·86	14·00
Methane	0·20	None.
	100·00	100·00

An equation suggested to represent the combustion of gun-cotton is—

$$2(C_6H_7O_2)O_3(NO_2)_3 = 9CO + 3CO_2 + 7H_2O + 3N_2$$

At the temperature of explosion, which varies from 3700° C. to 4400° C., the steam would be dissociated and would oxidise some of the carbon monoxide. Various observers give the volume of gas evolved on the explosion of 1 gram of gun-cotton at from 483 c.c. to 829 c.c.

Detailed information on the products, etc., will be found in the Appendix.

Pressure.—Estimations of the pressure developed by the detonation of gun-cotton differ greatly in value, Berthelot placing it as high as 24,000 atmospheres, or 160 tons on the square inch, whilst other authorities estimate it as not much more than half this pressure.

The experiments of Sir Frederick Abel show that the detonation of moist gun-cotton is rather quicker than of dry, whilst the work done by the same weight of cotton appears to be equal in either case. The presence, however, of water in the moist gun-cotton must use up a certain amount of the heat, but this will be accompanied by an increase in the volume of the gases owing to the extra hydrogen liberated. It has been proposed to soak the gun-cotton in paraffin instead of water in order to get over the trouble of evaporation, and this has been tried with fairly satisfactory results, but the addition of a hydrocarbon to a substance already containing too little oxygen for its complete combustion seems hardly advisable.

Nitro-glycerin.—This compound is a nitric derivative, and was discovered in 1847, when Sobrero, whilst experimenting with glycerin, found that by treating this substance with strong nitric acid he obtained a compound which, on account of its exploding on a sudden rise of temperature, he called "pyro-glycerin"; but its value as an explosive was not realised until 1863, when Alfred Nobel showed that by firing it by detonation an excessively powerful effect could be obtained.

Glycerin or glycerol—$C_3H_8O_3$—is a sweet, syrupy liquid having a specific gravity of 1·269 and a boiling point of 290° C., at which temperature, however, it undergoes partial decomposition. It is soluble in water and in alcohol, but it is insoluble in ether. It is contained in the liquor left after the separation of soap in the manufacture of that article, being one of the products formed when oils or fats are acted upon by alkalies, and is obtained in still larger quantities during the manufacture of palmitic acid for candle making.

The vegetable fat, palm oil, which chiefly consists of palmitin, when acted upon by superheated steam, is broken up into palmitic acid and glycerin, which can afterwards be separated.

$$\underset{\text{Palmitin}}{C_3H_5(C_{16}H_{31}O_2)_3} \quad + \quad \underset{\text{Steam}}{3H_2O} \quad =$$

$$\underset{\text{Palmitic acid}}{3H(C_{16}H_{31}O_2)} \quad + \quad \underset{\text{Glycerin}}{C_3H_5(HO)_3}$$

When acted upon by strong nitric acid, glycerin, like cellulose, is converted into a nitrate with simultaneous formation of water—

$$C_3H_5(HO)_3 \quad + \quad 3(HNO_3) \quad = \quad (C_3H_5)O_3(NO_2)_3 \quad + \quad 3(H_2O)$$

Manufacture.—In the manufacture of nitro-glycerin, a mixture of 992 lbs. of nitric acid, specific gravity 1·48, and 1,680 lbs. of sulphuric acid, specific gravity 1·84, is thoroughly cooled and run into the mixing vat made of chemically pure lead, all the joints of which are autogenously melted together. The glycerin is then slowly and carefully added by means of an injector which regulates the rate of supply, whilst the whole charge is kept well agitated by blowing air through it, which not only thoroughly mixes the glycerin and the acids but also prevents local heating. In this way 330 lbs. of glycerin are mixed in with the acids, the process taking about an hour, and every precaution is taken to prevent the temperature rising above a limit of 22° C. (71·6° F.), the mixture being cooled by cold water, which is run through a coil of lead pipes inside the vat. If by any chance the temperature should rise to a higher limit, a valve in the bottom of the vessel can be opened, and the whole charge run into a tank of water placed below it.

In the Government factory at Waltham Abbey several improvements have been made in the methods employed for nitrating the glycerin, and the nitration and separation are now carried out in one vessel shown in Fig. 42.

It is a cylindrical vessel made of autogenously soldered lead, with sloping bottom to assist in draining off the contents; and is fitted with the same arrangement of cooling coils and air injection tubes that were used in the old form of nitrating "egg."

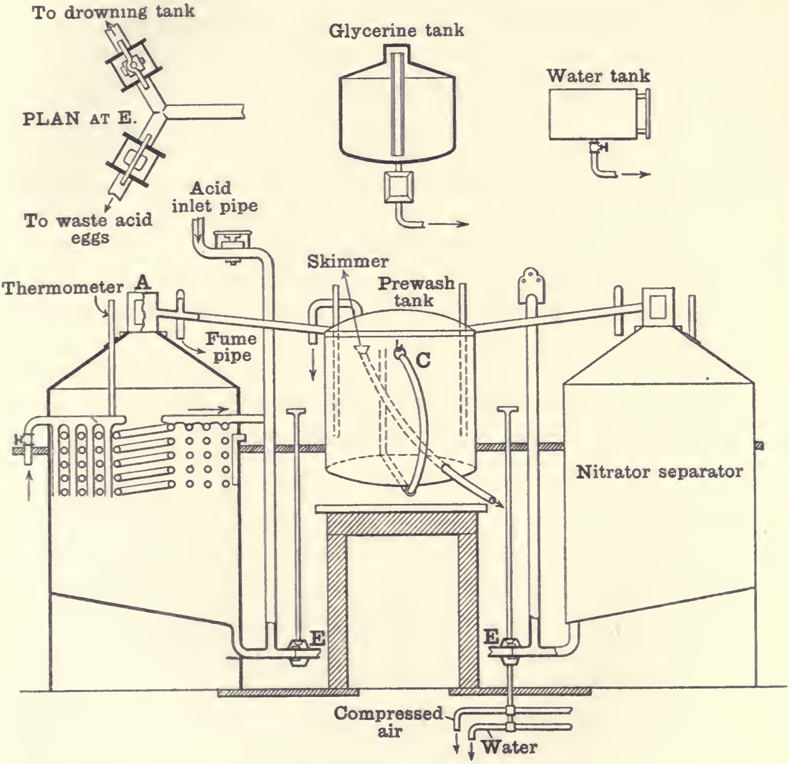


Fig. 42.—Nitro-glycerin plant.

The top of the vessel is conical, terminating in a cylinder, provided with an inspection window, and a side overflow pipe leading to the pre-washing tank (c). At the lowest point in the tank is a tubulure which by means of three branch pipes (Fig. 42) (A) can be utilised either for running the charge into the drawing tank in case of overheating, or running in or off the acids.

The nitrating acid is run into the vessel and cooled down by the coils, and the glycerin injector is then fitted into the top of the cylindrical cap and the nitration is effected, the fumes being carried off from the cap into a Guttmann condensing tower, in which about 18 lbs. of nitric acid is recovered for a ton of nitro-glycerin made.

When the nitration is completed the injector is removed, and the mixture is allowed to stand for a few minutes, when the nitro-glycerin begins to separate as an oily layer on the top of the acid, as although it is heavier than water, it is lighter than the mixed acids. Waste acid from a previous charge is now allowed to flow from an overhead tank in a gentle stream into the bottom of the vessel, and gradually forces up the liquid until the nitro-glycerin layer enters the cylinder and flows down into water in the pre-washing tank. When the separation is complete a sharp line of demarcation is seen through the inspection window between the nitro-glycerin and the acids.

In this apparatus all earthenware cocks are done away with so as to avoid any risk of friction, and the flow at outlets and inlets are governed by rubber tubes, the level of which can be altered to secure the desired results.

Purification.—In the pre-washing tank the nitro-glycerin flowing in from the separator is agitated with water by compressed air being blown through, and given three washings with water and one with water containing a little sodium carbonate.

The nitro-glycerin after this treatment is allowed to flow into the wash tank, where its final purification takes place by washing with a tepid 2·5 per cent. solution of soda ; it is then twice washed with still more dilute solutions, and finally with pure water, after which it does not contain more than 0·01 of alkali, and after filtration through salt or sponge is ready for testing and passing to store.

By calculation from the equation 100 parts of glycerin should yield 247 parts of nitro-glycerin, and the small loss in the Waltham Abbey process is shown by the yield being 229, whilst by the old process 215 was considered good.

The nitro-glycerin so made is tested for moisture, alkalinity, nitrogen content and stability by the Abel heat test (see p. 291), and should stand 180° F. for fifteen minutes before the iodide and starch paper indicator shows the liberation of oxides of nitrogen.

The waste acids are recovered by the same method as is used for the acids from the displacement process in making gun-cotton, and it is found that mixing 2 per cent. of water with them after they leave the separator prevents any further separation of nitro-glycerin, and the acids may be run direct to the recovery plant.

Properties.—Nitro-glycerin so prepared is an oily, colourless liquid, which has no odour and is insoluble in water, although it rapidly dissolves in ether, benzol, wood spirit, and hot alcohol, and from the solution so formed can again be precipitated on dilution with water.

It has a violent effect upon the system, acting in large doses like strychnine, whilst even traces produce vertigo, and, as it is absorbed through the skin, people working with it are frequently at first seriously affected, but after a time experience no ill effects and, it is said, present a more than usually healthy appearance.

When cautiously heated to 100° C. it slowly evaporates, at 200° C. it burns, and detonates at 257° C.* When a lighted match is applied to it, it burns quietly away, and when the light is removed the flame generally goes out ; indeed, a lighted match may be extinguished by plunging it into nitro-glycerin. It is, however, detonated by a sudden blow or by heating it to 257° C. Nitro-glycerin becomes solid at 4° C., and in this condition it is comparatively inert, hence it is necessary to thaw it before use, an operation attended with considerable risk.

It is stated that exposure to the direct rays of the sun will convert it into a very unstable and explosive substance, and also that the presence of ozone will sometimes cause its spontaneous decomposition.

Products.—When nitro-glycerin is exploded it is instantaneously decomposed into gaseous products, the probable decomposition being—

$$\begin{array}{ccccccccc} \text{Nitro-glycerin} & & \begin{array}{c}\text{Carbon}\\ \text{dioxide}\end{array} & & \text{Water} & & \text{Nitrogen} & & \text{Oxygen} \\ 2(C_3H_5)O_3(NO_2)_3 & = & 6(CO_2) & + & 5(H_2O) & + & 3N_2 & + & O \end{array}$$

showing that the amount of oxygen present is more than sufficient

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* The actual ignition point is very uncertain. Any quantity will invariably fire below 180° C.

for complete combustion, which is not the case in any other explosive compound.

Nobel has found that about 12,000 times its own volume of gas, calculated at normal temperature and pressure, is generated by the explosion of nitro-glycerin; whilst the heat evolved expands it to nearly eight times this volume. Its explosive force, volume for volume, is nearly thirteen times as great as gunpowder.

Downward Effect of High Explosives.—The rapidity of detonation of nitro-glycerin is very great, and it is this which gives rise to the downward effects noticeable in all nitro-glycerin or dynamite explosions.

Six cubic inches of nitro-glycerin when exploded would yield about a cubic yard of gas, and would require approximately $\frac{1}{40000}$th of a second for conversion into the gaseous form. A square yard of surface carries an atmospheric pressure of, roughly, nine tons, so that the gaseous products would have to lift nine tons to a height of one yard in $\frac{1}{40000}$th of a second, and the earth, being rigid, is broken up by the recoil from this enormous strain.

CHAPTER XVIII

SMOKELESS POWDERS

ALTHOUGH the idea of smokeless powders for warfare has always been a dream with strategists, it is only within recent years that they have become an absolute necessity, as with the introduction of quick-firing and machine guns into the Navy, it became necessary to have a powder giving little or no smoke if the guns are to be of any use for the objects for which they were intended. For instance, in repelling the attack of torpedo boats, the use of black or brown powder would entirely defeat the purpose of the guns, as after the first few shots the cloud of smoke would entirely obscure the whereabouts of the attacking force, and render, for some time at any rate, the further use of the guns abortive.

It must be clearly borne in mind that not only the projectile but also the products of combustion have to be expelled from the gun, these latter having ultimately even a higher velocity than the shot, and in using black powder the weight of the charge is far greater than with a smokeless powder. In powder also 57 per cent. of the charge is inert, whereas in the case of smokeless powder the whole is operative, and gives the charge a great gain in efficiency over the gunpowder.

Cause of Smoke.—The formation of smoke during the combustion of powder is entirely due to the presence amongst the products of combustion of solid compounds, which, although liquid at the time of explosion, rapidly solidify as the temperature falls, and with the black powders, potassium carbonate, potassium sulphate, and potassium disulphide are the products which cause the fouling of the gun, and, together with condensing water vapour, form the dense cloud of smoke which follows the firing of a shot. When using brown powder, although the smoke cloud appears at first to be as dense as with the black powder, it is noticed that it clears away far more rapidly. This is due to the fact that whereas the products of combustion of the black powder contain only 12·8 per cent. of water vapour, the products of combustion from the cocoa powder contain 38·5 per cent. of water vapour, which in condensing carries down with it, by absorption and solution, the finely-divided potassium salts.

Ammonium Nitrate Powder.—The fact that the solid residue from powders consists entirely of potassium compounds from the base of the salt potassium nitrate employed in powder, naturally suggested the idea of using some nitrate which would give up its oxygen for the combustion of the carbon and sulphur in the same way that saltpetre does, but should have as its base some body which would yield volatile or gaseous compounds. The only inorganic nitrate which would in any way answer this requirement is ammonium nitrate, and many attempts have been made to utilise this in forming a smokeless powder.

Unfortunately, however, ammonium nitrate is a highly deliquescent body, which has the property of so readily absorbing moisture from the atmosphere that the powder made with it would rapidly be converted into mud if exposed to atmospheric influences.

Amide Powder.—In order to obviate, as far as possible, this difficulty, F. Gans conceived the idea of replacing only a certain proportion of the potassium nitrate in the gunpowder by ammonium nitrate, imagining, by so doing, the hygroscopic character of the ammonium salt would be got over, whilst the formation of a volatile compound, called potassium amide, caused by the union of the potassium with the nitrogen and hydrogen of the ammonium, would occur, and being volatile, would render the products practically smokeless, and in view of this theoretic action he christened his compound "amide powder." His views, however, were founded upon considerations which have not stood the test of practice, as the powder so produced was hygroscopic, and by no means smokeless.

The most successful attempt to produce a smokeless powder by the use of ammonium nitrate was made by Mr. Heidemann, one of the original patentees of cocoa powder, whose large knowledge of powder-making and the requirements to be observed, enabled him to so modify Gans' idea as to obtain a powder which not only gave most excellent ballistics, but which was decidedly less hygroscopic than the ordinary ammonium nitrate powder, and gave but little smoke. This powder, like the cocoa powder, contains a certain definite amount of water as one of its constituents, and, with a comparatively dry atmosphere, shows no tendency to absorb more, but with a saturated atmosphere it rapidly shares the fate of the ammonium nitrate powders generally, and becomes pasty. In order to overcome this defect, the cartridges were enclosed in hermetically-sealed metal cases, so as to prevent any absorption taking place, but it was found the storage of these in ships' magazines caused the moisture already present in the powder to become unequally distributed in the cartridges, with the result that there was occasionally a want of uniformity in the action of the powder in firing, and a tendency to the occasional development of high pressure, and this was considered a drawback to its adoption in the Naval Service.

Early Attempts to Use Gun-cotton.—When Schönbein discovered gun-cotton, it seemed at first as if the question of a smokeless powder had been solved, but as soon as experiments came to be made, it was found that on account of its low density it occupied far too large a volume, whilst when it was rammed into cases, the explosion was often of so violent a character as to produce disastrous results. Many attempts were made by von Lenk to obviate this trouble by converting cotton threads into gun-cotton, and winding these threads with different degrees of tightness, generally upon a core of wood, but this system of taming the explosive power of the gun-cotton proved unreliable, and although von Lenk's system was introduced on a somewhat extensive scale, the unsatisfactory results obtained soon led to its abandonment.

Von Lenk's results having been investigated by Sir Frederick Abel, the experiments were repeated in England with wound cartridges of gun-cotton threads, but with no better results than had been obtained in Austria, and Abel having in the meantime completed the improvements in the manufacture of compressed gun-cotton discs, attempts were made to use these built up into cartridges with varied air spaces, with the object of regulating the rapidity of explosion. No certainty in results could, however, be obtained, and the attempts to utilise it were for the time abandoned.

Smokeless Sporting Powders.—About this period Messrs.

Prentice, of Stowmarket, and Colonel Schultze, in Prussia, had succeeded in making practically smokeless powders for sporting purposes. The Stowmarket preparation consisted of felt-like paper made of a mixture of gun-cotton and ordinary cotton, containing 30 per cent. of gun-cotton and 10 per cent. of ordinary cellulose, together with oxidising bodies, made in sheets which were afterwards rolled up into the cartridges. This cartridge depended to a great extent on the presence in it of moisture for the ballistics which it gave, the unchanged cellulose being itself hygroscopic and aiding hygroscopic action in the gun-cotton. It was impossible, however, to regulate the amount of moisture present, and when the cartridges had been kept in a warm place the moisture would become too low and the danger of detonation of the gun-cotton would increase, whilst if the cartridges had been kept in a damp place they were apt to burn more like squibs than explosives.

When this trouble was realised, the rolled cartridge was replaced by a cylindrical pellet of slightly compressed gun-cotton pulp, attempts being made to tame down the rapidity of the explosion, and also to waterproof it by impregnating it with a certain proportion of india-rubber, but neither of these cartridges gave sufficiently uniform results to fulfil Service requirements.

Schultze Powder.—The Schultze powder on the other hand consisted of granulated wood which, after purification by boiling with dilute sodium carbonate, was washed and treated with a solution of bleaching powder; the mass was then washed, dried, and soaked in the mixture of strong nitric and sulphuric acids for two or three hours, the temperature at the same time being kept as low as possible, and after getting rid of the free acid in a centrifugal machine, the nitrated wood was washed with water until free from acid, boiled with dilute sodium carbonate, and dried, after which it was steeped in a solution of the mixed nitrates of barium and potassium, and again dried at a low temperature.

E.C. Powder.—Another powder which became very popular for sporting purposes was the well-known E.C. powder, which was first made by Mr. Reid in 1882, and consisted of gun-cotton incorporated with 35 or 40 per cent. of the mixed nitrates of barium and potassium, the mass being granulated and gelatinised by means of mixtures of ether, alcohol, and benzoline, which gave a hard coating to the grain. In this powder the presence of gun-cotton constituted a source of trouble, as the action was occasionally unduly violent, and the hard coating resisted ignition by the flash, and necessitated the use of a powerful cap.

In 1888, the E.C. powder No. 2 was introduced by Mr. W. D. Borland, and in this powder the use of true gun-cotton was entirely done away with, the nitro-cellulose being completely soluble, and the hardness of the grain was obtained by treatment with a solvent containing camphor, which acted uniformly throughout the mass, whilst it left the surface in a slightly roughened condition, which enabled the flash to rapidly ignite the powder.

These powders gave very satisfactory results for sporting purposes, and also gave good ballistics with smooth-bore guns, but both the E.C. and Schultze powder left an ash which was considerably harder than that afforded by the old black powder, and which instead of forming a partial lubrication for the succeeding shot, tended to choke rifled guns, so interfering with accuracy in shooting. Moreover, these powders could not be made on a large scale with a sufficient degree of uniformity to fulfil the requirements of Service powders.

Influence of the Metallic Base on Smoke.—None of these powders were absolutely smokeless, as the inorganic nitrate used to supply the oxygen necessary for making up the deficiency in the nitro-cellulose always gave a certain amount of solid residue, but the amount of smoke given varied a great deal with the kind of nitrate used, the presence of potassium nitrate in the original powder undoubtedly making the smoke much denser than when other metallic nitrates were substituted for it, this being one of the reasons why barium nitrate is employed to replace some of the potassium nitrate in these compounds, and also, of course, because the barium nitrate slows down the combustion.

The Causes of Failure with Gun-cotton.—It has been shown that the compression of gun-cotton causes it to burn much more slowly when ignited under ordinary atmospheric conditions, and it was in this direction that all the early experiments tended, but it was soon found that in the chamber of a gun the pressure forced the flame first formed into the interior of the mass and produced detonation, which, giving no time for overcoming the *vis inertia* of the projectile, threw an enormous strain on the gun, and gave very unsatisfactory muzzle velocities. Many attempts were then made to so dilute and tame the gun-cotton by admixture with inert or less explosive substances so as to render it sufficiently slow for this purpose, but with little success, as inequality in ballistics and the risk of detonation always remained insuperable objections.

Destruction of Structure.—The first important step toward doing away with these troubles was the recognition that the cause of them was in the hollow fibre of the nitrated cotton, and that no matter how thoroughly the gun-cotton was disintegrated in the hollander during manufacture, or how closely the pulp was compressed in pressing the cartridges, discs, or slabs, you had merely shortened the tubes, and had not done away with them, and that it was only by absolute destruction of the structure of the cotton that the too rapid combustion could be checked and the risk of detonation avoided.

Tri-nitro-cellulose is soluble in ethyl acetate and nitro-benzene, whilst some other substances will convert it into a gelatinous mass, and by utilising such bodies to absolutely destroy the structure of the cotton, and by converting it into a solid substance, which can only burn regularly from the surface, the rate of combustion can be controlled, and the risk of detonation overcome. This method of taming the explosive has made the modern smokeless powder a practical possibility.

History.—The history of the present smokeless powders may be said to have its commencement when Mr. Alfred Nobel, who has done so much in the history of explosives of all kinds, showed in 1875 that when the two most powerful of the compound explosives were blended together their properties became beautifully tempered, so that, although the power of doing their full meed of work was still retained, the violence of the action was so far reduced that they became applicable for purposes for which neither of them alone could have been employed.

Blasting Gelatine.—He found that when nitro-cotton is thoroughly saturated and digested with nitro-glycerin the cotton loses all trace of its fibrous quality, and absorbing the nitro-glycerin, becomes converted into a gelatinous body having almost the character of a compound. The nitro-cotton, macerated with 90 per cent. of nitro-glycerin, and the mixture being kept warm, causes the formation of a plastic material from which neither of the components can be easily separated, and this substance, which has become of world-wide repute as a mining explosive under the name of blasting gelatine, will always be regarded with even greater interest as being the parent of the modern smokeless Service powders.

In January, 1888, Mr. Nobel took out a patent for using nitro-cellulose mixed with nitro-glycerin, with or without the addition of a retarding agent, to form a powder which could be relied upon for use in guns.

It had been found by experiments made in Austria for adapting blasting gelatine to military purposes, that this substance might be exploded by the penetration of a bullet or fragments of a shell into the transport waggon. Colonel Hess, whilst endeavouring to make it less susceptible to accidental explosion, found that by incorporating with the components a small proportion of camphor, and also by increasing the proportion of nitro-cotton used, the rapidity of the explosion of the material could be reduced, and the product made of a horn-like character, which had remarkable ballistic properties, and which was uniform and practically smokeless.

Some of the camphor, however, used in the substance remains in it, and this being volatile, its evaporation causes modifications in the ballistic properties of the powder, and attempts have been made to improve upon this by replacing the camphor by other substances which would play the same part as the camphor, but which would not have the same drawbacks.

Ballistite.—The powder so made by Nobel, and known by the name of Ballistite, was extensively used in Italy and Germany. As manufactured in Italy, it contained equal parts of nitro-cellulose and nitro-glycerin, with the addition of a half per cent. of aniline, and when used in the form of threads or cords was called "Filite." The German ballistite contained a rather larger percentage of nitro-cellulose, and the finished material was coated with graphite.

Mark I. Cordite.—In the above powders the collodion cotton (di-nitro-cellulose) is employed, as it was well known that nitro-glycerin alone does not dissolve the tri-nitro-cellulose; but whilst endeavouring to avoid slight imperfections which had been noticed in the behaviour of the ballistite, Sir Frederick Abel and

Professor Dewar found that if tri-nitro-cellulose and nitro-glycerin were mutually taken up by a liquid capable of dissolving them both, on evaporating off the solvent, the tri-nitro-cellulose and the nitro-glycerin remained behind in the most perfectly incorporated and gelatinised condition. It was on this principle that our English smokeless Service powder, Cordite, which contained 58 per cent. of nitro-glycerin, 37 per cent. of tri-nitro-cellulose, and 5 per cent. of vaseline, was introduced.

Cordite could be perfectly well made by incorporating tri-nitro-cellulose with nitro-glycerin by aid of such a solvent as acetone, but the perfect freedom from any solid or liquid products of combustion during the explosion of such a mixture leaves the bore of the gun so clean that great friction is set up between the metal of the lining and the bullet, with the result that metallic fouling of the bore, due to abrasion of the bullet, and wear of the lining due to the same cause takes place. It is chiefly to overcome this trouble that the vaseline or petroleum jelly is incorporated with the other ingredients, as it gives a thin film of solid matter in the bore and greatly reduces this trouble, besides giving the cordite the power of resisting water and facilitating the squeezing of the material into threads. Vaseline also plays an important part in rendering cordite more stable; its action in this respect being more fully dealt with later (p. 297).

Qualities to be sought in a Smokeless Powder.—Bernadou has arranged the positive and negative qualities of smokeless powders in the following convenient form :—

Positive.	Negative.
(1) Non-liability to detonation	Detonation.
(2) Development of minimum heat	Erosion.
(3) Formation of minimum residue	Smoke and bore deposit.
(4) Good keeping qualities	Decomposition.
(5) Maximum propulsive effect	Low value of $\frac{\text{velocity}}{\text{pressure}}$.

It has already been pointed out that the difficulty experienced with gun-cotton, owing to its liability to detonation, has been overcome by destroying its fibrous character. The pure nitro-cellulose powders first prepared belonged to one of two main classes—(*a*) those obtained from highly nitrated insoluble nitro-celluloses gelatinised by acetone; (*b*) those from soluble collodion cottons of medium nitration, gelatinised by ether-alcohol. The former class gave as a rule uncertain pressures, owing to brittleness, whilst the latter, owing to a deficiency of oxygen, gave smoke and bore deposits.

Naturally the difficulty of brittleness with the first would be overcome by toughening the material, and the second by the addition of some oxidising agent. Barium or potassium nitrate was therefore frequently incorporated, or, since nitro-glycerin is an explosive which has an excess of oxygen over that required for the oxidation of the carbon and hydrogen, this was also employed, as in ballistite and cordite.

With all such nitro-cellulose-nitro-glycerin powders, however, serious erosion was found to take place, and Sir Andrew Noble made a large number of experiments, and came to the conclusion that the principal factors determining its amount are —(1) the actual temperature of the products of combustion; (2) the motion of these products. But little erosive effect is produced, even by the most erosive powders, in closed vessels, or in those portions of chambers of guns where the motion of the gas is feeble or nil, but the case is widely different where there is rapid motion of the gases at high densities. It is not difficult to retain absolutely without leakage the products of explosions at very high pressures, but if there be any appreciable escape before the gases are cooled they instantly cut a way for themselves with astonishing rapidity, totally destroying the surfaces over or through which they pass.

The most erosive powders which have been used for charges in heavy guns were the brown prismatic powders, but there is one essential difference with the erosion produced by them and that with cordite. When the erosion is due to gunpowder the metal is pitted and grooves are formed, which are liable to develop into cracks, whilst with cordite this form of erosion is absent, and the action appears to consist of a simple washing away of the surface of the steel barrel by the enormously heated gases.

Experiments soon showed that it was the high percentage of nitro-glycerin present in the cordite which was doing the mischief, as it developed a temperature on burning well above the melting point of steel. Sir Andrew Noble then made a series of experiments which showed that in mixtures of nitro-cellulose and nitro-glycerin the temperature on explosion increased with increase of nitro-glycerin, whilst the volume of gas increased with increase in nitro-cellulose, and further experiment showed that by varying the size of the cords of explosive the same ballistics as with the cordite could be obtained with a mixture much poorer in nitro-glycerin.

The following table, corrected by Noble in 1905, shows the heat developed by Cordite Mark I, Cordite M.D., and a nitro-cellulose powder, with three different densities of charge :—

Density of charge.	Cordite Mark I.		Cordite M.D.		Nitro-cellulose.	
	a	*b*	*a*	*b*	*a*	*b*
0·45	5090	5090	4713	4624	4305	3954
0·40	4902	4970	4494	4411	4007	3890
0·35	4710	4860	4200	4215	4630	3795

The figures show the temperature of explosion in centigrade degrees, those under *a* being calculated from the pressures, whilst those under *b* from specific heats.

The Potential Energy of any explosive will depend on two factors, namely, the actual volume of the gas generated (calculated for comparison under standard conditions) and on the temperature developed on explosion, whereby the gases become enormously expanded. It has been shown that high temperatures are undesirable, hence to obtain the same potential energy the gas yield must be increased, either by actual chemical decomposition or increase of charge.

The production of carbon dioxide leads to high temperatures and low gas volumes (under standard conditions of measurement), whilst the production of carbon monoxide yields much lower temperatures but greater gas volume, thus a much greater gas volume (at 0° and 760 mm.) is obtained with low percentages of nitro-glycerin with nitro-cellulose, but since carbon dioxide is produced only in smaller quantities the actual temperature is low, the effect of increasing the nitro-glycerin being to produce larger and larger amounts of carbon dioxide with great increase of temperature, for the heat developed when carbon burns to one or other of its oxides is—

$$C + O = CO + 2472 \text{ calories.}$$
$$C + O_2 = CO_2 + 8140 \quad ,,$$

The researches of Mendeléeff, Lunge and others have shown that by careful attention to the ingredients and process of manufacture it is possible to obtain perfectly uniform nitro-cellulose, which shall be soluble in ether-alcohol, but insoluble in alcohol alone, which contains approximately 12·4 per cent. of nitrogen, and which theoretically yields carbon monoxide only, according to the following equation :—

$$C_{30}H_{38}O_{25}(NO_2)_{12} = 30CO + 19H_2O + 6N_2.$$

To this body Mendeléeff gives the name of *pyro-collodion.*

By proper adjustment of the charge, size of cord, etc., it is clear that a powder to give efficient propulsive effect within the limits of pressure permissible in a gun, may be prepared from either a suitable nitro-cellulose-nitro-glycerin mixture, or from a nitro-cellulose alone, with or without the addition of some metallic nitrate.

Keeping Qualities.—The pure nitro-cellulose powder has the advantage of greater homogeneity, but the important question of stability has yet to be considered. It is generally understood that the nitro-cellulose powders require very careful treatment in magazines ; many cases of serious decomposition have occurred, and for this reason foreign ships on which such powders are employed have to be provided with special means for keeping down the temperature of the magazine. The nitro-cellulose-nitro-glycerin powders appear to have a distinct advantage in this respect.

Weight of Charge.—Experiment shows that the potential energy increases far more rapidly with rise of temperature than it increases with rise of gas volume (calculated at 0° and 760 mm.), that is to say, that a given weight of nitro-cellulose-nitro-glycerin powder will develop a greater potential energy than the same weight of a pure-nitro cellulose powder. To again quote Noble's results (1905), for a density of charge 0·25—

	Cordite, Mark I.	Cordite, M.D.	Nitro-cellulose.
Volume of total gases per gram	871·3 c.c.	888·6 c.c.	922·3 c.c.
Temperature °C.	5086	4220	3667
Comparative potential energy	0·97	0·82	0·74

Clearly, then, to develop the same propulsive effect, larger charges must be used for M.D. cordite than for Mark I. cordite, and still larger charges for a nitro-cellulose powder. The effect of this is far-reaching, for not only will the cost of material be greater, but a type of gun suitable for a cordite powder would be quite unsuitable for the much greater charge of a nitro-cellulose powder, and further, the influence of increased bulk on magazine space must not be overlooked.

The Smokeless Powders of To-day.—The successful smokeless powders at present in use may be all divided into two classes—

1. Powders consisting of nitro-cellulose and nitro-glycerin either alone or mixed with some material to regulate the combustion.
2. Powders consisting of nitro-cellulose with regulating and sometimes oxidising materials, but no nitro-glycerin.

CORDITE.

It will be well now to consider the ingredients employed and the methods of manufacture of the principal smokeless powders.

We have already gone fully into the manufacture of gun-cotton and nitro-glycerin employed as the basis of the English Service powder, and besides these are used acetone as the blending agent, and vaseline, which is now recognised as one of the most important constituents acting, not only as a lubricant, but also as a stabiliser.

Acetone, which is used in making the cordite and also as a solvent in some other smokeless powders, is a compound having the formula C_3H_6O. It is a colourless, fragrant liquid, having a specific gravity of 0·79 and boiling at 56·3° C. or 133·3° Fahr. It is inflammable, burning with a luminous flame, and will mix with water, alcohol, and ether. It is essential, for purposes such as the making of smokeless powders, that it should be as pure as possible, as any traces of impurity would probably be left behind on its evaporation and remain in the powder. That used at Waltham Abbey has a specific gravity of 0·7965, and 98 per cent. of it distils off between 56·2 and 56·4° C. When such acetone is treated with a 0·1 per cent. solution of potassium permanganate, it should retain its rose colour for more than several minutes. In addition to this point, it should not have more than 0·005 per cent. of acidity nor contain more than 0·1 per cent. of aldehyde. The recovered acetone in the Waltham Abbey factory is so pure that it will stand the permanganate test for two or three days.

Vaseline.—Vaseline or mineral jelly used is obtained during the distillation of petroleum, and consists mainly of portions distilling at temperatures above 200° C.; it has a boiling point of about 278° C., and has been given the formula $C_{16}H_{34}$, but is probably a mixture of this with higher and lower members of the C_nH_{2n+2} group of hydrocarbons, and also contains unsaturated hydrocarbons.

Products of Explosion.—The composition of the early Mark I. cordite was—

Nitro-glycerin	58
Tri-nitro-cellulose	37
Vaseline	5
	100

The proportions of the atoms of carbon, hydrogen, nitrogen, and oxygen in the compounds forming it would approximately be $C_5H_8N_3O_{10}$.

Such a mixture of compounds might be expected to give on explosion—

$$2(C_5H_8N_3O_{10}) = 4CO_2 + 6CO + 6H_2O + 2H_2 + 3N_2$$

and this is fully borne out by an analysis of the permanent gases yielded by cordite on explosion—

	I.	II.	Calculated from Equation
Carbon dioxide	25·40 ..	24·9 ..	26·66
Carbon monoxide ..	37·62 ..	40·3 ..	40·00
Hydrogen	17·43 ..	14·8 ..	13·33
Nitrogen	19·55 ..	20·0 ..	20·00
	100·00	100·0	99·99

Drawback to Cordite.—Cordite at first appeared to be a perfect smokeless powder ; it gave excellent ballistics, its stability under trying conditions of temperature was better than with any other smokeless powder, and it showed no tendency to detonate or give unduly high pressures in the guns.

Erosion.—Soon, however, it became noticed that the enormously high temperature developed on firing large charges began to seriously erode the guns, and that this took place to a much more serious extent with large than with small guns, a rapid washing away of the surface of the bore taking place. It was at first hoped that by modifying the form of the driving band of the projectile this trouble might be got over, but directly an increase in muzzle velocity was required the trouble became accentuated, and the experience of the South African War showed that even the 4·7 guns had their shooting rendered inaccurate at long ranges by the erosion caused after a comparatively small number of rounds.

M.D. Cordite.—This led to the adoption of what is known as M.D. cordite, which has the composition—

Tri-nitro-cellulose	65
Nitro-glycerin	30
Vaseline	5
	100

Experience shows that this modification of cordite is, if anything, more stable, and that for charges of the same size the life of the gun is nearly doubled, the heat developed on explosion being reduced from 1253 calories per gram with cordite to about 1000 with the M.D. cordite.

In the Manufacture of M.D. Cordite as at present carried out the tri-nitro-cellulose and nitro-glycerin are manufactured by the processes described in the last chapter, the only variation being that in the last stage of manufacturing the gun-cotton free alkali is not added, and instead of the gun-cotton being highly compressed under a pressure of six tons, it is lightly compressed into small cylinders, in which condition it contains roughly 45 per cent. of moisture. When required for use the cylinders of gun-cotton are placed upon trays of copper wire gauze, arranged in the stoving or drying room in racks, and subjected to the action of warm air for 80 to 100 hours, in which period the moisture is reduced to 1 per cent.

It is then weighed out in lots of 24 lbs. 6 oz., which are put into brass-lined wooden boxes, and 11¼ lbs. of nitro-glycerin, which has been weighed out from store into gutta-percha jugs, are poured over the gun-cotton. The boxes containing these ingredients are removed to the mixing house, in which their contents are kneaded together by hand and then rubbed through half-inch mesh copper wire gauze, the nitro-glycerin being absorbed under these conditions by the gun-cotton, and the mixture being known as "*cordite paste.*"

The next stage is to thoroughly incorporate the cordite paste with the acetone, that is, to destroy the structure of the tri-nitro-cellulose and blend it with the nitro-glycerin. The incorporating machine consists of an iron box formed of two semicircular troughs open at the top. In each trough is a spindle carrying a propeller-shaped blade, the spindles being made to revolve in opposite directions, one twice as fast as the other. The lower portion of the incorporating box is water-jacketed in order to keep down the temperature, which is never allowed to exceed 104° F.

Half the acetone to be used having been put into the incorporating vessel, the cordite paste with the remainder of the acetone is added, a wooden cover is put on top of the machine to prevent evaporation of the acetone, and the spindles are then run for three hours. At this point 9½ lbs. of vaseline are added, and the incorporating is continued for another three hours, during the last fifteen minutes of which the blades are reversed in order to break up the mass, which is now called "*cordite dough.*" This dough is removed in barrels to the press-house, where it is compressed into cylinders which are placed under a hydraulic ram, the mass being forced out through dies into threads or sticks.

Below the die is an endless band carrying knife edges, the band travelling at the same rate as that at which the cordite issues from the dies. The band with the cordite on it passes under a roller so adjusted as to force the cordite on to the knife edges, which cut it into sticks of the required length. These lengths of cordite are arranged on trays and are stoved at 110° F. for periods varying from 272 hours up to 880 hours, according to their diameter, this removing the acetone. The acetone is now to a large extent recovered during the drying of the cordite and after rectifications is of a high degree of purity. About 50 per cent. of the amount put in the incorporating machines is available for further use. After this the cordite only needs to be blended so as to obtain uniform ballistics.

Tubular Cordite.—In order to reduce as far as possible the initial pressure when using cordite and to gain as great an increase as possible whilst the projectile travels along the bore of the gun, the cordite is sometimes made in tubes instead of in cords, for if the combustion can be started in the interior of the tubes a moderate initial velocity of gas is obtained which increases with increase of the burning surface. Larger charges can be more completely consumed in a given length of gun, thus enabling higher muzzle velocities to be obtained without waste of powder, the great disadvantage being the increase in bulk as compared with the cords for the same weight of charge.

In the manufacture of tubular cordite there are two practical difficulties, one of which is that in the flexible condition in which it comes from the die, it is difficult to cut it into lengths without pressing together to a certain extent the walls of the tube, which impedes regular ignition, and does away with much of the benefit derived from the form of the cordite, whilst the second is that it is difficult to obtain perfect smoothness and uniformity of the interior surface of the tube.

Smoke Haze from Cordite.—Although nitro-glycerin and gun-cotton are both of them absolutely smokeless, yet the rapid firing of a number of guns using this powder gives rise to a fog or haze, and with the increase in charges necessitated by the introduction of modified cordite, this has shown itself to be rather troublesome and hampers the use of the guns to a certain extent. This haze, which in some cases becomes a thick yellow cloud, is due to several factors. It consists of condensed water vapour, smoke from the powder primer, vaseline, and the cartridge bag, and oxide of copper from the driving bands ; and as the moisture, vaseline, and cartridge bagging increase directly with the charge, this trouble necessarily increases with the use of the modified cordite.

Stability Tests for Cordite.—The Abel heat test has already been mentioned in considering the keeping properties of gun-cotton, but is of such importance that a full description of the test and its application to testing smokeless powders is necessary.

The instability of the gun-cotton made in 1847 by the processes introduced by Schönbein and Bottcher was so great as to lead to the serious explosions which resulted in the abandonment of the manufacture of gun-cotton within two years of its discovery. Later, when Abel in 1864 introduced into England the improvements which had been devised by von Lenk and his own modifications, which had resulted from the discovery that this excessive instability was due to traces of acid retained in the capillaries of the cotton, it was realised that even after complete purification by washing and disintegration in the hollander and final treatment in the poaching machines, the compound was still liable to a gradual decomposition, which, however, was so slow as to give rise to but little danger. It was in consequence of this that the Abel heat test was introduced, and it is still the most valuable empirical test that we have, as although it will sometimes fail to give true indications with deteriorated cordites, and although the action may be nullified by the presence of such bodies as mercuric chloride in the nitro-compounds, it still is the only test occupying a sufficiently short period and capable of being carried out with sufficiently simple apparatus to make it of practical use for Service work.

Many attempts have been made to replace it or to alter the details of procedure, but in no case has the suggested method given results that could be compared with it for general utility, and it, therefore, very properly retains its pride of place as being the test applied in the first place to Service explosives. Although of a purely empirical character, results obtained with a large number of cordites which have been subjected to storage at various temperatures for varying length of time have clearly shown a close coincidence between the duration of the test and the storage conditions. It is, therefore, possible from the results obtained to determine whether the cordite is still sufficiently reliable to remain in magazines or whether it shall be relegated to other uses or destroyed.

At one time the ground cordite was exposed to the air for a period of 24 hours, but this illogical practice has been abandoned, and the freshly-ground material is subjected to the test with as little delay as possible.

In order to carry it out, a spherical copper water-bath, of about 8 inches in diameter, is filled to within a quarter of an inch of the top with water, which has preferably been purified by distillation, and is then heated carefully by any form of gas or spirit burner, the flame being regulated according to the reading of the thermometer immersed in the water, the temperature being kept constant at the required point. A copper lid, 6 inches in diameter, fits into the top of the water-bath, and is pierced with seven holes to receive a thermometer and six test tubes, which are 5¼ to 5½ inches long, and of such diameter that they will hold 20 to 22 c.c. of water when filled to a height of 5 inches. These test tubes are each closed by means of a cork, through which passes a glass rod terminating in a platinum wire hook, from which may be suspended a standard iodide of starch test paper, and before using the upper half of these is moistened with a mixture of equal parts of pure water and glycerin. The paper is then hung on the rod in such a way that it shall be vertical, and is so adjusted by the sliding rod that the lower edge is about halfway down the tube.

The nitro-compound to be tested is, after careful sampling, cut into small pieces and passed through a small grinding mill, the first portion being discarded, as it might contain foreign matter from the mill, which latter has to be taken to pieces and cleaned after each sample has been ground. A nest of sieves of standard size is supplied with the test, and the ground-up explosive is placed in the top sieve, and is then sifted, that portion which has passed through the top sieve and been stopped by the second being retained for the test.

Twenty-five grains of this sifted material are weighed out and put into one of the test tubes, and collected at the bottom by gently tapping the tube. The tubes are then placed in the water-bath by inserting the ends through the lid so that 2¾ inches shall be immersed in the water-bath, which is kept at a constant temperature of 160° F., the cork carrying the rod and test paper being then placed in position. Under these conditions, if properly arranged, the lower margin of the moistened paper should be about five-eighths of an inch above the surface of the cover.

The paper is carefully watched, and when the faint brown line, which after a time makes its appearance at the junction of the wet and dry portions of the paper equals in tint the brown line drawn on the standard tint paper supplied, the test is complete, and the time which elapses between the insertion of the test tube and the completion of the test is noted.

In using this test it must be remembered that the presence of any trace of acid from an extraneous source will render the test abortive, and the greatest care has, therefore, to be taken in keeping the various parts of the apparatus absolutely clean and handling the material as little as possible.

The preparation of the standard papers for use with the apparatus may be carried out as follows: 45 grains (3 grams) of white maize starch (corn flour) previously washed with cold water, are added to $8\frac{1}{2}$ oz. (250 c.c.) of distilled water; the mixture is stirred, heated to boiling, and kept gently boiling for ten minutes; 15 grains (1 gram) of pure potassium iodide (*i.e.* which has been crystallised from alcohol) are dissolved in $8\frac{1}{2}$ oz. of distilled water. The two solutions are thoroughly mixed and allowed to get cold. Strips or sheets of white English filter-paper, previously washed with water and re-dried, are dipped into the solution thus prepared, and allowed to remain in it for not less than ten seconds; they are then allowed to drain and dry in a place free from laboratory fumes and dust. The upper and lower margins of the strips or sheets are cut off, and the paper is preserved in well-stoppered or corked bottles, and in the dark. When the paper is freshly prepared, and as long as it remains in good condition, a drop of dilute acetic acid put on the paper with a glass rod produces no colouration. In process of time, however, the paper deteriorates, and the stronger the light to which the paper is exposed the sooner a drop of acid produces a brown or bluish colouration (a single hour of direct sunlight produced a marked effect), and whenever this is the case the paper should be rejected. On this account it is advisable not to prepare too much of the test paper at one time, but to prepare it fresh every month or so. The dimensions of the test-paper used are about $\frac{4}{10}$ inch by $\frac{8}{10}$ inch (10 mm. by 20 mm.).

To obtain the standard tint paper. A solution of caramel in water is made of such concentration that when diluted one hundred times (10 c.c. made up to 1 litre) the tint of this diluted solution equals the tint produced by the Nessler test in 100 c.c. of water containing 0·00075 gram of ammonia, or 0·00023505 gram of ammonium chloride. With this caramel solution lines are drawn on strips of white filter-paper (which paper must be carefully washed with distilled water in the first instance, to remove any traces of bleaching matter, and dried) by means of a clean quill pen. When the marks thus produced are dry, the paper is cut into pieces of the same size as the test paper previously described, in such a way that each piece has a brown line across it near the middle of its length, and only such strips are preserved in which the brown line has a breadth varying from $\frac{1}{2}$ mm. to 1 mm. ($\frac{1}{50}$ to $\frac{1}{25}$ inch).

For the testing of freshly-manufactured cordite in the Abel heat test, a heat of 180° F. for 30 minutes is required, but owing to the fall which takes place in the time it will stand the heat test after exposure to such temperatures as are found in Indian magazines, the official duration and temperature tests have been modified from time to time, the present minimum being five minutes for land service and four for naval purposes.

The formation of the line on the paper is due to the liberation of iodine from the potassium iodide by traces of nitrogen oxides given off under the influence of heat during the test. The oxides may already exist as such, or may be formed from nitrites produced by previous actions, which acted on by such acids as acetic and formic, would evolve oxides of nitrogen. A volatile body having the characteristics of a nitrite has been detected in cordites from India, and formic and acetic acids have been found in deteriorated cordite.

The Waltham Abbey silvered vessel test, introduced by Sir Frederick Nathan and Dr. Robertson, more nearly reproduces storage conditions, with the exception that the temperature to which the cordite is subjected is raised to 80° C. (176° F.) in order to bring about in a reasonable time the reaction which theory indicates as taking place in cordite kept at moderately elevated temperatures.

The vessel used in this test consists essentially of a spherical bulb of glass, silvered to reflect any heat evolved during the decomposition inwards upon the explosive itself, and so intensify the effect of spontaneous heating when this sets in. The bulb is surrounded by a vacuum jacket for the purpose of insulating the explosive contained in it, and of limiting in this way the dissipation of any heat evolved by exothermic changes on the one hand, and on the other, for the purpose of minimising the effect of accidental slight changes in the temperature of the water-bath, the latter effect being further restrained by silvering the outer shell. In the centre of the spherical mirror is situated the bulb of a thermometer; the stem of the thermometer passes through a cork in the neck of the vessel. Nearly at right angles to the neck of the vessel a side tube is attached, for the purpose of making observations on the colour of the gases evolved. For heating the vessel a bath is provided, furnished with immersed cylinders closed at the bottom and wide enough to admit the vessel to such a depth as the side tube will permit. To prevent draughts, the tops of the cylinders are covered with asbestos lids, pierced with a hole sufficiently large to admit the neck of the vessel. The bath is fitted with a gas regulator or other means for securing that the temperature of the bath is kept constant.

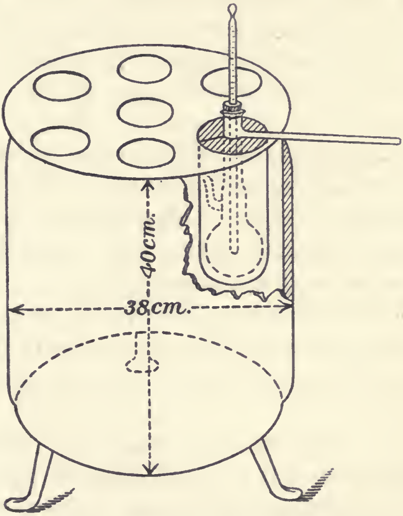


Fig. 43.—Silver vessel apparatus.

In using this apparatus, the explosive is ground to the same degree of fineness as in the Abel heat test, and 50 grams are employed. The temperature in the bath having been carefully regulated to 80° C., the flask is inserted in position, and the temperature kept constant night and day, readings of the thermometer being taken at intervals. A point is at length reached, which may vary from less than 100 hours with a very bad sample up to 600 hours with freshly-made cordite, when decomposition in the mass has just commenced, and an observer looking along the side tubulure sees brown fumes beginning to appear. As soon as this point is reached the thermometers are carefully watched, and it will be found that very shortly a rise in temperature makes itself manifest, and when this rise exceeds 2° C., the flask is withdrawn and the test is finished.

There is not the least doubt that the course taken by the action in this test is the same as that in store. In both cases there is a long period during which changes in composition are so slight as neither to affect the temperature nor evolve any notable quantity of oxides of nitrogen, and this is at length succeeded by a period of chemical activity, when rise of temperature sets in which would in store culminate in fire of the same order of violence in the silver vessel as those which have actually occurred in India and on board some of our ships (*Revenge*, *Perseus*, and *Fox*).

The rate of decomposition which takes place in cordite is dependent upon and increases in direct ratio with the temperature, and in the silver vessel test, by raising the temperature to 80° C., the process of decomposition taking place at ordinary temperatures is exactly reproduced, but is accelerated in a 1·7-fold increase in the rate of decomposition for a rise of 5° C., so that it is possible by knowing the rate of decomposition at any particular temperature to translate it into the rate which would take place at any other temperature.

If, therefore, the history of a sample of cordite is known, and the periods over which it has been stored in various magazines, and the average temperatures of those magazines, one can calculate the number of hours of decomposition at 80° C. to which the storage is equivalent. The proof of the accuracy of the silver vessel test is to be found in the fact that the life represented by the results obtained in the test closely approximates to the period calculated from the storage conditions, and it is possible to make a table by which the total residual life of cordite in store at any particular temperature can be calculated from the hours given by the silver vessel test at 80° C.

In practice, of course, the storage allowed for a tested sample of cordite would be curtailed by a safety margin of two or three years.

TABLE FOR CALCULATING TOTAL RESIDUAL LIFE OF CORDITE FROM HOURS IN SILVERED VESSEL TEST AT 80° C.

Hours in silvered vessel at 80° C.	100	200	300	400	500	600
Temperature of storage	Years	Years	Years	Years	Years	Years
60° F. ..	10·6	21·2	31·8	42·4	52·9	63·5
65 ..	7·9	15·8	23·5	31·7	39·6	47·6
70 ..	5·9	11·8	17·6	23·5	29·4	35·3
75 ..	4·4	8·8	13·1	17·5	22·0	26·3
80	3·3	6·6	9·9	13·2	16·4	19·7
85 ..	2·4	4·9	7·3	9·8	12·2	14·6
90 ..	1·9	3·7	5·6	7·5	9·4	11·2
95 ..	1·3	2·7	4·1	5·4	6·8	8·1
100 ..	1·0	2·0	3·0	4·0	5·0	6·0

Stabilising Action of Vaseline.—When mineral jelly or vaseline was first introduced as a constituent of cordite, it was done to give a sufficient quantity of solid matter in the products of explosion to protect the lining of the guns from metallic fouling, and also to waterproof the cordite and facilitate the squeezing into threads, but it was not until more recently that its important action in increasing the stability of cordite was suspected.

It used to be supposed that as nitrated bodies of the character used in smokeless powders underwent decomposition, nitrogen dioxide only was liberated, and this gas has little or no effect in increasing the rate of decomposition, but an extended research by Dr. Robertson and S. S. Napper showed that 40 per cent. of the nitrogen evolved during decomposition is in the form of nitrogen tetroxide, and that this gas is distinctly active in increasing the rate of decomposition.

Vaseline or mineral jelly has generally been looked upon as being a member of the paraffin series, in which case it would be inert in its action towards nitrogen tetroxide, but researches made at Waltham Abbey show that whilst there is a quantity of paraffins present in the jelly, the bulk of the material consists of hydrocarbons of the nature of naphthenes, with which the paraffins form an emulsion, and these naphthenes are nitrated by the nitrogen tetroxide.

This absorption of the nitrogen tetroxide gives greater stability to the composition, and as long as the nitrogen tetroxide is being absorbed by the naphthenes any rapid decomposition is held in check. That this is so is shown by the fact that if a cordite be prepared without mineral jelly it will only stand the silver vessel test for 83 hours,

with 2 per cent. it will stand the test for 263 hours
,, 3 ,, ,, ,, ,, 335 ,,

whilst the ordinary manufacture with 5 per cent. will stand for approximately 600 hours.

Foreign Smokeless Powders.—At one time England and Italy alone employed the nitro-glycerin-nitro-cellulose type of powder, the former cordite, the latter ballistite. Largely through the researches of Vieille, France was the first Power to adopt a simple nitro-cellulose powder, consisting of mixed soluble and insoluble nitro-celluloses gelatinised by a mixture of alcohol and ether. Later, Russia adopted a nitro-cellulose powder made entirely of soluble nitro-cellulose (pyro-collodion), and a similar powder is the standard American propellant. The Belgian and Swiss Service powders are gelatinised gun-cotton powders, the former gelatinised by amyl acetate, the latter by ethyl acetate.

The composition of Service powders in most countries is constantly undergoing modifications and improvements, and whilst those countries which adopted gelatinised nitro-cellulose still retain it for small arm and general propellant purposes, the tendency is all in the direction of the use of a nitro-glycerin-nitro-cellulose powder similar to M.D. cordite for the large modern guns. The German propellant for large guns contains 23 per cent. nitro-glycerin.

It appears that the drawback of erosion with such powders is more than counterbalanced by the larger charges of simple nitro-cellulose powders, the difficulty of removing the solvent from the larger sizes, the apparent lower stability, and the much greater risk of back-flash.

In most of the nitro-cellulose powders some "stabiliser" is introduced with the idea of it functioning in the same manner that vaseline does in cordite. Large numbers of organic substances may be employed which will take up the incipient products of decomposition. In the French B.N. powder, which has led to such serious disasters, the stabiliser was amyl alcohol (fusel oil). In addition to stabilisers, accelerators in the form of oxygen containing substances, such as barium nitrate, are also frequently introduced.

The manufacture of simple nitro-cellulose powders is carried out on the following lines.

The wet nitro-cellulose, containing about 10 per cent. of water, is passed through rollers to squeeze out as much water as possible, and the flaked mass is dried by adding to it a large excess of alcohol, which mixes with the water present, and by then subjecting the mass to pressure, the excess of alcohol and water is squeezed out, this process of drying being far superior to drying in a current of warm air, as this was found to give rise to a large quantity of dry nitrated dust, which rendered the atmosphere excessively explosive and gave rise to so much danger that it had to be abandoned. The method also has the advantage that the percentage of moisture left in the nitro-cellulose can be readily adjusted by altering the amount of alcohol added and the pressure in the dehydrating press.

The nitro-cellulose when removed from the dehydrating press is moist with alcohol, and is then transferred to the mixing machine where alcohol and ether are added. The mass is kneaded to a paste by revolving blades, the machine, however, having to be closed by an air-tight lid to prevent the evaporation of the solvents. After mixing for about half an hour the pasty mass is pressed into cylindrical blocks of uniform density, which are then placed in the hydraulic press from which the paste is forced out in the form of strips, tubes, or multi-perforated rods, and whilst still soft is cut to the required size. After this it is dried at a temperature not exceeding 100° F. to expel the excess of solvent.

LYDDITE.

Picric Acid, which was originally made by the action of nitric acid upon indigo, is now prepared far more cheaply by the action of nitric acid at a low temperature on carbolic acid obtained from coal tar.

Phenol, or carbolic acid—C_6H_5OH—is one of the compounds obtained from heavy tar oil, and is much used as a constituent of disinfecting powders and liquids. It is obtained in needle-shaped crystals, possessing a strong, tarry smell, and has a fusing point of 42° C., the liquid boiling at 182° C.; and when a small quantity of the fused acid is poured into nitric acid a violent action takes place, with evolution of red fumes. When this action has moderated, some of the strongest nitric acid is added, and the liquid boiled until red fumes nearly cease to be evolved; on cooling, a yellow substance called picric acid crystallises out, and can be purified by re-crystallising from water.

The change which takes place during the action of the nitric acid upon the carbolic acid may be represented as follows:—

$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Nitric acid}}{3(HNO_3)} = \underset{\text{Picric acid}}{C_6H_2(NO_2)_3OH} + \underset{\text{Water}}{3(H_2O)}$$

Owing to the violence of the reaction when direct nitration is employed the usual commercial process of manufacture is to mix the crystallised carbolic acid with an equal weight of concentrated sulphuric acid, and to heat the mixture in an iron vessel by steam coils to a temperature a little over 100° C.; after cooling the mixture is dissolved in twice its weight of water, and the solution is added gradually to three times its weight of nitric acid, specific gravity 1·4.

The acid is contained in earthenware pots standing in running water to prevent undue rise of temperature, and when fuming has ceased steam heat is applied to complete the nitration. On cooling down crystals of picric acid separate, and after washing with warm water are purified by recrystallisation.

This method of making picric acid is called the sulphonating process, and is now the one almost entirely employed.

Picric acid may be regarded as a nitro-substitution product, in which three atoms of the hydrogen in the original phenol are replaced by the radicle NO_2, and by the action of picric acid on metals or metallic bases, is obtained the class of salts known as picrates.

$$\underset{\text{Picric acid}}{C_6H_2(NO_2)_3OH} + \underset{\text{Potassium hydroxide}}{KHO} = \underset{\text{Potassium picrate}}{C_6H_2(NO_2)_3OK} + \underset{\text{Water}}{H_2O}$$

Many of these salts have the property of exploding when heated or struck.

Picric acid is a pale yellow crystalline solid, having the form of plates or prisms, and is but little soluble in cold water, although readily soluble in alcohol. It derives its name from its intensely bitter taste, and is extensively used as a dye for silk and wool, which it colours a fast yellow.

On heating the crystals of picric acid, they fuse at 119° C. with partial sublimation. It can only be exploded with difficulty by heat.

When exploded the decomposition is somewhat complicated.

Nitrogen, carbon dioxide, carbon monoxide, nitric acid, water vapour, and hydrocyanic acid are produced, and a residue of unburnt carbon left behind. An inspection of the formula for picric acid makes it at once evident that there is clearly not nearly enough oxygen for the complete combustion of the carbon and hydrogen present, and for this reason nearly all the picric powders and explosives consist of mixtures of picric acid or its salts, with oxidising substances of a character suitable for supplying this deficiency.

It is now more than thirty years ago since Désignolle first introduced potassium picrate and saltpetre for use as bursting charges for torpedoes and shells, and this was improved upon by Sir Frederick Abel, who substituted ammonium picrate for the potassium salt, the same composition also being adopted in Brugère's picric powder. Soon after this Dr. Sprengel showed that the picric acid by itself was capable of being detonated by mercuric fulminate, and in 1885 E. Turpin patented the use of picric acid for shells and torpedoes, and proposed to make it less sensitive to percussion by melting it and pouring it whilst hot into the shells, or by making the grains into a solid mass by means of collodion; in this way a very great weight of the explosive can be got into a small space on account of the high specific gravity of the fused mass.

The great drawback to picric acid is its acid nature which causes it to act on metals with formation of picrates, some of these, like lead picrate, being far more sensitive to friction and percussion than the acid itself.

Melinite contains picric acid as its chief constituent, mixed with some oxidising substance, or as stated by some authorities, merely made into a compact mass with collodion, and the explosive "Lyddite," which is used as a bursting charge in shells, consists of picric acid fused at 130° to 140° C., and cast into the shell, leaving a central core for the exploding priming.

The lyddite shells used in the South African campaign showed great diversity of behaviour, at one time exploding with tremendous effect, and at others giving a very low order of explosion and dense yellowish green fumes. This was due to the fact that for its proper explosion picric acid needs a powerful detonator, and fear of premature explosion of the shell in the gun prevented sufficiently strong detonators being used.

The cast acid is not so easily detonated as when it is in the form of powder, 3 grams of mercuric fulminate failing to detonate it, but by using a primer of gun-cotton, powdered picrate, or better still trinitro-toluene, it can be detonated with certainty.

Trinitro-cresol can be made from cresylic acid, another coal-tar derivative which is always found in heavy tar oil in company with carbolic acid, by an exactly similar sulphonating process to that used for making picric acid. Cresol or cresylic acid has the formula $C_6H_4.CH_3.OH$, and the trinitro-cresol is formed by the replacement of three atoms of hydrogen by nitryl, so that the formula for it is $C_6H_2(NO_2)_2.CH_3.OH$. It is used alone or mixed with potassium nitrate as a bursting charge for shells, and the explosive is known in France as "Cresylite," and in Austria as "Ecrasite." Like picric acid, it is a solid and melts at 107° C.

Trinitro-toluene is another valuable explosive much used for blasting explosives, and which, in the future, is quite likely to largely displace picric acid as a bursting charge for shells, as it has the advantages of having no acid properties, and therefore not attacking metals, whilst its fumes and dust do not affect those working with it. It is slightly less powerful in its explosive action than picric acid, since it contains a lower percentage of oxgyen. Its rate of detonation is 6700 metres per second, that of picric acid being 7100, but this is not altogether a disadvantage, as used as a bursting charge it gives rather larger fragments of shell, and, therefore, greater destructive effect.

Toluene, from which it is made, is obtained from coal tar, and comes over with benzene in the first fraction distilled. The toluene is converted into mono-nitro-toluene by nitrating it with a mixture of two parts of nitric acid, specific gravity 1·495, to three of sulphuric acid, specific gravity 1·84, three parts of mixed acids to one of toluene by weight being used.

The product from the first nitration is then converted into dinitro-toluene by a second nitration with twice its weight of the same acid mixture, and finally a third nitration yields the trinitro-toluene.

Toluene has the formula $C_6H_5.CH_3$ (methyl benzene), and the trinitro-toluene $C_6H_2(NO_2)_3.CH_3$; it dissolves readily in alcohol, from which it can be crystallised as yellow needles, the crystals darkening when exposed to light for some time.

When lighted it burns with a smoky flame, but cannot be exploded except by a mercuric fulminate detonator.

CHAPTER XIX

BLASTING EXPLOSIVES AND FULMINATES

In explosives for blasting purposes, the study of ballistic effects has to be abandoned for considerations of a totally different character. When the explosive is required by the engineer for such mechanical work as tunnelling and the removal of rocks and other obstacles in a waterway, or when such bodies are required for the purpose of bringing down masses of slate and stone in quarries, the primary points which claim attention are, firstly, safety in handling; secondly, the fitness of the explosive to do the work required of it, *i.e.* whether it shall have a shattering and disintegrating effect which shall allow of the ready removal of the *débris*, or shall partake more of an upheaval and steady push, which will separate the mass in blocks fitted for cutting into slabs or other forms; thirdly, during its combustion such an explosive must not give off gases which, in the confined and ill-ventilated spaces in which they have often to be used, are likely to be actively dangerous to the life and health of those exposed to the air contaminated by such fumes.

For use in coal mines, however, these points, although of great importance, are overshadowed by the question of safety, and the ideal in explosives for such work must also be free from the danger of causing explosion in the air of the mine. At one time explosions in mines were always attributed to the accidental ignition of mixtures of air and methane, to which the name of "fire-damp" is given, and undoubtedly this cause is the prime factor in this class of disaster, but the introduction of such precautions as safety lamps at once brought about a considerable reduction in the number of explosions taking place. Many disasters, however, still continued to occur under apparently mysterious circumstances, the conditions being such that any large proportion of methane in the air of the mine appeared practically impossible. Investigations of such explosions showed that coal dust, in a dry and finely powdered condition, had generally been present in the mine at the time of the explosion, and the coked residue of this dust was found afterwards on the surfaces exposed to the explosive wave. Years of experimental investigation by scientific men of the greatest ability proved the fact that air containing so small a proportion of methane as to be itself perfectly non-explosive, becomes a good explosive when holding dry and finely divided coal dust in suspension; and within the last few years explosions have taken place in mines which have always been celebrated for their freedom from any trace of methane. Further experiments made by Mr. H. Hall and Mr. W. Galloway, finally showed that the violent ignition of dust-laden air is possible by a blown-out shot, even if the air in the mine be free from any trace of methane.

In a paper by Dr. John Harger, read before the Institution of Mining Engineers in 1912, he showed that the ignition of a mixture of coal dust and air depended upon the percentage of oxygen in the air, and that, in fact, various kinds of coal dust had their ignition and explosion percentages, so that whilst an anthracite dust needs over the percentage present in air, and so is for all practical purposes non-explosive, others would ignite with only 17·5 per cent. of oxygen, but that below this point all fear of explosion ceased, and the presence of carbon dioxide rendered the dust still less sensitive.

History.—In the earlier days of mining, gunpowder was the only blasting agent employed, but the discovery by Alfred Nobel, in 1864, that nitro-glycerin could be used with tremendous effect for blasting purposes, and his patenting it under the name of "Nobel's blasting oil," gave rise to an entirely new era, and when, in 1866, the dangerous character of this substance led to legislative restrictions, it was Nobel who complied with the requirements of the time by converting his blasting oil into the powerful and effective explosive which will be treated later under the name of dynamite.

During the succeeding years many attempts were made to modify and improve upon this idea, but the next great era in blasting explosives may be taken as commencing in 1873, when Dr. Sprengel read a paper before the Chemical Society on a new class of explosives. In this paper he pointed out that in the then existing explosives there were considerable variations between the amount of available oxygen present and the amount of combustible matter to be burnt by it, and that the proportions, as a rule, were not such as to give the highest explosive value, some of these bodies, as in the case of gun-cotton, containing too small an amount of oxygen for complete combustion, whilst nitroglycerin contains more than sufficient. He suggested that higher explosive values could be obtained by employing mixtures which might either be solid, liquid, or the two combined, one of which should be a hydrocarbon, containing the elements carbon and hydrogen in a condition favourable to their rapid combination with oxygen, whilst the second should be an easily decomposable compound, which could be made available for supplying the necessary oxygen for the combustion of the hydrocarbon, and which could be mixed with it in the proportions necessary to give the highest explosive value.

Amongst the advantages claimed for such explosives is the important one of safety in transit, as the mixing of the ingredients need take place only when the body is required for use, and the two constituents when separate being non-explosive, there would be no danger until such admixture was made. Dr. Sprengel showed also that mixtures of potassium chlorate and such bodies as benzene, petroleum, and phenol could be detonated and exploded with great violence. This class of explosives, named after the inventor, "Sprengel explosives," was largely adopted for blasting purposes. The principal were—

Rack-a-rock, a mixture of potassium chlorate and petroleum, or, in some cases, nitro-benzene, which obtained notoriety from being the material used in the Hell-gate explosions, when the rocks at the mouth of New York Harbour were destroyed.

Hellhoffite, a mixture of nitrated tar oils with the strongest nitric acid.

Oxonite, containing picric acid and nitric acid, which are mixed just before use.

The next era in blasting explosives may be taken as dating from 1875, when Nobel in December of that year took out his first patent for blasting gelatine, a substance which figures so prominently in the foregoing pages as the parent of our successful Service explosive.

In discussing the composition and properties of these explosives it will be convenient to divide them into three classes—

(1) Blasting powders of the same character as gunpowder; (2) Sprengel explosives; (3) nitro-glycerin explosives; which will cover all the explosives most used for blasting purposes, with the exception of tonite, which is a mixture of nitro-cotton with mineral nitrates.

Blasting Powder.—Under the first heading come ordinary gunpowder, and also the commoner forms of blasting powder, in which the sulphur is considerably increased at the expense of the potassium nitrate, these still forming 58 per cent. of the blasting explosives in use.

The following table gives an idea of the composition of such powders :—

	England	France	Italy
Potassium nitrate	65	62	70
Sulphur	20	20	18
Charcoal	15	18	12

The result of this alteration of composition is to increase the volume of permanent gases given off by the powder, and at the same time to reduce the heat energy of the explosion; but in obtaining a slight lowering of temperature, the poisonous constituent of the products of combustion, carbon monoxide, is increased to a very serious extent.

The following table gives a clear idea of the alteration brought about in the composition of the products of combustion by the increase in the amount of sulphur present, and reduction in the potassium nitrate :—

	Gunpowder, fine grain	Mining powder
Carbon dioxide	50·62	32·15
Carbon monoxide	10·47	33·75
Nitrogen	33·20	19·03
Sulphuretted hydrogen	2·48	7·10
Methane	0·19	2·73
Hydrogen	2·96	5·24
Oxygen	0·08	0·00
	100·00	100·00

Bobbinite is a gunpowder in which the sulphur has been reduced to 2 per cent., and starch and paraffin wax added to increase the safety in use in coal mines. Its composition is—

Potassium nitrate	66·0
Charcoal	20·0
Sulphur	2·0
Starch	8·5
Paraffin	3·0
Moisture	0·5
	100·0

The mixture is pressed into pellets and coated with paraffin wax, and is much used, as it does not break the coal as much as most of the safety explosives, but it evolves a large percentage of carbon monoxide on explosion.

In order to ensure safety in mines in which gas is known to occur, or which from their dryness are liable to coal dust, only "permitted" explosives that have passed the Home Office tests are allowed. The use of gunpowder in such mines is prohibited, but bobbinite is on the permitted list, with the new regulations, however, as to testing now being carried out by the Home Office, it will probably fail to pass the drastic test of being fired direct without tamping into coal dust and air and coal gas and air.

The old test on which the present permitted list is passed consisted in firing shots from the test cannon into a mixture of 15 per cent. coal gas and 85 per cent. air, the cartridge being stemmed in the cannon with a definite column of dried china clay. If the gas mixture was not fired in twenty consecutive shots with 12 inches of stemming and ten shots with 9 inches of stemming, no residue being left, the strength of the charge being equal to 4 ounces of Dynamite No. 1, then the explosive was "permitted."

In the second class of "Sprengel explosives," in the sense of the ingredients being mixed immediately before they are used, none are employed in England, but their place has been taken by what are now known as ammonium nitrate explosives, and which also have the advantage of being included in the present "permitted list" for use in fiery mines.

Roburite, as introduced by Dr. Carl Roth, was a simple mixture of ammonium nitrate with chlorinated meta-di-nitro-benzene, but its composition now is—

Ammonium nitrate	87
Chlorinated compound	1
Di-nitro-benzene	12
	100

The ammonium nitrate is first dried and ground, then heated in a closed steam-jacketed vessel to a temperature of 80° C.; the melted organic compound is added, and the whole stirred until an intimate mixture is obtained. On cooling, the yellow powder is ready for use, and is stored in air-tight canisters or is made up into cartridges. Owing to the deliquescent nature of the ammonium nitrate, the finished explosive must be kept out of contact with the atmosphere, and for this reason the cartridges are waterproofed by dipping them in melted wax.

This mixture is not exploded by ordinary percussion, firing, or electric sparks. If a layer of the explosive is struck a heavy blow with a hammer, the portion directly receiving the blow is decomposed owing to the heat developed, but no detonation whatever takes place, nor are those portions of the substance around the spot struck in any way affected; whilst, if roburite be mixed with gunpowder and the gunpowder be then ignited, the latter explodes and scatters the roburite without firing it.

The roburite can only be exploded by a specially powerful detonator, and on decomposition the gases evolved contain no combustible constituents, but consist only of carbon dioxide, water, and nitrogen, with a small trace of hydrochloric acid gas, which is at once condensed by the large volume of water vapour evolved, and gives rise to no inconvenience.

The only objection that can be raised to it is that the nitro-benzenes are all poisonous, and that the manufacture, therefore, is liable to be injurious to the workmen unless proper precautions are taken.

There are many other explosives of the same character, using such nitrated organic compounds as di-nitro-naphthalene, tri-nitro-toluene, etc., to mix with the ammonium nitrate, whilst potassium or sodium nitrates often replace some of the latter.

The third class of blasting explosives consists of nitro-glycerin absorbed by various substances, which will render it less liable to accidental detonation.

For blasting purposes nitro-glycerin was at one time very extensively used; the fact of its being unaffected by moisture gave it a great advantage, whilst the rapidity of its explosion made it only necessary to prepare a bole-hole, partly fill it with nitro-glycerin, and then fill up the hole with water; the water forming just as good a tamping for the nitro-glycerin, when fired by detonation, as if the hole had been plugged with wood or metal.

The use of nitro-glycerin for blasting purposes is, however, attended with several inconveniences; being fluid it can only be used in downward bore-holes, whilst its transport in the liquid form has given rise to many accidents; finally, the liquid state is not very suitable for detonation, as the fluid yields to the sudden blow, and is often scattered instead of being completely exploded, so reducing its power, and becoming a source of danger in subsequent operations. In order to avoid these drawbacks, Nobel made the nitro-glycerin into certain plastic preparations by mixing it with various absorbent substances, and these mixtures, in many cases, have a higher explosive power than the nitro-glycerin itself.

Dynamite.—These nitro-glycerin preparations to which Nobel gave the name of dynamite may be divided into two classes: first, those containing non-explosive absorbents; and, secondly, those with explosive absorbents. The majority of these will be considered below.

When first working in this direction, in 1866, Nobel used charcoal as an absorbent for nitro-glycerin, and, encouraged by the success of his experiments, tried various other bodies which were capable of taking up and holding the nitro-glycerin, and he came to the conclusion that the infusorial earth first found at Oberlohe, in Hanover, gave the most satisfactory results. This earth consisted of the remains of diatoms, and contained 95 per cent. of silica, which is so finely divided as to be free from any grit, and which, after having been heated to a moderate temperature to remove moisture and organic matter, can be ground and sifted.

This substance is called kieselguhr, and is mixed with three times its weight of nitro-glycerin, the mixture being made by hand kneading. It is sometimes squeezed by hand through the meshes of a coarse sieve, and sometimes is forced out of a metal tube by means of a peculiarly constructed Archimedean screw, the resulting mass being cut into lengths to form cartridges of the required size.

During the mixing of the substance 8 per cent. of sodium carbonate, barium sulphate, mica, talc, ochre, and ammonium carbonate, are allowed to be added to it. This substance is generally known by the name of dynamite No 1. In the large factory at Ardeer, the kieselguhr employed comes from Aberdeenshire, and is of considerable purity, containing 98 per cent.

of silica, whilst in France a similar earth, called "Rhandanite," is employed.

The finished dynamite is a semi-plastic substance of a reddish-brown colour, containing 75 per cent. of nitro-glycerin and has a specific gravity, as made at Ardeer, of about 1·6. Under normal conditions dynamite can be set fire to by the application of a flame, and even when in considerable quantity can be burnt in this way without explosion, but, like nitro-glycerin, if the temperature rises above a certain limit, the combustion increases in rapidity until the temperature of detonation is reached.

This phenomenon of the increase in the rate of combustion and consequent increase in temperature is found in all substances capable of undergoing detonation. If a mixture of nitrogen dioxide and carbon disulphide be inflamed in an open-mouthed jar, not more than eight or ten inches in height, it burns quietly, emitting a most brilliant light, but if a long cylinder be employed, the flash of light is seen in the upper part of the cylinder, whilst the mixture in the lower portion violently explodes. The same phenomenon may be observed when burning mixtures of acetylene and air, as with a long tube or cylinder containing a mixture, the combustion will often commence quietly with deposition of large volumes of carbon, but the flame rapidly becomes quicker and quicker until the last portion of the mixture detonates and generally breaks the vessel to pieces. In the case of gun-cotton also, it is well known that small quantities burn away perfectly quietly, but large masses will first burn in the ordinary way, then the temperature generated will often rise until the remainder explodes.

Dynamite, like nitro-glycerin, freezes at a temperature of about 4° C. The frozen cartridges are less sensitive to shock and detonation, and therefore have to be thawed before use for blasting purposes, and it has been found that frozen dynamite burns very slowly, the first portion of the heat being used to thaw the substance before combustion takes place, but the burning frozen dynamite cartridges are much more likely to explode than when the dynamite is in its ordinary state.

Dynamite is not so easily detonated by shock as nitro-glycerin, and Berthelot states that this is due to the inert mass present having a cushioning effect upon the mechanical force of the blow, the energy imparted being divided between the absorbent and the nitro-glycerin, and for the same reason the dynamite is less crushing in its action than nitro-glycerin, because the heat evolved in its detonation is shared between the products of explosion and the inert body present.

Experiments made by Sir Frederick Abel gave a velocity of propagation of detonation in dynamite as 20,000 feet per second, but the experiments having been made with half-inch cartridges placed end to end in a continuous train, forty-two feet in length, the break in the homogeneous nature of the train may have introduced error into the result.

It is interesting to note that experiments made by General Abbott in submarine mining, show that the intensity of the action of such dynamite containing 75 per cent. of nitro-glycerin is greater than that of nitro-glycerin itself, and a confirmation of this was obtained in the fact that Sir Frederick Abel found the rate of detonation of dynamite was much quicker than that of nitro-glycerin ; this, however, being to a certain extent due to the liquid particles of the latter having a tendency to escape from the blow of the detonator.

One of the great troubles with kieselguhr dynamite is that under certain conditions some of the nitro-glycerin will exude from it, this being specially the case when wet or placed in water.

Lithofracteur is composed of nitro-glycerin mixed with an equal weight of a mixture of sawdust, kieselguhr, and barium nitrate, and generally also contains a small trace of sulphur.

Carbonite consists of twenty-five parts of nitro-glycerin mixed with no less than forty parts of wood meal, and about thirty-four parts of sodium or potassium nitrate, and there are about thirty explosives of much the same character (see p. 313).

All these mixtures, unless properly protected, are liable to the great drawback of occasionally exuding nitro-glycerin, especially if water be present, and then they become highly dangerous to use, whilst another serious drawback is their liability to freeze, which will take place by continued exposure to a temperature of 4° C., or even slightly higher.

Blasting Gelatine.—The other class of dynamite explosives, namely, nitro-glycerin absorbed by an explosive agent, was invented by Mr. A. Nobel, who discovered that nitrated cotton would dissolve in nitro-glycerin with the formation of a solid product. In practice, ninety-three parts of nitro-glycerin are heated in a copper water-bath to about 45° C., and seven parts of nitrated cotton—a mixture of mono- and di-nitro-cellulose—stirred in gradually. As the cotton dissolves the mixture gelatinises, and on cooling solidifies. This substance, called " blasting gelatine," is semi-transparent, of specific gravity 1·5 to 1·6, and is not altered by submergence in water. It freezes at 4° C., but, unlike kieselguhr dynamite, it is very easily exploded in this state by shock. A bullet *may* be fired through a heap of unfrozen cartridges of blasting gelatine without any explosion, whilst similarly fired through frozen cartridges it never fails in exploding them.

Gelatine Dynamite and Gelignite are prepared by adding potassium nitrate and wood meal to the blasting gelatine in varying proportions.

The addition of 4 per cent. of camphor to the blasting gelatine increases the solidity, and at the same time makes the mixture less sensitive to shock. This preparation is made and sold under the name of camphorated gelatine.

Nitro-magnite, dyna-magnite, forcite, Giant powder, Vulcan powder, Atlas powder, Judson powder, Hercules powder, and Lignin dynamite, are all modifications of the above forms of dynamite and blasting gelatine that have been used here or abroad.

Safety Explosives.—It has been shown (p. 307) that for coal mining, especially where dust or fire-damp are found in the mine, only " permitted " explosives are allowed, and as it is certain that every explosive, if used in a sufficiently large charge, will, under certain circumstances, give rise to an explosion of fire-damp or dust and air, succeeding generations of legislators have been making the tests that the explosives have to satisfy more and more drastic in their attempts to attain the impossible—absolute security.

The routine adopted to get an explosive on the permitted list for the last fifteen years has been to submit it to the Home Office, it is then analysed and tested by friction and heat to make sure it is sufficiently insensitive to give safety in handling, and it has then to undergo the practical test at Woolwich of firing from a cannon into a mixture of air and 15 per cent. coal gas (p. 307), the cartridge being tamped as it would be in firing in the mine. If it passes this test it is tried for power in the ballistic pendulum, which consists of a mortar or cannon hung on a pendulum. A fixed charge with a definite amount of tamping is then fired, and the swing of the pendulum, induced by the recoil, is measured, and gives a comparison with a standard explosive—Dynamite No. 1.

The following list gives the names of the explosives that passed this test :—

ENGLISH PERMITTED LIST, 1912.

Nitro-glycerin explosives.

Arctic carbonite
Arkite
Britonite
Cambrite
Carbonite
Celtite
Cliffite
Clydite
Cornish powder
Dominite
Dragonite
Extra carbonite
Fracturite
Haylite No. 1
Kolax
Kynite
Kynite condensed
Nobel carbonite
Normanite
Oaklite No. 1
Phœnix powder
Pitite
Rexite
Rippite
Russelite
Samsonite
Stowite
Swalite
Tutol
Victorite

Ammonium nitrate explosives.

Ammonite
Amvis
Aphosite
Bellite No. 1
Bellite No. 3
Curtisite
Dahmenite A
Dreadnought powder
Electronite
Faversham powder
Fortex
Good luck
Kentite
Minite
Negro powder
Odite
Ripping ammonal
Roburite No. 3
St. Helen's powder
Stomonal
Titanite No. 1
Virite
Westfalite No. 1
Westfalite No. 2
Withnell powder

Mixed.

Bobbinite
Colliery steelite
Excellite
Monobel
Nobel Ammonia powder
Oaklite No. 2
Permonite

The nitro-glycerin explosives differ more in name than nature, nearly all of them consisting of nitro-glycerin mixed with potassium nitrate and some form of carbonaceous compound, such as starch, wood meal, etc. The potassium nitrate by its decomposition absorbs heat and supplies only enough oxygen to the carbonaceous material to burn it to carbon monoxide, so reducing the high temperature of explosion of the nitro-glycerin. An example of this class of "permitted" explosives is—

Carbonite, which has the composition—

Nitro-glycerin	25·0
Potassium nitrate	30·5
Barium nitrate	4·0
Wood meal	40·0
Sodium carbonate	0·5
	100·0

Now nitro-glycerin has a calorific value of about 1600 calories per kilo., but the heat abstracted by the decomposition of the potassium nitrate and low heat of combustion of the carbon in the wood meal, when burnt to carbon monoxide, bring down the calorific value of carbonite to 576 calories per kilo.

Of the second class, Roburite No. 3 has already been described, and may be taken as the type, whilst the third or mixed class consists of explosives like bobbinite, a powder explosive; colliery steelite, a mixture chiefly consisting of resin and potassium chlorate; or mixtures which really belong to the ammonium nitrate class, but have 4 or 5 per cent. of nitro-glycerin mixed with them to ensure complete detonation.

On the Continent and in America explosives for coal mining have for some time past been tested for safety by firing them unstemmed into testing galleries containing first a mixture of air with 8 per cent. of pit gas, and then into a mixture of air and fine coal dust, it being found that the mixtures separately are more sensitive than when coal dust is suspended in a mixture of air and gas, the reason being that to render air and coal dust explosive the air must contain over 19 per cent. of oxygen, and the admixture of gas by lowering the percentage renders the test less sensitive.

The Home Office, in order to fall into line with other countries, is now altering the method of testing, and has erected a well-arranged station at Rotherham, where, in future, all explosives for the permitted list will be tested in the same way as above, *i.e.* by firing the charge untamped into a mixture first of gas and air and then into coal dust and air.

This will have the effect of condemning a very large percentage of the present permitted explosives, as tamping exercises a most powerful effect in preventing the ignition of gas or dust and air mixtures, and some explosives which untamped fire the mixtures with 50 grams, will pass with ten times that charge when tamped.

In the new test the size of the charge necessary to ignite either of the mixtures will be arrived at by gradually increasing the charge, 2 oz. at a time, and the biggest charge which fails to ignite either will be known as the "maximum charge," or *charge limite,* as it is called on the Continent.

The Rotherham test will in one respect at least be more severe than in some of the Continental galleries, as the explosion chamber is less in diameter, and this exercises a marked difference in making the test more sensitive, whilst the igniting point of coal gas and air is slightly lower than that of pit gas, which consists chiefly of methane.

It seems a pity that whilst the authorities were making such a drastic change in attempting to increase the safety from explosions, they should not have taken steps to also prevent the introduction of explosives which give large volumes of carbon monoxide, which is not only one of the most deadly poisons, but also in even small traces makes dusty air highly explosive, and it is to be feared that watering down the explosives to reduce them to a point that will enable them to pass the Rotherham test, will give rise to more than one unforeseen danger in other directions.

The temperature of explosion is always high, as will be seen from the following table of the temperatures developed by the more prominent explosives :—

	°C.
Blasting gelatine	3220
Nitro-glycerin	3170
Dynamite	2940
Gun-cotton	2650
Tonite	2648
Picric acid	2620
Gunpowder	2200
Roburite	2100

The temperature at which mixtures of methane and air ignite is between 650° and 700° C., and although the temperatures of explosion are so enormously high, they only occasionally ignite an inflammable mixture of the gases, this being due to the fact that in order to ignite fire-damp, not only must the temperature of ignition be reached, but it must be sustained for several seconds before the gases inflame, and as the explosion by detonation is instantaneous, ignition does not occur ; if, however, some of the charge burns instead of detonating, the gaseous mixture is fired.

Bichel has shown that the important factors in bringing about explosion in a gaseous mixture are (*a*) the length of the flame, (*b*) its duration, (*c*) its temperature. The ratio of the duration of the flame to the rate of detonation (called the "after-flame ratio") is an excellent indication of the relative safety of blasting explosives ; where this is high, as in blasting gelatine, the explosion is extremely likely to cause ignition of fire-damp, whilst when it is low, as in the usual " safety " explosives, the risk is reduced to a minimum.

With mixtures of carbon monoxide and air, however, if coal dust be present, ignition takes place directly the required temperature is reached (650° C.).

FULMINATES AND DETONATORS.

Fulminates.—Nearly all explosives are now fired by means of a cap or detonator, which generally consists of a small copper cylinder charged with one of the class of bodies called fulminates, or mixtures in which they play an important part. The fulminate generally used is mercuric fulminate ($HgC_2N_2O_2$), made by acting upon mercury with nitric acid and alcohol. It may be made on a small scale by dissolving 3 grams of mercury in 36 grams (27·7 c.c.) of nitric acid having a specific gravity of 1·36. As soon as it is all dissolved, and whilst the solution is still yellow from presence of nitrous fumes, take 34·5 grams (43 c.c.) of 90 per cent. alcohol, and add one-half; a violent action takes place, and when this ceases, the second portion of alcohol is added, and the mixture allowed to stand, when the mercuric fulminate crystallises out in small needle-shaped crystals, which have a greyish colour from the presence of a trace of free mercury.

When made on a large scale the operation is a little different, the mercury being dissolved in the nitric acid and the solution allowed to cool; the alcohol is then added in one operation, which is carried out in an open shed in a large retort, and the escaping fumes condensed and utilised. The fulminate so obtained is well washed with distilled or rain water until free from all acid, and is stored whilst still containing 20 per cent. of moisture.

The changes taking place during the formation of mercuric fulminate are not very thoroughly understood, but the general action may be looked upon as resulting in the solution of mercury in nitric acid with the production of mercuric nitrate and nitrous acid, these products further reacting with the alcohol—

$$\overset{\text{Mercuric nitrate}}{Hg(NO_3)_2} + \overset{\text{Nitrous acid}}{2(HNO_2)} + \overset{\text{Alcohol}}{C_2H_6O} = \overset{\text{Mercuric fulminate}}{HgC_2N_2O_2}$$

$$+ \overset{\text{Water}}{3(H_2O)} + \overset{\text{Nitric acid}}{2(HNO_3)}$$

Mercuric fulminate is very heavy, having a specific gravity of 4·4, and it is easily detonated either by a blow, by friction, by touching it with a wire heated to 190° C., by an electric spark, or by contact with strong sulphuric or nitric acids, when it is instantaneously decomposed into—

$$\underset{\text{Mercuric fulminate}}{HgC_2N_2O_2} = \underset{\text{Mercury}}{Hg} + \underset{\text{Carbon monoxide}}{2(CO)} + \underset{\text{Nitrogen}}{N_2}$$

with a sharp flash and evolution of greyish fumes of mercury. The rapidity of its explosion is so great that, when exploded in contact with any easily decomposable body, the vibration which it sets up travels through the mass with the rapidity of sound and affects the whole almost instantaneously, giving rise in many cases to the most rapid form of explosion, known as detonation. Berthelot has shown that even stable gases, such as nitrogen dioxide, acetylene, and cyanogen, can be decomposed into their elementary constituents by the detonation of mercuric fulminate.

The high specific gravity of mercuric fulminate (4·4) and the rapidity of its explosion make it the best detonating agent in practice, besides which, volume for volume, it is the most powerful of the explosives.

One gram of the fulminate yields 235 cubic centimetres of gas, or 1030 times its own volume of gas measured at normal temperature and pressure, whilst the 403 units of heat evolved expand this volume enormously, and it has been calculated that the pressure generated at the moment of explosion is over 6000 atmospheres.

If a small train of mercuric fulminate is laid on a metal plate and some gunpowder is placed on it and the fulminate fired, the powder will be scattered but not ignited, the explosion being too rapid to communicate itself to the powder; if, however, a little finely powdered potassium chlorate is mixed with the fulminate, the flame will be increased and the powder ignited. This can be explained when it is considered that carbon monoxide, which is evolved by the decomposition of the fulminate, is oxidised to carbon dioxide by the oxygen from the chlorate, thus increasing the flame and the temperature.

Advantage is taken of this fact in the preparation of composition for percussion caps, in which the fulminate is mixed with potassium chlorate, and sometimes with antimony sulphide, glass powder being often added to increase the friction and so make the cap more sensitive to percussion. A small quantity of the mixture having been put into the cap or detonator, a drop of shellac dissolved in spirit is added, which causes the mixture to adhere to the metal and also gives it a waterproof coating.

Nobel's detonators contain a mixture of 70 per cent. fulminate and 30 per cent. potassium chlorate, and fulminate is also employed in varying charges in all the Service fuses.

The detonator is ignited either by the insertion of a piece of slow burning fuse, or by electricity.

In the Service in firing by electricity low tension fuses are used. These consist of a small primer, containing a few grains of powdered gun-cotton mixed with a little gunpowder, which is in touch with a small bridge of fine platinum or iron wire connected with the ends of two wires communicating with the poles of a battery. On passing the current the wire fuses and ignites the priming mixture, which causes the ignition of the mercuric fulminate, and this in turn brings about the detonation of the explosive. For blasting purposes high tension fuses are generally employed when firing by electricity. In this case a priming mixture, composed of an intimate mixture of native antimony sulphide, copper sulphide and potassium chlorate, is ignited by means of a spark passing between the terminals of two wires connected with a magneto machine, the mixture being confined in a small paper case which is inserted into the detonator.

Silver fulminate ($Ag_2C_2N_2O_2$) is made in the same way as mercuric fulminate, silver being used instead of mercury; it is, however, far more sensitive and dangerous than the mercuric salt, and is only used in small quantities for "pull" and "throw down" crackers.

Detonators made of tetra-nitro-methyl-aniline, known as "tetryl detonators," are now largely used with some safety explosives.

CHAPTER XX

SULPHUR AND SULPHUR COMPOUNDS

Sulphur is one of the few elements found uncombined in Nature, large quantities occurring as deposits in most volcanic districts, and it was from beds of this native sulphur found in Sicily that for many years the sulphur was obtained for the sulphuric acid and gunpowder factories in this country; but the imposition of a heavy tax upon the export caused manufacturers to seek other sources of supply. At the present time most of the sulphur used in this country is obtained from iron pyrites, a double sulphide of iron and copper, which is obtained in considerable quantities in various parts of the world, and from which sulphur can be obtained by a process of distillation. The sulphides of the metals are as a rule their most common ores, and besides the enormous amount of sulphur combined as sulphide, it is also extensively distributed in combination with metals and oxygen as sulphates, such as gypsum (calcium sulphate), heavy spar (barium sulphate), Epsom salts (magnesium sulphate), etc.

To obtain sulphur from the mixture of marl, limestone or gypsum with which it is found native, a heap is generally made and some of the sulphur kindled, which by its combustion melts the remainder, and on choking out the fire the melted sulphur runs from the bottom of the heap; or the crude mixture may be heated in iron vessels by superheated steam which melts the sulphur, causing it to flow away from the impurities with which it was mixed, and it is then run into wooden moulds.

When iron pyrites is heated out of contact with air, it gives off one-third of its sulphur, a reaction which may be represented by—

$$\underset{\text{Iron pyrites}}{3FeS_2} = \underset{\text{Triferric tetra-sulphide}}{Fe_3S_4} + \underset{\text{Sulphur}}{S_2}$$

The purification of the crude sulphur is effected by distillation, a type of plant commonly used for the purpose being shown in Fig. 44.

The crude material is melted in the pot (A) by the waste heat from the fire-place below, and suitable quantities can be run from time to time into the retort (B), from which it distils as vapour into the large condensation chamber (C). The first quantities of vapour passing into a cool chamber condense in a fine crystalline form (*flowers of sulphur*), but as the chamber becomes hot the whole of the sulphur passing into it condenses as a liquid which is run off by means of a suitable plug (D) into cylindrical wooden moulds, forming *roll sulphur*.

Sulphur is remarkable for the number of different forms in which it can exist and the changes which it undergoes when heated.

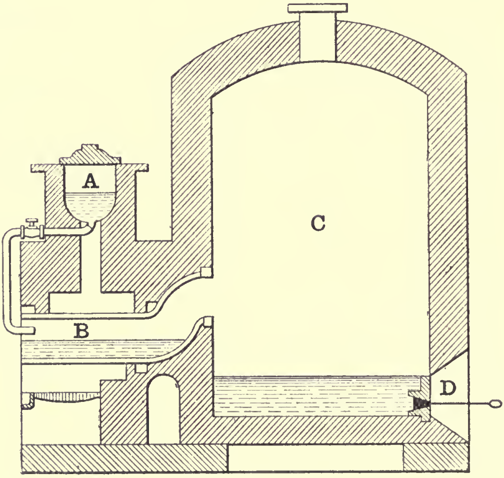


Fig. 44.—Sulphur refining.

Modifications of Sulphur.—At very low temperatures sulphur is nearly white, but at ordinary temperatures it has a straw-yellow colour; when heated to 115° C. it melts to an amber coloured liquid, which is as fluid as water, and on allowing this to cool a crust forms on the outside of the mass. If holes are broken in this crust, and the still fluid portion is poured out from the interior, the remaining sulphur is found to have crystallised in needle-shaped oblique prisms which are perfectly transparent when freshly made, but which soon become opaque on keeping, due to the mass having become converted into minute rhombic octahedra, a change attended with evolution of heat.

On heating sulphur above 115° C., it gradually darkens in colour and becomes more and more viscid, until at 180° C., it is nearly black and so thick that the vessel in which it has been melted can be turned upside down without any running out. Some change in condition of the sulphur evidently occurs about this point, as, if a thermometer is immersed in the sulphur, it remains stationary, although heat is being poured into the sulphur, showing that heat is being rendered latent; after a short time, however, the temperature again begins to rise, the viscid sulphur becoming more and more liquid, until at 250° C. it can again be freely poured out, although it is not so liquid as at 115° C. If sulphur liquefied at 260° C. is poured in a thin stream into a large vessel of water, it forms an elastic semi-transparent mass, very much resembling india-rubber; but this plastic form is not permanent, and on keeping gradually becomes yellow and brittle, being reconverted to the crystalline condition, and if the mass be broken up and examined under a magnifying glass the particles will be seen to be octahedral in form.

This change from the plastic to the crystalline form is attended with evolution of the heat rendered latent at 180° C., and the two forms of sulphur exhibit such wide differences in their behaviour that they are looked upon as allotropic modifications of the element. Plastic sulphur is only partly soluble in carbon disulphide, but both the crystalline varieties readily dissolve, and if the solvent is allowed to spontaneously evaporate, the sulphur is left in octahedral crystals of the same form as that in which it is found native. The crystalline sulphur soluble in carbon disulphide has been shown to be electro-negative to the insoluble forms of sulphur. On continuing to heat sulphur above 260° C., no further change takes place until 444° C. is reached, when it boils and is converted into vapour.

Three chief forms of sulphur are described—the octahedral, the prismatic, and the plastic or "*amorphous*" (*i.e.* without crystalline form), while the fact that it forms two distinct kinds of crystals causes it to be classed with those substances which are called "*dimorphous*" (having two crystalline forms). Sulphur has an atomic weight of 32. The existence of various forms of sulphur may to a certain extent be explained by the presence of a varying number of atoms in the molecule, and this idea is supported by the density of sulphur vapour, which at 500° C. is 96, but steadily diminishes with increase of temperature above 700° C. and becomes constant at 1000° C. when it is 32. At 500° C. therefore the molecule of sulphur must contain six atoms instead of two, and it is quite possible that at lower temperatures a further increase in the number of atoms in the molecule may take place.

Sulphur in its combining power very much resembles oxygen, and it will enter directly into combination with all the non-metals, with the exception of nitrogen, and with most of the metals.

Compounds of Sulphur.

Hydrogen Sulphide or **Sulphuretted Hydrogen** (H_2S) was discovered by Scheele in 1777, and exists free in Nature in the gases evolved from volcanoes, in certain mineral waters, such as those of Harrogate, and is formed when organic substances containing sulphur undergo putrefactive decay, hence its presence in sewer gas, stale eggs, etc.

Sulphuretted hydrogen can be made by the direct combination of its constituents, the gas being produced when hydrogen is passed over or through boiling sulphur; the method usually employed for its preparation, however, consists of decomposing a metallic sulphide with an acid.

When ferrous sulphide (made by fusing together sulphur and iron) is acted upon by dilute sulphuric or hydrochloric acid, the gas is evolved in abundance, with formation of a sulphate or chloride of the metal, the action taking place in the cold—

$$\overset{\substack{\text{Ferrous}\\\text{sulphide}}}{FeS} + \overset{\text{Sulphuric acid}}{H_2SO_4} = \overset{\substack{\text{Ferrous}\\\text{sulphate}}}{FeSO_4} + \overset{\substack{\text{Hydrogen}\\\text{sulphide}}}{H_2S}$$

This method is usually adopted in making the gas for laboratory use; but since the iron sulphide invariably contains particles of metallic iron, hydrogen always contaminates the gas. Pure sulphuretted hydrogen can be obtained by heating together antimony sulphide and hydrochloric acid.

$$\overset{\substack{\text{Antimony}\\\text{sulphide}}}{Sb_2S_3} + \overset{\substack{\text{Hydrochloric}\\\text{acid}}}{6(HCl)} = \overset{\substack{\text{Antimony}\\\text{chloride}}}{2(SbCl_3)} + \overset{\substack{\text{Hydrogen}\\\text{sulphide}}}{3(H_2S)}$$

Properties.—Sulphuretted hydrogen is a colourless gas, having a sweet taste and the odour of rotten eggs, and when present in the air in any quantity is very poisonous. Under a pressure of 17 atmospheres, or at —74° C., it may be condensed to a colourless liquid which freezes at —86° C. The gas can be decomposed by heat and is freely soluble in water, which dissolves 4·37 times its bulk of the gas at 0° C. It has a feeble acid reaction, and burns in oxygen or air. If the supply of oxygen is abundant, the sulphuretted hydrogen burns forming water and sulphur dioxide—

$$\overset{\text{Sulphuretted hydrogen}}{H_2S} + \overset{\text{Air}}{3(N_4 + O)} = \overset{\text{Water}}{H_2O} + \overset{\text{Sulphur dioxide}}{SO_2} + \overset{\text{Nitrogen}}{6N_2}$$

If, however, the supply of air is small and the quantity of oxygen therefore limited, the hydrogen burns forming water, and sulphur is deposited.

The gas is decomposed by chlorine, bromine or iodine, with deposition of sulphur—

$$\overset{\text{Sulphuretted hydrogen}}{2(H_2S)} + \overset{\text{Chlorine}}{2Cl_2} = \overset{\text{Hydrochloric acid}}{4(HCl)} + \overset{\text{Sulphur}}{S_2}$$

It is also decomposed by nitric and sulphurous acids.

The tarnishing of silver in the air of towns is due to the traces of sulphuretted hydrogen present, for which silver has a great affinity, combining with it to form black silver sulphide.

The action of sulphuretted hydrogen on solutions of metallic salts is of great value in analysis, and it is for this purpose that the gas is chiefly used. By its aid the metals are separated into three main groups :—1. Metals, the sulphides of which are insoluble in dilute hydrochloric acid ; 2. Metals which form sulphides soluble in dilute hydrochloric acid, but insoluble in neutral or alkaline solutions ; and 3. Metals which form sulphides soluble in water.

Composition.—The composition of sulphuretted hydrogen can be ascertained by heating metallic tin in a known volume of the gas, when the tin combines with the sulphur forming a solid sulphide, whilst the liberated hydrogen occupies the same volume as the gas taken—

$$\underset{\text{2 vols.}}{\overset{\text{Sulphuretted hydrogen}}{SH_2}} + \overset{\text{Tin}}{Sn} = \overset{\text{Stannous sulphide}}{SnS} + \underset{\text{2 vols.}}{\overset{\text{Hydrogen}}{H_2}}$$

therefore, like steam, sulphuretted hydrogen contains its own volume of hydrogen.

The molecular weight of the gas is 34 and its density 17. An aqueous solution of sulphuretted hydrogen has the same chemical properties as the gas itself, and in many cases is a very convenient solution for use in analysis, but it must be remembered that a solution of the gas rapidly oxidises, the oxygen originally dissolved in the water and absorbed from the air combining with the hydrogen, whilst sulphur is precipitated.

Sulphuretted hydrogen can be detected at once by its fœtid odour, and by its turning a piece of paper moistened with lead acetate solution black, owing to the formation of black lead sulphide.

THE OXIDES OF SULPHUR.

Sulphur combines with oxygen in two proportions to form sulphur dioxide (SO_2) and sulphur trioxide (SO_3).

Sulphur Dioxide, sulphurous anhydride, or sulphurous acid as it is sometimes called, has been known from the earliest times, Homer and Pliny mentioning the irritating nature of the fumes given off by burning sulphur, whilst its properties were investigated by Stahl and by Priestley in 1774, the latter demonstrating its true composition by the combustion of sulphur in oxygen. Like sulphuretted hydrogen, it is found free in the gases issuing from volcanoes, and is always formed when sulphur or sulphur compounds are burnt in air or oxygen—

$$\overset{\text{Sulphur}}{S_2} + \overset{\text{Oxygen}}{2O_2} = \overset{\text{Sulphur dioxide}}{2(SO_2)}$$

Preparation.—When the gas is required pure, it is prepared by heating a metal such as mercury or copper with strong sulphuric acid, when—

$$\overset{\text{Copper}}{Cu} + \overset{\text{Sulphuric acid}}{2(H_2SO_4)} = \overset{\text{Copper sulphate}}{CuSO_4} + \overset{\text{Sulphur dioxide}}{SO_2} + \overset{\text{Water}}{2(H_2O)}$$

In the same way when strong sulphuric acid is heated with carbon or organic matter, sulphur dioxide is evolved, but in this case carbon dioxide is formed at the same time.

$$\overset{\text{Carbon}}{C} + \overset{\text{Sulphuric acid}}{2(H_2SO_4)} = \overset{\text{Carbon dioxide}}{CO_2} + \overset{\text{Sulphur dioxide}}{2(SO_2)} + \overset{\text{Water}}{2(H_2O)}$$

Properties.—It is a colourless gas, having a strong, pungent odour and an acid taste and reaction; it is freely soluble in water and in alcohol, and can be reduced to a liquid by a pressure of three atmospheres, or by a temperature of −18° C. and can be solidified at −76° C. Liquid sulphur dioxide will dissolve phosphorus, sulphur and iodine. Sulphur dioxide has a molecular weight of 64 and a density of 32.

Nearly all classes of coal contain small traces of sulphur, which, during combustion, is converted into sulphur dioxide and escapes into the air; when present in even small traces, it acts mostly injuriously upon vegetable life, one part in 10,000 of air being fatal to plants, whilst four parts in 10,000 render air irrespirable.

The gas does not burn or support combustion; indeed, its power of extinguishing fire has led to its use in several of the so-called "grenades" and "fire-extinguishers," and a handful of sulphur thrown on the fire in the grate is one of the oldest and best known remedies for a chimney on fire.

Moist sulphur dioxide has a strongly acid reaction, and its solution in water may be looked upon as a sulphurous acid (H_2SO_3), as although this compound has not been isolated, yet when the solution is acted upon by bases, hydrogen is replaced by the metal of the base, and the class of salts called sulphites is obtained.

$$\underset{\text{Sulphurous acid}}{H_2SO_3} + \underset{\text{Sodium oxide}}{Na_2O} = \underset{\text{Sodium sulphite}}{Na_2SO_3} + \underset{\text{Water}}{H_2O}$$

Sulphurous acid when left exposed to air gradually takes up oxygen and becomes sulphuric acid (H_2SO_4), and this tendency to undergo oxidation renders sulphurous acid a powerful reducing agent.

Bleaching.—Moist sulphur dioxide or sulphurous acid is also a powerful bleaching agent, but does not so completely destroy the colouring matter as in the case of bleaching by chlorine, for the colour may in many cases be restored by acting upon the substance with a stronger acid or an alkali, an example of this being the turning yellow of blankets, the wool of which has been bleached with sulphurous acid. It is largely used for bleaching straw, wool, and silk, and is also employed as a deodoriser and as an antiseptic to prevent fermentation and decay.

Sulphur Trioxide.—Under ordinary conditions sulphur dioxide will not directly combine with more oxygen, but if a mixture of sulphur dioxide and oxygen be passed over heated platinum or platinised asbestos, the strong surface action exercised by the platinum causes combination to take place, and dense white fumes of sulphur trioxide (SO_3) are formed. The trioxide is most conveniently prepared by warming Nordhausen sulphuric acid, which consists of sulphur trioxide dissolved in sulphuric acid. Under the influence of heat the sulphur trioxide is driven off, and may be condensed in a cooled receiver.

$$\underset{\text{Nordhausen acid}}{H_2S_2O_7} = \underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Sulphur trioxide}}{SO_3}$$

Sulphur trioxide is a white silky crystalline body, having a specific gravity of 1·95 and melting at temperatures varying between 15° C. and 32° C., according to its crystalline condition; when exposed to air it yields dense white fumes, and absorbing moisture, rapidly becomes liquid. At a high temperature it is decomposed into oxygen and sulphur dioxide. When free from moisture it is not acid to dry litmus, but becomes acid immediately on absorbing moisture. On bringing it in contact with water it combines with it energetically, giving off great heat and hissing as if red hot iron had been plunged into the water, instantly forming sulphuric acid (H_2SO_4), a method now largely employed for the commercial production of sulphuric acid.

$$\underset{\text{Sulphur trioxide}}{SO_3} + \underset{\text{Water}}{H_2O} = \underset{\text{Sulphuric acid}}{H_2SO_4}$$

Sulphuric acid, hydrogen sulphate or oil of vitriol (H_2SO_4) is the most important of the acids.

It is used to an enormous extent in the arts and manufactures; indeed, so many industries are dependent upon it that Liebig has said with considerable truth that "the civilisation of a country may be roughly gauged by the amount of sulphuric acid manufactured in it."

The old chamber method of manufacturing sulphuric acid may be said to date from 1786, when Dr. Roebuck made the acid by burning sulphur with saltpetre in leaden vessels and condensing the fumes in water. Large quantities are now made by the "contact" process, whereby sulphur dioxide is directly converted into the sulphuric anhydride SO_3.

The principle of the older method at present employed is the same as that of Roebuck's process, and is that whilst sulphur dioxide is not able, even in presence of water, to rapidly absorb oxygen from the air, it can readily take it from some of the oxides of nitrogen, which, in turn, can again take oxygen from the air, and may in this way be made the medium for rapidly oxidising sulphur dioxide in the presence of water, with formation of sulphuric acid. The manufacture of sulphuric acid therefore involves four distinct processes: (*a*) the generation of sulphur dioxide in large quantities, (*b*) the constant production of small quantities of oxides of nitrogen, (*c*) the generation of steam, (*d*) provision of large chambers in which these various gases can interact with the formation of sulphuric acid.

The usual arrangement in a modern sulphuric acid works is illustrated in a diagrammatic manner in Fig. 45. Iron pyrites is thrown into heated chambers (A) to which there is easy access of air, which maintains the combustion of the sulphur present in the pyrites to sulphur dioxide. This gas, together with air and excess of nitrogen, passes through the tower (E) (to be described later), along the large main (*e*), near the bottom of which another smaller pipe leads in the gases from the nitre pots (B). These pots are situated over a smaller series of pyrites burners, the hot gases from which circulating around them generate nitric acid from a mixture of nitre (sodium nitrate) and sulphuric acid.

The sulphur dioxide and nitric acid interact with the production of sulphuric acid and nitrogen tetroxide.

$$\underset{\text{Sulphur dioxide}}{SO_2} + \underset{\text{Nitric acid}}{2(HNO_3)} = \underset{\text{Sulphuric acid}}{H_2SO_4} + \underset{\text{Nitrogen tetroxide}}{2(NO_2)}$$

A mixture of sulphur dioxide, oxides of nitrogen, oxygen and nitrogen (derived from the air), is sent into the large lead-lined chamber (D) where it meets with a plentiful supply of steam generated in the boilers (C) and delivered by small pipes (*c c*). In most modern works three of these large lead-lined chambers are used, the gases passing through each in succession, steam being blown into each chamber. Here the gases interact with the formation of sulphuric acid, which condenses on the walls of the chamber. This acid is known as "*chamber acid*" and contains from 62 to 70 per cent. of sulphuric acid.

The gases escaping from the chamber by the flue (*d*) should be free from sulphur dioxide, but will contain considerable quantities of oxides of nitrogen which have been added in excess of the amount required, and to absorb these the escaping gases are passed upwards through a brick tower, called the "*Gay Lussac*" tower (F), which is filled with coke, and down this cold strong sulphuric acid flows from the tank 3. The nitrous fumes are absorbed by the acid, producing nitro-sulphonic acid.

The nitrogen oxides absorbed in this way can be recovered by causing the hot gases from the pyrites burner to act upon the acid, this being accomplished in the "*Glover's*" or "*denitrating*" tower (E), already referred to. This is filled with flints,

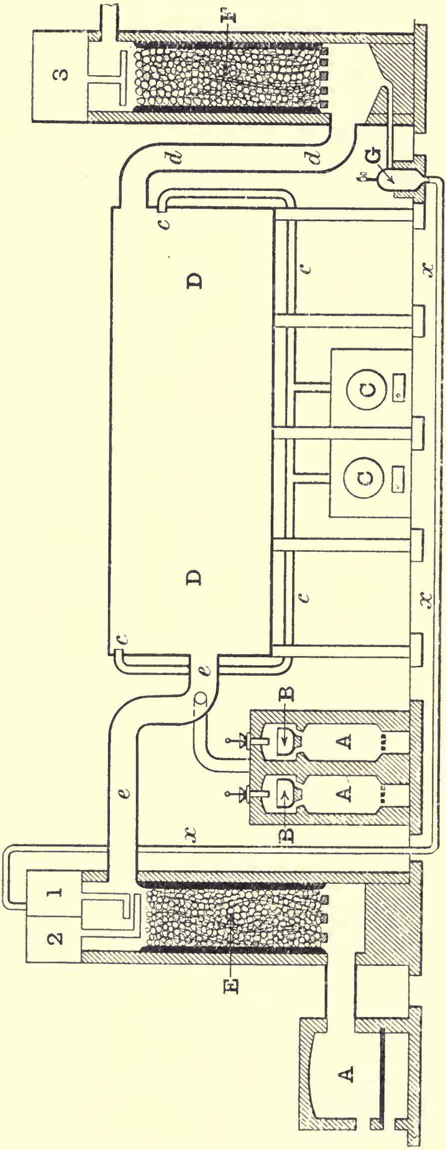
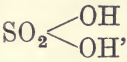
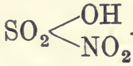


FIG. 45.—Diagram of sulphuric acid plant.

A A. Pyrites burners.
B B. Nitre pots.
C C. Boilers.
D D. Lead chamber.
E. Glover's Tower.
F. Gay Lussac Tower.
x x. Pipe conveying acid to Tank 1.
c c. Steam Pipes.
2. Chamber acid tank.

and the acid charged with nitrogen oxides is forced by air pressure in (G) through the pipe (*xx*) into a tank (1) situated at the top of the tower. The second tank (2) contains "chamber" acid, and the mixed acids flowing down over the flints meet the hot ascending gas current, the acid from the Gay Lussac tower becoming denitrated, whilst at the same time the weak chamber acid is considerably strengthened by evaporation of water. Such an arrangement permits of very economical working.

Chemical Reactions during the Manufacture.—It has already been shown that the gases entering the chamber are a mixture of sulphur dioxide, nitrogen tetroxide, oxygen and nitrogen (from the air), and here they meet with an excess of steam. The net result is the formation of sulphuric acid, but intermediate products are undoubtedly formed, and on this point divergent views are held. Should a deficiency of steam be present, a compound nitro-sulphuric acid—which may be regarded as sulphuric acid,  $SO_2<{}^{OH}_{OH}$, in which one OH group has been replaced by NO_2, giving  $SO_2<{}^{OH}_{NO_2}$—separates as white crystals known as "*Chamber crystals.*" The formation of this body must therefore be looked upon as one of the intermediate reactions.

$$(1)\quad \overset{\text{Sulphur dioxide}}{2(SO_2)} + \overset{\text{Nitrogen tetroxide}}{3(NO_2)} + \overset{\text{Steam}}{H_2O} = \overset{\text{Nitro-sulphonic acid}}{2(SO_2OH.NO_2)} + \overset{\text{Nitrogen dioxide}}{NO}$$

When this nitro-sulphonic acid meets with sufficient water, it undergoes decomposition with the formation of sulphuric acid and the liberation of a mixture of nitrogen di- and tetroxides.

$$(2)\quad \overset{\text{Nitro-sulphonic acid}}{2(SO_2.OH.NO_2)} + \overset{\text{Steam}}{H_2O} = \overset{\text{Sulphuric acid}}{2(H_2SO_4)} + \overset{\text{Nitrogen dioxide}}{NO} + \overset{\text{Nitrogen tetroxide}}{NO_2}$$

The nitrogen dioxide formed in accordance with equations (1) and (2) now takes up more oxygen from the air forming nitrogen tetroxide, which reacts again in accordance with equation (1).

$$(3)\quad \overset{\text{Nitrogen dioxide}}{NO} + \overset{\text{Oxygen}}{O} = \overset{\text{Nitrogen tetroxide}}{NO_2}$$

The further course of the reactions in the acid chambers may be looked upon as a continual taking up of oxygen from the air by the nitrogen dioxide, and reduction of the nitrogen tetroxide formed by the sulphur dioxide and water, with formation of sulphuric acid and liberation of nitrogen dioxide, which is again ready to perform its function as a carrier of oxygen from the air to the sulphur dioxide and water. The water needed in the reaction is blown into the chambers either in a fine spray or as steam, and condensing, carries down the sulphuric acid to the floor of the chambers.

It is evident that, theoretically, the small amount of oxides of nitrogen first introduced should be able to convert an unlimited amount of sulphur dioxide into sulphuric acid, but in order to supply the oxygen necessary to the reaction, very large quantities of air must be drawn into the chambers and the residual nitrogen must be removed, and the constant removal of the nitrogen from the chambers carries away a large percentage of the nitrous fumes, necessitating their constant renewal.

The acid formed in the chambers is not allowed to attain a higher specific gravity than 1·55, as above this point of concentration it would absorb the nitrous fumes. After a preliminary concentration in the denitrating tower, it is run into lead evaporating pans, and flame and hot air are allowed to play over the surface of the acid, water being evaporated and the specific gravity of the acid raised to 1·71, beyond which it is impossible to concentrate it in leaden vessels, as the hot acid would attack the lead. This strength of acid is sold for many manufacturing purposes and is technically known as B.O.V. (brown oil of vitriol), the colour being due to the presence of small quantities of carbonised organic matter.

Further concentration is effected in glass or platinum stills, until dense fumes of sulphur trioxide begin to escape, when the acid is drawn off and has now a density of 1·84.

In the contact process, sulphur dioxide is made by burning sulphur, spent oxide from the purification of gas, or pyrites in air, and the gas is freed from dust, arsenic and other impurities. The dry, clean sulphur dioxide mixed with air is then passed through tubes filled with platinised asbestos, kept at a temperature of 400° C., when the sulphur dioxide takes up another atom of oxygen from the air forming a mist of sulphur trioxide, which is dissolved in diluted sulphuric acid.

Properties.—The concentrated sulphuric acid is a heavy, oily liquid, having no smell and an intensely corrosive action; it boils at 388° C., and at this temperature gives off clouds of white fumes; it has a great affinity for water, and when mixed with it evolves great heat and combines forming definite hydrates. If left exposed to air it rapidly increases in volume from the absorption of water vapour from the air, and this property makes it valuable as a desiccating (drying) agent, as substances containing moisture can be placed over a pan or dish of the acid under an air-tight glass shade, the acid drying the air in a confined space and so promoting evaporation from the substance to be dried. Similarly, gases which are not acted upon by the acid can be effectually dried by passing them through tubes containing (ignited) pumice stone saturated with the strongest acid, a large surface thus being presented to the passing gases. This affinity for water is also shown in the action of the strong acid on substances of organic origin, containing besides carbon, oxygen and hydrogen in the proportions necessary to form water, when the combination of the hydrogen and oxygen is determined by the presence of the acid, and in many cases the carbon is liberated. The action is well illustrated by pouring an equal volume of the strongest sulphuric acid into a saturated sugar syrup, when the sugar is decomposed, the hydrogen and oxygen extracted as water by the acid, and a spongy mass of carbon occupying many times the bulk of the original liquid is obtained.

$$\overset{\text{Sugar}}{C_{12}H_{22}O_{11}} + \overset{\text{Sulphuric acid}}{xH_2SO_4} = \overset{\text{Dilute acid}}{xH_2SO_4,11(H_2O)} + \overset{\text{Carbon}}{12C}$$

At a red heat the vapour of sulphuric acid is decomposed into steam, sulphur dioxide and oxygen, and this has been proposed as a method for the preparation of oxygen, as it can readily be freed from the sulphur dioxide by washing with an alkaline solution.

With the exception of gold and platinum all the metals are acted upon by boiling concentrated sulphuric acid, a sulphate of the metal being formed and sulphur dioxide liberated.

$$\overset{\text{Mercury}}{Hg} + \overset{\substack{\text{Sulphuric}\\ \text{acid}}}{2(H_2SO_4)} = \overset{\substack{\text{Mercuric}\\ \text{sulphate}}}{HgSO_4} + \overset{\substack{\text{Sulphur}\\ \text{dioxide}}}{SO_2} + \overset{\text{Water}}{2(H_2O)}$$

Sulphuric acid, even very dilute, exercises a "rotting" action on fabrics, the acid becoming concentrated by evaporation, soon completely destroys the fibre. When unsized paper is soaked in a cold mixture of two volumes of concentrated sulphuric acid and one volume of water, it is converted into a substance called "vegetable parchment," which must be freed from acid by well washing with water; it is a tough translucent substance much used for covering jam pots, and other purposes, for which animal parchment was at one time employed.

Sulphates.—The large and important class of salts called sulphates consists of the acid radicle (SO_4) in combination with metals. The hydrogen of the acid can be replaced in two stages by a monad metal forming two classes of salts corresponding to the formulæ—

$NaHSO_4$ (Sodium hydrogen sulphate),
Na_2SO_4 (Sodium sulphate).

Sulphuric acid and its salts, when in solution, may be recognised by their giving a white precipitate with soluble barium salts; this precipitate is barium sulphate, which is practically insoluble in all acids.

Sulphur forms many other compounds of great scientific and industrial importance, but which do not come within the scope of the present work.

CHAPTER XXI

THE HALOGENS

The four elements, fluorine, chlorine, bromine, and iodine, constitute the halogen (salt-forming) elements, so-called from their occurrence in a large number of common salts. They combine directly with metals to form salts. These elements exhibit a gradual difference in properties and in their power of combining with other elements, fluorine having the greatest affinity for metals and iodine the least. The stability of the compounds formed in combining with oxygen is in reverse order, iodine forming the strongest compound, whilst fluorine is the only element which does not combine with oxygen, and this gradual gradation of affinity is also accompanied by a gradation in physical properties.

	Fluorine	Chlorine	Bromine	Iodine
Atomic weight ..	19	35·5	80	127
Physical state ..	gas	gas	liquid	solid
Colour	colourless	yellow	brown	black
Boiling point ..	..	.. −33°	+63°	+200°
Fusing point ..	..	.. ..	−7°	+113°

The consideration of these elements is taken in order of their importance.

CHLORINE.

Chlorine gas was discovered in 1774 by Scheele, and its elementary character was proved by Thénard and Davy in 1809–1810.

It is never found free in Nature, but abundantly in combination with sodium and other metals, and is found in all animal secretions.

Preparation.—The gas is most easily prepared by heating together a mixture of black oxide of manganese (the mineral pyrolusite) and strong hydrochloric acid, the reaction taking place in two stages—

$$\overset{\text{Pyrolusite}}{MnO_2} + \overset{\text{Hydrochloric acid}}{4(HCl)} = \overset{\text{Manganese tetrachloride}}{MnCl_4} + \overset{\text{Water}}{2(H_2O)}$$

Manganese tetrachloride, existing only at low temperatures, breaks up on warming into manganous chloride and chlorine gas.

$$\overset{\text{Manganese tetrachloride}}{MnCl_4} = \overset{\text{Manganous chloride}}{MnCl_2} + \overset{\text{Chlorine}}{Cl_2}$$

This is the method by which Scheele first prepared chlorine, and it is still employed as the most convenient laboratory method for making the gas. When used on a manufacturing scale the manganous chloride is again converted into the black oxide by treating with lime, which forms calcium chloride and manganese oxide (MnO), the latter being oxidised to the black oxide (MnO_2) by mixing with more lime and blowing air through the mixture (Weldon's process).

It can be prepared from common salt by mixing the salt (sodium chloride) with pyrolusite and sulphuric acid and warming the mixture—

$$\overset{\text{Sodium chloride}}{2(NaCl)} + \overset{\text{Pyrolusite}}{MnO_2} + \overset{\text{Sulphuric acid}}{2(H_2SO_4)}$$

$$= \overset{\text{Sodium sulphate}}{Na_2SO_4} + \overset{\text{Manganous sulphate}}{MnSO_4} + \overset{\text{Water}}{2(H_2O)} + \overset{\text{Chlorine}}{Cl_2}$$

On a manufacturing scale it is now largely prepared by "Deacon's process." A mixture of air and hydrochloric acid gas is passed over heated fire-bricks saturated with copper chloride or sulphate, when the alternate formation and decomposition of copper chloride gives chlorine gas. The final action may be represented as—

$$\overset{\text{Hydrochloric acid}}{2(HCl)} + \overset{\text{Air}}{(N_4+O)} = \overset{\text{Water}}{H_2O} + \overset{\text{Nitrogen}}{2N_2} + \overset{\text{Chlorine}}{Cl_2}$$

The chlorine obtained is mixed with twice its volume of nitrogen, but for the processes in which it is employed this does not matter.

Properties.—Chlorine is a yellowish-green gas which is volume for volume 35·5 times heavier than hydrogen; it has an insupportable odour, and when inhaled in even very minute traces causes great irritation of the mucous lining of the throat and lungs, air containing 5 per cent. of it rapidly proving fatal to animals.

It can be liquefied under a pressure of six atmospheres at 0° C. At ordinary temperatures, water dissolves a little more than 2·5 times its volume of the gas, and if the solution be cooled down to 0° C., crystals of a solid hydrate separate from the solution, their composition being ($Cl_2.10H_2O$).

Chlorine gas is not combustible in air or oxygen, and will only support the combustion of certain metals, or substances rich in hydrogen, combining with the hydrogen of the body to form hydrochloric acid whilst the carbon is deposited; in some cases spontaneous combustion takes place, as when blotting-paper moistened with turpentine is plunged into the gas.

Chlorine does not combine directly with either carbon or oxygen; phosphorus catches fire spontaneously in it, forming chiefly phosphorus trichloride (PCl_3), and sulphur will burn feebly in it; whilst selenium, boron and silicon will combine with it when heated.

Chlorine has an intense affinity for hydrogen and the metals, a mixture of equal volumes of chlorine and hydrogen combining with explosion when subjected to direct sunlight; whilst many metals, like antimony or copper, in a fine state of division, spontaneously ignite when thrown into the gas, chlorides of the metals being produced.

When a solution of chlorine in water is exposed to daylight it rapidly loses its characteristic yellow colour and becomes colourless, oxygen being at the same time liberated, an action due to the chlorine under the influence of light decomposing the water—

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

Bleaching.—The affinity of chlorine for hydrogen makes chlorine a very powerful oxidising agent, as when it comes in contact with any moist substance which can be readily oxidised, the chlorine combines with the hydrogen of the moisture, forming hydrochloric acid, whilst the nascent oxygen combines with the oxidisable substance.

This explains why it is that moist chlorine will bleach many colouring matters, whilst the dry gas has no effect upon them; the bleaching action of chlorine being an oxidation at the expense of the oxygen of the water present. Colours bleached by chlorine are destroyed, and cannot, as in the case of bleaching by sulphur dioxide, be restored.

COMPOUNDS OF CHLORINE.

Hydrochloric Acid (HCl).—The formation of this gas by the direct combination of hydrogen and chlorine has already been referred to. So great is the affinity of the two elements for each other, that if they are mixed in equal volumes, and exposed to any light rich in the chemically active rays which are found at the violet end of the spectrum, such as direct sunlight, the light from burning magnesium, or the flash obtained by igniting a mixture of carbon disulphide vapour and nitrogen dioxide, the two gases combine with explosion, whilst even in diffused daylight they gradually combine without explosion, in each case forming their own volume of hydrochloric acid gas. A mixture of the two gases, however, may be kept for an indefinite period in the dark, but will combine when brought into the light, or under the influence of heat or an electric spark.

Hydrochloric acid is found in volcanic gases, and also occasionally in the spring waters of volcanic districts, whilst its salts are amongst the most important natural compounds.

Preparation.—For laboratory use it is always prepared by acting upon salt with sulphuric acid, when—

$$\overset{\text{Sodium chloride}}{NaCl} + \overset{\text{Sulphuric acid}}{H_2SO_4} = \overset{\text{Sodium hydrogen sulphate}}{NaHSO_4} + \overset{\text{Hydrochloric acid gas}}{HCl}$$

an interchange taking place between the sodium and one atom of hydrogen of the sulphuric acid, with formation of hydrochloric acid gas and sodium hydrogen sulphate.

In preparing the gas in this way it is found convenient to fuse the salt before using it, in order to reduce the surface exposed, and thus prevent the excessive frothing which attends the use of ordinary table salt.

At temperatures which can be safely employed in a glass flask the above reaction takes place, but at a higher temperature, such as is attained in the salt cake furnace of the soda manufacturer, both atoms of hydrogen in the sulphuric acid can be replaced by sodium, and double the volume of hydrochloric acid gas is obtained—

$$\overset{\text{Sodium chloride}}{2(NaCl)} + \overset{\text{Sulphuric acid}}{H_2SO_4} = \overset{\text{Sodium sulphate}}{Na_2SO_4} + \overset{\text{Hydrochloric acid}}{2(HCl)}$$

The gas so obtained must be collected over mercury or by downward displacement, as it is so intensely soluble in water that it would be impossible to utilise it for its collection. The molecular weight of the gas is 36·5 and its density 18·25.

Properties.—It is a transparent, colourless gas with a suffocating odour and acid taste; it forms dense fumes on escaping into the air. These fumes are due to the gas attracting moisture from the air and condensing it, the gas itself being extremely soluble in water.

Hydrochloric acid gas can be condensed to a liquid by a pressure of forty atmospheres, and the anhydrous liquid has few of the properties of the solution of the gas in water; it has little or no action upon the metals, it hardly affects dry litmus, and has no action upon calcium carbonate or on quicklime.

Composition.—The composition of hydrochloric acid gas can be proved by confining a known volume of hydrochloric acid gas over mercury in a bent tube (A, Fig. 46), and passing up into it a pellet of potassium on the end of a platinum wire (B). The potassium at once commences to absorb the chlorine of the hydrochloric acid gas, combining with it to form potassium chloride; and if the potassium be gently heated by a spirit-lamp flame to prevent any absorption of hydrogen, exactly half the gas will disappear, leaving only pure hydrogen behind. Another proof is that if saturated hydrochloric acid solution is decomposed by a galvanic current in a Hofmann's electrolytic apparatus (Fig. 47), using carbon electrodes, equal volumes of hydrogen and chlorine will be evolved.

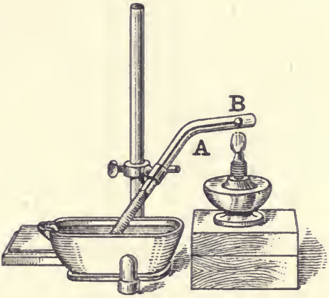


FIG. 46.—Composition of hydrochloric acid.

Commercial Hydrochloric Acid.—The liquid hydrochloric acid of commerce, called *muriatic acid*, or *spirits of salt*, is a solution of the gas in water. One pint of water at ordinary temperature will absorb nearly 500 pints of hydrochloric acid gas, forming $1\frac{1}{3}$ pint of the solution, having a specific gravity of 1·21.

If the strongest acid, having a specific gravity of 1·21, is cooled down to − 18° C., it deposits crystals having the composition $HCl.4(H_2O)$.

This acid is produced in enormous quantities in the alkali works, where common salt is decomposed by sulphuric acid as a preliminary step in the manufacture of sodium carbonate.

When this gas is present in the air in even small traces (1 in 25,000) it has a most destructive effect upon vegetation, causing the leaves to quickly wither and shrivel up, an effect which is supposed to be due to the attraction which the acid gas has for moisture. The effect of traces of this gas in the air may be seen in the pottery districts, where large areas are practically denuded of vegetation by the hydrochloric acid evolved during the process of salt glazing. As a consequence the alkali maker is compelled by Act of Parliament to condense the hydrochloric acid gas evolved, otherwise it would escape into the air, and wither up all the vegetation in the neighbourhood. The gas is condensed by making it pass up a tower containing lumps of coke, over which water is slowly trickling down; the water dissolves the hydrochloric acid gas, and the solution is drawn off at the bottom of the tower.

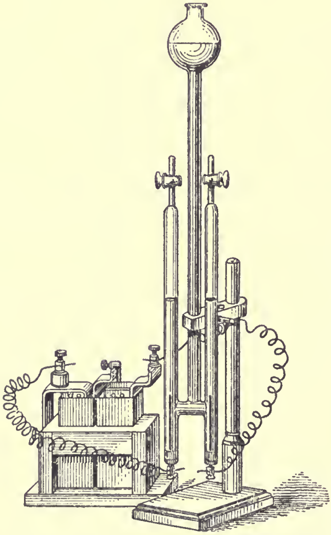


Fig. 47.—Electrolysis of hydrochloric acid.

Pure hydrochloric acid solution is colourless, but the crude acid nearly always has a yellow colour, due to the presence of iron.

Chlorides.—Most of the metals, with the exception of gold and platinum, are acted upon by hydrochloric acid, forming a chloride of the metal, which is also obtained when a metallic oxide is acted on by the acid. The molecule of hydrochloric acid containing only one atom of hydrogen, no acid salts can be formed.

Chlorides in solution can be detected by their forming a white precipitate with soluble silver salts, which is insoluble in nitric acid but soluble in ammonia, whilst all chlorides when heated with manganese dioxide and sulphuric acid evolve chlorine.

In its great affinity for the metals, chlorine resembles oxygen, and as a rule, the more closely elements resemble each other the less will be their affinity for each other, and chlorine cannot be made to combine directly with oxygen, although by indirect processes it forms several oxides.

Chlorine Monoxide.—If dry chlorine gas be passed over dry precipitated mercuric oxide, a substance called chlorine monoxide passes off and may be condensed as a red liquid in a tube surrounded with ice and salt.

$$\overset{\substack{\text{Mercuric}\\\text{oxide}}}{2(HgO)} + \overset{\text{Chlorine}}{2Cl_2} = \overset{\substack{\text{Mercuric}\\\text{oxychloride}}}{HgO,HgCl_2} + \overset{\substack{\text{Chlorine}\\\text{monoxide}}}{Cl_2O}$$

This liquid boils at $+19°$ C., and any elevation of temperature causes it to explode; it is rapidly absorbed by water, and the solution is supposed to contain hypochlorous acid, which, however, has not been isolated, although its salts are well known in an impure condition.

$$\overset{\text{Chlorine monoxide}}{Cl_2O} + \overset{\text{Water}}{H_2O} = \overset{\text{Hypochlorous acid}}{2(HClO)}$$

Bleaching Powder.—The most important compound of chlorine is "bleaching powder," the "chloride of lime" of the oil shops. This is made by taking freshly burnt quicklime, free from iron, and slaking it, sifting to remove lumps, and spreading it in thin layers on stone shelves fitted in a stone, brick, or sometimes lead chamber, the shelves being so arranged that they are open alternately back and front, so that gas passing through the chamber traverses the surface of each shelf; small openings with glass doors are made in the side of the chamber, so that the operation can be watched and the lime raked over once or twice during its conversion into bleaching powder. Chlorine gas is now generated in a stone "still," and the gas is made to pass over the slaked lime, care being taken to keep the temperature as low as possible, as the heat, which would be developed if the absorption went on too rapidly, would reduce the strength of the bleaching powder owing to the formation of calcium chlorate instead of calcium hypochlorite. The operation is continued for about thirty-six hours, by which time it is complete, and the bleaching powder contains from 30 to 39 per cent. of chlorine which can be rendered available for bleaching purposes.

Dry bleaching powder consists mainly of a substance intermediate in composition between calcium chloride (Cl-Ca-Cl) and hypochlorite (ClO-Ca-OCl), namely calcium chloro-hypochlorite (Cl-Ca-OCl).

It derives its value as a bleaching preparation from the ease with which it parts with a portion of its chlorine, the moisture and carbon dioxide of the air quickly bringing this about when the material is left exposed.

When acted upon by water, calcium hypochlorite is formed, together with calcium chloride.

Calcium chloro-hypochlorite		Calcium chloride		Calcium hypochlorite
$2[Ca(OCl)Cl]$	$=$	$CaCl_2$	$+$	$Ca(OCl)_2$

The bleaching action results from the decomposition of this calcium hypochlorite with dilute acids, hypochlorous acid being first liberated (*a*), which then undergoes further decomposition with the liberation of chlorine (*b*).

	Calcium hypochlorite		Hydrochloric acid		Calcium chloride		Hypochlorous acid
(*a*)	$Ca(OCl)_2$	$+$	$2(HCl)$	$=$	$CaCl_2$	$+$	$2(HClO)$
(*b*)	$2(HClO)$	$+$	$2(HCl)$	$=$	$2(H_2O)$	$+$	$2Cl_2$

In using it on a large scale a solution of the bleaching powder in water is taken, and the fabrics to be bleached are dipped into it, and after being allowed to soak for some hours, are then transferred for a short time to a tank containing very dilute acid, by which the chlorine is liberated in the material itself. When the bleaching is completed, which may require two or three dippings, the articles are well washed and boiled in a dilute solution of sodium carbonate, to remove the colouring matter rendered soluble by the chlorine, and to get rid of all traces of free acid, which, if allowed to remain, would render the fabric rotten.

Bleaching powder is of value as a disinfectant, breaking up moisture, and thus oxidising and destroying organic germs; it also decomposes noxious gases, like sulphuretted hydrogen, taking the hydrogen to form hydrochloric acid and depositing the sulphur.

Potassium Chlorate $KClO_3$.—If chlorine gas is passed into cold dilute potassium hydroxide solution, chlorine is absorbed, and a mixture of potassium chloride and hypochlorite is formed which is technically known as "Eau de Javelle," and which was the first artificial bleaching agent used.

$$\overset{\text{Potassium hydroxide}}{2(KOH)} + \overset{\text{Chlorine}}{Cl_2} = \overset{\text{Potassium chloride}}{KCl} + \overset{\text{Potassium hypochlorite}}{KClO} + \overset{\text{Water}}{H_2O}$$

If this solution be boiled, the hypochlorite breaks up into potassium chloride and chlorate—

$$\overset{\text{Potassium hypochlorite}}{3(KClO)} = \overset{\text{Potassium chloride}}{2(KCl)} + \overset{\text{Potassium chlorate}}{KClO_3}$$

Potassium chlorate may be formed in one operation by passing chlorine into a hot strong solution of potassium hydroxide—

$$\overset{\text{Potassium hydroxide}}{6(KHO)} + \overset{\text{Chlorine}}{3Cl_2} = \overset{\text{Potassium chloride}}{5(KCl)} + \overset{\text{Potassium chlorate}}{KClO_3} + \overset{\text{Water}}{3(H_2O)}$$

If this solution be concentrated and allowed to stand, the potassium chloride, which is soluble in three times its weight of cold water, remains in solution, whilst the chlorate, requiring sixteen times its weight of cold water to dissolve it, separates out in tabular crystals.

On a manufacturing scale a paste of potassium carbonate and slaked lime is saturated with chlorine, and treated with boiling water, which dissolves out the calcium chloride and potassium chlorate formed, and the former salt being very soluble in water, the chlorate is easily separated by crystallisation.

Potassium chlorate ($KClO_3$) is derived from an acid called chloric acid ($HClO_3$) by replacing the atom of hydrogen by potassium, and in the same way the class of salts called chlorates may all be built up.

The chlorates, like the nitrates, are all strong oxidising agents acting, however, at lower temperatures, because they part with their oxygen more easily; the oxidation by potassium chlorate is also much more violent than the action of the nitrate, the chlorate being an endothermic compound.

A few grains of sulphur mixed with potassium chlorate and rubbed in a mortar detonates violently, and before the introduction of mercuric fulminate this mixture was used for percussion caps, for which, however, it was ill adapted, as it caused serious corrosion of the nipple of the gun.

A mixture of antimony sulphide and potassium chlorate will detonate when struck with a hammer, and is used in friction tubes for firing cannon. Friction tubes consist of a quill tube filled with powder, in the upper part of which a small rasp surrounded by the mixture is fixed, and on rapidly pulling this out by means of a cord the friction fires the mixture, which in turn ignites the powder. For military use the tube is of copper.

Potassium chlorate has been employed as an ingredient of explosives, but many compositions in which it plays a part are liable to spontaneous combustion, added to which its effects are so uncertain and violent that it is rarely licensed as an explosive in England.

BROMINE ($Br = 80$) AND IODINE ($I = 127$).

The elements bromine and iodine so strongly resemble chlorine in all their properties that the three are classed together with fluorine, these elements being commonly called "*the halogens,*" or salt producers, from the fact that when an atom of one of them exists in combination with an atom of potassium or sodium, the compound strongly resembles sodium chloride or common salt in properties.

The principal source of sodium chloride is sea water, and the salts of bromine and iodine are also obtained from it.

Bromine was discovered in 1826 by Balard, who obtained it from the solution left after concentrating sea water and crystallising out the sodium chloride, and at first, supposed it to be a compound of iodine and chlorine. Like chlorine, it never occurs free in Nature, and its salts are found in company with the chlorides in sea water, and more plentifully in the waters of many mineral springs.

Bromine is now almost entirely prepared from the mother liquors obtained after crystallising out the potassium salts which occur in large deposits as *Carnallite* ($KCl, MgCl_2, 6H_2O$), at Stassfurt. The present process is a continuous one, the solution containing the bromides (mainly as magnesium bromide) passing downwards through a tower filled with balls, to give a large liquid area, and meeting an ascending current of chlorine, which replaces the bromine, forming magnesium chloride.

$$\underset{\text{Magnesium bromide}}{MgBr_2} + \underset{\text{Chlorine}}{Cl_2} = \underset{\text{Magnesium chloride}}{MgCl_2} + \underset{\text{Bromine}}{Br_2}$$

The bromine is condensed in a suitable apparatus, the last traces which escape condensation being removed by passing over moist iron. The bromine is afterwards purified by distillation.

Properties.—Bromine and mercury are the only two elements liquid at ordinary temperatures.

The vapour has an excessively corrosive and irritating smell and acid taste, and is an active poison. Volume for volume bromine vapour is eighty times as heavy as hydrogen. Liquid bromine boils at 63° C. and solidifies at —20° C., and is soluble in water, 34 parts of water dissolving one of bromine.

The vapour of bromine, like chlorine, only supports the combustion of substances rich in hydrogen, and it also bleaches certain colours by oxidation in the presence of moisture.

Hydrobromic Acid.—Bromine combines with hydrogen to form hydrobromic acid (HBr), but the tendency to combine is much feebler than is the case with chlorine, the mixed gases having to be passed through a red-hot tube to make them unite.

Hydrobromic acid forms the class of salts called bromides, much used in medicine and photography, but for other purposes it is of but little practical use, and the same remark applies to the compounds formed by bromine and oxygen.

Iodine was discovered in 1812 by Courtois, and like bromine, it occurs chiefly in sea and certain mineral spring waters. Sea water contains only about one part of iodine compounds in 250,000 parts of water, but seaweeds during their growth collect the traces from the sea water, and when the weeds are collected and burnt, the iodides are found in the ash. On the coast of Scotland and the neighbouring islands, enormous quantities of seaweed are collected and burnt, and the ash which is called "kelp" is then exhausted with water, and on evaporating the solution potassium sulphate crystallises out; this is removed, and on further concentration and cooling a crop of crystals of potassium chloride, together with sodium sulphate, chloride and carbonate, is obtained.

The mother liquor, which contains bromides as well as iodides, is then mixed with sulphuric acid and is put into a retort, manganese dioxide is added, and the retorts are heated, when the iodine distils over as a violet vapour, which is condensed in cooled receivers as a greyish-black shining solid, crystallising in metallic-looking scales.

$$\overset{\text{Potassium iodide}}{2(KI)} + \overset{\text{Manganese dioxide}}{MnO_2} + \overset{\text{Sulphuric acid}}{2(H_2SO_4)}$$
$$= \overset{\text{Manganous sulphate}}{MnSO_4} + \overset{\text{Potassium sulphate}}{K_2SO_4} + \overset{\text{Water}}{2(H_2O)} + \overset{\text{Iodine}}{I_2}$$

When no more iodine distils over, more manganese dioxide is added and the temperature raised, when the bromine present in the liquid distils over.

Practically all the iodine at the present time is obtained from crude Chili saltpetre (*Caliche*), which contains notable quantities, chiefly as sodium iodate. By successive crystallisations the sodium nitrate is removed, leaving a mother liquor which contains about 20 per cent. of sodium iodate. To recover the iodine from this, a solution of sodium hydrogen sulphite (obtained by passing the sulphur dioxide, obtained on burning crude sulphur, into a solution of sodium carbonate) is added, when a somewhat complex change takes place as represented by the following equation :—

$$\overset{\substack{\text{Sodium}\\ \text{iodate}}}{2(NaIO_3)} + \overset{\substack{\text{Sodium hydro-}\\ \text{gen sulphite}}}{5(NaHSO_3)}$$
$$= \overset{\substack{\text{Sodium hydro-}\\ \text{gen sulphate}}}{3(NaHSO_4)} + \overset{\substack{\text{Sodium}\\ \text{sulphate}}}{2(Na_2SO_4)} + \overset{\text{Water}}{H_2O} + \overset{\text{Iodine}}{I_2}$$

The iodine is allowed to settle, is washed and purified by distillation.

Properties.—The iodine so obtained is purified by resublimation, and is generally found in rhomboidal plates, having a lustre like graphite. It melts at 113° C., and boils at 200° C., being converted into a magnificent violet vapour, which is 127 times heavier, bulk for bulk, than hydrogen. It is but little soluble in water, 7000 parts dissolving only one of iodine, but is readily soluble in alcohol, ether, carbon disulphide, or the alkaline iodides. Iodine and the iodides are much used in medicine and photography, but neither the element nor its compounds with hydrogen or oxygen have many practical applications.

Iodine has not so strong an affinity for hydrogen or the metals as either chlorine or bromine, both of which will turn it out of combination. Of these three elements, chlorine has the strongest affinity for hydrogen and the metals, and iodine the feeblest, bromine being intermediate in its affinity. This order is reversed in their combinations with oxygen, iodine being the strongest, and chlorine the weakest.

The fact that iodine can be liberated from its compounds by the addition of a drop of chlorine water can be utilised as a very delicate test for the iodides. If an iodide is mixed with a dilute solution of starch no change in colour takes place, but if a drop of chlorine water be now added, the iodine will at once be liberated and blue iodide of starch will be formed, even if the quantity of iodine present be exceedingly small.

FLUORINE (F = 19).

The compounds of this element have been recognised as containing it since the close of the last century, but its affinity for nearly all other substances is so great that, in spite of the many attempts to isolate it, it remained unknown in the free state until 1887, when it was obtained by Moissan by electrolysing pure hydrofluoric acid, in which potassium hydrofluoride had been dissolved to render it a better conductor of electricity, a platinum **U** tube being employed (Fig. 48). An electrode of platinum-iridium alloy was used as the positive pole, whilst the negative consisted of platinum only ; the **U** tube was provided with stoppers of fluor-spar, and platinum delivery tubes were used for the gaseous products. Under these conditions, and at a temperature of —23° C., fluorine was obtained as a colourless gas which decomposes water, liberating oxygen and combining with the hydrogen to form hydrofluoric acid ; when brought in

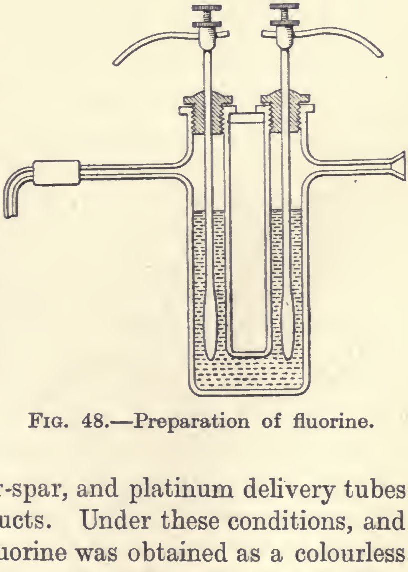


FIG. 48.—Preparation of fluorine.

contact with hydrogen gas it exploded, even in the dark, and combined with most of the elements with combustion, oxygen and carbon alone being unaffected by it.

Fluorine occurs in Nature chiefly in combination with calcium as calcium fluoride (CaF_2), found in enormous quantities as fluor or Derbyshire spar, which forms crystals belonging to the cubical system, and is often very beautifully coloured by traces of metallic oxides.

Hydrofluoric Acid.—Fluor-spar has been used from the earliest ages as a flux in metallurgical processes, and rather more than a century ago it was discovered that when it was heated with sulphuric acid, fumes were given off, which had the property of rapidly corroding glass, and these fumes were afterwards shown by Gay-Lussac and Thénard to consist of a compound containing hydrogen united with the then not yet isolated element fluorine.

This method is still that employed for its preparation, and the reaction which takes place may be represented as—

$$\begin{array}{ccccccc} \text{Calcium fluoride} & & \text{Sulphuric acid} & & \text{Calcium sulphate} & & \text{Hydrofluoric acid} \\ CaF_2 & + & H_2SO_4 & = & CaSO_4 & + & 2(HF) \end{array}$$

The hydrofluoric acid obtained, which contains one part by weight of hydrogen combined with nineteen parts by weight of fluorine, forms dense white fumes when in contact with air. When prepared by this method the escaping vapour can be condensed to a liquid by passing it through a tube cooled by a mixture of ice and salt, and the liquid so obtained was long considered to be liquid hydrofluoric acid, but is, in reality, a concentrated solution of hydrofluoric acid gas in water.

The anhydrous acid may be obtained from this by distilling it with phosphorus pentoxide, the liquid boiling at 19·5° C., and when perfectly anhydrous has little or no action on glass, but in solution, or in the presence of moisture, it rapidly attacks it, dissolving out some of the silica from it and forming a compound called silicon fluoride.

Hydrofluoric acid, in many of its properties, bears a strong resemblance to hydrochloric acid, but its action upon glass and substances containing silica distinguishes it from all other compounds.

In consequence of this property, it cannot be prepared in vessels of glass or porcelain, and retorts of lead or platinum are usually employed in its production, whilst it must be kept in bottles of lead, india-rubber, or paraffin wax.

Etching on Glass.—It is largely used for etching patterns upon glass, and for this purpose may be used either as vapour or solution, the latter being preferable, as it is much more manageable. The surface of the glass is first coated with a thin film of wax, and the pattern, drawn upon the wax with a sharp pointed tool, the solution of hydrofluoric acid is poured over it, and attacks the exposed glass, whilst it has no action on the wax. When etched to a sufficient depth, the acid is washed off with water, and the wax removed by scraping and washing the plate with turpentine.

In using hydrofluoric acid, care must be taken to avoid its contact with the skin, as it produces very painful wounds. Hydrofluoric acid in solution dissolves all the metals with the exception of gold, platinum, and mercury ; silver and lead forming fluorides of the metals soluble in water.

The fluorides of the alkalies slowly corrode glass when left in contact with them, and liquids for drawing or writing on glass can be prepared by mixing a solution of ammonium or potassium fluoride with sulphuric acid.

CHAPTER XXII

SILICON AND ITS COMPOUNDS

SILICON (Si = 28).

QUARTZ was believed to be an element until, in 1813, Sir Humphry Davy succeeded in decomposing it, and demonstrated that it was the oxide of an element called silicon, which can be obtained by acting on a compound called potassium silicofluoride at a high temperature with sodium or potassium, either of which combine with fluorine to form a fluoride, whilst the silicon is set free, and on treating the mass with water the fluorides are dissolved, the silicon being left as a brown amorphous powder.

$$\overset{\substack{\text{Potassium}\\\text{silicofluoride}}}{K_2SiF_6} \quad + \quad \overset{\text{Potassium}}{2K_2} \quad = \quad \overset{\substack{\text{Potassium}\\\text{fluoride}}}{6(KF)} \quad + \quad \overset{\text{Silicon}}{Si}$$

Silicon is not acted upon by any acid except by hydrofluoric, with which it forms silicon fluoride, hydrogen being evolved—

$$\overset{\text{Silicon}}{Si} \quad + \quad \overset{\text{Hydrofluoric acid}}{4(HF)} \quad = \quad \overset{\text{Silicon fluoride}}{SiF_4} \quad + \quad \overset{\text{Hydrogen}}{2H_2}$$

It burns with considerable brilliancy in air or oxygen gas, forming silica (SiO_2), which fuses on its surface and stops the combustion. Silicon has an atomic weight of 28.

If the potassium silicofluoride is fused with potassium and zinc, the silicon as it is liberated, dissolves in the molten zinc, and on cooling deposits in the mass as black shining crystals. These can be separated from the zinc by acting upon the mass with hydrochloric acid and afterwards separately with nitric and hydrofluoric acids, which dissolve the metal but leave the crystals of silicon unaltered.

The crystals consist of black shining octahedra, having a specific gravity of 2·49, and are excessively hard. They will not burn in oxygen and are unaffected by acids, except a mixture of hydrofluoric and nitric acids. When heated in chlorine gas, silicon forms a chloride, and nitrogen also enters into direct combination with silicon at high temperatures to form silicon nitride.

In many of its properties silicon very closely resembles carbon, but unlike carbon it forms only one compound with hydrogen, which catches fire spontaneously on coming in contact with air.

Silicon hydride (SiH_4) or siliciuretted hydrogen is prepared by fusing anhydrous magnesium chloride with sodium silicofluoride and sodium, together with a flux of salt. The mixture is heated until the sodium flame ceases to be visible, and on allowing the mass to cool, and breaking it out of the crucible used, a grey mass of magnesium silicide is found at the bottom, with a layer of fused chloride and fluoride of sodium above it. If the magnesium silicide is now roughly powdered and is treated with dilute hydrochloric acid, silicon hydride is evolved which fires spontaneously on contact with air and burns with a bright flame, giving off white fumes consisting of silica.

Silica (SiO_2), also called silicic acid and silicon dioxide, is by far the most important compound which this element forms, and constitutes a large portion of the crust of the globe. The purest form of silica is called rock crystal, from its transparency, and occurs crystallised in six-sided prisms generally terminating in six-sided pyramids. These crystals, coloured by certain metallic oxides, form various precious stones such as the amethyst, jasper, agate, catseye, onyx, opal, chalcedony, carnelian, etc. Silver sand is nearly pure silica, whilst the ordinary forms of yellow sand are silica coloured with iron.

Flint is a form of silica found in the chalk formation, and silica is one of the chief constituents of many forms of rock. Most forms of silica are intensely hard, rock crystal scratching glass nearly as easily as the diamond ; and all ordinary natural forms of silica are insoluble in water. Silica, however, is found dissolved in certain springs, whilst its presence in straw, bamboo canes, and other vegetable fibres, shows that under some conditions it must be soluble.

At high temperatures silica may be fused, and a large number of articles for technical and laboratory purposes are now made of pure silica. Such material is resistant to acids, and may be quenched from a white heat without cracking.

Silicic Acid and Silicates.—Silica, although insoluble in water, is an acid anhydride and by fusion with basic materials yields silicates. These are of immense importance in practice, glass consists of a mixture of silicates, and in metallurgy they constitute the bulk of the slags.

Silicic acid (H_2SiO_3) may be obtained by fusing silica with sodium carbonate, thus forming sodium silicate, a salt soluble in water and finding extensive applications as "water-glass." On pouring the solution into dilute hydrochloric acid, sodium chloride and silicic acid are obtained in solution. To obtain the acid the solution must be "dialysed." Membranes such as parchment are impermeable to the molecules of certain forms of matter in solution, but the molecules (or ions) of most crystallisable salts easily pass through. The latter are hence known as "*crystalloids*" and the materials which fail to pass as "*colloids*." Silicic acid belongs to the latter class, so that by pouring a solution prepared as described into a vessel with a parchment bottom with water on the outside, the sodium chloride and excess of hydrochloric acid pass into the water, the solution of silicic acid remaining in the dialyser.

If this solution be allowed to concentrate over sulphuric acid in a vacuum, it is converted into a gelatinous mass when it contains about 14 per cent. of silicic acid, and this shrinks and gives off more moisture until a glass-like mass having the composition (H_2SiO_3) is left. This substance will not again dissolve in water, is but slightly soluble in hydrochloric acid, and if it is heated so as to expel all water, it becomes totally insoluble in the acid.

If instead of pouring the solution of sodium silicate into dilute acid, strong hydrochloric acid had been added *to* the silicate, the silicic acid would have separated as a jelly-like mass.

Glass is a mixture in varying proportions of silicates of potash, soda, lime, lead oxide, baryta, magnesia, and alumina. If silica, which occurs nearly pure in Nature as silver sand and quartz, is fused at a high temperature with sodium carbonate, a glassy mass of sodium silicate is obtained; but this is slowly acted upon and dissolved by water, and is, therefore, useless as glass, for it would be incapable of resisting the moisture in the atmosphere; but if a small quantity of lime or oxide of lead is fused with it, a glass is obtained which will resist almost entirely atmospheric influences.

The readiness with which glass will fuse depends upon the silicates it contains, the presence of lead, for instance, causing the glass to melt at a lower temperature than a glass containing lime.

Plate glass and ordinary window glass consist chiefly of silicates of lime and soda.

Bohemian glass is a double silicate of potash and lime, the more fusible kind required for making ornaments, vases, etc., containing also silicate of alumina. Flint glass, of which tumblers, wine glasses, etc., are made, consists of a double silicate of potash and lead; it is called flint glass because the silica used in its composition consists of ground flints.

Window glass is made by fusing together at a high temperature 100 parts of sand with about 35 parts of sodium carbonate and 35 parts of chalk (calcium carbonate). The sand, at the high temperature, expels the carbon dioxide as gas from the sodium carbonate and calcium carbonate, and silicates of sodium and calcium are formed.

Sheet glass is made by blowing a long spheroidal bottle, which, when the ends are cut off, leaves a large cylinder of glass. This is split down one side by touching it with a wet rod, and is then again softened in the furnace, and spread out flat upon an iron plate, giving a sheet of glass, which is less brilliant than crown glass, and the surface being wave-marked, has to be worked up by grinding and polishing.

Plate glass, which is now most used, is formed from a mixture of 300 parts of pure silver sand, 100 parts of sodium carbonate, 15 parts of lime, and 300 parts of broken fragments of glass, called "cullet," and a little white arsenic. The mixture when fused and converted into glass is poured on to a heated metal table and is spread out to the required thickness by means of a heavy metal roller, being afterwards placed in the annealing oven, where it remains for a week or a fortnight.

The annealing oven is first heated to a dull red heat, and after all air openings have been closed it is allowed to cool down slowly to the temperature of the surrounding atmosphere. The plates are then taken out, ground true and polished, and are fit for use.

The process of annealing is of the greatest importance, for glass allowed to cool too rapidly is liable to crack and fly to pieces.

The glass of which wine bottles are made is of the commonest description, consisting of silicate of lime mixed with the silicates of the alkalies, and of iron and alumina, and it is to the iron present that it owes its dark colour.

When glass has been heated to the softening point and is kept at that temperature for some time without fusion, and then allowed to cool, it is found to be converted into a white opaque mass much resembling china, which is called "Réaumur's porcelain." This change is called "devitrification," and is due to the crystallisation of the silicates contained in the mass. Many materials are used to colour glass; in painted glass the colouring matter is merely laid on and then burnt into the surface of the glass, whilst in stained glass the colouring matter is mixed with the ingredients during manufacture. The ornamentation of cut glass is effected by grinding it, and designs are etched upon it by means of hydrofluoric acid, which dissolves out the silica from the glass, in this way eating into it.

Clay.—One of the most important natural silicates is aluminium silicate, which is the basis of all clays, and also occurs in a more or less pure condition in slate, pumice stone, and fuller's earth.

Clay varies very much in composition, china clay or kaolin being nearly pure hydrated aluminium silicate, whilst the commoner kinds of yellow clay contain considerable quantities of iron. The plastic properties of the different kinds of clay render it specially adapted for moulding into various forms; its use for the manufacture of pottery dates from a very early period in the world's history.

Pottery.—If a well-kneaded specimen of clay be chosen it may be readily moulded into any required form, but when heated it has the property of shrinking; so that on baking the vessel would crack and lose its shape. To obviate this it is mixed with a certain proportion of sand, chalk, or bone ash, which prevents shrinkage, but renders the baked vessels very brittle; to overcome this difficulty, some "felspar" (a silicate of alumina and potash) is added, which fuses at the temperature employed in baking the ware, and thus forms a cement, binding the particles of infusible clay into a compact mass. The vessel made of this mixture, when baked, retains its shape and does not crack, but it has the disadvantage of being porous, and is therefore unfit for ordinary use. To prevent this it must be glazed, that is, coated with some easily fusible material, which will form a thin coating of glass on the surface.

Porcelain.—In the manufacture of porcelain, 62 parts of kaolin, 4 parts of chalk, 17 parts of sand, and 17 parts of felspar are ground to the finest possible powder in water, and are allowed to stand until the coarser particles have settled down to the bottom of the grinding vat. The creamy fluids containing the finer particles in suspension are mixed in the proper proportions, and are allowed to settle; the sludge deposited at the bottom is drained until it reaches the right consistence, and is then thoroughly mixed and kneaded. The paste so prepared is now ready for making porcelain, but it has been found that it improves greatly by keeping for a considerable space of time in a damp place, the organic impurities which it contains being destroyed. Before the paste is used for moulding, it is again worked up and kneaded by hand.

The moulds used in the process of shaping are always made of a porous material, capable of absorbing the moisture from the clay, generally plaster of Paris. When the pattern is very complex, the mould is made in several pieces, but for round objects it is made in two parts. When the paste has been sufficiently dried by the absorption of its moisture by the mould, the latter is removed by separating its two halves, leaving the work complete. The articles are then air dried, and afterwards packed in cylindrical cases of refractory clay, which are arranged in a furnace or kiln and baked, the temperature being allowed to rise very gradually.

When sufficiently baked, the "biscuit porcelain," as it is now called, has to be glazed, and this is done by dipping it into a very finely ground mixture of felspar and quartz, suspended in vinegar and water. The porous ware absorbs the water, and leaves a coating of felspar and quartz on its surface, which on heating a second time in the kiln, fuses and forms a glaze, partly penetrating the ware, and partly remaining as a varnish on the surface. It is very important that the glaze employed should have the same rate of expansion with heat as the porcelain; otherwise, as it cooled, the glaze would crack.

In colouring wares of this kind, if a uniform tint is required, the materials for producing it are mixed with the glaze; but coloured designs are painted upon the ware after glazing, and are generally composed of coloured glasses, ground with turpentine, which colours, when again heated in the kiln, fuse into the glaze.

Stone ware is a much coarser description of porcelain, containing both iron and lime, to the presence of which it owes its colour and fusibility, and it is covered with a glaze of sodium silicate which is produced by the process known as "salt glazing." The articles are coated, by dipping, with a thin film of sand, and are then intensely heated in the kiln, into which some damp salt is thrown. The water present is decomposed, its hydrogen taking the chlorine from the salt to form hydrochloric acid, whilst its oxygen combines with the sodium of the salt to form sodium oxide, which, coming in contact with the silica on the surface of the ware, forms a glaze of sodium silicate.

Staffordshire ware, of which common plates, etc., are made, is manufactured from a description of white clay of less value than kaolin; it is mixed with ground flints, and is fired at a high temperature, and after being dipped in a highly fusible glaze, consisting of lead oxide, ground flints, and a little clay, it is again fired at a lower temperature.

Earthenware vessels and pipes are made from common clay, mixed with a certain proportion of marl and sand, and they are glazed with a mixture of from four to five parts of clay with six to seven parts of lead oxide.

Bricks are also made of common clay, mixed when necessary with sand, and they, as in the case of common earthenware, owe their colour to the iron which they contain.

Building Materials.—In choosing building materials, those substances should be employed which offer the greatest resistance to atmospheric influences.

The causes which tend to produce decay in building materials are two: First, the disintegrating action of rain and frost; and secondly, the solvent action on certain ingredients of the materials exercised by carbon dioxide and acid impurities dissolved in rain water, or suspended in the moisture present in the air as fog or mist. As a rule, these two factors of decay act together; the weathering action first rendering the surface of the stone rough and porous, and this gives a coign of vantage for the lodgment of the rain with its gaseous impurities, which, dissolving out carbonates of calcium and magnesium, further disintegrates the surface, and causes scaling and pitting of the stone.

This being the case, it is evident that the smoother and harder the surface of the materials employed the less rapid will be the decay; and also that the vertical walls of a building, as they allow the water to freely run off from their surface, will be less exposed to these actions, and will therefore resist them better than ledges and horizontal surfaces, which, holding water, will be acted upon to a greater extent.

This is fully borne out by experience, and in buildings of sandstone and limestone it is nearly always found to be these portions which are first attacked.

It has been noticed that many of the ancient monuments of Greece and Egypt, even now, show but slight traces of decay as compared with the buildings to be found in this country, and the difference is partly due to the greater resistance afforded by the surface of the materials used, but to an even greater extent, to the much smaller quantity of rain which falls in those countries and to the purity of the atmosphere.

The building stones used in this country are—

1. Granite.
2. Sandstone or freestone.
3. Limestone.
4. Magnesium limestone or dolomite.

Granite is by far the most lasting of the building stones, and consists of from 65 to 80 per cent. of silica, which seems to act as a cement in building together mica and felspar, the whole mass being of a crystalline character. The chief granite yielding districts of England are Devon, Cornwall, and Cumberland, whilst Scotland and Wales also furnish large quantities. The Devon and Cornwall granite has been largely used—Westminster, Waterloo, and London bridges, the Thames Embankment, the London docks, Keyham docks and the Portland breakwater being built of it; whilst in Scotland, the Aberdeen and Peterhead quarries supply some of the most valuable stone.

The fine surface and power of resisting disintegration possessed by granite, render it the best building stone we possess, but owing to its great hardness it is so difficult to work that it is employed only for massive and simple work, where great resistance to wear and tear is required.

The Sandstones consist essentially of particles of silica, *i.e.* sand which has been probably formed by the disintegration of older rocks, and has collected in deposits, becoming consolidated into a hard mass by the carbonates of calcium and magnesium, the percentage of silica present varying from 84 to 93 per cent., whilst the carbonates binding it together vary from less than 1 per cent. up to nearly 13 per cent.

The sandstones are largely used for building purposes in Scotland, where they are employed to a great extent, especially in Glasgow and Edinburgh, but carbon dioxide dissolved in rain water is able to rapidly dissolve out the cementing carbonates, and so cause disintegration of the surface.

The Limestones are perhaps those most generally in use, and consist of calcium carbonate, with small and varying quantities of other substances, such as silica and alumina, and their power of resisting the atmospheric influences depends entirely upon their density and compactness of structure.

Marble, which is the most compact form of limestone, will resist the action of the atmosphere for centuries, whilst the more porous kinds are rapidly acted upon.

Portland stone, of which St. Paul's is built, is, next to marble, the most durable, and Bath stone also resists atmospheric action for a considerable period.

Dolomite, or magnesium limestone, is a double carbonate of calcium and magnesium, and is much used because it is easily sawn into blocks, and can be readily carved ; but it is also rapidly acted upon by the water and carbon dioxide in the air. The magnesium limestone, of which the Houses of Parliament are built, contains about 50 per cent. of calcium carbonate, 40 per cent. of magnesium carbonate, and some silica and alumina.

In manufacturing towns much damage is caused to such stone by the sulphuric acid in the air, formed by the combustion of coal containing small traces of sulphur.

Mortar is a mixture of one part of freshly-slaked lime with two of sand, mixed with water to the consistence of a thin paste ; the hardening of mortar at first depends upon the conversion of some of the lime into carbonate by the absorption of carbon dioxide from the air ; whilst, after the lapse of a considerable time, a still further hardening takes place, due to the formation of calcium silicate.

Cements or hydraulic mortars are made by heating together very finely divided chalk and clay, when carbon dioxide is expelled and silicates of calcium and aluminium are formed, together with a compound of alumina and lime; when this cement is mixed with water, combination takes place, the cement setting as a hard mass of hydrated double silicates, upon which more water has no effect.

In the manufacture of Portland cement, instead of ordinary clay, river mud is used.

Silicon Tetrafluoride.—When silica or silicates are acted upon by hydrofluoric acid, or by a mixture of fluor-spar and concentrated sulphuric acid, a gas is evolved which fumes in air and has a pungent odour. This gas is a compound of silicon and fluorine, and may be looked upon as being silica in which the two atoms of oxygen have been replaced by four atoms of fluorine. It is called silicon tetrafluoride.

$$\overset{\text{Silica}}{SiO_2} + \overset{\text{Hydrofluoric acid}}{4(HF)} = \overset{\text{Silicon tetrafluoride}}{SiF_4} + \overset{\text{Water}}{2(H_2O)}$$

or—

$$\overset{\text{Silica}}{SiO_2} + \overset{\text{Calcium fluoride}}{2(CaF_2)} + \overset{\text{Sulphuric acid}}{2(H_2SO_4)}$$
$$= \overset{\text{Calcium sulphate}}{2(CaSO_4)} + \overset{\text{Silicon tetrafluoride}}{SiF_4} + \overset{\text{Water}}{2(H_2O)}$$

Hydrofluosilicic Acid.—When brought in contact with water, it at once undergoes decomposition with formation of silica, which is deposited, whilst an acid containing hydrogen, silicon and fluorine, called hydrofluosilicic acid, is formed—

$$\overset{\text{Silicon tetrafluoride}}{3(SiF_4)} + \overset{\text{Water}}{2(H_2O)} = \overset{\text{Hydrofluosilicic acid}}{2(H_2SiF_6)} + \overset{\text{Silica}}{SiO_2}$$

This acid is prepared most conveniently by heating together a mixture of sand, fluor-spar, and sulphuric acid in a stoneware bottle, and leading the silicon tetrafluoride produced through a wide delivery tube, dipping into a small cup of mercury placed at the bottom of a vessel of water, thus guarding against obstruction of the exit tube by silica. Each bubble of gas as it passes up through the mercury is decomposed immediately it comes in contact with the water, and after a few hours the water becomes thick with the gelatinous mass of separated silica, and if this be filtered off, the clear filtrate will contain the hydrofluosilicic acid (H_2SiF_6).

BORON ($B = 11$).

Boron is an element which closely resembles silicon; it is obtained from boracic acid by fusing it with potassium as a brown amorphous powder, which on fusion with aluminium, combines with some of it and forms octahedral crystals resembling the diamond in hardness and power of refracting light. Boron differs from most of the other elements in combining directly with nitrogen when heated to redness in the gas, forming a nitride.

In certain parts of the volcanic districts of Northern Italy, jets of steam issue with considerable violence from the ground, and are found to contain a compound of hydrogen, boron, and oxygen, called *boracic acid,* which can be obtained in the crystalline form, having the composition (H_3BO_3). It is largely used for antiseptic purposes, as it prevents decay and putrefaction.

Boracic acid forms a few salts, the most important of which is sodium biborate or borax ($Na_2B_4O_7$), which is used to a considerable extent for cleaning metallic surfaces, from which, when fused, it has the power of dissolving metallic oxides, and also for glazing certain kinds of stoneware.

CHAPTER XXIII

PHOSPHORUS AND ARSENIC

PHOSPHORUS (31).

OWING to its intense affinity for oxygen, phosphorus is never found free in Nature, but occurs in large quantities combined with metals of the alkaline earths, the commonest being tricalcium phosphate $Ca_3(PO_4)_2$. By the disintegration of the minerals containing phosphates, the latter pass into the soil, and are absorbed by plants, appearing principally in the seed. The minerals phosphorite, coprolite, and apatite, also contain phosphorus. In the animal kingdom, the element appears to be a very necessary ingredient in the brain and other centres of nervous action; in bones about 60 per cent. of the total weight consists of mineral phosphate, and it is from the ashes of burnt bones that phosphorus itself is usually obtained.

Phosphorus was probably discovered in the seventeenth century by Brandt, who obtained it by heating the residue left after the evaporation of urine with sand. Later on Gahn discovered the existence of calcium phosphate in bones, and Scheele showed how phosphorus could be obtained from this substance.

The bones are heated with water under pressure, which dissolves out the ossein or soluble organic matter, and this is either purified for domestic or photographic use, or sent into the market as glue. The mineral matter left is heated to redness in the air, and the white ash remaining is called bone ash, and consists chiefly of tricalcium phosphate. Bone ash is also obtained by calcining animal charcoal after its decolorising power has been exhausted to such an extent that it cannot be sufficiently revived by re-burning.

Manufacture of Phosphorus.—Bone ash and mineral phosphates containing as little iron and alumina as possible, are used as the crude material, and after being ground to a fine powder, this is treated in a mixer with sulphuric acid of 1·55 specific gravity, until the whole of the lime is converted into calcium sulphate with liberation of phosphoric acid—

$$\overset{\text{Tricalcium phosphate}}{Ca_3(PO_4)_2} + \overset{\text{Sulphuric acid}}{3(H_2SO_4)} = \overset{\text{Calcium sulphate}}{3(CaSO_4)} + \overset{\text{Phosphoric acid}}{2(H_3PO_4)}$$

The phosphoric acid is then filtered off and concentrated by steam evaporation to a syrup, which is mixed with sawdust, coarsely powdered charcoal or coke, and is dried at a dull red heat in a cast-iron vessel. This heating converts the phosphoric acid into metaphosphoric acid by driving off one molecular proportion of water.

$$\overset{\text{Phosphoric acid}}{H_3PO_4} = \overset{\text{Metaphosphoric acid}}{HPO_3} + \overset{\text{Water}}{H_2O}$$

The dried mixture is then distilled in fireclay retorts, about three feet long and eight inches in diameter; two-inch iron pipes are luted into the mouths of the retorts and are made to dip under the surface of water.

At a white heat, the reduction of the metaphosphoric acid takes place—

$$\overset{\text{Metaphosphoric acid}}{4(HPO_3)} + \overset{\text{Carbon}}{12C} = \overset{\text{Carbon monoxide}}{12(CO)} + \overset{\text{Hydrogen}}{2H_2} + \overset{\text{Phosphorus}}{P_4}$$

The phosphorus vapour distilling over in the atmosphere of carbon monoxide and hydrogen is condensed to the solid state in the water.

The introduction of the electric furnace has now considerably modified the process of manufacture, and is used at some of the largest works for the continuous production of phosphorus.

The calcium phosphate either as mineral or bone ash is mixed with carbon and a flux, and is then fed in through a hopper to a closed chamber lined with refractory fire-brick, where the mixture is acted upon by the arc, the phosphorus distilling off through an outlet pipe to the condenser, whilst the slag is from time to time tapped and run off. This process gives a considerable saving, as the use of sulphuric acid is done away with, handling of the materials is reduced to a minimum, and the concentration of the phosphoric acid is rendered unnecessary.

Purification.—The phosphorus so obtained is generally very impure, and is again melted under warm water to which four per cent. of potassium bichromate is added, and the mixture well stirred; dilute sulphuric acid is then added, and the chromic acid so liberated oxidises the impurities and causes them to separate, leaving the phosphorus nearly pure and colourless.

Sometimes also purification is effected by redistilling the phosphorus from iron retorts at as low a temperature as possible.

The melted phosphorus is cast into sticks under warm water, or if for match manufacture into cheese-shaped masses.

Properties.—The phosphorus so obtained is almost colourless and transparent, but when exposed to light it gradually acquires an opaque red coating, partly due to its conversion into a sub-oxide of phosphorus, and partly to the formation of the red variety of the element.

Phosphorus melts at 44° C., and it has an intense affinity for oxygen, inflaming at a temperature of 60° C., and for this reason has to be kept under water. It is soluble in carbon disulphide and also in chloride of sulphur. If the solution in disulphide be allowed to stand in contact with air, the solvent evaporates off, and leaves the phosphorus in so fine a state of division that it spontaneously ignites.

Red Phosphorus.—If ordinary phosphorus be kept at a temperature of 230° C. for some hours in an atmosphere incapable of acting chemically upon it, such as of nitrogen or carbon dioxide, it gradually changes to a dark red mass, having the same chemical composition, but totally distinct in all its properties from yellow phosphorus. It undergoes no change when exposed to air or light, and may be heated to 250° C. before it ignites, at which temperature it is reconverted into ordinary phosphorus. Unlike the ordinary phosphorus it is insoluble in carbon disulphide, unattacked by chlorine or iodine at ordinary temperatures and non-poisonous.

The density of phosphorus, as vapour, is 62, and its molecular weight is therefore 124, but it can be proved from its hydrogen compounds that the atomic weight of the element is 31. It follows therefore that the molecule consists of four atoms, and inasmuch as dissociation does not take place even at 1040° C., it is evident that the molecule has this composition. Phosphorus enters largely into the composition of the paste with which lucifer matches are tipped.

Matches.—In the manufacture of lucifer matches, even-grained white pine is split up by machinery into splints twice the length of the matches to be made; these are then wound round and round, by machinery, with a thick woollen or leather band, which leaves an inch of splint projecting at each end, and the thickness of which separates the splints one from the other. Several hundred splints having been in this way rolled up into a firm compact bundle and the ends all levelled, the bundles are passed with one set of ends downward, over hot plates to warm the wood, and dipped in shallow pans containing melted paraffin wax; the bundles are turned over and the other ends heated and dipped. When the paraffin has hardened, they are ready for the next process of tipping them with the match composition, made by mixing phosphorus and either potassium nitrate or chlorate, red lead, lead dioxide, or manganese dioxide, together with gum or glue enough to make a thin paste, to which sometimes some colouring matter, such as vermilion or Prussian blue, is added.

In such a composition, there is present the highly inflammable phosphorus and a compound containing oxygen, and friction is sufficient to set up chemical action between the two—the heat evolved by the combination of the phosphorus and oxygen to form phosphoric pentoxide being sufficient to inflame the paraffin or sulphur on the splint, and this in turn ignites the wood.

In England, potassium chlorate is generally used as the oxidising agent, such mixtures generally exploding slightly when the matches are struck, whilst on the Continent nitrate of potassium or lead and a little red lead or lead dioxide are often used instead, these matches igniting quietly and being known as "silent matches."

If phosphorus, even in the red form, is mixed with potassium chlorate, it forms a most dangerous explosive, which detonates violently on subjection to the lightest friction or blow, but in the match mixture, the particles of phosphorus and chlorate are coated with the glue used, and are thus preserved from intimate contact until friction is applied.

The match mixture is spread as a thin paste on tables made of iron, and heated by steam, the depth of mixture being gauged by a thin rim over which a flatting tool is passed. The ends of the splints already coated with paraffin are dipped in the mixture, and the wheels of splints are strung on spindles in small fireproof chambers to dry, a rapid draught of warm air being created by revolving fans. When dry the bundles are unrolled by machinery and taken to the "boxing" benches, where women take a handful of the matches, cut them in half by means of a sharp-hinged knife, and pack them into the boxes with marvellous rapidity.

At this stage of the operations, firing of the matches often takes place during frosty weather, when the air is crisp and dry, but under ordinary atmospheric conditions the loss from this cause is very small.

Safety Matches.—Bryant & May's "safety matches" contain no phosphorus in the head of the match, the tipping mixture consisting of antimony trisulphide, potassium chlorate and powdered glass, mixed into a paste with glue.

This mixture will explode when struck a sharp blow, and will ignite when subjected to very great friction, a long steady stroke across a sheet of glass being sufficient to ignite the safety matches, but they are not sufficiently sensitive to ignite with ordinary friction, doing so at once, however, when rubbed against the composition on the side of the box, which contains amorphous phosphorus mixed with glass.

The manufacture of safety matches is in all respects the same as that described above, with the exception of the composition of the mixture used for the tips.

Wax Matches.—In the manufacture of wax vestas, cotton is wound off from the hank, and is passed in bundles of about a dozen strands through a melted mixture of stearin, containing either paraffin wax or gum dammar to harden it; the cotton is passed through several times until it has taken up the required amount of the wax mixture, and is then made uniform in size, and polished on the outside by passing through a warm metal plate pierced with holes of the required size.

At Messrs. Bryant & May's manufactory, 800 miles of this taper can be made in a day.

The taper is passed on to the cutting machine, where in one operation it is cut to the required length for the matches, and clamped in frames with thin wooden battens between the rows, each frame holding 7,200 matches; the frames are taken to the dipping table, dipped in the mixture, dried in racks in fireproof chambers, and are then ready to be unpacked from the frames and put in the boxes.

In all accounts of the match industry great stress is laid upon the painful and disfiguring diseases (called by the operatives "Phossy Jaw") of the bones of the face induced by constant contact with the fumes of phosphorus in a match factory, but of late years it has been found that attention to cleanliness of person amongst the operatives does away, to a large extent, with what undoubtedly was a great evil, and in such factories as Messrs. Bryant & May's, where scrupulous cleanliness is enforced, it has practically disappeared. Red amorphous phosphorus, as it does not give off fumes, tends to reduce the danger, but in nearly all factories a larger quantity of ordinary than red phosphorus is still used.

Many attempts have been made, from time to time, to do away with the use of phosphorus in matches, but the action of the compounds used (which generally contain antimony sulphide and potassium chlorate as a basis) is not sufficiently certain to lead to their general adoption.

COMPOUNDS OF PHOSPHORUS.

Phosphorus does not directly combine with hydrogen, but by indirect means three compounds can be obtained, only one of which, however, is of any practical importance.

Hydrogen Phosphide (PH_3), phosphuretted hydrogen or phosphine, consists of hydrogen and phosphorus combined together in the proportion of thirty-one parts by weight of phosphorus to three of hydrogen, to which the formula (PH_3) has been assigned.

A few pieces of ordinary phosphorus are placed in a retort (Fig. 49), connected with a hydrogen generator; the air is completely driven out by hydrogen. The mouth of the retort being placed under the surface of water and the retort and its contents heated, a gas is evolved, which escapes a bubble at a time, and each bubble as it comes in contact with air spontaneously inflames with a flash of white light and formation of rings of smoke, consisting of phosphorus pentoxide, formed by the combustion of the phosphorus with the oxygen of the air. If instead of allowing the gas to escape into air it is collected in a cylinder over water, it will be seen to contain some oily drops, and also will deposit a yellow solid on the side of the cylinder. The liquid and solid are the other two "phosphines," the liquid having the composition (P_2H_4), and the solid the probable composition (P_4H_2), and it is to the presence of the liquid compound that the spontaneous inflammability of the phosphuretted hydrogen is due.

The formation of the gas may be represented as follows :—

Phosphorus		Sodium hydroxide		Water		Sodium hypophosphite		Phosphuretted hydrogen
P_4	$+$	$3(NaHO)$	$+$	$3(H_2O)$	$=$	$3(NaH_2PO_2)$	$+$	PH_3

If the evolved gas is passed through a tube cooled by a freezing mixture, the liquid phosphine (P_2H_4) condenses, and the phosphuretted hydrogen loses its power of igniting spontaneously. The liquid phosphine can also be removed by employing an alcoholic solution of potash, instead of an aqueous solution, when it is absorbed and kept back by the alcohol.

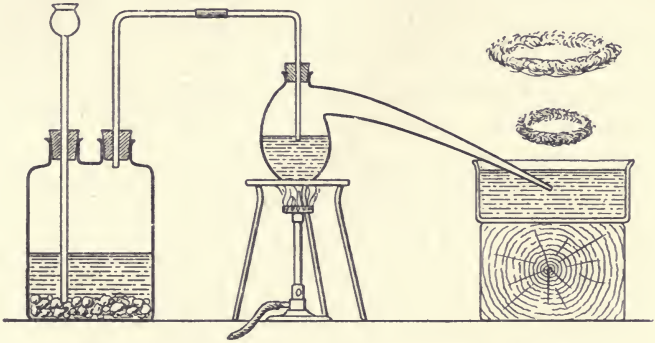


FIG. 49.—Preparation of phosphuretted hydrogen.

When quicklime and phosphorus are heated to bright redness in an air-tight crucible, or the vapour of phosphorus is passed over heated quicklime, a dark brown solid is obtained containing calcium phosphide. If this substance be thrown on to water, it decomposes with formation of liquid phosphine.

Calcium phosphide		Water		Calcium hydroxide		Phosphine
$2CaP$	$+$	$4H_2O$	$=$	$2[Ca(HO)_2]$	$+$	P_2H_4

The liquid phosphine is very unstable and at once splits up into the solid phosphine and phosphuretted hydrogen, which ignites on coming into contact with the air.

Calcium phosphide rapidly deteriorates when exposed to air, being partially decomposed by the moisture present in it. This substance is used in "Holmes' lights," which consist of sealed cartridges containing calcium phosphide. To use them the seal is torn off and they are attached to the buoy or other object, the position of which is to be made visible when in the water. The water decomposes the phosphide, and the flash of the burning phosphuretted hydrogen reveals the whereabouts of the floating object at night, whilst the heavy white smoke serves as a guide by day.

Phosphuretted hydrogen is a colourless gas with a very disgusting odour, resembling putrid fish. Its molecular weight is 34 and density 17.

In composition it resemble ammonia gas, and forms compounds analogous to those of ammonium. For instance, it combines with hydrogen iodide (HI) to form phosphonium iodide (PH_4I), corresponding to ammonium iodide (NH_4I).

Oxides of Phosphorus.—Phosphorus forms two well-defined oxides, viz.—

Phosphorus trioxide, P_2O_3.
Phosphorus pentoxide, P_2O_5.

Phosphorus trioxide is a white, deliquescent powder formed by the slow oxidation of phosphorus in a limited supply of dry air. If the trioxide be heated to a high temperature in a sealed tube, it forms phosphorus pentoxide and phosphorus.

The trioxide dissolves in water to form phosphorous acid—

$$\underset{\text{Phosphorus trioxide}}{P_2O_3} + \underset{\text{Water}}{3(H_2O)} = \underset{\text{Phosphorous acid}}{2(H_3PO_3)}$$

The solution is a very powerful reducing agent.

Phosphorus pentoxide (P_2O_5) is formed when phosphorus is burnt in dry air or oxygen; it is a white flaky solid having an intense avidity for moisture. If left exposed to air, it rapidly deliquesces, and is used as a dehydrating agent, as it will abstract moisture from nearly all bodies which contain it, even sulphuric and nitric acids being dehydrated by it.

It may be sublimed unchanged, and when heated with charcoal it breaks up into phosphorus and carbon monoxide.

Phosphoric Acids.—The pentoxide combines with water in three proportions, forming:

Metaphosphoric acid, $P_2O_5.H_2O = 2(HPO_3)$
Pyrophosphoric acid, $P_2O_5.2(H_2O) = (H_4P_2O_7)$
Orthophosphoric acid, $P_2O_5.3(H_2O) = 2(H_3PO_4)$.

Of these three acids the most important is orthophosphoric acid, or ordinary phosphoric acid (H_3PO_4). It is tribasic, and forms three classes of salts, as—

Monosodium orthophosphate = NaH_2PO_4
Disodium orthophosphate = Na_2HPO_4
Trisodium orthophosphate = Na_3PO_4.

The atoms of hydrogen can also be replaced by different monad metals as in microcosmic salt, which is hydroammonium sodium phosphate ($H.NH_4.NaPO_4$).

If orthophosphoric acid be heated to 215°, two molecules lose one molecule of water, and pyrophosphoric is formed, thus—

Orthophosphoric acid		Water		Pyrophosphoric acid
$2(H_3PO_4)$	$=$	H_2O	$+$	$H_4P_2O_7$

This acid is tetrabasic, and forms four series of salts with monad metals.

If the orthophosphoric acid be heated to redness, one molecule of the acid loses one molecule of water, and metaphosphoric acid is formed, thus—

Orthophosphoric acid		Water		Metaphosphoric acid
H_3PO_4	$=$	H_2O	$+$	HPO_3

This acid is also prepared by dissolving the pentoxide slowly in water. It is monobasic and forms only one class of salts. All these acids are deliquescent and very soluble in water. They are distinguished by the following tests :—

Orthophosphoric acid, when neutralised, gives a white precipitate with barium chloride, and a yellow one with silver nitrate. Neither the acid nor any of the salts coagulate albumen.

Pyrophosphoric acid does not coagulate albumen, and gives white precipitates with silver nitrate and with barium chloride, only in neutral solutions.

Metaphosphoric acid coagulates albumen, and gives a white precipitate with barium chloride or silver nitrate.

Chlorine readily combines with phosphorus to form the *trichloride* (PCl_3). It is a colourless fuming liquid, decomposed by water into phosphorus and hydrochloric acids—

Phosphorus trichloride		Water		Hydrochloric acid		Phosphorous acid
PCl_3	$+$	$3(H_2O)$	$=$	$3(HCl)$	$+$	H_3PO_3

The trichloride readily absorbs chlorine to form *phosphorus pentachloride* (PCl_5), which is a yellowish crystalline solid. If this substance be exposed to moist air, it forms phosphorus oxychloride ($POCl_3$).

ARSENIC (As = 75)

Is often classed amongst the metals on account of its lustre and other physical properties which it possesses. It is incapable of forming a base with oxygen, and the general character of its chemical combinations justifies its consideration with the non-metals. Being a complete analogue of phosphorus, it is best studied after that element.

The element is found in combination with iron as mispickel ($FeS_2.FeAs_2$), also as realgar (As_2S_2), and yellow orpiment (As_2S_3). The ore is roasted, and the fumes of arsenic trioxide are collected and reduced with charcoal in covered crucibles, arsenic subliming in the upper part of the apparatus.

Arsenic oxidises slightly in moist air, is very brittle and crystalline. At 180° C. it volatilises without fusion, and its vapour density is twice as great as its atomic weight, consequently its molecule is assumed to contain four atoms instead of two. The vapour has the peculiar odour of garlic.

Oxides.—On heating, arsenic readily combines with oxygen to form the *trioxide* (As_2O_3). Arsenic trioxide dissolves to a small extent in water to form arsenious acid (H_3AsO_3), but this is not known in the free state. It combines with metals to form arsenites.

If arsenic or the trioxide be warmed with nitric acid, the *pentoxide* is formed (As_2O_5). This oxide combines with three molecules of water to form arsenic acid (H_3AsO_4), which forms salts called arsenates, corresponding to the phosphates.

Arsenic trioxide, or white arsenic, is employed in the manufacture of glass, in the preparation of colouring matters, as a constituent of sheep dipping compositions, fly papers, vermin killers, and in arsenical soap, which is used for the preservation of skins and natural history objects.

Commercial white arsenic is a fine white powder so closely resembling flour in appearance that it has occasionally been substituted for it, with disastrous results. It is, however, so heavy (sp. gr. 3·8) that it can easily be distinguished from flour, and under the microscope is seen to consist of glassy crystalline fragments.

White arsenic is, fortunately, only very slightly soluble in water; a cold saturated solution containing only 2·5 grams of the oxide in a litre of water. In event, then, of the oxide being thrown into water, but little dissolves; and if the mixture be stirred and swallowed, the insolubility of the oxide aids the treatment by antidotes, the chances of success being greater than in the case of easily soluble metallic poisons. The smallest dose, attended with fatal results, is about two grains.

The employment of arsenic as a constituent of green colouring matter is now, happily, to a great extent, a thing of the past; but it has been recklessly employed in wall papers, lamp shades, and even as a colouring matter for confectionery.

If zinc, alloyed with arsenic, be acted on by dilute sulphuric acid, the hydrogen given off is mixed with an excessively poisonous gas called *arsenuretted hydrogen* (AsH_3). This gas is readily decomposed on heating, arsenic being deposited. It burns with a livid flame forming arsenic trioxide and water. If a cold surface be depressed on the flame, so as to lower the temperature of the gas, a mirror of arsenic is obtained (Marsh's test).

If arsenious acid be distilled with strong hydrochloric acid, *arsenious chloride* is obtained ($AsCl_3$). This affords an excellent method of determining the presence of arsenic in certain cases, the material being boiled with strong hydrochloric acid in a retort, the distillate is diluted with water and sulphuretted hydrogen gas passed through. If any arsenic be present, a yellow precipitate of the sulphide (As_2S_3) will be obtained. This method, however, is useless in determining the presence of arsenic when mixed with organic matter, on account of the frothing up of the mixture when boiled. The simplest way is to acidify with hydrochloric acid, place in the mixture a strip of clean copper on which a narrow strip of platinum foil has been wound, and warm gently. If any arsenic be present, it will be deposited on the copper. To determine its presence the copper is carefully wiped and dried, and heated in an open tube. The arsenic will oxidise to trioxide, which volatilises, and the crystals formed can be dissolved and tested in the usual way (Reinsch's test).

CHAPTER XXIV

THE METALS

The elements are for the sake of convenience divided into two groups, the non-metallic elements and the metallic; but it must be clearly borne in mind that no natural line of demarcation of this kind exists, and that the properties of the elements exhibit a gradual transition from those elements which are unmistakably non-metallic in their characteristics to those which have equally definite metallic properties, so that with some elements, such as arsenic, a certain amount of doubt exists as to which division they should belong.

Physically, metals are recognised by their lustre and power of conducting heat and electricity, whilst the chemical definition of a metal is "*an element capable of forming a base by union with oxygen.*"

Nearly all the metals used in the arts and manufactures are found in Nature combined with other substances; indeed, gold and platinum, both of them rare metals, which have very little affinity for other elements or compounds, are the only exceptions to this; the remaining metals, although small quantities may be sometimes found uncombined, practically exist only in combination. If a piece of iron is exposed to the action of moist air, the iron rusts, that is, becomes finally converted into a compound of iron with the oxygen of the air, called oxide of iron; the whole of the original metal being eaten away if exposed for a sufficiently long period. Again, if a silver vessel is exposed to the air, it slowly becomes tarnished, due to the formation of sulphide of silver on its surface, caused by traces of sulphuretted hydrogen in the atmosphere. It is therefore evident that the ordinary metals are in a more or less reactive condition, and, if left to themselves, are ready to unite with certain other substances to form compounds; and it is for this reason that these metals are not generally found in a pure state in Nature.

The native compounds of the metals are called "minerals" or *ores*, and the art of extracting metals from their ores is called "metallurgy."

The principal ores are, as a rule, oxides, sulphides, carbonates, arsenides and silicates of the metals, and most of them have been formed at a high temperature. These compounds hardly ever occur in a separate state, but are more or less mixed with other minerals, and in nearly all metallurgical operations, the ore from which the metal is to be extracted has to undergo several mechanical operations in order to free it as far as possible from these extraneous matters, *the gangue*, before it can be subjected to the particular chemical operations which isolate the metals from the elements with which they are combined.

The removal of the gangue by mechanical means is seldom complete, so that it is necessary to cause it to combine with other materials during the operation of smelting so that it may be separated as a "*slag*" from the molten metal. Materials added for this purpose are termed "*fluxes*," and the general principle underlying the selection of a flux are those based upon the mutual reaction of bases and acids, for the slags are really salts formed at a high temperature by the combination of basic and acidic oxides. An acid gangue demands a basic flux; a basic gangue must be fluxed by silica.

Slags are essentially fusible silicates, formed by the combination of silica (SiO_2), which is an acidic oxide, with such basic oxides as lime (CaO), alumina (Al_2O_3), etc., to form silicates of the type $CaO.SiO_2$ and $Al_2O_3.3SiO_2$. The fusion point of such simple silicates as the above is, however, high, but it is found that silicates containing more than one basic oxide are far more easily fused, and the process of fluxing is directed to the formation of the most fusible slag, since its separation by gravity from the metal is more easily accomplished. A typical double silicate of this nature is $3CaO.Al_2O_3.3SiO_2$, which melts at 1400° C.

The formation of a suitable slag is also essential to the economical production of most metals, for in the absence of suitable bases like CaO, Al_2O_3, etc., any excess of silica will combine with the oxide of the metal under process of extraction, leading to considerable working losses.

The metallurgical processes are nearly all chemical reactions carried on between dry materials at a high temperature; where fusion takes place they are based upon reactions occurring between the fused materials. Such processes may be divided into two main classes, roasting and smelting.

The *roasting* may be either (*a*) *roasting and reducing,* as when oxide of iron is heated to a temperature short of its melting point in contact with gases capable of abstracting its oxygen and leaving metallic iron; or (*b*) *roasting and oxidising,* as when sulphide of copper is roasted in a current of air, when the oxygen of the air converts the sulphur into sulphur dioxide, and the copper into oxide of copper. The reducing or oxidising nature of the action is determined by the kind of furnace used and the proportions of air, fuel and ore taking part in the operation.

In roasting operations the temperature employed is not allowed to rise to the melting point of the materials used; but in *smelting,* sufficient heat is generated to melt the substances. In the liquid state they then react upon one another, forming new compounds, and in some cases liberating the metal, as when oxide, sulphide and sulphate of lead are melted together and produce metallic lead with liberation of gaseous sulphur dioxide.

By the term "oxidation" we imply an action in which the oxidisable element or compound combines with the element oxygen, as when iron rusts, or carbon burns in oxygen gas; while the term "reduction" means the abstraction of oxygen, or some element resembling oxygen in its behaviour, such as sulphur, from a compound; as, for instance, when copper oxide is heated in a stream of hydrogen gas, the hydrogen takes the oxygen from the copper oxide to form water and "reduces" the copper oxide to metallic copper. Again, iron heated in the presence of molten lead sulphide combines with the sulphur and so reduces the lead from its ore.

In all metallurgical processes the most valuable reducing agent in use is carbon, the solid itself reducing many metallic oxides when heated in contact with them, whilst a still more powerful effect results from its partial combustion to carbon monoxide, this gas having great reducing properties. Not only therefore does carbon, in the form of coke, charcoal, or coal, supply the necessary heat to carry on the process, but it also plays an effective chemical part.

General Properties of the Metals.—With the exception of mercury, all the metals are solid at ordinary temperatures; most of them have definite crystalline structures, and are possessed of a certain power of reflecting light called metallic lustre, which, however, they exhibit only when in compact masses and not when in a fine state of division.

For a metal to exhibit lustre in a high degree, it follows that its surface must not easily be acted upon by the atmosphere, thus gold, platinum and highly burnished steel have a high lustre, whilst such metals as lead have but little lustre.

Colour is also an important characteristic of metals, and determines mainly their use for certain purposes; for example, the great advantage in coins of having marked differences in colour, and again for ornamental work in metals.

However, practically all metals in common use derive their great value from their more purely mechanical properties; their strength; the ease with which they can be worked to the desired shape; their fusibility, and such properties; and for most purposes strength must be the first consideration.

When a piece of metal is subjected to a stretching force (*stress*), a certain amount of extension (*strain*) is produced, this being proportional to the stress up to a certain point. If the stretching force is no longer applied, the metal returns to its original dimensions, that is, it has *elasticity*. After reaching this *limit of elasticity*, the strain increases in greater rapidity than the stress, and now on releasing the metal from the tension it no longer attains its original dimensions, in fact it has become permanently distorted. Further stretching leads to actual rupture of the metal, and the stress applied, in tons per square inch, to bring about this result is taken as the measure of the *tensile strength* of the metal. Between the point when permanent distortion and actual rupture occurs, there may be a short or long period depending greatly on the particular metal. A metal which goes on stretching for some time before rupture is said to have high extensibility, for example copper, a property which permits of much work being done on the metal by hammering, rolling, etc., whilst hard steel, although having high tensile strength, has little extensibility, consequently it cannot be *appreciably* beaten out or rolled when cold.

A large number of factors influence the actual tensile strength of any metal, such for example as the amount of work which has been done on it, and therefore values for the tensile strength must not be regarded as fixed points in the same way that the melting point may be. For instance, cast copper has a tensile strength of about eight tons, whilst that of sheet copper amounts to some fifteen tons, and of copper wire to twenty-eight tons.

The tensile strength also is largely influenced by the presence of foreign substances; thus with steels it increases with the increase of carbon present, but the actual effect of various other elements it is more convenient to consider when dealing with the properties of the individual metals.

The Malleability is a measure of that property which certain metals possess of being rolled or beaten out into sheets, and will naturally be largely dependent on the extensibility of the metal. The influence of temperature on malleability is very great, thus zinc is not malleable at ordinary temperatures, but can readily be rolled at 150° C.; again, ordinary brass is malleable at the normal temperature, but Muntz metal, containing a higher percentage of zinc, must be rolled hot.

A metal is said to be *ductile* when it can be readily drawn down into wire, a condition which will depend mainly on the softness of the metal and on its tensile strength, since it has to resist the pull necessary to draw it through die plates of diminishing section. A metal, therefore, which is extremely malleable (soft) may not possess the necessary strength to permit of it being drawn into wire, for example lead. Iron or mild steel, on the other hand, although not particularly soft, have such high tensile strength that they may easily be drawn down very fine, a process which greatly increases the tensile strength, thus a piano wire of 0·0284 inch diameter had a tensile strength equivalent to 211 tons per square inch.

The *Specific Gravity* of metals varies greatly and is frequently a determining factor in their suitability for many purposes, thus the high specific gravity of gold enables a high value to be attained in a small compass in coinage, whilst the low specific gravity of aluminium, combined with its relative strength, gives the metal many advantages for certain special purposes, examples of which are its use in the framework of balloons and for overhead conductors for high voltage currents, it being extensively employed for this latter purpose in the big power works at Niagara.

Any treatment of the metal which tends to bring the particles closer together, such as rolling, hammering or pressing, will naturally increase the specific gravity.

The specific gravity of the metals as compared with water varies considerably, lithium being the lightest, whilst osmium and iridium are the heaviest.

SPECIFIC GRAVITIES OF COMMON METALS.

Lithium	0·50	Cobalt	8·5
Potassium	0·86	Cadmium	8·6
Sodium	0·97	Copper	8·9
Calcium	1·58	Bismuth	9·8
Magnesium	1·75	Silver	10·5
Aluminium	2·56	Lead	11·4
Barium	3·75	Mercury	13·59
Antimony	6·7	Gold	19·3
Zinc	7·1	Platinum	21·5
Tin	7·3	Iridium	22·4
Iron	7·8	Osmium	22·4

Metals may be divided into two groups according to their specific gravities, those below five being called the "light metals," whilst those of higher density are called the "heavy metals." The light metals generally exhibit considerable chemical energy and oxidise readily, forming strong basic oxides, whilst the heavy metals are less energetic and form weaker basic compounds.

The metals are all conductors of heat and electricity, two properties in which they are in somewhat close agreement, as will be seen from the table below. The high conductivity of copper makes it particularly valuable for electrical purposes, but here the influence of even traces of impurity is very great. The resistance increases rapidly with rise of temperature, and the converse is true with lowering of temperature, in fact at extremely low temperatures, such as that of boiling liquid air, all pure metals become practically ideal conductors, but this does not apply in the case of alloys.

CONDUCTIVITY OF THE COMMONER METALS FOR HEAT AND ELECTRICITY.

Metal	Heat	Electricity
Silver	100	100
Copper	73·6	77·4
Gold	53·2	55·9
Aluminium	31·0	34·0
Tin	14·8	17·0
Iron	11·9	14·4
Lead	8·5	7·7
Platinum	8·4	10·5
Bismuth	1·8	1·2

The Fusibility of metals and alloys is of great practical importance, since those which can be brought readily to the liquid condition may be employed for the production of castings, as with iron, brass, gun-metal, etc., whilst the ready fusibility of the alloys containing tin and antimony, together with the slight expansion they undergo on setting, render them extremely valuable for type in printing. On the other hand, the high melting point of platinum is of the greatest value, since it enables crucibles, etc., of this metal to be employed in the laboratory without fear of fusion ; and again, to cite a more common example, the infusibility of wrought iron makes it the best of all the common metals for use as fire bars.

All metals are fusible, but their points of fusion vary very widely, as shown in the following table :—

MELTING POINT OF COMMON METALS.

Metal	Melts at °C.	Metal	Melts at °C.
Mercury	−39	Aluminium	654
Potassium	+62	Silver	962
Sodium	97	Gold	1065
Tin	232	Copper	1085
Bismuth	270	Cast iron	1150
Cadmium	321	Nickel	1484
Lead	327	Wrought iron	1500
Zinc	419	Platinum	1780
Antimony	630	Iridium	1950

STRUCTURE OF METALS AND ALLOYS.

It is at once apparent that many of the physical properties of the metals will, to a large extent, be dependent on their actual structure, and it can readily be shown by even a superficial examination that many mechanical operations have a profound influence on the structure. Although in accordance with our usual system of classification all metals, with the exception of mercury, are regarded as solids, the fact must not be overlooked that metals generally do not exhibit that extreme rigidity which is associated with the ideal solid, for in all of them a certain amount of internal movement or " flow " can be brought about, depending on their "extensibility." Lead, for example, is commonly "squirted" under a pressure of some thirty-three tons to the square inch, behaving as a viscous fluid, and further examples of this flow are seen in the striking of medals, in planing, polishing and "spinning."

The appearance of the fractured surface of a bar of metal has always been the worker's guide to the quality of the metal and the timing of the operations involved in its production, and the fracture is a rough indication of the molecular arrangement in the metal. Zinc, for example, exhibits a highly crystalline fracture, whilst that of hard steel shows an extremely fine grain; wrought iron, on the other hand, having a fibrous fracture.

The structure as exhibited by the fracture will be greatly influenced by the treatment to which the metal has been subjected. Slow cooling, allowing as it does the particles to arrange themselves, generally tends to the production of a coarse fracture, a fact well illustrated in the differences observed in the case of a large casting, the more solid parts of which having taken the longest time to cool, develop a relatively coarse structure, as shown by the fracture. When metal is "chilled" in casting, the outer portion will exhibit a fine fracture.

The introduction of the microscope into the study of the structure of metals by Dr. Sorby in 1864, marked a period of great advance in metallurgy generally, and now the micro-structure of metals forms an important branch of the study, and has done much to throw light on many hitherto obscure problems. For the purpose of examination, the metal is first highly polished, in which process frequently considerable structure becomes visible, since the softer portions are more readily rubbed away, but generally it is necessary to further develop the structure by suitably etching, for during the polishing a "flow" is produced in the surface layers and a uniform film of metal results which must be removed before the true crystalline structure beneath is revealed. In other cases differences of composition, etc., become manifest through a staining action of the reagent employed.

The application of the microscope to the study of metals may be in two directions—first, to the study of the structure and mode of crystallisation of pure metals and to the constituent bodies of which an alloy is generally composed, and the effect of mechanical and heat treatment on the structure; secondly, to diseases of metals which may have resulted from over-heating, to the "decay" or corrosion of metals in use, to the study of the causes of the well-known " fatigue " which some metals exhibit, and finally to the consideration of failures arising through the separation (segregation) of impurities, such as manganese sulphide in steels.

A pure metal is found to be built up of a number of grains of varying size and roughly polyhedral in shape, and an exactly similar structure is exhibited in certain alloys where only one constituent is present, for it then behaves as a pure metal (Fig. 2, Plate III). When a molten metal is allowed to slowly cool crystallisation starts almost simultaneously from a number of points and proceeds in several directions producing a large number of fern-like growths radiating from centres. That this is so may be shown by pouring off the still fluid portions. Crystallisation of this type is known as *dendritric,* and is illustrated by Fig. 1, Plate I, where the crystals are those on the surface of a cast block of antimony, and similar dendritic structure is exhibited in cast brass. Such growths proceed from different centres until they interfere with each other and finally the space between the branching growths fills up with solidified metal. Obviously such a method of the growth of crystals will lead to the production of individual grains of the irregular polyhedral shape referred to above.

By more deeply etching these polyhedral crystals further light is thrown on their nature. It is now found that light is reflected from them at very different angles and the appearance in Fig. 3, Plate III, is noted, where the specimen is under oblique illumination. On bringing the light upon the surface from the opposite side, the bright crystal faces in the first case become the dark surfaces in the second. Closer examination at higher magnification shows that this is due to each grain being built up of infinitely small crystals all arranged in the same axial relation to each other in the same grain, which axial relation is different in nearly every crystal, and the bright or dark appearance is due to the reflection of light from these minute surfaces all parallel to one another in a given crystal.

Mechanical treatment of the metal breaks up this natural conformation, and moreover intertwines adjacent crystals ; finally, all crystalline structure is lost and the metal becomes hard. This is illustrated in the case of hard rolled brass (Fig. 1, Plate III). On annealing by heating for a brief period the polygonal structure is again developed (Fig. 2, Plate III), and by longer annealing so that the conditions are favourable to the arrangement of the minute crystals in their most normal position, the dead soft brass shows the structure already described (Fig. 3, Plate III). When raised to incipient fusion the dendritic structure of cast brass is once more developed.

This normal crystalline structure of the grains exercises an important influence on the behaviour of a metal under strain, and has thrown much light upon the well-known fatigue which metals, subjected for long periods to alternating strains, exhibit. Ewing and Rosenhain examined pieces of metal under the microscope whilst actually being strained, and showed that while each grain was extended slightly no actual disarrangement of the regular crystal formation in the grain took place, and they liken the conditions to that existing when a pack of cards is distorted by a slight slip of each card over the adjacent ones. Parallel lines would be developed, when viewed from the end, and such lines (" slip bands ") were noted on the surface of strained metals. Given a continual slipping to and fro through frequent straining in use, lines of potential weakness would develop and may ultimately result in fracture.

In the study of the nature of steel and alloys the microscope has proved an invaluable adjunct to other methods, and has led to a very great extension of our knowledge of these important commercial metals and the conditions in which the constituents actually exist, and upon this the specific properties are dependent. The consideration of this important subject is deferred to the later chapter on " Alloys."

CHAPTER XXV

IRON AND STEEL

Iron ($Fe = 56$).

Iron is by far the most important of the metallic elements; its strength with comparative lightness, its fusibility in certain forms, the possibility of welding masses of it together, and the hardness which can be imparted to it, make the applications of the metal extremely varied. Further, the comparative ease with which the metal may be reduced from its ores, and the wide and abundant distribution of these ores, make the first cost of the metal very low.

Metallic iron is met with in the form of meteorites, metallic masses which occasionally fall upon the earth from unknown sources, and which generally contain small quantities of other metals, such as nickel, cobalt, chromium, etc.

The chief native compounds which are sufficiently abundant to make them valuable as a source of the metal are :—

		Percentage of iron in pure ore
Magnetic iron ore	Fe_3O_4	72
Specular iron ore	Fe_2O_3	70
Red hæmatite		
Brown hæmatite	$2(Fe_2O_3).3(H_2O)$	60
Spathic iron ore	$FeCO_3$	48
Clay ironstone	$FeCO_3$, mixed with clay,	17 to 48
Iron pyrites	FeS_2	46

These ores all contain certain quantities of foreign impurities, some of which, like sulphur and phosphorus, are nearly always present and exert a deleterious influence on the metal obtained from them. The magnetic iron ore, specular ore, and red hæmatite are the purest ores, and it is from these, therefore, that the best iron is obtained, whilst the difficulty in separating the sulphur prevents iron pyrites from being used as a source of the metal.

Magnetic and specular iron ore, however, do not exist in sufficiently large quantities in England for them to be much used, and the density of the red hæmatite offers considerable obstacles to its easy reduction, so that the most commonly used ores in this country are the brown hæmatite, the spathic iron ore, and the clay ironstone ; in spite of the low percentage of metal present in the latter ore, it is the one from which by far the largest proportion of iron is made in this country.

Production of Pig Iron in the Blast Furnace.—Many simple forms of furnace have been employed in the production of iron, which, by varying the working conditions, may be obtained in almost any of its well-recognised forms, but for all practical purposes the pig iron as produced in the ordinary practice of smelting in the blast furnace may be regarded as the parent body from which all the different grades are obtained, ranging from wrought iron, which is nearly free from carbon, to a high carbon steel.

The general relationship between the various commercial forms of iron and steel to the parent pig iron is shown overleaf.

The reduction of a simple oxide of iron by means of charcoal in a suitable small furnace is an easy operation, the iron so produced being of remarkable purity, and charcoal iron is still produced for special purposes in this way. The majority of the iron ores are, however, not in bulk the simple bodies represented by the preceding formulæ, but contain varying amounts of foreign mineral matter which complicate the process of production. It is necessary with most ores to carry out preliminary purification by washing, calcining, etc., and to make a careful computation of the character and amount of the flux to be added for the removal of the remaining foreign substances in the form of slag. The possible formation of a very fusible slag which ferrous oxide (FeO) forms with silica has to be especially guarded against as this would lead to large working losses of iron.

Preparation of the Ore.—In the case of the purer ores, the hæmatites and magnetites, no preliminary treatment is required, but poor clay ores are frequently washed, or in some cases " weathered " in order that the sulphur present as pyrites may be largely oxidised and washed away. Ores containing carbon dioxide require a preliminary calcination, which drives off water and carbon dioxide, rendering the ore more porous, and at the

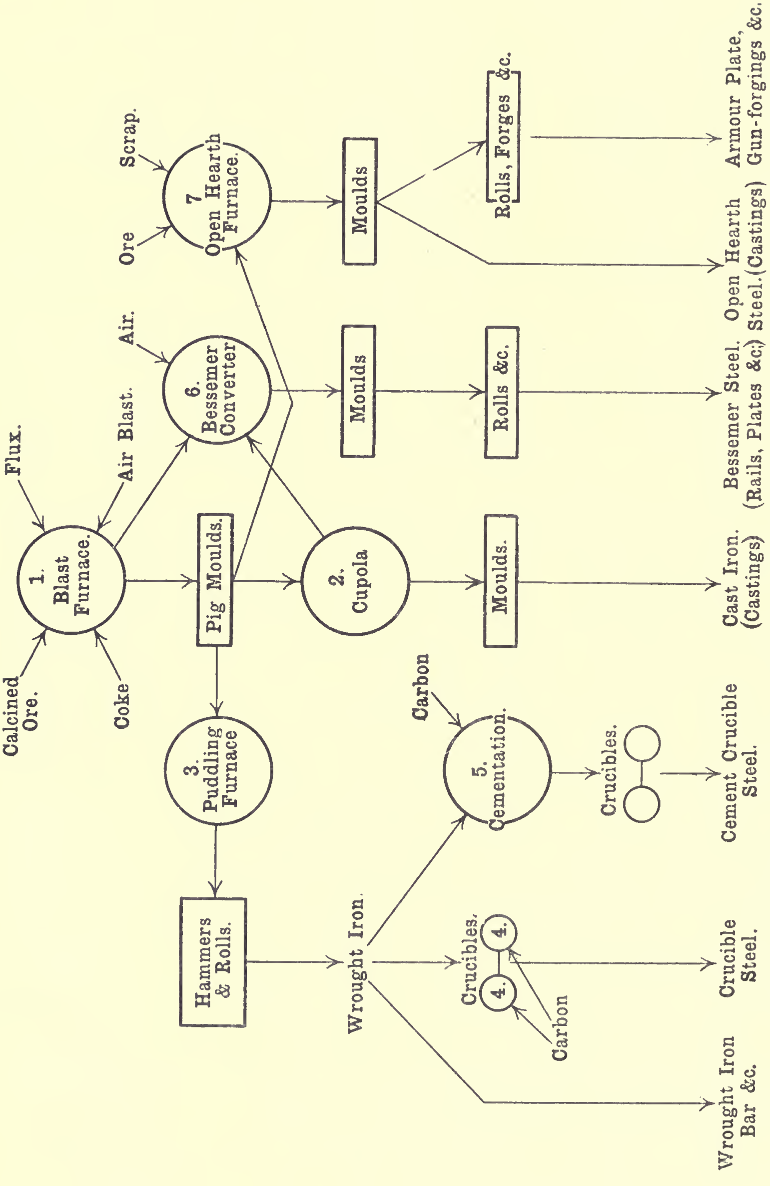


FIG. 50.—Diagram showing relationship between commercial irons and steels and pig iron.

same time converting any ferrous oxide (FeO) into ferric oxide (Fe_2O_3), an important consideration in view of the ease with which the former combines with silica to produce the fusible slag already mentioned.

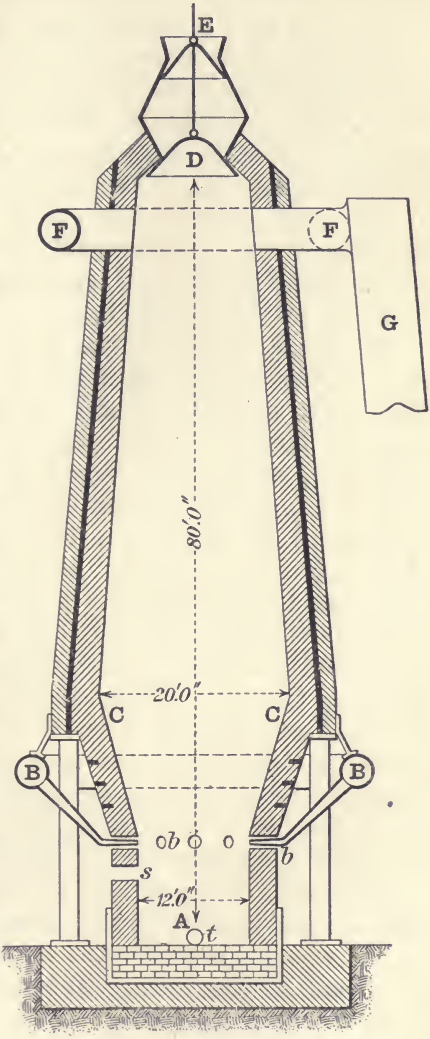


Fig. 51.—Diagram of blast furnace.

The Blast Furnace.—The general shape and arrangement of the blast furnace is shown in Fig. 51. It consists essentially of two long conical parts placed base to base, the upper and longer constituting the body of the furnace and the lower, where the furnace narrows, the "bosches" (C). Below the bosches is the hearth (A), of cylindrical shape. The top part, where the charge is introduced, is known as the "throat." The whole of the interior is built up of fire-brick, and between the brick and the outer casing of iron plates a layer of mould or similar loose material is packed, which will yield to the expansion and contraction of the brick.

At one time the throat of the furnace was always open and the combustible gases were allowed to burn to waste. The utilisation of these gases was introduced in 1845, and the arrangement for their collection on the most modern system is illustrated at F and D. Large gas outlets are provided just beneath the throat, and the furnace top is closed by double inverted cones (D) and (E), each working below a hopper. These are mechanically operated when material has to be introduced, and it is arranged so that at no time are both bells simultaneously depressed. The escaping gases are led away by the down-comer (G). The temperature of the escaping gases is usually between 150° and 270° C.

The blast is introduced into the furnace a little above the level to which the metal and slag may rise, through a number of water-cooled "twyers"(*b*) which are supplied from the blast ring (B), a circular pipe running round the furnace. The air supplied for each ton of iron produced amounts to some 4–5 tons, so that very large blowing engines are required in a modern installation, and it is common to provide for the delivery of 50,000 cubic feet of free air per minute. The pressure of the blast at the twyers is from 6–15 lbs.

For certain classes of iron the blast is used cold, but a very great improvement in blast furnace practice resulted from the introduction of the hot blast by Neilson in 1829, the output of a particular furnace being greatly increased, the fuel consumption diminished, whilst at the same time certain classes of coal could be used directly in the furnace without previous coking. Two stoves are built close to each blast furnace, these being arranged with a suitable checkerwork of fire-brick; through one of these the hot waste gases are being led with the air necessary for combustion, thus heating up the one stove, whilst the air blast is being forced through the other stove in the reverse direction, taking up the heat from the hot fire-brick within. Control over the temperature of the blast is now usually maintained by a suitable self-recording pyrometer, the valves controlling the stoves being operated to reverse the gas and air current, when the temperature of the blast has reached the minimum permissible. The initial temperature of the blast is frequently above 800° C.

The hearth of the furnace is provided with a tap hole (*t*) at its lowest part for running off the iron produced, and at the highest level to which it is permissible for the slag to rise, on account of the twyers, a "slag notch" (*s*) is constructed. Through this the slag is regularly removed.

The general arrangement of a modern blast furnace plant is shown in diagrammatic form in Fig. 52. The ore, fuel, and flux are conveyed to the top of the furnace either by an inclined skip-way or by lifts; the charging arrangements are automatic. The blast is supplied from the blowers, operated by a portion of the waste gas, to one or other of the hot blast stoves, heated by

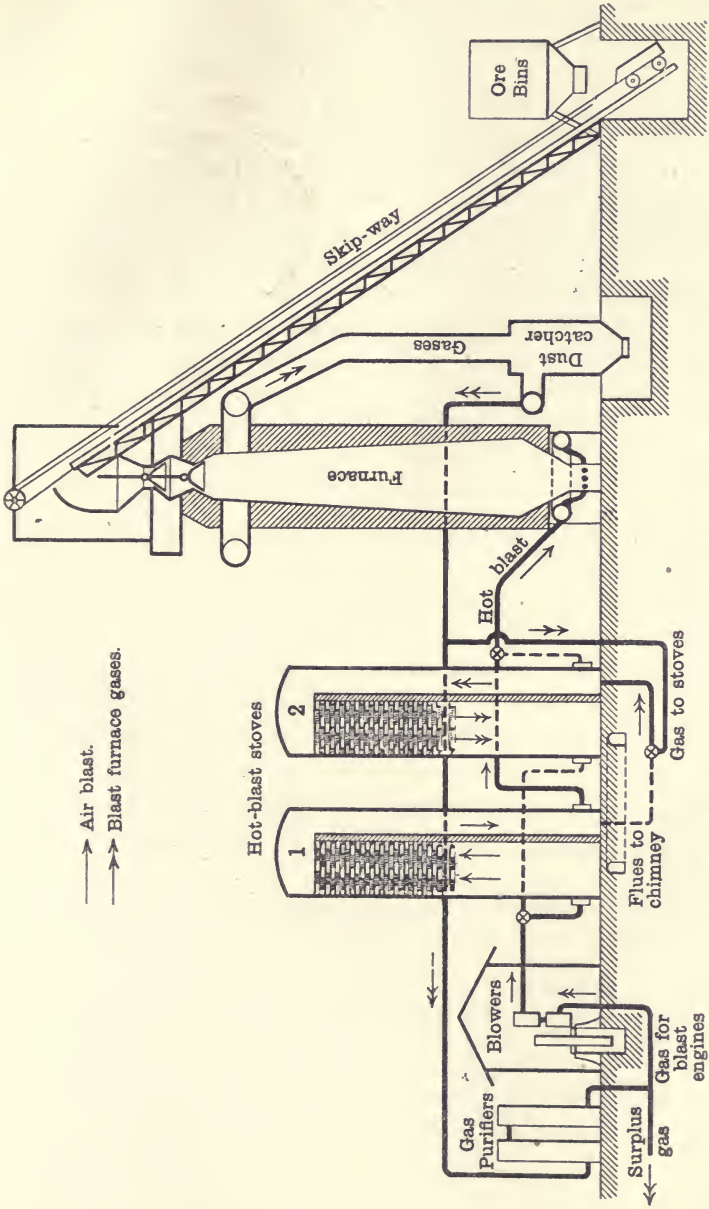


FIG. 52.—General arrangement of blast furnace plant.

another portion of the waste gas. In Fig. 52, stove 1 is heating the blast, which is indicated throughout by single arrows ; stove 2 is heating up by the combustion of a portion of the waste gases, shown by double arrows. The rest of the waste gases pass on through long pipes of large diameter to the gas purifying plant, from which a portion supplies the necessary power for the blowing engines. An important point is the removal of dust carried over by the gases ; this is partly accomplished by deposition in the dust catcher and in the long length of pipes the gas is made to traverse, the final portions being removed in a centrifugal washer by means of water.

The composition of the waste gases averages : CO_2, 12 per cent. ; CO, 30 per cent. ; nitrogen, 58 per cent., and its calorific value is about 90 B.Th.U. per cubic foot. About 165,000 to 170,000 cubic feet are produced per ton of iron and about one-third is available with modern installations for power purposes outside that employed in operating the entire plant.

Charge for the Furnace.—This may conveniently be divided under three headings—

(*a*) The ore or a mixture of ores.
(*b*) The fuel, usually specially prepared coke.
(*c*) The flux, which, as already pointed out, depends on the nature of the ore. Frequently the blending of a clay ironstone (acidic), with a calcareous ore (basic) is all that is needed.

In general terms, for the production of one ton of metal a solid charge of some three tons of ore, fuel, and flux will be required.

A typical charge for the production of 1 ton of Cleveland pig iron is—

Charge.		Products.	
Calcined ironstone	48 cwt.	Pig iron	20 cwt.
Limestone ..	12 ,,	Slag	30 ,,
Coke	20 ,,	Gases	130 ,,
Air	100 ,,		
	9 tons.		9 tons.

The furnace, when once " blown in," is kept in blast for years, the ore, flux and fuel being regularly charged in proper proportions, control of which is maintained by constant analysis of the metal and slag. In most modern forms of furnace a "closed" hearth is employed, the molten iron settling to the bottom, and over it the fused slag, which flows away continuously through a suitable *slag-notch.* The composition of the slag is very variable, depending upon the composition of the ore, the working conditions, etc. A good slag approximates to $6(2CaO.SiO_2) + 2Al_2O_3.SiO_2$. The metal is tapped every twelve hours, being run off through sand channels into sand moulds, placed at right angles to the channels, where it solidifies into "pigs," which are U-shaped in section, and weigh from 1 to 1½ cwts. each. A considerable quantity of slag passes off with the metal. In order to remove this an iron plate is pushed down in the sand walls of the channels so that a dam is formed beneath which the iron flows.

A high average output for an English hot blast furnace may be taken as 1000 tons weekly, whilst in American practice 2500 tons is common.

Reactions in the Blast Furnace.—These may be most conveniently divided under two heads: (*a*) those changes taking place in the ascending gas current; (*b*) those in the descending charge.

(*a*) The oxygen of the blast on entering at the twyers, at once combines with the carbon of the fuel forming carbon dioxide; this at the very high temperature becomes dissociated into carbon monoxide and oxygen, the latter combining with a further amount of carbon forming more carbon monoxide.

Carbon		Oxygen		Carbon dioxide
C	$+$	O_2	$=$	CO_2
Carbon dioxide		Carbon monoxide		Oxygen
CO_2	$=$	CO	$+$	O
Carbon		Oxygen		Carbon monoxide
C	$+$	O	$=$	CO

This is clearly shown by the fact that neither free oxygen nor carbon dioxide is found in the ascending gases a short distance above the twyers.

As the gas current ascends, carbon dioxide is found in increasing quantities, and this is believed to be due mainly to the decomposition of carbon monoxide into carbon dioxide and *free carbon* when in contact with hot spongy iron, the particles of the latter becoming impregnated with carbon.

$$\overset{\text{Iron}}{Fe} + \overset{\text{Carbon monoxide}}{2(CO)} = \overset{\text{Iron}}{Fe} + \overset{\text{Carbon}}{C} + \overset{\text{Carbon dioxide}}{CO_2}$$

Certain subsidiary changes in the gases also go on at the same time; thus in the body of the furnace carbon dioxide is constantly combining with more carbon to form carbon monoxide, and again when carbonates are present (as when limestone is used as a flux), carbon dioxide is evolved in the higher parts of the body. In general, a high percentage of carbon monoxide must be maintained in the furnace for the successful production of iron.

(*b*) Considering next the changes in the descending charge of solid materials: in the upper part of the furnace, before the material reaches even a low red heat reduction of the Fe_2O_3 of the ore takes place, chiefly according to the following equations:—

$$(1)\ 2(Fe_2O_3) + 8(CO) = 7(CO_2) + 4Fe + C$$
$$(2)\ Fe_2O_3 + CO = 2(FeO) + CO_2$$

At a slightly higher temperature reduction by solid carbon is also set up.

$$(3)\ Fe_2O_3 + 3C = 2Fe + 3(CO)$$

Ferrous oxide (FeO) is more resistant to the reducing action of carbon or carbon monoxide than is Fe_2O_3, and requires to reach a full red heat for its reduction.

It has been shown by equation (1) that carbon becomes set free from carbon monoxide at the low temperature at the top of the charge. Lower down the reduced spongy iron acting on CO sets free a further quantity of carbon, according to the equation—

$$(4)\ Fe + 2(CO) = Fe + C + CO_2$$

It is the carbon separated by these decompositions and deposited in a finely divided state throughout the spongy reduced iron which afterwards furnishes the high carbon content characteristic of pig irons.

As the charge passes downwards little further change is noted until the smelting zone is reached, all the reducing effect being confined to probably the first 20–25 feet from the top. The limestone, added for fluxing, breaks up about the centre of the furnace into lime (CaO) and CO_2. At the bosches fusion commences, the iron trickling down over and completing its saturation with carbon, and here the slag begins to form. Here, also, the impurities silicon, manganese, phosphorus and sulphur will be set free and taken up by the iron, the following being the principal reactions :—

$$(a)\ SiO_2 + 2C = Si + 2(CO)$$

This is favoured by high temperature, so that with a hotter blast or high ratio of fuel to ore there will be greater tendency to high silicon iron, and this indirectly determines that the iron is "grey," containing much free (graphitic) carbon. On the contrary a basic slag, since it combines with SiO_2, will render the iron less grey.

$$(b)\qquad P_2O_5 + 5C = P_2 + 5(CO)$$
$$(c)\ FeS + CaO + C = CaS + Fe + CO$$

This last reaction is of special importance, illustrating the effect of excess of lime at high temperatures in removing the objectionable sulphur. This enters the furnace mainly as pyrites (FeS or FeS_2) in the coke. At a low temperature lime and pyrites do not act as in equation (*c*), so that sulphur passes into the iron, rendering it hard and white. An increase in the fuel favours the reaction by giving a higher temperature, and although this involves the introduction of a greater total amount of sulphur into the furnace, very little passes into the iron, the bulk going to the slag.

PIG IRON.

The material as obtained from the blast furnace is known as "*pig iron*"; after re-melting and casting it is known as "*cast iron*," though no chemical difference is to be found between them.

In each case a considerable quantity of carbon is present, the actual amount as well as its condition (whether free or combined) depending on the other elements present. Pure molten iron can dissolve about 7 per cent. of carbon, the maximum in pig or cast iron being about 4·5 per cent. (Howe). Chromium and manganese increase the amount of carbon iron can dissolve.

When the molten iron solidifies, the dissolved carbon may be thrown almost completely out of solution as plates of graphite, or it may remain almost wholly in the combined state, when the iron will be white, the rate of cooling and the presence of other elements (especially the latter) having a marked influence on the condition of the carbon. Slow cooling and the presence of silicon and aluminium set the carbon free, producing a soft grey iron, whilst rapid cooling and the presence of sulphur, manganese and chromium produce a hard white iron.

Pig iron is commercially graded according to the appearance of its fracture, the greyest iron (containing most free carbon) being termed No. 1, whilst the hard white iron is the last of the series. The general classification in this country is—

No. 1
No. 2
No. 3
No. 4 (Foundry)
No. 4 (Forge)
Mottled
White

The influence of the working conditions in a blast furnace on the character of the iron is great; as shown above, high temperatures, that is a high fuel ratio to the ore or a hotter blast, the more silicon in the iron; low fuel ratio means a poor white iron, high in sulphur.

The differences existing between grey and white pig iron are very marked.

Since grey cast iron is nearly pure iron with free carbon distributed throughout it, it is comparatively soft and can be easily worked; it has a higher fusing point than white iron, but when fused is more liquid, and expands at the moment of solidification due to the liberation of the bulky graphite.

White iron has a higher specific gravity than the grey, 7·6 sp. gr. white iron—about 7 sp. gr. grey iron—and is excessively hard and brittle; it fuses at a lower temperature than the grey iron, but is never so liquid or so well adapted for taking castings as the grey. The hardness of white iron is so marked that it can be cut only with special tools.

If molten grey iron is suddenly cooled, the graphite which has redissolved in the liquid metal has not time to separate, and the casting becomes in consequence extremely hard and of the appearance of white iron. This is taken advantage of in "*chill casting*," by which shot and shell cast from grey iron have the apex and outer skin of metal made as hard as steel by casting them in iron moulds. The hard material so produced is very brittle, but since the interior portion has cooled more slowly, this interior consists of tough grey iron, which gives it any necessary support. Great judgment is needed in selecting a suitable iron for chilling, one which gives a slightly mottled fracture when cast in sand being best.

The relative proportions of free carbon (graphite) and combined carbon (as cementite) in irons containing approximately the same carbon is as follows :—

	Grey	Mottled	White
Graphite	3·4	2·2	0·1
Combined carbon	0·1	1·4	3·2

Cast Iron.—This is the cheapest form in which iron can be commercially applied, its great value being due to the ease with which it can be melted and the exactness with which it takes the form of the mould, since on solidifying slight expansion takes place. Since the contraction of the solidified metal exceeds the expansion on solidification allowance is made for this in the patterns, usually one-eighth of an inch to the foot.

As compared with cast steel it has the following advantages ; less cost in production of the moulds, smaller losses in casting, and further the castings do not require the careful annealing which steel castings must undergo. The disadvantages of cast iron are principally its lack of ductility and malleability ; it can therefore only be worked to shape by cutting away.

An iron simply containing carbon, which may be termed "pure cast iron," is quite unsuitable for casting purposes, the small amounts of other elements present in ordinary cast iron, notably silicon, conferring upon the metal its much desired characteristics. "Pure cast iron" lacks fluidity, and castings in it contain many blow-holes.

It is seldom that one class of iron is employed for castings, since the desired amounts of those constituents which tend to produce good results can be obtained only by blending, whilst further the use of mixed irons places the iron-founder in a more independent position as regards supplies.

The metal is usually melted down in a cupola with about one-quarter of its weight of fuel, the fuel and metal being charged in alternate layers, together with a little lime to assist in slagging off any impurities, when the iron undergoes certain changes, the silicon being reduced, owing to oxidation, whilst the sulphur is increased, since a certain amount is generally absorbed from the fuel. Further, the total amount of carbon is somewhat reduced, whilst the alteration in the silicon and sulphur both tend to the production of white iron having the carbon in a combined condition, hence the metal becomes harder. A soft grey iron, in fact, is considerably improved in strength.

Care has to be exercised in the selection of a metal suitable to the size of the casting it is intended to produce, a coarse grained iron, in a large casting, developing a still coarser grain in slow cooling, hence weakness, whilst the same iron might be well suited for small castings, where the rapid cooling of the metal produces a closer grain. Silicon being the main determining factor in the liberation of graphite, it follows that a low silicon iron is most suitable for a large casting which will solidify slowly, whilst to get the same amount of graphite in a small casting a highly siliceous iron must be employed.

The influence of foreign elements on the properties of cast iron is very marked. Silicon prevents the formation of carbon monoxide, the main cause of "blow-holes," and so produces sounder work, besides increasing the fluidity of the metal. For very fine work, where strength is not of prime importance, a fair amount of phosphorus may be present, since it promotes fluidity and diminishes shrinkage. With less than 1 per cent. of phosphorus, the accompanying weakness is more than counterbalanced by the greater soundness of the castings. Manganese is frequently employed as a softener for hard irons, counteracting as it does the tendency of sulphur to keep the carbon in a combined state.

In regard to mechanical properties, cast iron may be obtained which offers greater resistance to crushing than any other material, special irons showing a crushing strength of little less than 100 tons per square inch, though the average for British irons is about 40 tons (Turner). A tensile strength of 10 tons per square inch may readily be obtained, and as high as 21·2 tons has been recorded. The average transverse strength may be taken as 20 cwts., though South Staffordshire founders have obtained iron standing 40 cwts. with fair regularity (Turner).

A notable property of grey iron is the large permanent increase in volume which it undergoes on alternately heating to a red heat and cooling—conditions which occur in the use of cast-iron pans, etc. A bar heated and cooled 27 times increased in volume over 40 per cent. and suffered a great decrease in strength.

Malleable Cast Iron.—Although castings in ordinary foundry iron may be so cheaply produced, their value is greatly discounted for many purposes by the lack of strength of the material. White cast iron is by nature hard and brittle, whilst grey iron containing large plates of graphite offers lines of cleavage along which a break readily occurs. White cast iron can, however, in small masses be converted into a tough malleable substance by prolonged heating, usually with some gentle oxidising substance, a process first described by Réaumer in 1722. The tensile strength of malleable cast iron may range from 40,000 to 60,000 lbs. per square inch. Under proper treatment, the carbon, which in the original casting is wholly in a state of combination, becomes converted into a specially fine-grained form of graphite, a certain portion of it at the same time being oxidised, so that the malleable iron obtained always contains less total carbon than the original. At the same time the sulphur present passes out into the surrounding oxidising material, and it may be the loss of this sulphur which largely determines the appearance of the carbon in a free condition in the malleable iron.

Prolonged heating alone, the metal being protected from the action of hot gases by surrounding it with any inert material, will also bring about dissociation of the carbon-iron compound, but better results are obtained by using a gentle oxidising body such as hæmatite ore, and hence this is now universally employed.

The most successful results are obtained with special hæmatite iron which has been freed from silicon, and containing about 3 per cent. of carbon, mainly combined. The castings are made in green sand, being afterwards thoroughly cleaned, when they are packed into iron boxes and surrounded with hæmatite broken down to a coarse grain. If all the hæmatite be fresh, it exerts too powerful an oxidising action and the malleable casting is uneven in quality, hence it is usual to employ mostly old ore with a proportion of new. The charged boxes are then closed and heated up for several hours at a temperature of 800–875° C., the length of time being determined by the size of the castings. When cooled down the castings show a fine grey fracture ; they may be easily worked with a file and are fairly malleable. Malleable cast iron, however, cannot be welded, and it is liable to suffer from defects, owing to blow-holes in the original casting.

WROUGHT IRON.

The large quantities of foreign matter present in cast iron diminish its toughness and tensile strength, and render it unfit for use in many applications of the metal, and in order to give it the property of toughness, it is converted into a purified form called "wrought iron." This may be regarded as commercially pure iron, but it is always associated with small quantities of slag, which, from the subsequent rolling the metal undergoes, confers upon it a fibrous texture to which the special properties of wrought iron may be ascribed.

Wrought iron melts at a very high temperature (hence its use for furnace bars, etc.), but before melting passes through a pasty stage which permits of its being welded. When cold it is ductile (distinction from cast iron), whilst if heated and suddenly quenched it cannot be appreciably hardened (distinction from steel). It is prepared from cast iron by removing the impurities with which the latter is associated, such as carbon, silicon, phosphorus, etc. This purification is based on the fact that when cast iron is heated in contact with oxide of iron, the carbon and silicon combine with the oxygen of the oxide of iron, carbon monoxide being evolved as a gas, and the silicon combines with the oxygen to form silica, which unites with another part of the oxide of iron to form a slag; this being very fusible, can easily be separated from the metal. It is essential that the slag shall be of a highly basic character. Bessemer first introduced his process with the view of producing soft wrought iron by a simpler process than that of "puddling," but the metal so obtained, being free from slag, had not the fibrous character necessary in wrought iron, and so the process is now employed entirely in the production of steel, which, however, may contain so little carbon (mild steel) as to approach wrought iron in this respect.

Several direct methods of producing wrought iron from the ore have been tried, but far the greater part of this material is produced by the "*puddling process*." At one time the pig iron was always treated by the "dry" puddling process, which involved the use of white pig, since this could be obtained as a pasty mass, the surface of which was oxidised by the excess of air in the furnace, this oxide being well worked into the mass by the workman to carry the oxygen necessary for the oxidation of carbon, silicon, and phosphorus, to all parts. When only grey pig iron was available, it was necessary to first convert it into white iron in a "finery." It will be noted that the necessary oxygen had to be first absorbed by the pasty iron from the air. A great advance on this method was introduced by Hall in 1830, when he employed oxides of iron produced in other ways for the oxidation of the impurities, carrying out the process with the iron in a fluid condition, instead of a pasty one. The carbon monoxide produced by the interaction of the iron oxide and carbon of the pig caused violent boiling, hence this "wet" process came to be known as *pig-boiling*.

Reverberatory furnaces are employed in both puddling processes, that for pig-boiling having a bed consisting of cast-iron plates, which are "fettled" with suitable basic slags, some consisting of the roasted slag obtained during the working of the process, and a certain portion, above this in the lower part of the bed, of "hammer slag." The essential point is that the molten iron has always below it free oxides of iron from which the impurities in the iron may draw oxygen to assist in their oxidation. The process is usually conducted in four stages :—

1. The furnace having been heated up, has a charge of from ½ to 1 cwt. of hammer slag thrown into it and then some 4½ cwts. of broken pig iron, which is allowed to melt down slowly, the molten iron and slag being well mixed. At this stage the silicon is mainly oxidised together with much of the manganese, and normally about half the phosphorus originally present is removed.

2. The whole having become fluid is now kept in this condition for about half an hour, with constant rabbling, when the remaining silicon and manganese are oxidised, and also a considerable amount of the phosphorus.

3. The temperature is now reduced and the mass well rabbled to bring the oxide of iron into intimate contact with the molten metal. The carbon is rapidly oxidised with the evolution of carbon monoxide, which gives the metal the appearance of "boiling." Quantities of slag (*tap cinder*) are produced, and flow out into suitable trucks, this cinder being frequently calcined to be afterwards employed in fettling the furnace.

The violence of the reaction will have ceased in about half an hour, and the metal "comes to nature," showing the process to be complete.

4. All that now remains is for the workman to raise the

temperature sufficiently to thoroughly soften the almost pure pasty iron in the furnace, in order that he may work it into " blooms " of a size suitable for the subsequent treatment.

The changes brought about may be briefly summarised. Silicon and manganese are almost completely oxidised and removed in the slags. Of the phosphorus originally present some 75 to 80 per cent. will have disappeared and possibly 50 per cent. of the sulphur, whilst the carbon will have been reduced from some 3 per cent. to less than one-tenth of this quantity. The removal of phosphorus and sulphur depends entirely on the slag being of a highly basic character.

Gas-fired puddling furnaces on the regenerative principle are now extensively used, and when the success of the Bessemer process was assured, large numbers of patents were taken out for furnaces in which the puddling process was carried out mechanically, it being hoped to thus stave off the threatened extermination of the process. Few of these mechanical appliances have remained in use, and since the character of puddled iron is much superior for special purposes to the soft iron which can be produced by the Bessemer process, the manufacture by " puddling " still holds its own.

Treatment of the Puddled Iron.—The blooms obtained are far from uniform and are impregnated with large quantities of slag. To remove this, it may be hammered or squeezed. The hammering was formerly entirely performed by " *helves*," a type of heavy hammer, usually weighing some six tons, which was raised by four cams on a rotating axle and allowed to fall on the bloom below. Rotary squeezers and steam hammers are generally employed at the present time, since greater masses of metal can be worked under them, and the process is quicker. The slag forced out of the blooms is termed " hammer slag," and is charged into the puddling furnace (see p. 395). The hammered iron is now taken to the rolls and after passing through the first pair is termed " No 1 iron," or puddled bar. This is far from uniform, containing considerable quantities of slag. To produce greater homogeneity the bars are cut into short lengths, " piled " together in bundles and reheated, when they are again hammered to weld them together, and passed through the rolls, giving " No. 2 " or " merchant " bar. By again repeating the process a still better quality iron (No. 3) is obtained. Compound bars can be obtained by suitable selection of the irons and arrangement of the short bars in the pile, thus the centre bars may be of high tensile strength, whilst the outer bars may be of a tough iron.

Wrought iron is of a very fibrous nature, is ductile, fusible only at very high temperatures. Its good working properties at the forge and the ease with which it welds render it unsurpassable for smiths' work. Because of its high fusion point it is used for furnace bars and other purposes where the metal must get highly heated. In a dead soft condition it is employed in dynamos, motors, etc. The tensile strength may vary from 18 to 30 tons, and it is usual to specify for 17 to 26 tons, according to the size and quality required.

STEEL.

The cheap production of steel which has been rendered possible during the last sixty years through the inventions of Bessemer and Siemens has had an enormous influence on the whole commercial development of the world, and it is almost impossible to mention any great industry which has not benefited by the introduction of this material in a cheap form. For constructional work, for ship-building, rails, guns, and a thousand other industries, it has proved invaluable. Before the announcement of Bessemer's great discovery at Cheltenham in 1856, the total steel produced in this country was 51,000 tons (1855), the price being about £50 per ton, whilst Sheffield alone produces some 830,000 tons annually at a price of £4 and upwards (Roberts-Austen).

The first boiler in which Bessemer steel-plates were employed was constructed in 1860, and steel rails were tried about the same time, and found to outlast in many cases twenty iron rails. In 1863 two steel barges were built, and in 1864 a 400-ton paddle-steamer, to be followed shortly after by a ship of 1250 tons (Turner).

Before the introduction of the mild steels produced by the Bessemer and Open Hearth processes, the definition of steel was a simple matter. On the one hand was wrought iron containing less than 0·2 per cent. of carbon, which could not be hardened on quenching, yet could be welded and forged hot; and on the other hand, cast iron containing from 2·5 to 4 per cent. of carbon; a material which could not be forged hot and could only be employed in the form of castings. Between these two varieties of iron came steel, which could be forged hot and whose special characteristic was that it could be hardened on quenching, such steel containing an amount of carbon intermediate between that in wrought and cast iron. That steel could be made by dissolving wrought iron in molten cast iron was shown by Réaumer in 1722.

Much of the steel produced by modern methods contains so little carbon that it cannot be appreciably hardened by quenching, in fact it only differs from wrought iron in the absence of a fibrous structure, and in having been cast whilst in a molten state. Harbord defines such steel as "purified pig iron in which the carbon and other impurities present have been reduced to such a point that the ingot cast is capable of being forged or rolled into blooms, slabs, etc."

Production of Steel.—Since ordinary steel is an intermediate body between pig iron and wrought iron, its production would be a fairly simple matter if, in the puddling of iron, the process could be stopped before the whole or nearly the whole of the carbon had undergone oxidation. *Puddled steel* was produced in this way from an iron containing much carbon and manganese, the latter serving to protect the carbon from too rapid oxidation, but clearly the great difficulty of knowing exactly the right point at which to check the process in order that the desired quantity of carbon might remain in the product was very great, and so the process never became general. It is usual to completely oxidise out the carbon and produce wrought iron, afterwards treating the bars by the *cementation process* in such a way that the requisite amount of carbon is taken up by the pure iron. It was by this process that practically all steel was produced before the introduction of the Bessemer and Open Hearth processes, and for some purposes, such as cutlery, tools, etc., steel is still produced by cementation, although crucible steel made directly from iron and carbon has largely superseded it.

The process depends on the fact that at a high temperature iron in contact with carbonaceous matter absorbs a certain amount of carbon, the quantity being largely dependent on the length of time the materials are kept in contact at the requisite temperature. Carbon monoxide was at one time supposed to play an important part in the process, but since if pure iron and carbon be heated together in a vacuum the carbon is found to penetrate the iron, producing steel, and again if cylinders of pure iron are shrunk on to hard steel cores and heated out of contact with air, diffusion of the carbon into the soft iron is easily seen, it may be assumed that diffusion is what actually occurs in practice.

The cementation furnace has in the interior two rectangular pots, which are usually some 12 feet in length and 3 feet in cross section, which are heated by fires below, the heat being uniformly distributed by suitable flues. For the manufacture of the highest quality steel, Swedish iron is employed, hammered bars being preferred to those which have been rolled. A layer of charcoal is placed in the bottom of the pot, and then the iron bars are laid in with spaces between each bar, another layer of charcoal and more bars being added until the pot is full; the top is then well covered with the sediment from grindstone troughs, termed "wheel swarf," which fuses and protects the contents from oxidation. There is a hole at the end of each pot, in order that a trial bar may be withdrawn and examined to see how the carburisation is progressing.

The furnaces are slowly heated up and maintained at a temperature somewhat over 1000° C. for several days, according to the carbon content required in the finished steel, when the furnaces are allowed to cool down slowly. The bars of steel obtained are, from their appearance, termed *blister steel,* the blisters being produced by the interaction of the carbon with small quantities of slag present in the original bar, with the production of carbon monoxide. It is highly important that air shall not reach the bars during the process, for it leads to the oxidation of the carbon in the outer layers (aired bars).

As might be expected, the amount of carbon in the outer portion of the bar will be much greater than in the interior; in fact, if the process is only carried on a few days for the production of mild steel, the interior portion will still be soft iron. This combined carbon is in the form of *cementite,* a name obviously derived from this process. Fine needle-shaped crystals of this constituent are seen in high carbon steels and a section of such steel is shown in Fig. 1, Pl. V. With an "aired" bar, on the other hand, the outer layers are practically free from carbon.

The cemented bars are afterwards made up into faggots, heated (with suitable precautions to prevent oxidation) and drawn out under the hammer, thus producing *shear steel.* Occasionally these bars of shear steel are folded on themselves, reheated and hammered to produce *double shear steel.* The material is afterwards drawn into suitably thin form for cutlery and other purposes.

Crucible Steel.—Shear steel is naturally anything but uniform throughout, and a great advance was made in the production of steel when Huntsman (1740) introduced the melting down and casting into suitable ingots of the shear steel. For this purpose crucibles or pots are employed which hold about 56 pounds of the broken up shear steel, and this is melted down in a special furnace.

For mild steels fireclay pots are employed, since their use does not lead to the introduction of more carbon, whilst for the harder steels it is usual to employ pots made by mixing Ceylon graphite with fireclay. In melting, the amount of carbon present is generally reduced, and the use of pots containing carbon minimises this loss.

Large quantities of crucible steel are now made by the direct solution of carbon in molten wrought iron, a process far more economical in time and fuel than the cementation process. Most tool steels are now made by melting the wrought iron in the crucibles, adding the carbon and necessary " physic " (manganese, etc.), and for the special alloy steels, the other elements such as chromium, tungsten, vanadium, etc.

The molten steel is poured into long iron moulds of square section, with a slight taper. Great judgment is required in " teeming " into the moulds. The steel is allowed to remain in the pots until it is " killed," that is until it will pour without the evolution of gases (principally carbon monoxide) which causes the metal to pour " fiery " and become full of blowholes. If allowed to remain too long in the pots it pours " dead " and the metal is brittle and unworkable. These changes are due to the absorption of silicon from the silica (SiO_2) of the pot. Silicon promotes soundness by its interaction with carbon monoxide, whereby it forms silica and sets free the carbon. On long standing so much silicon passes from the pot into the metal that it completely spoils the steel, in which only the merest traces of silicon should be present.

When poured at the proper time the ingot " pipes," that is a hollow cone is formed in the upper part due to the great contraction of the steel on solidification. The evolution of gas on the metal solidifying would obviously be against the tendency to contraction so that a good pipe is evidence of sound metal. After removing the "pipe" until sound metal is reached, the ingot is reheated and rolled or forged to the desired section.

The percentage of carbon in crucible steels ranges from 0·5 to 2 per cent., the amount or "temper" varying with the particular work which the steel is being prepared for, thus "razor temper" indicates 1·5 per cent. of carbon; "chisel temper," 1 per cent. "die temper," 0·75 per cent.

CASE HARDENING.

The case hardening of iron and the production of armour plate are but special applications of the process of cementation. In both it is desirable to leave a tough interior or backing of soft steel, whilst the surface shall be capable of being rendered exceedingly hard.

For the former the articles, having been machined to the approximate requirements, are packed into iron boxes with material to supply the requisite carbon, some of which it is desirable to have as hydrocarbon vapours, charred leather or material to which a certain amount of oil has been added, being excellent for the purpose. The box is then closed with a lid, which is luted into place, and the whole raised in temperature. The depth to which the carbon penetrates depends on the time the materials are kept heated in contact with each other. The contents of the boxes are now turned out into water, a sieve being usually placed a few inches below the surface to catch the "cemented" articles, which by this treatment become hardened. Various colours can be given to the pieces according to the height from which they are allowed to fall into the water, owing to more or less oxidation in their passage through the air. Any slight distortion is removed by grinding.

The production of armour plate is described later (p. 425).

CHAPTER XXVI

STEEL (*continued*)

THE BESSEMER PROCESS.

THIS has proved to be one of the most important inventions in metallurgy, and its influence on the extended use of steel has already been referred to. The oxidation of carbon and other constituents in pig iron by blowing air upon the molten metal was known for generations, and employed in the old "finery" hearth. Bessemer's original idea was to blow air through the metal and so prepare it for use in the puddling furnace; he does not appear to have recognised at first the possibility of producing such a high temperature that the oxidation could be carried to completion, whilst the heat developed maintained the metal in a fluid condition. The practically pure iron thus obtained required the addition of carbon in suitable quantities to convert it into varying grades of steel, but such pure steel proved unworkable, owing to the amount of oxide left in. The addition of manganese, which acts as a "deoxidiser" by reducing the oxide of iron, the manganese oxide passing into the slag, is essential.

The process is carried out in a "converter" (Fig. 53), consisting in the most modern forms of three portions—the bottom section, which is easily removable, the body and the nose. Since the bottom section will only stand from twelve to fifteen "blows," whilst the upper portions will last several months, it is a great advantage to have the former easily replaceable. The bottoms are usually mounted on cars, which can be run under the converter and brought into position by a hydraulic ram, when they are clamped into place. The whole converter is built up of either mild steel or wrought iron plates, and is lined with a fireclay lining, "ganister," a special form of clay, being usually employed. The converter may have the nose situated either eccentrically or concentrically, the former being usually employed for the "acid" process, the latter for the "basic."

The converter can be rotated on trunnions, the air blast being conveyed down one arm (A) at a pressure of 20 to 25 lbs. into the blast box at the bottom of the converter, whence it is delivered through fireclay twyers (B) in the bottom of the vessel. There are several of these twyers arranged in the bottom, each having from twelve to eighteen holes in it.

When charging, the nose of the converter is turned down in order that the twyers may be above the level of the molten iron which is poured in, sometimes from the blast furnace direct or a suitable mixer which may hold iron from several furnaces, so ensuring uniformity in the charge; or from a special cupola in which the pig is melted down. The blast is now turned on and the converter rotated to a vertical position. During the first period of the blow, the slag-forming stage, it is mainly the manganese and silicon which undergo oxidation, their respective oxides uniting with iron oxides to form slags. This period is characterised by the appearance of the flame issuing from the mouth of the converter, which is irregular and of violet colour, but gradually increases and becomes more yellow.

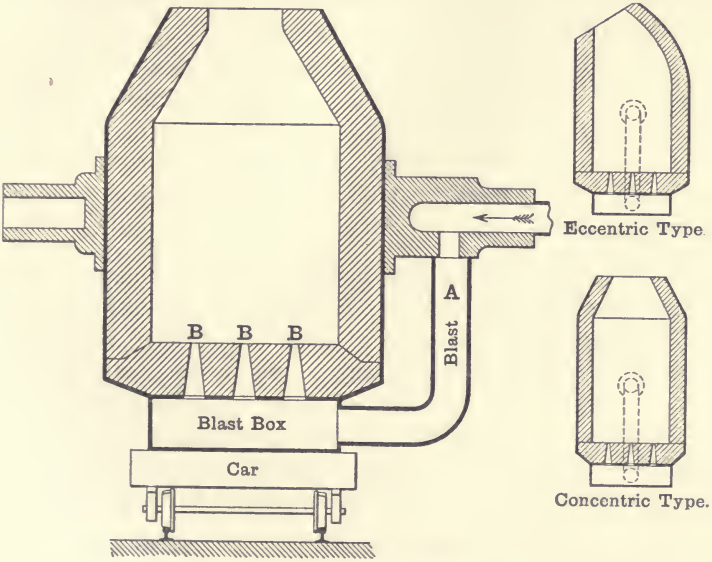


FIG. 53.—Bessemer Converters.

In the second period the oxidation of manganese and silicon continues, but the main reaction is the conversion of carbon into carbon monoxide, the escape of which gas is responsible for the "boil" of the metal. The gas burns at the mouth of the converter as a brilliant large flame, and quantities of metal and slag are ejected.

The third period is marked by the dropping of the flame, since very little carbon now remains to give rise to carbon monoxide. Remaining traces of silicon and manganese are oxidised away, and the blow comes to an end in about twenty minutes from the commencement. The general changes taking place during the process are evident from the analyses below :—

	Carbon	Silicon	Manganese	Sulphur	Phosphorus
Pig as used ..	3·93	1·96	3·46	0·02	0·040
5 mins. blow ..	2·46	0·44	1·64	trace	0·040
10 ,, ,, ..	0·90	0·11	0·43	trace	0·045
15 ,, ,, ..	0·09	0·03	0·11	trace	0·045
After spiegel added	0·25	0·03	0·16	trace	0·045

The iron is practically free from manganese, silicon, carbon, etc., and the charge has now to be "finished" by suitable "additions," depending on the class of steel it is desired to produce. Manganese is absolutely necessary to make the steel workable, and to introduce this, together with the requisite carbon, either *ferro-manganese* or *spiegeleisen* is added. These are manganese-iron alloys produced by specially smelting manganiferous iron ores in the blast furnace. Their composition is approximately—

	Ferro-manganese	Spiegeleisen
Manganese ..	70–80 ..	.. 10–45 per cent.
Carbon	6 ..	.. 5 ,,

To introduce into the steel the requisite amount of manganese, less ferro-manganese is required, hence less carbon is at the same time introduced. Ferro-manganese is therefore added in lumps for mild steel. On the other hand, for hard steel where more carbon is required, spiegel is employed, and since the quantity added is greater, it is always melted first. When the charge has had time to properly mix it is poured into the casting ladle, which, being mounted on a suitable rotating platform, can be brought successively over the ingot moulds. The more modern practice is to swing the casting ladle over the first of a series of cars into which the metal is run (car casting), a second car being pushed forward to replace the first when full, and so on.

The removal of phosphorus and sulphur in this process is practically negligible, whilst the temperature necessary to keep the bath fluid, in spite of the cooling effect of the large volumes of air passed through, is derived mainly from the combustion of the silicon. It follows that to produce a good steel the iron employed must be free from more than traces of phosphorus and sulphur, but contain a fair proportion of silicon. Too much of the latter, however, causes the metal to blow hot.

The Tropenas Converter.—This type is particularly suitable for producing small quantities of special steels for a foundry, and has the advantage of turning out the metal at a higher temperature, and, therefore, in a more fluid state, than the ordinary Bessemer converter. Such Tropenas converters are employed in the shell factory at Woolwich Arsenal, the capacity of each being two tons.

In these converters the first oxidation is effected by the blast acting downwards on the surface of the metal, it is only in the later stages of the process that the air passes through the bath. The twyer box is arranged about one-third the height of the converter from the bottom, there being two rows of twyers, one row a few inches above the other.

For carbon steel shells the purest hæmatite pig and good scrap steel are melted in cupolas and run into the converter. Since the scrap is deficient in silicon some ferro-silicon is also thrown into the converter, otherwise the requisite temperature would not be attained. The converter is partly turned up, and an air blast directed on the metal from the lower twyers. Later, the converter is brought to the vertical position, the other row of twyers put in operation, and the changes completed by the air passing through the bath. The operation lasts about twenty-five minutes, and owing to the oxidation of the carbon yielding a much higher percentage of carbon dioxide than in the Bessemer blow, the finished metal is hotter and pours in a more fluid condition.

For special steels the proper alloys are melted down in pots, poured into the converter, which is turned down for the purpose at the finish of the blow, brought back into the vertical position to promote mixing, and then poured into the ladle.

Basic Bessemer Process.—The acid Bessemer process is only suitable for the treatment of iron containing but little phosphorus and sulphur, since it does not eliminate these undesirable elements, hence until Thomas and Gilchrist introduced their basic method in 1878, the pig irons available were somewhat limited. Enormous quantities of good steel are now produced by the basic method from phosphoric irons.

The whole success of the process depends upon getting the phosphorus into combination with a suitable base (usually lime) in the form of phosphate, in which condition it occurs in the "basic slag" produced. This slag has proved a valuable asset, since it is largely used as a manure. Silica in any quantity is undesirable in the slag on account of its acid properties, hence whilst a siliceous pig iron is requisite for the acid Bessemer process, the quantity of silica present in pig iron for the basic process should not exceed 1 per cent., whilst the phosphorus may be present in considerable amount in order to develop the heat necessary for success.

The converters are of the concentric type and are of larger capacity than those employed in the acid process. The lining is of calcined dolomite, a calcium-magnesium carbonate. To form the basic slag, 3 to 4 cwts. of lime are thrown into the converter per ton of metal, which is afterwards run in and the blow commenced. There is little difference observed in the appearance at the mouth of the converter until the flame "drops," and up to this point manganese, silicon and carbon have alone been oxidised. The blow is now continued for some three or four minutes longer—the "*after blow,*" and it is during this period that the phosphorus is oxidised to phosphorus pentoxide, which combines with the lime forming a calcium phosphate $(CaO)_4.P_2O_5$. The point at which this is completed is determined by taking a sample of the metal, cooling it and fracturing.

In recarburising it is essential that no reducing element, such as carbon, shall come in contact with the slag, otherwise phosphorus and some sulphur will pass back into the metal and ruin it. The reduction of calcium phosphate by carbon may be expressed as—

$$2(3CaO.P_2O_5) + 5C = 6(CaO.P_2O_5) + 5CO + 2P$$

The slag is poured off as completely as possible, and when the metal is poured any remaining slag is held back by a suitable dam. Recarburisation must, therefore, be carried out in the ladle and not in the converter itself.

The general character of the changes in the process are shown below :—

	Carbon	Manganese	Silicon	Sulphur	Phosphorus
Melted metal ...	3·6	0·7	1·7	0·06	1·6
6 mins. blow ..	3·4	0·6	0·3	0·06	1·6
12 ,, ,, ...	0·9	0·3	trace	0·05	1·4
14 ,, ,, ...	0·1	0·1	trace	0·05	0·15
Completed ..	trace	trace	absent	0·03	0·07

THE OPEN HEARTH PROCESS.

Steel made by this process has proved the only serious competitor to that produced by the Bessemer process, and Open Hearth steel is generally preferred to the same class as prepared in the converter. There is not the same risk of over-oxidation, and throughout the production repeated samples can be examined which makes the product a more reliable material.

Siemens conceived the idea of oxidising the impurities in pig iron by the addition of iron ore, whilst in France, Martin worked out a process by which the silicon, carbon, etc., in the pig were partially oxidised, but mainly diluted, by the addition of wrought iron or mild steel scrap. The great difficulty was to maintain a sufficiently high temperature for the reaction, and this Siemens overcame by the introduction of gas firing on a " regenerative " system, by which both the combustible gases and the air needed for their combustion are raised to a high temperature before combination.

The common practice of to-day is to employ both ore and scrap, the whole being melted down in a large rectangular hearth (A, Fig. 54) lined with either silica bricks and sand or basic material, for the process may be either " acid " or " basic," just as in the case of the Bessemer process. The large hearths employed by many firms have a capacity of 45 tons. These are generally built on independent foundations from the regenerators (B,B′,C,C′) and opening at either end of the hearth are the gas and air ports, the air ports being slightly in excess of those for gas. The gas from the producer is led through the gas regenerator (B), whilst the air supply is heated up in (C), the combustible and the supporter of combustion not meeting until they arrive at the furnace proper. The hot products of combustion, after passing over the hearth, are drawn through the other pair of regenerators (B′), (C′), heating them to the requisite temperature, when the controlling valves are reversed, and the gas and air currents sent through in the opposite direction.

The charge varies greatly with the nature of the pig, the scrap available, etc., but usually some 75 to 80 per cent. of pig is charged into the furnace, and 20 to 30 per cent. of heavy scrap charged on top of it, when the whole is slowly melted down, some of the impurities undergoing oxidation. Practically the whole of the manganese, from 35 to 50 per cent. of the silicon, and up to 30 per cent. of the carbon, are removed in this stage. Pure hæmatite is now thrown in, causing the liquid to undergo a violent boiling, due to the oxidation of the carbon with the evolution of carbon monoxide.

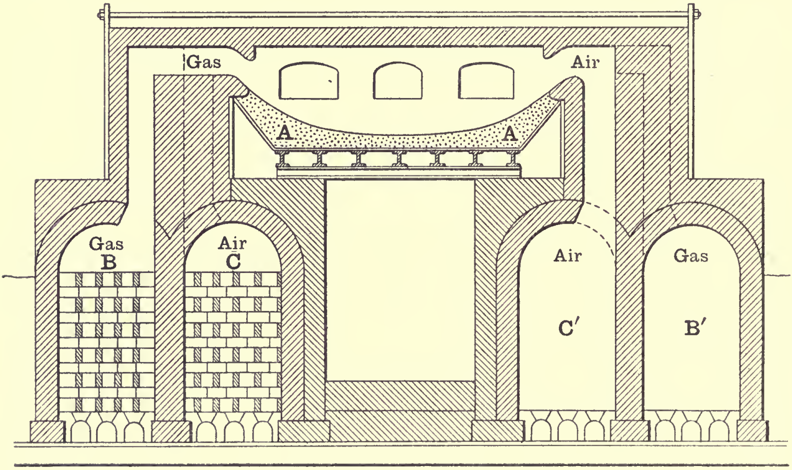


FIG. 54.—Open hearth steel furnace.

$$3C \quad + \quad Fe_2O_3 \quad = \quad 2Fe \quad + \quad 3(CO)$$

In this way the carbon is reduced until the metal is "dead soft," a few pigs of iron are thrown in to keep up a gentle "boil," and then the furnace is tapped, the necessary "additions" of ferro-manganese for mild steel being made to the stream of metal as it flows to the casting ladle. If spiegeleisen is employed for hard steels, it is charged into the furnace before tapping and well rabbled in. Pig iron, or a mixture of pig and spiegel, is also employed in recarburising for high carbon steels.

In order to ensure soundness and the absence of blow-holes it is now the common practice to add a few ingots of aluminium to the metal when run into the casting ladle.

Like the acid Bessemer process, the above method of working does not remove phosphorus or sulphur; indeed, owing to concentration, the amount in the finished steel exceeds that in the original pig iron. It is, therefore, necessary to select a high-class pig iron for working by this process. Since the heat for the operation is derived from external sources, and is not dependent upon oxidising reactions in the bath of metal, a lower silicon content in the pig iron as compared with that requisite for the Bessemer process, is desirable.

The use of "scrap" is not only economical, because the large quantities produced in subsequent treatment of the ingots, etc., can be utilised, but also by reason of the shortening of the time for a heat through the reduction of the total quantity of impurity in the charge which has to be oxidised out. A corresponding reduction in fuel costs follows.

Basic Open Hearth Process.—Large quantities of steel are made by working under basic conditions, the reactions being, in the main, very similar to those in the basic Bessemer process, depending on the maintenance of a highly basic slag containing a fair proportion of lime, with which the phosphorus and some sulphur enter into combination. The lining of the hearth is calcined dolomite. The usual method of charging is to cover the bottom of the hearth with steel scrap, and on this throw the necessary lime and ore, covering this again with the main part of the scrap and pig iron. The whole is melted down in about two hours, and then a further addition of scrap and pig is made.

During the melting down the silicon is almost entirely removed, and a part of the manganese and carbon. Judgment is required to ensure that the carbon has not been entirely eliminated until all the phosphorus has passed into the slag, otherwise the bath goes off the boil, and the intimate contact with the basic slag, so essential to the process, does not take place.

Recarburisation must in this case be effected in the tapped metal, since the introduction of carbon, in the presence of the basic slag, would reduce the phosphorus and cause it to pass back into the steel, just as in the basic Bessemer process.

In the basic Bessemer process much of the heat for the reactions is due to the oxidation of phosphorus, which must, therefore, be fairly high, generally over 1 per cent. In the basic Open Hearth process, much lower phosphorus is desirable, since the heat is derived from external sources.

In many modern Open Hearth plants tilting furnaces are employed; these have the advantages of overcoming troubles and delays with the tap hole, the slag can be removed at any time, and the metal tapped off more expeditiously than through a tap hole. They are more particularly suitable for the basic process, and with a method of partial pouring of the metal, as in the Talbot process, considerable economies are effected in time and cost. In this process, the metal having been completely oxidised, the slag is poured off, and then about one-third of the metal, which is recarburised as usual. Ore and lime are charged in, and then fresh molten pig iron is run in to replace the poured metal, this fresh bath being worked down as before.

Comparison of the Steel from Bessemer and Open Hearth Processes.—It has already been indicated that for each of the above certain classes of pig iron are particularly adapted, and one of the four methods of working enable almost any grade of iron to be converted into good steel.

In the Open Hearth processes the bath of metal being large, and the time of the operation prolonged, more complete control of the process and product is possible, since there is time for taking samples and ascertaining the exact state of the bath by rapid methods of chemical analysis. Acid Open Hearth steel is always specified for where the best material only is permissible, as for armour plate, gun forgings, etc. Basic Open Hearth steel is admitted for ship plates, boiler tubes, etc. In general basic steel carries more oxygen in the ladle and is more liable to blow-holes.

The Bessemer processes offer certain advantages, and are largely employed for general rolling mill work, such as rails, etc. The frequent and small makes, from one or more converters, poured into the moulds of a train, form a most convenient sequence of ingots for the mill to deal with. The large floor space demanded, the large makes and the infrequent tappings in the Open Hearth processes are not so favourable for rolling mill practice.

ELECTRIC STEEL REFINING.

Whilst on theoretical grounds there is nothing against the use of electric furnaces for the direct reduction of iron ores in suitable furnaces, and the refining of pig irons by similar means, considerations of cost are totally against these methods. The cost of the production of steel in such furnaces by melting suitable pig iron with scrap, or pure iron and carburising, also compares unfavourably with Bessemer and Open Hearth costs. The present scope of electrical methods seems confined to the super-refining of steels produced by these latter processes, for it permits of the complete removal of both the remaining phosphorus and sulphur. Steels refined in such furnaces are equal to the best crucible steel, and special alloy steels are easily made, especially those which contain valuable and readily oxidised rare elements.

The general principle of the refining is the washing of the molten metal with successive lots of liquid highly basic slags of strong oxidising power. Such slags are only fusible at very high temperatures, and it is here that the advantage of the high temperature of the electric arc is manifest. The oxidation of phosphorus by a slag rich in oxides of iron is similar to that taking place in the basic Open Hearth process, as is also the absorption of the phosphorus pentoxide by the free lime in the slag. Sulphur can be only partly removed in the Open Hearth process, and at the best its removal is erratic, since the requisite temperature for the reaction

$$\mathrm{C} + (\mathrm{Fe.Mn})\mathrm{S} + \mathrm{CaO} = \mathrm{CaS} + \mathrm{Fe.Mn} + \mathrm{CO}$$

cannot be properly attained, but which is easily carried out in an arc furnace.

Metal super-refined in the electric furnace must be recarburised by ferro-manganese for low carbon steels. For high carbon steels a mixture of pure iron and carbon which have been fritted together by heat is employed, in some cases a pure high silicon pig iron is employed.

DEFECTS IN THE FINISHED STEEL AND THEIR REMEDIAL TREATMENT.

Honeycombing.—However good in composition a steel may be when tapped from the furnace, the subsequent treatment to which it is subjected has an enormous influence on its value. Great trouble arises with low carbon steels, owing to the amount of gases, chiefly carbon monoxide, which are dissolved, causing general unsoundness in the ingots, since these dissolved gases are liberated at the moment of solidification. In some cases, known in the works as "wild heats," the liberation of gas is so copious that the metal boils over. Generally speaking, even the best ingots have small "blow-holes," but since the inside surfaces are clean, they are readily united when properly worked under the hammer or press. Should the blow-holes occur near the surface of an ingot, cracks are likely to develop under the hammer or press or in the rolls; the metal being exposed, oxidises and the cracks do not weld up. Similarly situated blow-holes in steel castings are very objectionable, as there is every chance of the tool cutting into them during machining.

Naturally, any substances which will cause the molten steel to dissolve less gas, or which will be acted on by dissolved gas, will tend to promote soundness in the casting, effects well known to be brought about by silicon and aluminium, the addition of a few ounces of the latter per ton being now common practice.

Fluid compression is also used to attain the same object, the metal being poured into suitably strong moulds, and whilst still fluid, placed in a hydraulic press. Quantities of gas are forced out, and the resulting ingot is much sounder; but after working ingots of the same steel, pressed and unpressed, of course no difference would be expected in them, one great advantage, however, is that a much larger portion of the ingot is available for use if produced under pressure.

Piping.—With high carbon steels, blow-holes or "honeycombing" do not occur, but owing to the great contraction of such steel in cooling, the ingot is always found to have a conical hollow, extending for some distance downwards from the top, termed a "pipe." Piping may be reduced by elongating the ingot mould into a fireclay top in which part of the metal remains fluid and serves as a feeder to the ingot proper below. In large steel castings the "riser" or feeder must be so arranged and be of sufficient size to take the pipe, which is afterwards cut off. Owing to this and the occurrence of slag in the upper parts, much metal has to be sacrificed, and at the bottom of the ingot, due to chilling, the metal is also unsatisfactory, so that the Admiralty require that 30 per cent. from the top and 3 per cent. from the bottom shall be removed from ingots.

Segregation.—This is one of the greatest troubles with steel, especially in large masses. Segregation is the separation of certain constituents during solidification, leading to lack of uniformity. It is due to the presence of lower melting compounds which, by the prior solidification of the higher melting constituents, become concentrated in the last portions of metal to solidify, which will invariably be around the pipe. In large masses where the solidification is most prolonged, segregation will be most prominent.

Carbon segregation is very common, and is due to the melting point of steel being generally lowered by increase of carbon so that the central portions of an ingot, and especially those portions immediately around the pipe, will be richer in carbon than the general steel of the piece. As these parts are cut away, and as the distribution of carbon in the remaining portion is not excessively uneven, carbon segregation is not serious.

Segregates of sulphur, phosphorus and manganese constituents are, however, very serious, as is also that of silicon as silicides. Flaws develop on forging at these segregates, and frequently bad scoring on the interior of drawn boiler tubes may be traced to the same cause. The patch of metal in which the segregate occurs possesses all the bad properties of a highly inferior steel, although the average composition of the metal is excellent, and analysis of drillings fails to reveal this latent trouble. The best method of detecting sulphur segregation is to obtain a good surface on the steel and squeeze down upon it a sheet of ordinary photographic bromide paper which has been soaked in dilute hydrochloric or sulphuric acid (1 part of acid to 10 parts of water). After five minutes the paper is removed, and where sulphur compounds were beneath the evolved sulphuretted hydrogen will have produced a brown skin. The paper must be washed and then fixed in " hypo " as usual. A sulphur print of a transverse section of a rolled bar for making boiler tubes is shown in Fig. 1, Plate VII. The analysis of this steel showed no abnormal sulphur content, but the steel failed in practice, the cause of failure being revealed by the segregates shown in the sulphur print.

Under a high power microscope the segregates may be detected, and a photograph of sulphur segregates is given in Fig. 2, Plate VI. In this case the segregates appear as light-grey circular globules. In Fig. 2, Plate VII, another segregate of regular form, believed to be a silicide, is illustrated.

Obviously the formation of segregates around the pipe causes purification of the sound part of the metal, so that if the sacrificed upper part of an ingot carries all the segregates, the segregation has in reality been beneficial.

Steel castings are liable to fracture from the shrinkage on solidification, which amounts to some $\frac{3}{16}$ths of a linear inch per foot, and in any case the casting will have developed considerable internal stresses, which must be removed by proper annealing.

The value of the steel, in other form than castings, is very largely dependent upon the amount of work which has been done on the hot metal during the finishing stages, such as forging, rolling, etc. The cooled ingots are very slowly heated up in suitable gas-fired furnaces so that they are thoroughly softened right through, and then, according to their size, or the purpose for which they are intended, forged under a steam hammer or hydraulic press, and frequently then rolled, or with smaller ingots taken down in " cogging " mills to a smaller section before passing to the finishing rolls.

It is very essential that the working shall be thorough right through the metal, otherwise the interior portions will be markedly inferior to the better worked exterior. The blow from a hammer is not nearly so penetrative in soft metal as the steady squeeze of the hydraulic press giving a pressure of some 5 to 6 tons per square inch. For this reason all large ingots for armour plate, large guns, etc., are worked under big presses. The failure of rolls to properly work the interior of a bar is well illustrated in Fig. 1, Plate VII, where the sulphur print shows the existence of an unworked portion of the square section of the original ingot, although the reduction had been from an ingot of average measurement of 15 inches square to a round bar $3\frac{1}{4}$ inches in diameter.

Great attention must also be paid to the finishing temperature of the metal when it leaves the rolls, as this largely determines the tensile strength, etc. It is common practice to cool with water to a low red heat for the finishing passes.

PROPERTIES OF IRON AND STEEL.

Pure iron is a soft malleable metal of considerable tensile strength. Its specific gravity is 7·88, and it fuses at about 1600° C. In the presence of moisture and air it readily rusts, and decomposes water at its boiling point with the formation of triferric tetroxide (Fe_3O_4). It dissolves in hydrochloric and sulphuric acids, with the production of ferrous salts. With nitric acids its reactions are somewhat remarkable. When the acid is fairly strong, no action takes place, the metal being termed "passive," and even on the addition of water there is no sign of chemical activity. If now the surface be scratched, at once violent action is set up. With dilute nitric acid a ferrous salt is formed and hydrogen liberated, but with strong acid a ferric salt and nitrogen dioxide are the products.

Wrought iron more nearly approaches pure iron in its composition and properties than any other commercial form of the metal. Like the pure metal, it cannot be hardened by quenching.

If a rod of practically carbonless iron be taken, having a small hole bored in it into which a thermo-junction may be inserted, and the metal be slowly and regularly heated up in a furnace, certain well-marked periods of rest are observed during the heating, and corresponding points also in the cooling; and well-defined changes in physical properties occur at these points. This is generally regarded as indicating certain allotropic changes in the iron, but as the subject is so closely connected with the influence of carbon on iron, the further consideration of the question will be dealt with later (p. 500).

INFLUENCE OF OTHER ELEMENTS ON IRON.

Carbon.—This element has by far the greatest influence on the properties of iron, determining as it does the capability of the metal to be hardened and tempered, its power of becoming permanently magnetised, its melting point and tensile strength, in fact all those properties associated with the different classes of iron and steel.

In a fused condition carbon can dissolve to the extent of 7 per cent. in iron, but on solidifying, a certain proportion is thrown out, so that the maximum found in solid iron is 4·6 per cent. This carbon may be free, as in grey cast iron, where it occurs mainly as plates of graphite, or it may be in combination as a definite carbide, cementite (Fe_3C), as in white cast iron. Certain elements have great influence in determining its condition; thus silicon causes it to separate "free," whilst sulphur maintains it in combination. Other elements influence the amount of carbon which iron is capable of retaining, thus manganese considerably increases the amount.

Within limits, the amount of carbon is proportional to the hardness it is possible to impart to a steel, and likewise to its power of retaining magnetism. The tensile strength is also greatly increased with increase of carbon present.

The very important influences of this element were not understood until the question came to be studied by careful temperature measurements, aided by microscopic examination of the various specimens which had been subjected to well ascertained thermal treatment, but since steel is regarded as an iron-carbon alloy, the full consideration of its structure under varying conditions of heat treatment is deferred until alloys are discussed in a later chapter (p. 501).

Phosphorus, Sulphur, and Silicon.—Both the former elements have great influence on the quality of iron and steel, and as already mentioned, the Bessemer process could be applied only to iron free from phosphorus until the introduction by Thomas and Gilchrist of the basic method, which permitted its elimination. Sulphur again is so objectionable that every care has to be taken to avoid its introduction, principally through the fuel in smelting, so that for the best qualities charcoal is employed, whilst coking the coal, thereby eliminating much of the sulphur, is general practice.

Phosphorus generally makes iron "cold short" (brittle when cold), and very liable to fracture under shock. In tool steel it seriously interferes with proper tempering, and a fine cutting edge cannot be obtained with such steel.

The influence of phosphorus is considerably modified by the amount of carbon present, and generally in mild steels very erratic behaviour is noticed, so that well under 0·1 per cent. is all that can be allowed in such steel. With the high carbon steels this element should be almost entirely absent.

It has been shown that if an ingot of steel is allowed to solidify partially and is then submitted to hydraulic pressure, the metal extruded is much richer in phosphorus than the average content of the original steel; in other words, there is a "phosphorus eutectic," and the presence of this causes distinct segregation of metal rich in phosphorus.

In cast iron the element is not so objectionable, since it promotes soundness in the casting and hence greater combined strength.

Sulphur.—This renders iron "red short" (incapable of being worked at a red heat without cracking), and when much is present the iron has no welding property.

The "red shortness" in the case of steel is at once detected by the bad rolling qualities of the metal, but this is very largely counteracted by manganese.

Silicon may render iron both "cold short" and "red short," but the actual amount causing these effects depends on the amount of carbon present; a small amount of carbon may carry with it far more silicon without ill-effect than a higher proportion of carbon. Its effect in causing carbon to separate in the form of graphite in pig iron has already been mentioned. Generally speaking, the amount of this element ever likely to occur in mild steel will never be sufficient to have injurious effects. Its presence in small amounts in molten steel promotes soundness in the ingots, silicon acting as a powerful deoxidiser.

True silicon steel is dealt with later (p. 420).

Aluminium.—The use of this metal in promoting soundness in steel castings through its energetic deoxidising action has already been referred to (p. 412), and since the metal acts much as manganese does in regard to sulphur, it is now being employed to correct for sulphur in cases where it is not desired to introduce carbon to the metal, as must inevitably be the case when spiegel or ferro-manganese is employed.

Aluminium has no effect on the hardening properties of steel. Like silicon, it tends to the liberation of carbon as graphite.

ALLOY STEELS.

The important influence which varying amounts of other metals have on steel has within recent years received much attention, and most valuable materials for certain special purposes have been the outcome of these researches, notably the steels suitable for armour piercing projectiles, armour plates, and the "self-hardening" steels now coming into such general use. Although these may be looked upon as true alloys, yet they are of such a special class that it is desirable to deal briefly with their properties under " steel," rather than under " alloys " generally.

In the first place, a clear distinction must be drawn between the influence of other metals when the quantities present are merely those incidental to the production of the steel, and those special alloys in which the foreign element has been purposely added in suitable proportions to produce certain results.

Manganese was the first metal to be introduced largely into the metallurgy of steel, Heath having noticed in 1839 the improvement effected by its presence in small amounts.

Manganese has been termed the " physic " of the steel-maker, its greatest use in small quantities being for counteracting the bad effects of sulphur, and at the same time it facilitates the removal of some of this element, since it makes the slags more fusible, and therefore more easily worked out of the metal. It will be remembered that manganese, either as spiegel or ferromanganese, is always added to the steel produced by either the Bessemer or Open Hearth processes, the finished metal containing from 0·3 to 1·0 per cent.

Its general effect in mild steel is to increase tensile strength. Less manganese is usually found in high carbon steels than in mild steels, and its presence in any but small quantities is undesirable, since the steel is liable to fracture on quenching.

Above 2 per cent. will justify the metal being classed as *manganese steel,* but when less than 7 per cent. is present the metal is worthless on account of its brittleness. Between 7 and 20 per cent. we have the valuable manganese steel, a material of extraordinary strength and toughness. The influence of heat treatment on manganese steel is remarkable. Heated to about 1000° C. and quenched, the metal is soft and capable of being worked. On now heating to a bright red and cooling in air the metal is hardened. Manganese steel is unmagnetisable.

Although the material is so valuable, its use is limited, owing to the difficulty of working it. Its hardness and resistance to wear, combined with good ductility, render it particularly suitable for rails on curves, rock crushing machinery, burglar proof safes, etc.

Nickel.—The introduction of this metal was made by Riley in 1889, and it has proved a most valuable alloy, being very tough and having great power of resisting shock, properties which make it particularly suitable for armour plate, propeller shafts, gun steel, etc.

The practical range for the proportion of nickel lies between 1·5 and 4·5 per cent.; the usual range is between 2·0–3·75 per cent. The presence of nickel enables iron to take up a greater amount of carbon, hence such metal may be rendered extremely hard by quenching. Its greatest effect, however, is in raising the elastic limit, the elongation and the reduction of area. This is well seen in the table below from the results by Hadfield, for steels containing 0·13–0·19 per cent. of carbon, where U shows the unannealed steel and A the annealed steels.

HADFIELD'S RESULTS FOR NICKEL STEELS.

Nickel per cent.	Tensile strength.		Elastic limit.		Elong. on 2 in.		Reduction of area on 2 in.	
Ordinary steel.	U. Tons. 33	A. Tons. 35	U. Per cent. 16·5	A. Per cent. 17·5	U. Per cent. 18	A. Per cent. 22	U. Per cent. 30	A. Per cent. 35
0·95	33	27	25	20	31	41	53	63
1·92	34	31	26	22	33	36	55	53
3·82	37	33	28	25	30	35	54	55
5·81	41	37	28	28	27	33	40	51

Nickel makes the metal more fluid so that sounder castings are obtained, and the close fine grain of nickel steel gives resistance to shock on impact, which is particularly serviceable in armour plate. Carbon segregation is hindered by nickel, but with higher percentages of nickel than usual, trouble has been experienced with segregation of sulphur and phosphorus. Little appears to be gained in ductility and resistance to shock by exceeding 3 per cent. One of the most important properties of nickel steel is its resistance to repeated alternating stresses, such as occur in propeller shafts, motor shafts, etc. It is stated that 3·5 per cent. of nickel confers about six times the life to steel as far as this "fatigue" is concerned.

High nickel steels possess peculiar properties in relation to expansion by heat, the 36 per cent. alloy (*Invar*) is practically non-expansive, and is valuable for standards of length, pendulum rods, etc. The 42 per cent. alloy has almost the same coefficient of expansion as glass, and is used for "armoured glass."

Nickel steel resists corrosion far better than ordinary carbon steel; this attribute, together with its special mechanical properties, renders it very suitable for wire hawsers, etc.

Chromium without much carbon has little influence on iron, but with about 1 per cent. of carbon and about 3 per cent. of chromium a metal very suitable for armour-piercing projectiles is obtained. These contain usually 2–2·75 per cent. chromium, and 0·9–1 per cent. carbon. The maximum amount of chromium which can be employed is under 5 per cent. Chrome steel is difficult to work hot and to weld, owing to the formation of chromium sesquioxide (Cr_2O_3).

Chromium raises the critical point of steel, but the changes taking place when steel cools through its critical range are greatly retarded by chromium, consequently, for a given carbon content, it is possible on quenching a chrome steel to obtain a much greater degree of hardness (p. 422).

Chromium and nickel are frequently employed together in steels; the nickel increases the toughness, and the chromium and carbon act as hardening agents. Such steels are almost universally employed for armour plate.

Silicon Steel.—These steels are those to which silicon has been added with a view to producing alloy steels. Owing to the method of manufacturing steel, the amount of silicon ordinarily present is negligible. Hadfield found the best composition of silicon steel is attained with 2·75 per cent. silicon, with low carbon, manganese, etc. Silicon steels are not of importance from the workshop point, but possess remarkable magnetic properties, which render them very valuable. Silicon steel has greater permeability to magnetism than the purest iron, and this is combined with high electrical resistance (low hysteresis). This means high efficiency in a dynamo or motor with reduction of eddy currents.

Tungsten is now a metal of great importance in the production of "self-hardening" steels, and since it greatly improves the steel in its power of retaining magnetism, tungsten steel is being employed for permanent magnets.

On iron it has little influence, but on steel it confers great hardness, but such steels must not be quenched, otherwise they crack. By heating to nearly a welding heat and cooling in an air blast, great hardness may be obtained. Tungsten steel is fragile, and therefore only suitable for tools where no "jarring" is likely to occur in their use. *Mushet* or self-hardening steel contains from 5 to 8 per cent. of tungsten, the carbon ranging from 1·5 to 2·3 per cent.

Magnet Steels contain from 4–5 per cent. of tungsten, and 0·5–0·7 per cent. carbon. Heated to redness and quenched such steel will retain magnetism better than any simple carbon steel.

Vanadium, a somewhat rare element, is now being employed for the production of steels suitable for special purpose, and owing to the very small quantities of vanadium required, such steel compares well in the matter of price with nickel steels. It is found advantageous to use chromium in conjunction with vanadium, Open Hearth steel forming the basis. Most of the chrome-vanadium steel is employed in the motor industry, since it offers great resistance to shock and alternation of stress. It will possibly find extended use for connecting rods, etc., in marine engines.

The ordinary type contains roughly 1 per cent. of chromium and 0·15 per cent. of vanadium. Such steel when rolled has a tensile strength of some fifty tons; it can be bent double cold, and offers great resistance to alternations of stress, to fatigue and torsion. The best results, in respect to the latter qualities, are obtained by annealing at a full cherry red, when the tensile strength, etc., is somewhat reduced, though still equal to 3 per cent. nickel steel.

Special chrome-vanadium steels are now being made to resist torsion, for springs, and for case-hardening, where a particularly tough core is desired.

Self-hardening Steels.—These in addition to tungsten generally contain small amounts of chromium and molybdenum, with usually under 1 per cent. of carbon. Ordinary hard carbon steel begins to undergo softening, that is the hardenite present begins to change into pearlite, at a little over 400° C., hence the speed at which tools of such steel can work is low on account of the heating. Many of the newer "self-hardening" steels can be used at a low red heat without losing their hardness and cutting properties, a fact which is rapidly having a great influence on workshop practice and machinery. At the Paris Exhibition (1900) such tool steel was shown in operation taking cuts on mild steel at the rate of 150 feet per minute, 60 feet on medium steel, and 15 feet on very hard steel. The time saved in the shops by such practice is enormous, and naturally the general introduction of high speed machinery, of a heavier type than that commonly employed, suitable for this class of tool, is only a question of time. The success of many of these special steels lies, not so much perhaps in their composition, but in the heat treatment to which they have been subjected. Usually this consists in heating up to quite high temperatures (well over 1000° C.), and then allowing the material to cool down slowly and regularly whilst the surface is protected from atmospheric oxidation.

The composition of some English high speed tools was approximately between the following limits :—

	Carbon	Chromium	Tungsten
Minimum	0·6	2·5	9·5 per cent.
Maximum	1·0	7·0	23·0 ,,

THE HEAT TREATMENT OF STEEL.

This may be defined as including the whole of the thermal conditions to which steel is subjected from the time when it is cast until it leaves the factory. Although the subject is closely connected and intimately dependent on the constituent bodies which go to make up steel, and which are dealt with fully under "Alloys," it is convenient to consider the question briefly here.

Hardening.—In the cooling of a moderately high carbon steel it is noted that at a certain temperature there is an arrest in the rate of cooling, in some cases an actual rise of temperature, the steel heats up and *recalesces.* The temperature at which this occurs is known as the "critical point." Quenched above this point the steel is hard ; quenched below it, no hardness is found. Quenching, therefore, preserves in the cold steel most of the conditions of composition existing at the temperature of quenching. The hard steel is also brittle.

Tempering.—This is known also as "letting down." Although the critical point is usually in the neighbourhood of 700° C., it is found that the hardness begins to be impaired when the steel is heated to 200° C., and the excessive brittleness reduced. This brittleness renders the steel so fragile to shock that it becomes necessary to "temper" it for use in tools, etc., and the guiding principle of tempering will be to maintain the maximum of hardness, so that the cutting edge may be preserved, combined with sufficient temper to resist breaking. A cutting tool which will not be subject to shock will require little letting down; a saw, in which there is much bending moment in use, must be let down much further.

The proper temperature for tempering is judged by the colour of the oxide film which is formed on the bright metal on reheating, so that the hard steel is polished, carefully heated up until the edge attains the necessary colour, and then quenched. The following shows some common tempering colours with the corresponding temperatures :—

Razors, taps, dies, etc.	Straw ...	230° C.
Punches, chisels, etc.	Purple ..	275°
Swords, coiled springs, etc. ..	Light blue	288°
Hand saws	Nearly black	316°

For great uniformity baths of lead or alloys kept at a definite temperature are employed.

The most generally accepted theory to account for these changes is that above the critical temperature the carbon exists in a form of solution in the iron, and by quenching this is more or less preserved. The condition is, however, abnormal, and unstable; it is maintained only by the rigidity with which the molecules are possessed. The low temperature of tempering is sufficient to relax this state of rigidity and permit the carbon and iron to form, more or less according to the temperature, those combinations which are normal and stable.

It follows that the more rapid the quenching the more perfectly preserved is the abnormal hard condition. Mercury, because of its great heat conductivity, quenches most rapidly, then iced brine, water, and least of all, oil. In the latter case much of the carbon and iron have time to pass into the stable condition. The influence of mass will necessarily greatly influence the rate of cooling on which the hardness depends.

Annealing.—This process is intended to remove the large internal strains set up during the cooling of large castings, etc., more especially those of steel, and strains due to working.

The metal must be slowly heated up and maintained at the annealing temperature—a low red heat is sufficient to remove strains—until the metal is at the same temperature throughout, and then allowed to cool down very slowly without any local chilling. Large steel castings require several days at the proper temperature, and must be very slowly cooled down.

Annealing does not greatly affect the tensile strength of steel, but the metal is softened, has an improved elastic limit and elongation, and offers greater resistance to shock.

Quenching with subsequent reheating.—All steel which is to be employed for purposes where the highest mechanical properties are demanded, especially resistance to shock, is greatly improved by first quenching (preferably in oil) at a temperature above the critical point, and then subsequently reheating to below the critical point and allowing to cool. The net effect is a considerable increase in the elastic limit. This is shown by the following results for 0·34 carbon steel (Brinel) :—

	Tensile strength	Elastic limit	Elongation
Normal steel	35 tons	12 per cent.	23·6 per cent.
Annealed at 850° C. ..	34 ,,	14 ,,	26·2 ,,
Water quenched at 850° C. then reheated to 550° C.	57 ,,	26 ,,	11·0 ,,
Oil quenched at 850° C. then reheated to 550° C.	46 ,,	27·5 ,,	18·0 ,,

From the results of a large number of forgings after oil quenching and reheating it appears that the tensile strength is increased from 20–25 per cent., the elastic limit about 50 per cent., whilst the elongation is diminished, but is still good.

Each variety of steel demands its own special treatment to give the best results, but the usual practice for armour plate and gun forgings is to oil quench at 850° C., and subsequently anneal at 610°–660° C. Shell steel, containing 0·45–0·55 carbon, is oil quenched at 800° and annealed at 750°, with slow cooling in the furnace. Alloy steels require more special treatment.

Overheated and burnt Steel.—Steel maintained at a high temperature for a considerable period develops such a coarse grain that its properties are seriously impaired ; if heated to a temperature still higher, just short of its melting point, the more easily fused parts may flow and leave cavities. The latter condition (*burnt steel*) is hopeless, but simple overheated steel may be restored by either reheating to just above its critical point, when all previous structure is obliterated, and the new structure, as regards coarseness, is that consistent with the temperature to which it has been reheated; or working again will break up the coarse grain, and the final grain will be dependent on the finishing temperature of the last operation.

Manufacture of Armour Plate and Gun Forgings.—The face hardening of mild steel for use as armour plate was introduced by Harvey, hence the process is frequently termed "Harveyising." The metal now employed is acid Open Hearth nickel steel, and generally contains also chromium and manganese, sometimes also tungsten. A usual composition is nickel, 2 per cent.; chromium, 1 per cent.; carbon, 0·3–0·35 per cent.

The steel is run from the casting ladle into large iron ingot moulds of rectangular shape; for large plates the mould may take 120 tons of metal. After cooling the ingot is reheated in a gas-fired furnace and taken to the hydraulic press where the necessary removal of the top is made, and the remaining sound part reduced to a slab of sufficient thickness for the rolls. In the latter the slab is reduced to the desired thickness; during the finishing stages of rolling brushwood is plentifully strewed on the plate and passes with it under the rolls. This, together with jets of water directed on both sides, serves to remove the mill scale which forms through oxidation. The rolled plate is considerably larger than the required size, as during further operations "scrap" must be cut off.

The plate is now carburised in a special furnace, the bed of which can be run in and out on a tramway. The iron body of the car has a fire-brick covering of some thickness, and above this fire-brick is built up so as to leave a number of flues running the long way of the furnace. The first plate is placed so that it rests on these piers of fire-brick, then a thick layer of carbonaceous material is spread on it, and finally the upper plate is laid on. In this way the carbonaceous material lies between the two plates and is under considerable pressure, which materially assists in the process. Fire-brick walls are built up at the sides and a thick layer of sand covers in the top. When in the furnace, the burning gases from the producers pass above the upper plate and are drawn back underneath the lower plate through the flues provided. The plates are maintained at a high temperature (about 1200° C.) for some seven or eight days, when they are allowed to cool down.

After carburising, the plate being still soft, it is bent to the required shape at the press, and undergoes a further heating to above the recalescence point, being then oil quenched, and, finally, reheated to below the recalescence point. This treatment, as already shown, considerably increases the tensile strength and elastic limit of steel.

Any drilling, etc., on the face of the plate must be carried out before the final hardening. The whole success of the plate depends now on its being properly hardened, a process requiring great experience to obtain the rest results. The plate is reheated in a gas-fired furnace in such a way that, whilst the face attains a temperature well above the recalescent point, in order that quenching may harden it, the back portion of the plate is kept below this point, hence preserving the advantages derived from the preceding heat treatment.

Water is then forced at a pressure of about 10 lbs. from suitable jets both against the front and back of the plate, hundreds of tons of water being required for the larger plates. The hardened surface may be from 1 to 1½ inches in depth, this depending upon the temperature and length of time the plate was in contact with the carbon, and is so hard that a steel punch is broken when driven against it. The surface layers may contain up to 1·35 per cent. of carbon.

The net result is the production of a plate having an extremely hard but tough face, whilst the back of the plate is soft, but has high tensile strength and elasticity.

The oxy-acetylene blow pipe is now used with great success in cutting the plates, the temperature of the flame being so high and localised that the metal is melted out, making a clean cut.

Simpson has invented a process by which it is claimed that perfect union between a high carbon plate and a low carbon backing plate may be obtained, thus enabling any thickness of facing plate to be used. The two plates are placed together with a sheet of copper between and suitable material to act as a flux. On heating above the melting point of copper, this metal alloys with the steel, and a perfect union is obtained.

In making gun tubes the ingots are octagonal, to facilitate forging into the round. The ingot is mounted in a lathe, and the unsound top and bottom portions cut off. The centre is then ‘ trepanned ” out right through the ingot by a special circular tool on which several cutters are arranged. The trepanned ingot is mounted on a long bar, which forms a mandril and is heated up in a gas furnace and gradually forged out under the press. Three heats are usually required for an A tube for a 12-inch gun.

The forging is machined up and bored, and is then subjected to a similar heat treatment by oil quenching and annealing to armour plate. The shrinking together of tubes is accomplished by heating the outer tube to a low red heat, lowering in place over the inner tube, which is placed in a vertical position in a shrinking pit, and then forcing water under pressure from jets in pipes arranged circularly around the hot tube, commencing at the bottom (the breech end), the sprinkler being slowly brought up to the muzzle end as the lower parts take up position.

COMPOUNDS OF IRON.

Iron forms three well-defined oxides :—

Ferrous oxide (FeO) ;
Triferric tetroxide (Fe_3O_4) ;
Ferric oxide (Fe_2O_3) ;

and in addition may exist in combination as FeO_3 forming *ferrates*, the oxide and these salts being analogous to chromium trioxide (CrO_3), and the chromates.

Ferrous and ferric oxides alone form salts when treated with acids, the oxygen being replaced by proportionate amounts of various acid radicles, giving two distinct series of salts—

	Ferrous salts (FeO)	Ferric salts (Fe_2O_3)
Chlorides ..	$FeCl_2$ or Fe_2Cl_4 ..	$FeCl_3$ or Fe_2Cl_6
Sulphide ..	FeS	Fe_2S_3
Sulphate ..	$FeSO_4$	$Fe_2(SO_4)_3$
Nitrate ..	$Fe(NO_3)_2$	$Fe(NO_3)_3$
Carbonate ..	$FeCO_3$	Not known.

Ferrous salts are generally unstable, showing a marked tendency to pass into the ferric condition ; when in solution ferrous salts are readily converted into ferric salts by the action of an oxidising agent, such as nitric acid. Similarly chlorine will convert ferrous chloride into ferric chloride.

Oxides.—*Ferrous Oxide* (FeO) is extremely unstable, and when slightly warmed in air at once takes fire, forming ferric oxide.

Ferric Oxide (Fe_2O_3) forms one of the chief sources of iron (p. 380). It is largely employed as *rouge*, for polishing purposes, also as a colouring material for glass, porcelain, etc., and in paints (Venetian red).

Ferric oxide is readily prepared by heating either of the sulphates, the oxalate or hydroxide.

Triferric tetroxide (Fe_3O_4) is also a valuable ore of iron (magnetite), and is frequently termed magnetic oxide of iron, since masses of it occur naturally having strong magnetic properties (lode-stone).

It is the oxide formed when steam is decomposed by red-hot iron, or when iron burns in oxygen. Since it is intermediate in composition between ferrous and ferric oxide, it may be regarded as FeO, Fe_2O_3.

Hydroxides.—All the oxides may be obtained associated with water in the form of hydroxides.

Ferrous Hydroxide $Fe(HO)_2$ is obtained as a white precipitate when potassium hydroxide is added to ferrous salts in solution, but all the materials must be free from dissolved oxygen, otherwise the substance rapidly undergoes oxidation. The dry hydroxide, obtained in an atmosphere free from oxygen, absorbs this gas so rapidly when exposed to air that considerable heat is developed.

Ferric Hydroxide $Fe_2(HO)_6$ is easily prepared by adding either ammonia or potassium hydroxide to solutions of ferric salts. The colour of the precipitate varies somewhat with the conditions of preparation, the usual colour being reddish-brown.

When iron rusts in moist air, the ultimate hydroxide formed has the composition $2Fe_2O_3, 3H_2O$.

Chlorides.—*Ferrous chloride* ($FeCl_2$) may be obtained in solution by the action of hydrochloric acid on iron, whilst if chlorine be passed over an excess of iron, the chloride may be obtained by sublimation as colourless crystals. It has the composition Fe_2Cl_4 at low temperatures, but dissociates into $2FeCl_2$ on heating.

Ferric Chloride ($FeCl_3$) is a yellow solid which can be easily fused. Below a full red heat, the vapour density shows it to have the composition Fe_2Cl_6, but above this, it dissociates into $2FeCl_3$. Ferric chloride is largely employed in the laboratory.

Ferrous Sulphate ($FeSO_4$) usually crystallises with seven molecules of water, and in this form is known as *green vitriol.* On exposure to air, the crystals readily lose some of their water and become covered with a white powder, consisting of the less highly hydrated salt. By heating ferrous sulphate, it yields Nordhausen sulphuric acid ($H_2SO_4.SO_3$) and ferric oxide.

CHAPTER XXVII

COPPER

COPPER ($Cu=63$).

COPPER has been known from earliest times, being used in the form of an alloy "bronze," for making tools and weapons long before any methods were discovered for the extraction of iron from its ores. It derives its name from the island of Cyprus. It is found native in the metallic form in Wales, Cornwall, and more abundantly in the neighbourhood of Lake Superior and also in New Mexico, and the copper produced by smelting the former deposit rivals the best that can be obtained by smelting ores.

Next to iron, copper is the metal of greatest industrial importance, and of the "common" metals its market price is second only to that of tin. It owes its general application to its extreme malleability and ductility, and for electrical purposes its high conductivity is of great value. Its application in the form of alloys is very great.

The most important ore of copper is "copper pyrites," which is a double sulphide of copper and iron, which, when pure, may be represented as (Cu_2S, Fe_2S_3) ; it is nearly always, however, mixed with arsenical pyrites and other minerals, the percentage of copper which it contains varying considerably. The rich Bratzberg ore from Norway contains as much as 23 per cent. of the metal, whilst the ordinary grey Cornish ore contains about 6 per cent.

Amongst the other less important ores of copper are malachite, a basic cupric carbonate [$CuCO_3.Cu(HO)_2$], red copper ore or cuprous oxide (Cu_2O), and black oxide (CuO) found in the north of Chili.

Metallurgy of Copper.—This is generally a very complex process, for the ores are so highly laden with foreign bodies extremely detrimental to copper, that their complete elimination is a matter of very great importance. Further, the amount of earthy matter usually present with the ore leads to complications.

The different methods of obtaining the metal may be divided into two main classes :—

(*a*) Those which depend on the reducing action of copper sulphide ;

(*b*) Those in which reduction is effected by carbon monoxide.

The Welsh Method, as practised in the district around Swansea, is dependent on the former, and by this method by far the largest proportion of the world's copper is produced. The process is very complicated, but certain main factors will indicate the general bearing of each stage.

1. In a mixture of copper and iron sulphides, under suitable conditions the iron sulphides will be oxidised in far greater ratio than the copper sulphide.

2. Copper oxide (CuO), and ferrous oxide (FeO), readily form fusible slags with silica (SiO_2).

3. At a high temperature a mixture of copper sulphide and oxide interact with the production of the metal.

First process.—This is intended to expel, as far as possible, volatile substances, such as arsenic, antimony, etc., and then to oxidise, as fully as possible, the iron sulphide.

$$\overset{\text{Copper pyrites}}{Cu_2S.Fe_2S_3} + \overset{\text{Oxygen}}{4O_2} = \overset{\text{Copper sulphide}}{Cu_2S} + \overset{\substack{\text{Ferrous}\\ \text{oxide}}}{2(FeO)} + \overset{\substack{\text{Sulphur}\\ \text{dioxide}}}{3(SO_2)}$$

In practice some of the iron sulphide escapes oxidation, whilst a little of the copper sulphide becomes oxidised (Cu_2O).

To accomplish this, charges of from 3 to 3½ tons of ore are roasted in a reverberatory furnace with free access of air for twelve hours.

The roasted ore averages some 10 to 13 per cent. of copper.

Second process.—To form a slag by the combination of the ferrous oxide with silica, which can be withdrawn, thus concentrating the copper sulphide. Slags from the fourth process are added, in order that the copper in them may be recovered.

The roasted ore is heated in another reverberatory furnace (*ore furnace*), so constructed, that a temperature sufficient to bring about fusion is attainable, silica being added to form the slag. The mass when fused evolves sulphur dioxide, and the slag separating, permits of the *coarse metal* being run off into water so becoming granulated.

The coarse metal contains from 30 to 40 per cent. of copper.

Third process.—To oxidise the remainder of the iron sulphide the granulated coarse metal is roasted as in the first process.

Fourth process is intended to bring about practically the same result as in the second process, namely the removal of iron as silicate. Slags from the fifth and sixth processes are added to recover the copper from them.

After fusion the matte produced (*fine metal*) contains from 60 to 80 per cent. of copper, whilst the slags contain from 3 to 4 per cent. of the metal. If there is over 75 per cent., free copper, as "*moss,*" is seen.

As already mentioned, the slag from this process being rich in copper, goes back to the second process.

Fifth process.—The fine metal is nearly pure copper sulphide (Cu_2S). In this process, a portion must be converted by oxidation into a mixture of cuprous oxide (Cu_2O) and cupric oxide (CuO), when on raising the temperature it will react with the remaining sulphide to produce the metal.

$$\overset{\text{Copper sulphide}}{Cu_2S} + \overset{\text{Cuprous oxide}}{2(Cu_2O)} = \overset{\text{Copper}}{6Cu} + \overset{\text{Sulphur dioxide}}{SO_2}$$

$$\overset{\text{Copper sulphide}}{Cu_2S} + \overset{\text{Cupric oxide}}{2(CuO)} = \overset{\text{Copper}}{4Cu} + \overset{\text{Sulphur dioxide}}{SO_2}$$

To bring about these changes, the metal is heated without fusion, with plentiful air supply for four hours; the excess of air is now shut off by dampers, and the temperature raised until the mass fuses, when vigorous action sets in, *blister* copper containing about 98 per cent. of the metal remaining, the slags containing 17 to 20 per cent.

Sixth process.—The blister copper contains such impurities as sulphur, arsenic and iron, and this process is intended to oxidise these finally, so that they may be removed as slag. Since a considerable quantity of the copper is also oxidised, the slag is very rich in copper, and is returned for treatment in the fourth process.

After roasting for some hours to bring about the oxidation, the metal is melted and well rabbled, the slag being removed. Cuprous oxide is formed, and being dissolved in the molten copper, renders it "dry." To remove this oxide, the metal is stirred with a green wood pole (poling), when the hydrocarbon gases evolved reduce the oxide, producing *tough pitch* metal. 30 to 40 per cent. of copper is found in the slag.

Production of Copper Mattes in the Blast Furnace.—Great advances have been made in America in the production of copper mattes directly in suitable blast furnaces. The richer sulphide ores may be charged directly into the furnace, but the poor ores are generally first crushed and washed to remove earthy matter. A suitable mixture of the ore with slags from subsequent processes is made, so that the matte produced may contain about 30 per cent. of copper, 2 to 3 cwt. of coke per ton being necessary for smelting.

The furnaces are from 6 to 10 feet high, made of iron and provided with a water jacket. The hearth is usually oblong or rectangular and must not exceed 4 feet across, otherwise the blast from the twyers will not pass through the fused matte. The air blast is supplied at from 1 to 1½ inches of mercury. As the matte is produced it passes to the lower part of the hearth together with the slag, but the two are generally allowed to flow out into a fore-hearth of special pattern, being divided into two chambers by a partition, one chamber having about twice the capacity of the other, the two communicating by a hole at the bottom of the partition. The larger chamber goes under the tap hole of the furnace, the hole in the partition being temporarily closed. A mixture of matte and slag collects and the former settles to the bottom. When nearly full the second chamber is put into communication with the first, and matte only flows into it. The process is now continuous, for matte free from slag continually passes into the smaller chamber from which it overflows into suitable moulds, whilst the separated slag overflows similarly from the larger chamber.

The matte produced may then be treated by the Welsh method.

Bessemerising Copper Mattes.—The success of the Bessemer process in the case of iron naturally led to its being tried for the oxidation of copper mattes, and although many difficulties had to be overcome, notably that of maintaining a sufficiently high temperature, the process is now being largely worked, and its success greatly simplifies the production of the metal.

One of the most successful converters is in the form of a cylinder, open at the ends and capable of being turned on its long axis in order that slag and the metal may be poured from a suitable spout.

Twyers pass at an angle through the walls and lining, being so placed that by rotation of the cylinder they may be either below or above the surface of the metal in the converter. A very thick siliceous lining has to be employed, as this is the only source of silica present to flux out the iron compounds.

Care has to be taken that the matte contains about the right amount of copper, which should be between 50 and 55 per cent. The molten matte is charged in with the twyers well above the level it will rise to, then the blast is turned on and the converter turned to deliver the blast through the matte. The reactions which ensue are :—

(*a*) Oxidation of iron sulphide and formation of an iron slag which is poured.

$$\overset{\text{Iron sulphide}}{2(FeS)} + \overset{\text{Oxygen}}{3O_2} = \overset{\text{Ferrous oxide}}{2(FeO)} + \overset{\text{Sulphur dioxide}}{2(SO_2)}$$

(*b*) Partial oxidation of the copper sulphide to oxide :—

$$\overset{\text{Copper sulphide}}{2(Cu_2S)} + \overset{\text{Oxygen}}{3O_2} = \overset{\text{Cuprous oxide}}{2(Cu_2O)} + \overset{\text{Sulphur dioxide}}{2(SO_2)}$$

(*c*) Interaction between the copper oxide and sulphide, with the production of the metal, exactly as in the fifth stage of the Welsh process where " blister " copper results :—

$$\overset{\text{Copper oxide}}{2(Cu_2O)} + \overset{\text{Copper sulphide}}{Cu_2S} = \overset{\text{Copper}}{6Cu} + \overset{\text{Sulphur dioxide}}{SO_2}$$

Even in South Wales the Bessemer converter is replacing the older reverberatory furnace, the usual practice being to charge with 7½ tons of fluid matte, containing 45 per cent. of copper, and to reduce the metal in six " blows."

Extraction of Copper from Spent Pyrites.—A great deal of copper and silver is obtained from the pyrites after it has been roasted for the production of sulphur dioxide in the manufacture of sulphuric acid (p. 327). It is estimated that half a million tons are employed annually in this industry, and since much of it averages 3 per cent. of copper in addition to silver, the extraction of these metals from what would otherwise be a waste product is of considerable importance.

The method usually employed is a " wet " one, the ore after grinding being mixed with common salt (NaCl) and roasted.

The copper sulphide becomes oxidised to sulphate, and then this interacts with the sodium chloride, forming copper chloride.

$$\overset{\text{Copper sulphide}}{CuS} + \overset{\text{Oxygen}}{2O_2} = \overset{\text{Copper sulphate}}{CuSO_4}$$

$$\overset{\text{Copper sulphate}}{CuSO_4} + \overset{\text{Sodium chloride}}{2(NaCl)} = \overset{\text{Copper chloride}}{CuCl_2} + \overset{\text{Sodium sulphate}}{Na_2SO_4}$$

Any silver present is also converted into silver chloride. The mass is now extracted with hot water in vats with false bottoms, when the copper and silver chlorides pass into solution, the latter dissolving in the brine, since it is not soluble in water alone.

Several methods may be employed for recovering the silver; one involves its deposition on copper plates immersed in the solution; another its conversion into silver iodide by the addition of zinc iodide, the copper afterwards being recovered by passing the solution on to iron scrap where it is deposited. The copper so obtained is very impure (*cement copper*) and is usually purified electrolytically.

Commercial Copper.—The most common impurities are iron, arsenic, antimony and bismuth, whilst occasionally sulphur, tin and lead are present. Since these have a marked influence on the properties and value of the metal, brief reference must be made to their effect.

The presence of iron, whilst increasing the tensile strength, makes the metal harder and hence impairs its malleability and ductility.

The effect of arsenic is most pronounced, and copper obtained from ores, such as some of the Spanish ores, is quite unfitted for electric conduction, some specimens having only one-seventh the conductivity of pure copper. The effect of arsenic on the mechanical properties is not great, and where the metal has to stand high temperatures arsenic is frequently added.

The influence of most impurities on the electric conductivity of copper is very great, and Sir Wm. Preece has stated that a cable made of the pure copper now employed will carry twice the number of messages that a similar cable made of less pure copper would carry in the early days of submarine telegraphy.

Bismuth, besides seriously impairing the quality of copper, also injuriously affects its conductivity, and, according to Lord Kelvin, 0·1 per cent. in a cable would render it useless.

Electrolytic Refinement of Copper.—A considerable amount of copper is now sent into the market after refinement by electrodeposition, cement copper especially being treated in this manner. By a suitable adjustment of current and strength of solution very pure copper indeed can be deposited, though the process is of necessity a slow one. The crude copper plates form the anodes in a bath containing copper sulphate with sulphuric acid, and sheets of pure copper the kathodes. On passing the current copper goes into solution, a like amount being simultaneously deposited at the kathode, whilst at the same time iron, nickel and zinc also dissolve, but with suitable current are not deposited. In acid solution neither gold nor silver dissolves, and they remain on the surface of the anodes as a slimy deposit which can subsequently be treated for their recovery.

Properties.—Copper has a specific gravity of 8·92; it melts at 1085° C., and expands as it solidifies; it is very malleable, and can be beaten out to thin leaf, or drawn out into wire. In tenacity or strength it ranks next to iron, but it is very inferior to it; a copper wire, one-tenth of an inch in diameter, will support only between 380 and 390 lbs., whilst a similar iron wire will carry just over 700 lbs. It is a good conductor of heat and electricity.

When copper is in the molten state it can absorb various gases, such as carbon monoxide, which escape as the metal solidifies, rendering the mass porous; further, the molten metal is very sluggish, and consequently pure copper is rarely used for castings.

Copper is very largely used in alloys with other metals, these being dealt with in the special chapter on Alloys (p. 508).

Copper resists the action of pure water or dry air, but when exposed for any length of time to moist air, the surface first becomes dimmed by a thin coating of copper oxide, and this then takes up carbon dioxide from the air and is converted into a basic copper carbonate, often erroneously called "verdigris." This action has occasionally led to very serious results from the use of copper vessels for culinary purposes; clean bright copper surfaces are not affected by the preparation of food in contact with them, but the oxide or carbonate is readily dissolved by such substances, and is a virulent poison.

Of the three common acids, nitric has by far the most violent action on copper; when concentrated the attack is very brief, since the nitrate formed on the surface protects the metal from further attack. On the addition of water the action becomes very vigorous, since the film of nitrate dissolves in the water, leaving a fresh surface of the metal exposed, when nitrogen dioxide is set free. In the cold, sulphuric and hydrochloric acids have little or no action, but on warming the former produces copper sulphate with the evolution of sulphur dioxide, and the latter, when boiled with finely-divided copper, forms cuprous chloride (Cu_2Cl_2), hydrogen being evolved.

Finely divided copper has the peculiar property of forming a compound with nitrogen tetroxide (Cu_2NO_2), which decomposes with water.

COMPOUNDS OF COPPER.

Oxides.—Two well defined oxides are known, cuprous oxide (Cu_2O) and cupric oxide (CuO).

Cuprous Oxide is found as the mineral *cuprite*.

If a cupric salt be boiled with a reducing agent, such as grape sugar, in the presence of an alkali, a red powder is obtained consisting of cuprous oxide (Cu_2O). This oxide is very unstable. It is dissolved by melted glass, and imparts to it a ruby colour. The cuprous compounds are generally colourless and insoluble in water; readily soluble in ammonia and hydrochloric acid, absorbing oxygen rapidly and yielding cupric compounds.

Cupric Oxide is formed as a black film on the metal when it is heated in the air, or by igniting the nitrate. This oxide readily dissolves in acids, forming cupric salts. From the ease with which it parts with oxygen when heated in contact with organic bodies, it is largely employed in analytical work.

Hydroxide $Cu(HO)_2$.—By adding potassium or sodium hydroxide to a cupric salt, a greenish-blue precipitate of cupric hydroxide forms, which is converted into the black cupric oxide when the solution is boiled.

The hydroxide is soluble in ammonia to a deep blue solution, which under proper conditions will dissolve cellulose, whilst under other conditions it converts it into a parchment-like substance (*vegetable parchment*).

Chlorides.—Two chlorides, corresponding to the two oxides are known.

Cuprous Chloride (Cu_2Cl_2) is obtained when the metal or cuprous oxide is dissolved in hydrochloric acid. It is a white crystalline body, insoluble in water, but readily soluble to colourless solutions in hydrochloric acid or ammonium hydroxide. The former is largely employed in gas analysis for the absorption of carbon monoxide, with which it forms a compound, $Cu_2Cl_2.CO.2H_2O$. The ammonia solution turns rapidly blue on exposure to air, owing to absorption of oxygen.

Cupric Chloride ($CuCl_2$) is prepared by dissolving cupric oxide in hydrochloric acid. It forms blue crystals ($CuCl_2.2H_2O$) which are soluble in alcohol.

Copper Nitrate.—[$Cu(NO_3)_2.3H_2O$] is readily formed by dissolving copper in nitric acid and crystallising. It is an oxidising substance, and as such is used in dyeing.

Copper Sulphate or blue vitriol ($CuSO_4.5H_2O$) is obtained on a large scale by roasting copper pyrites and extracting the mass with dilute sulphuric acid.

This salt on being heated loses its water and becomes white. This anhydrous salt is sometimes used to abstract the last traces of water from alcohol and other organic liquids.

Sulphate of copper is much used by the dyer and calico printer; besides which, it is employed as the source of copper in the electrotype process, and also in certain forms of galvanic battery.

CHAPTER XXVIII

LEAD, TIN, ZINC, CADMIUM AND MERCURY

LEAD is probably never found free in Nature. Its principal ores are galena (PbS), which is very widely distributed throughout the world, including many parts of the British Isles ; and the carbonate ($PbCO_3$) or white lead ore found in Spain, and near Aix-la-Chapelle.

Metallurgy.—The chemical principles involved in the reduction of the metal from the sulphide are similar to those in the production of copper, namely, roasting to convert some of the sulphide into oxide and then fusion, in order that the oxide and sulphide may interact to produce the metal.

$$\overset{\text{Lead sulphide}}{2(PbS)} + \overset{\text{Oxygen}}{3O_2} = \overset{\text{Lead oxide}}{2(PbO)} + \overset{\text{Sulphur dioxide}}{2(SO_2)}$$

$$\overset{\text{Lead oxide}}{2(PbO)} + \overset{\text{Lead sulphide}}{PbS} = \overset{\text{Lead}}{3Pb} + \overset{\text{Sulphur dioxide}}{SO_2}$$

At the same time some of the lead sulphide becomes oxidised to the sulphate, which is also capable of mutual reduction with the lead sulphide.

$$\overset{\text{Lead sulphide}}{PbS} + \overset{\text{Oxygen}}{2O_2} = \overset{\text{Lead sulphate}}{PbSO_4}$$

$$\overset{\text{Lead sulphate}}{PbSO_4} + \overset{\text{Lead sulphide}}{PbS} = \overset{\text{Lead}}{2Pb} + \overset{\text{Sulphur dioxide}}{2(SO)_2}$$

The process adopted to bring about these reactions varies greatly with the locality, the method common in this country being that in which the operations are carried out in a suitable reverberatory furnace, having a depression in the bed for the molten metal to run into.

There are really four stages in the treatment of each batch of ore. During the first the ore is gently roasted together with skimmings from a subsequent stage, which interact, causing lead to flow out, and the metal separated at this stage carries with it considerable quantities of silver.

The temperature is now raised, when the metal is rapidly produced. The slag is thickened, by the addition of lime, raked out of the hollow and spread well over the hearth. The temperature is raised still further, more lime being added. Some of the lead oxide will have combined with silica to form a fusible slag, which is decomposed by the lime, and the lead oxide so liberated can then react with more of the lead sulphide.

In the final "heat," the highest temperature is attained, and the metal is tapped out into an iron pot, the slag being further thickened with lime, and since it carries a considerable amount of lead, this is afterwards recovered on the "slag hearth."

On the Scotch hearth, the ore is charged on to the fuel (usually a mixture of peat and coal) and an air blast is used, but the reactions are very similar to those just described. The process is only capable of dealing with small quantities of the ore at a time, but it is a continuous one, the reduced metal constantly flowing away through a suitable channel in an iron plate in front of the furnace.

Blast furnaces of the type described under copper (p. 433) are now largely employed for extracting lead. Carbon from the fuel is capable of effecting the reduction of lead oxides, but is ineffective with the sulphide, as is usually the case with partially roasted galena. In this case a rich iron ore is usually mixed with the charge, when at the temperature of the furnace, iron is reduced, and this interacts with the lead sulphide, liberating the lead.

In all lead smelting operations a great deal of dust and fume is produced, and long flues have to be provided, in order that the dust and fume may settle out.

Softening Crude Lead.—Owing to the presence of small amounts of copper, iron, antimony, etc., the lead obtained by either of the above processes is rendered hard and quite unsuitable for many purposes. To soften the metal, quantities up to 150 tons are melted in a special reverberatory furnace—the "calcining furnace"—a plentiful supply of air being admitted, when a rich dross collects, owing to oxidation of the impurities, this dross being constantly removed. The operation is continued until a sample shows the metal to have been sufficiently softened. In the latter stages much lead undergoes oxidation, but the metal is easily recovered from this dross.

Since galena always contains a notable proportion of silver, the recovery of this precious metal from the crude lead is an important matter. The methods employed are dealt with under silver (see p. 459).

Properties.—Lead is bluish-white or grey in colour; it is extremely malleable and ductile, but is of slight tenacity; it is so soft that it may be easily cut with a knife, and leaves a mark if rubbed on paper. Lead expands greatly when heated, and does not on cooling always return to its original dimensions. It melts at 327° C., and partially volatilises at a bright red heat. The metal slowly oxidises in moist air, and, consequently, clean surfaces soon tarnish. Lead in contact with aerated water soon becomes oxidised, forming the white hydrated monoxide $Pb(HO)_2$, which is slightly soluble in water; the corrosive action is increased if ammonium salts are present, but is retarded by the presence of sulphates, phosphates and carbonates, owing to the formation of insoluble salts which coat the surface of the metal with a thin film, and protect it from further action. A large excess of carbon dioxide will, however, even then, increase the solvent action. For some waters this action prevents lead being used either for storing or distribution, as the dissolved lead salts are very poisonous, and act as a cumulative poison in the system. Lead cisterns should never be used for storing rain-water. Lead is employed in several alloys, which will be described in a subsequent chapter (p. 317).

The high specific gravity as well as the fusibility of lead recommends it for the making of projectiles for small arms, which are then usually coated with a nickel alloy sheath. Bullets intended to be discharged from smooth-bore small arms, are hardened by the addition of antimony, in order to give them greater penetration. In the manufacture of small shot for fowling pieces, the lead is alloyed with about 5 per cent. of arsenic, which enables the alloy to take a spherical shape when the melted metal is dropped through a colander into water. It is necessary, however, to cool down the drops before they fall into the water, and this is accomplished by allowing the molten metal to drop through the air from a height of 100 to 150 feet, according to the size of the shot. It is probable that the presence of arsenic diminishes the power of the liquid lead to contract as it cools after the outer surface has solidified. The shot are dried on a hot plate, and polished by friction in a revolving drum containing a small quantity of plumbago.

Lead is easily dissolved by dilute nitric acid, but the action of strong nitric acid is stopped by a coating of fine crystals of lead nitrate. Dilute hydrochloric and sulphuric acids do not attack lead, but when hot and concentrated readily form the chloride and sulphate of the metal.

COMPOUNDS OF LEAD.

Oxides.—Oxygen combines with lead in five proportions, three only of the oxides being important. *Lead monoxide* (PbO) is formed by the oxidation of metallic lead in air ; at a moderate heat a yellowish powder, called *massicot,* is obtained ; at a higher temperature, a reddish powder, which yields a crystalline mass called *litharge,* when fused. This oxide is the only one that forms salts ; the salts of lead being easily obtained by acting on the oxide with the corresponding acid, *e.g.*—

$$\overset{\text{Lead oxide}}{PbO} + \overset{\text{Acetic acid}}{2(HC_2H_3O_2)} = \overset{\text{Lead acetate}}{Pb(C_2H_3O_2)_2} + \overset{\text{Water}}{H_2O}$$

$$\overset{\text{Lead oxide}}{PbO} + \overset{\text{Nitric acid}}{2(HNO_3)} = \overset{\text{Lead nitrate}}{Pb(NO_3)_2} + \overset{\text{Water}}{H_2O}$$

The monoxide is largely used in the Arts in the manufacture of lead pigments, of lead plaster, of flint glass, etc.

Red Lead or **Minium** (Pb_3O_4) is a bright red heavy powder, prepared by prolonged heating of the monoxide at a dull red heat in a current of air. It appears to be a compound of two molecules of monoxide and one molecule of dioxide of lead ; for if red lead be acted on by nitric acid, the acid dissolves out the monoxide to form lead nitrate, and the dioxide is left as a brown powder. Red lead is largely used as a pigment, and in the manufacture of glass.

The *dioxide,* or *lead peroxide* (PbO_2), is best prepared from red lead, as stated above :

$$\overset{\text{Red lead}}{Pb_3O_4} + \overset{\text{Nitric acid}}{4(HNO_3)} = \overset{\text{Lead nitrate}}{2[Pb(NO_3)_2]} + \overset{\text{Lead dioxide}}{PbO_2} + \overset{\text{Water}}{2(H_2O)}$$

The dioxide is left as a dark brown heavy powder. When heated strongly it gives off half its oxygen, and the monoxide is left.

If heated with hydrochloric acid, lead chloride and chlorine gas are formed :

$$\overset{\text{Lead dioxide}}{PbO_2} + \overset{\text{Hydrochloric acid}}{4(HCl)} = \overset{\text{Lead chloride}}{PbCl_2} + \overset{\text{Chlorine}}{Cl_2} + \overset{\text{Water}}{2(H_2O)}$$

White Lead.—The most important salt of lead is the basic carbonate $[2PbCO_3.Pb(HO)_2]$ known as *white lead.* It is a very heavy powder, almost insoluble in water, but is more soluble if carbon dioxide be dissolved in the water. It is much used as a pigment, and possesses special advantages as such, on account of which, in spite of its very poisonous character, and that it is blackened by sulphuretted hydrogen, it has not been superseded by zinc white (ZnO) or baryta white ($BaSO_4$). White lead has the property of combining to a certain extent with oils and varnishes, and gives the paint the property of what is known as covering well. A great deal depends, however, on the way the white lead is prepared. (See " Pigments," p. 549.)

Lead Chloride ($PbCl_2$) is always formed when a chloride is added to a strong solution of a soluble lead salt :

$$\overset{\text{Lead nitrate}}{Pb(NO_3)_2} + \overset{\text{Sodium chloride}}{2(NaCl)} = \overset{\text{Lead chloride}}{PbCl_2} + \overset{\text{Sodium nitrate}}{2(NaNO_3)}$$

The precipitated lead chloride is a heavy white crystalline substance, soluble in hot water. A number of oxychlorides are known, some of which are of value as pigments, *e.g.* Pattinson's white oxychloride ($PbCl.OH$), and Turner's patent yellow ($PbCl_2.7PbO$), sometimes called " Paris " patent or mineral yellow.

Lead salts are easily distinguished by their turning black when brought into contact with sulphuretted hydrogen gas ; in fact, a most minute trace of this gas is easily detected by holding a piece of moistened lead paper (made by wetting blotting paper with a solution of lead acetate) in the gas, the blackening being due to the formation of black lead sulphide.

TIN ($Sn = 118$).

Tin has been known and used from the earliest times. Pliny relates that the Phœnicians were in the habit of trading both with Spain and Great Britain for tin. In this country it still occurs abundantly in Cornwall, and is also found in considerable quantities in Malacca, India and Mexico. Its chief and only important ore is tinstone (SnO_2).

Production.—The tinstone as found in England is nearly always mixed with a large quantity of foreign substances such as quartz, earthy matters, pyrites, etc., and whilst the extraction of the metal is simple, the ore being readily reduced by carbon, in order to remove these it has first to undergo a series of preliminary operations.

The purer portions are picked out by hand and are put on one side, whilst the residue is crushed in stamping mills, and the lighter portions, consisting of the earthy impurities, are washed away by exposure to a stream of water. This also gets rid of some of the pyrites, as the tinstone being very hard remains in larger pieces than the more friable sulphides ; and as the specific gravity of the tinstone is 6·5, which is far higher than that of any of the substances mixed with it, it is possible to treat successfully even the poorest ores by this process.

The washed ore is now roasted to expel arsenic and also to break up any of the mixed sulphides of iron and copper (pyrites) which may remain in it. These latter are left as iron oxide and sulphide and sulphate of copper, and on allowing the roasted ore to stand exposed to the action of air and moisture, the copper sulphide is converted into soluble sulphate, which can be removed by washing with water.

The ore so treated now contains from 60 to 70 per cent. of tin, and the metal is obtained from it by mixing it with one-sixth of its weight of charcoal and a small quantity of lime ; the mixture is then carefully heated in a reverberatory furnace. The carbon unites with the oxygen of the ore and escapes, while the metal separates :

$$\begin{array}{ccccccc} \text{Tinstone} & & \text{Carbon} & & \text{Carbon monoxide} & & \text{Tin} \\ SnO_2 & + & 2C & = & 2(CO) & + & Sn \end{array}$$

The temperature is then raised, and the added lime forms a slag with any siliceous matter that may have been present in the ore, and this collects on the top, the metallic tin sinking through it, and being drawn off from the bottom. This metal is cast into ingots, and is purified by the operations of *liquation* and *poling.* The ingots are heated up in a reverberatory furnace, care being taken that the temperature does not rise too high, when the metal fuses and flows away from the impurities, which have a higher melting point. The metal now requires to be exposed whilst in the molten condition to the oxidising action of the air for the remaining impurities to be oxidised. This is usually accomplished by holding down in the metal logs of wet wood, the steam and gases which are evolved serving to violently agitate the metal and so expose a great surface. The longer this process takes the purer the resulting metal, the best metal being known as "grain tin" from the fact that it occurs in irregular crystalline fragments, which are produced by allowing ingots heated to just below the melting point to fall from a height, when they readily break up.

Properties.—Tin is a somewhat soft, malleable metal. It emits a peculiar sound (*creaking* or *cry*) when bent, owing to its crystalline structure. It has the lowest melting point of any of the metals in common use, about 232° C. On exposure to damp air it is scarcely altered, and one of its greatest uses is in the production of *tin plate*. It is also used in many alloys, such as gun-metal, solder, pewter, etc.

The action of acids on tin is variable. Strong hydrochloric acid attacks it, forming stannous chloride ($SnCl_2$), and liberating hydrogen. Dilute sulphuric acid has little action on it. With nitric acid much depends on the strength of the acid and conditions under which it acts. Thus strong nitric acid scarcely acts at all; on diluting, somewhat violent action sets in, and if the temperature is allowed to rise, a yellowish insoluble body, metastannic acid, is obtained, but if the solution is kept quite cold it remains clear.

COMPOUNDS OF TIN.

Oxides.—Tin forms two oxides—stannous oxide (SnO) and stannic oxide (SnO_2), and in the same way forms two classes of salts, in one of which it behaves as a dyad, whilst in the other it is tetrad.

Stannous oxide dissolves in sodium hydroxide, forming a salt, *sodium stannite,* whilst the compound from stannic oxide is *sodium stannate* ($Na_2SnO_3.4H_2O$). Both these salts are extensively used by the calico printer.

Chlorides.—*Stannous Chloride* ($SnCl_2$) is also much used for calico printing, and is prepared by dissolving tin in hydrochloric acid.

Stannic Chloride ($SnCl_4$) can be obtained by heating tin in a current of dry chlorine gas, or boiling stannous chloride with aqua regia.

Sulphides.—*Stannous Sulphide* (SnS) is readily obtained by heating the metal with sulphur. When sulphuretted hydrogen is passed into solutions of stannous salts, a hydrated form of this sulphide is precipitated as a dark brown mass, readily soluble in sodium hydroxide and strong hydrochloric acid. As prepared from its elements, it is a dark grey crystalline powder, not very soluble in hydrochloric acid.

Stannic Sulphide (SnS_2) is used for decorative purposes under the name of mosaic gold, and is prepared by subliming a mixture of tin amalgam with sulphur and sal ammoniac, when the mosaic gold is left in the form of beautiful yellow scales.

ZINC ($Zn = 65$).

Zinc.—Metallic zinc is never found native; it occurs in combination with sulphur as *zinc blende* (ZnS), and as carbonate of zinc in *calamine* ($ZnCO_3$).

Zinc blende, or *black jack* as it is called by the miners, is found in considerable quantities in this country, but calamine is imported principally from Spain and the United States.

Production.—The metallurgy of zinc is very simple, since the metal is easily reduced from its oxide by heating with carbon; the zinc being volatile then distils off, and can be condensed in suitable receivers. The temperature at which reduction of the oxide takes place is well above the boiling point of the zinc.

The first step, therefore, in the production of the metal from either calamine or zinc blende, is to convert these into the oxide, for zinc sulphide is unreduced by carbon at any temperature. With calamine, simple treatment in a kiln, much after the manner of preparing lime from limestone, is all that is necessary. In the case of the blende, this must be roasted in a reverberatory furnace with free access of air, when the sulphur is wholly removed as sulphur dioxide, zinc oxide being left behind.

$$\underset{\text{Calamine}}{ZnCO_3} = \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Zinc oxide}}{ZnO}$$

$$\underset{\text{Zinc blende}}{2(ZnS)} + \underset{\text{Oxygen}}{3O_2} = \underset{\text{Sulphur dioxide}}{2(SO_2)} + \underset{\text{Zinc oxide}}{2(ZnO)}$$

This zinc oxide is then mixed with finely powdered coal, and is heated in fireclay retorts, when, at a red heat, the metallic zinc distils over and is condensed.

$$\overset{\text{Zinc oxide}}{\mathrm{ZnO}} + \overset{\text{Carbon}}{\mathrm{C}} = \overset{\text{Carbon monoxide}}{\mathrm{CO}} + \overset{\text{Zinc}}{\mathrm{Zn}}$$

In all the processes for extracting zinc, the general chemical reactions are the same, but different forms of furnace, retorts and receivers are employed.

Belgian Process.—The process mostly used in this country is known as the "Belgian process," in which the oxide mixed with coal is charged into fireclay cylinders about 4 ft. 6 in. long and 8 in. diameter, closed at one end. Such cylinders hold about 1 cwt. of the mixed ore and coal, and from forty to eighty of these retorts are arranged in tiers over the same fire (Fig. 55). Fireclay receivers from 2 to 3 ft. long (B) are now luted on, and distillation commenced.

The flame of carbon monoxide soon makes its appearance at the mouth of the tube, and shortly acquires a characteristic bluish-white colour, indicating that the metal has commenced to distil off. The greater part of the zinc condenses in the fireclay condenser (B), but in order to catch any which passes this point, an iron cylinder (C) is attached. About every two hours this cylinder is taken off and the mixed dust of zinc and its oxide cleared out, the workman at the same time removing the metal condensed in (B) with an iron ladle.

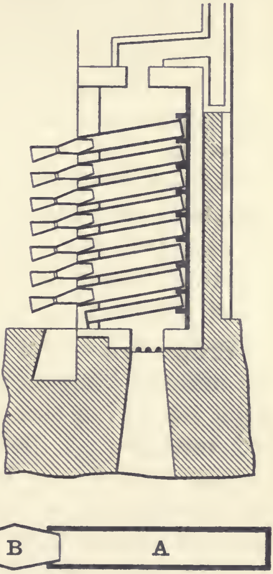


Fig. 55.—Belgian zinc furnace.

About 3 or 4 cwt. of coal is required to produce the metal from 1 cwt. of ore by this process, and the loss of zinc usually amounts to over 10 per cent. The time occupied in working through a charge is about twelve hours.

Silesian Process.—In this process the mixture of ore and coal is thrown into muffles about 4 to 5 ft. long, with flat bottoms, a number of these being arranged in pairs in one furnace, the grate of which runs along between the closed ends. Condensation is now usually effected in three long horizontal tubes, connected alternately at the ends, so that the vapours circulate properly through them.

The shape of the muffles used in this process offers certain advantages over the Belgian retorts, and these are sometimes used in conjunction with similar condensing arrangements to those in the latter process, giving to the compound method the term Belgian-Silesian process.

The remelted zinc is generally cast into slabs or ingots, which are commercially termed *spelter*.

It has been proposed to use the mixture of zinc and oxide obtained in the condensing cones as a basis for paint intended for ironwork.

Both at the ordinary temperature of the air and high temperatures, zinc is so brittle that it cannot be rolled, but at a temperature between 100° and 150° C., it becomes sufficiently malleable to permit of it being rolled down to quite a thin foil. Above 200° C. it is so brittle that it may be pounded in a mortar.

Properties.—Zinc is a bluish-white, hard, lustrous metal. At ordinary temperatures zinc is brittle, but when heated to about 150° C. it is both malleable and ductile. It melts at 412° C., and volatilises at 1040° C. Its specific gravity is about 7·0, varying from 6·8 to 7·1. Zinc undergoes very little change in air, but in contact with water charged with carbon dioxide it becomes coated with a film of oxycarbonate of zinc. When strongly heated in air or oxygen it burns with a bluish-white flame, forming zinc oxide. One of the chief applications of zinc is for coating iron, in order to protect the latter metal from the corrosive action of moist air. Iron so coated is called "Galvanised Iron," and when exposed to air the outer surface of the zinc becomes converted into zinc oxide, which slowly forms a basic carbonate by absorbing carbon dioxide, and this thin film, not being porous, protects the metal below it from further action.

COMPOUNDS OF ZINC.

Oxide (ZnO).—Only one oxide of zinc is known. This body is a white powder, formed by burning the vapour of the metal in air, and is used as a pigment (Chinese white). The colour not being affected by impurities in the air, especially sulphuretted hydrogen, it is frequently used in the place of white lead.

Hydroxide [$Zn(HO)_2$] is formed when ammonia is added to a solution of a zinc salt. By adding sodium or potassium hydroxides, the same precipitate is formed, but in each case dissolves in excess of the reagent, forming compounds of the type $Na_2O.ZnO$.

Chloride ($ZnCl_2$) is readily produced by the solution of the metal in hydrochloric acid. It is a white deliquescent solid, and is used as a caustic. It is also used as a disinfecting agent (Sir W. Burnett's fluid) to absorb the offensive gases, such as ammonia gas and sulphuretted hydrogen, emitted by organic matter during putrefactive decay. The chloride is also used to clean metallic surfaces which are to be soldered together.

Sulphate ($ZnSO_4.7H_2O$) is similarly produced by the action of sulphuric acid on the metal. This salt is isomorphous with magnesium sulphate (Epsom salts), and this has led to fatal mistakes, the former salt being poisonous. In small quantities it is used in medicine as an emetic.

Sulphide (ZnS) when found native is black, owing to the presence of sulphide of iron. When prepared in a pure state, either by precipitation from a soluble zinc salt with an alkaline sulphide, or by fusing together zinc dust and sulphur, it is quite white, but turns yellow if heated.

CADMIUM (Cd = 112).

This metal is always found in small quantities associated with zinc in its ores, and where the quantity is sufficient for recovery, the first portions of zinc collected are again mixed with carbon and redistilled. The rich cadmium-zinc alloy is dissolved in dilute sulphuric acid and precipitated as sulphide by sulphuretted hydrogen. This cadmium sulphide is dissolved in hydrochloric acid, sodium carbonate added and the precipitated cadmium carbonate dried, mixed with charcoal and redistilled, when the pure metal is obtained. Cadmium strongly resembles zinc in its physical and chemical properties; it melts at 228° C., and is converted into a vapour at 860° C.

The metal itself is employed in many fusible alloys, but its chief use is in the form of the sulphide, of which the pigment "cadmium yellow" consists. *Cadmium sulphide* (CdS) is easily precipitated by passing sulphuretted hydrogen through an alkaline solution of one of its salts. The *iodide* and *bromide of cadmium* are used in photography.

MERCURY (HYDRARGYRUM, Hg = 200).

Mercury, also called quicksilver, occurs chiefly as sulphide in the mineral *cinnabar* (HgS), from which the metal is obtained by mixing the ore with lime or scrap iron and distilling.

$$4(HgS) + 4(CaO) = 3(CaS) + CaSO_4 + 4Hg$$
$$HgS + Fe = FeS + Hg$$

The mercury vapour is led along cool passages where it condenses. Mercury is the only metal which is liquid at ordinary temperatures. It is almost silver white, of bright metallic lustre, and extremely mobile. It freezes at —40° and boils at 357·5° C., but volatilises at all temperatures. Metallic mercury is used for the manufacture of thermometers, barometers and other physical apparatus; for the collection of certain gases, the preparation of mirrors, and for the extraction of gold and silver from their ores.

All the ordinary metals with the exception of iron and platinum dissolve in mercury, yielding alloys which are known as *amalgams*. These amalgams are liquid at ordinary temperatures if the mercury is in excess, but are otherwise solid or semi-solid.

An amalgam of mercury 4 parts, bismuth 2 parts, lead and tin each 1 part, is employed for silvering mirrors. This is applied to the under surface of the glass and the excess of mercury drained off, and after the lapse of a few weeks a solid metallic coating is left on the glass, containing about 20 per cent. of mercury. For electrical purposes an amalgam of one part of zinc, one of tin and three parts of mercury is employed, whilst in dentistry, amalgams of mercury with gold, zinc or cadmium are used.

COMPOUNDS OF MERCURY.

Mercury forms two classes of compounds, namely, *mercurous* and *mercuric*. The mercurous are the most unstable, and have a great tendency to break up, forming the higher compound and metallic mercury.

Oxides.—*Mercurous Oxide* (Hg_2O) is a black heavy powder, easily decomposed into mercury and mercuric oxide by heat or light, and is prepared by precipitating a mercurous salt with sodium hydroxide.

Mercuric Oxide, or red oxide of mercury (HgO), is a red crystalline solid when prepared by heating mercury in air for some hours to a temperature near its boiling point. If this red oxide be heated to a higher temperature, it splits up again into oxygen gas and mercury. When the oxide is prepared by precipitating a mercuric salt with sodium hydroxide, it comes down as a yellow amorphous powder, and being in a finer state of division, is chemically more active than the crystalline variety.

Chlorides.—The most important salts of mercury are the chlorides. To prepare these, mercuric sulphate is taken ; this is obtained by boiling mercury and sulphuric acid together :—

$$\overset{\text{Mercury}}{Hg} + \overset{\text{Sulphuric acid}}{2(H_2SO_4)} = \overset{\text{Mercuric sulphate}}{HgSO_4} + \overset{\text{Sulphur dioxide}}{SO_2} + \overset{\text{Water}}{2(H_2O)}$$

Mercuric sulphate is formed and sulphur dioxide gas is given off. The mercuric sulphate is crystallised out and ground up with sodium chloride, and the mixture heated up in a retort. The *mercuric chloride* ($HgCl_2$), or corrosive sublimate, as it is sometimes called, distils over and sodium sulphate is left behind. Mercuric chloride is a crystalline salt, soluble in water, very poisonous, and is used as an antiseptic.

Mercurous Chloride, or calomel (Hg_2Cl_2), is a white salt insoluble in water and dilute acids, readily decomposed by alkalies. It is prepared in the same manner as mercuric chloride, only to the mixture of mercuric sulphate and sodium chloride some metallic mercury is added and an intimate mixture made. The mixture is distilled, calomel comes over, and is condensed in an atmosphere of steam, this causing the powder to fall in a fine state of division.

$$\overset{\text{Mercuric sulphate}}{HgSO_4} + \overset{\text{Sodium chloride}}{2(NaCl)} + \overset{\text{Mercury}}{Hg} = \overset{\text{Mercurous chloride}}{Hg_2Cl_2} + \overset{\text{Sodium sulphate}}{Na_2SO_4}$$

Calomel is largely used in medicine, and consequently great care must be taken to ensure the absence of corrosive sublimate, the presence of which may be readily tested by placing some calomel moistened with alcohol on a polished knife-blade, which will be blackened by the slightest trace of corrosive sublimate.

Iodides.—The iodides of this metal may be easily prepared by treating a soluble mercurous or mercuric salt with potassium iodide, and are recognised by their characteristic colours, *mercurous iodide* (Hg_2I_2), being yellowish-green, and *mercuric iodide* (HgI_2), a brilliant scarlet ; the latter salt is, however, soluble in excess of either potassium iodide or the mercuric salt. An alkaline solution of mercuric iodide in potassium iodide is known as Nessler's solution, and is a delicate test for ammonia both free and combined.

Nitrates.—The nitrates are readily prepared by dissolving mercury in nitric acid. If the mercury be in excess, *mercurous nitrate* [$Hg_2(NO_3)_2$], is formed ; if the acid be in excess, *mercuric nitrate* [$Hg(NO_3)_2$], is formed. Both these salts are soluble in water.

Sulphide.—*Mercuric sulphide* (HgS) may be precipitated by sulphuretted hydrogen from solution of a mercuric salt as a black precipitate, and is insoluble in nitric acid. The native sulphide, *cinnabar*, is red, and when ground to a fine powder constitutes the pigment vermilion.

The brilliant colour can be produced from the black variety artificially by two distinct processes. In the dry process, mercury and sulphur are heated together and the black mass formed is then sublimed, and the vermilion is ground under water. The wet process consists in digesting amorphous mercury sulphide with an alkaline sulphide, great care being taken to regulate the temperature. A brilliant vermilion may also be prepared by heating freshly precipitated " white precipitate " with ammonium polysulphide at a temperature of 45° C.

If ammonia solution be added to a metallic salt, the hydroxide of that metal is generally precipitated, but with the salts of mercury this is not the case, for if a solution of mercuric chloride be added to ammonia, an *amido* compound is formed, in which one atom of the chlorine is replaced by the amidogen group (NH_2), and has the formula ($HgCl.NH_2$) ; the common name for this substance is *white precipitate.*

CHAPTER XXIX

ALUMINIUM, GOLD, SILVER, PLATINUM

ALUMINIUM ($Al = 27$).

ALUMINIUM is one of the most abundant elements; it is never found in the free state, but occurs chiefly as silicate and oxide in felspar and all the older rocks, also in clay, marl, slate, and cryolite (a double fluoride of aluminium and sodium found in Greenland in large quantities).

Although aluminium occurs so abundantly in Nature, yet only during recent years has it been possible to produce it on anything like an extensive scale. Even at the highest temperatures attainable in an ordinary furnace, carbon or other reducing agents fail to free it from its compounds. The first commercially successful method was that of Deville, in which he reduced the double chloride of aluminium and sodium ($Al_2Cl_6.2NaCl$) by means of metallic sodium, but such a process was necessarily very costly, and now the metal is entirely produced by electrolysis.

Production.—The electric furnace (Fig. 56) consists of a rectangular box with a carbon lining, which forms the negative pole, and the positive pole is made up of a number of carbon rods about 3 inches in cross-section, separated from each other and held in a suitable holder of copper.

A fused bath of cryolite ($Al_2F_6.6NaF$) and fluor spar (CaF_2) is first prepared by packing this mixture around the carbon rods, an arc being then struck and the poles gradually parted, so that the whole mass is gradually brought to fusion, the carbon anode dipping into this liquid bath.

The material to be reduced is now added in the form of pure alumina (Al_2O_3), which dissolving in the bath, undergoes electrolysis, the fused aluminium sinking to the bottom as it is set free, where means are provided for its removal. Fresh alumina is charged in from time to time, so that the process is a continuous one.

Care has to be taken in the preparation of the aluminium oxide employed. This is carried out by taking a variety of clay known as "*bauxite*," which contains from 30 to 50 per cent. of alumina, together with iron, silica, etc., and roasting this with "soda ash," so producing sodium aluminate ($Al_2O_3.3Na_2O$), carbon dioxide escaping during the process. On extracting the mass with water, the sodium aluminate goes into solution, leaving behind the iron oxide. On passing carbon dioxide through this solution aluminium hydroxide is precipitated, and from this water is easily driven out, leaving the oxide.

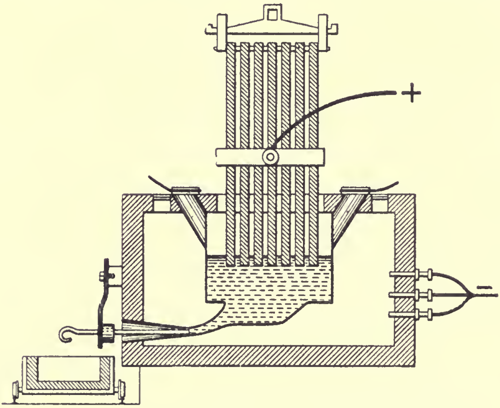


Fig. 56.—Electric furnace for aluminium.

$$\overset{\text{Sodium aluminate}}{Al_2O_3.3Na_2O} + \overset{\text{Water}}{3(H_2O)} + \overset{\text{Carbon dioxide}}{3CO_2} = \overset{\text{Sodium carbonate}}{3(Na_2CO_3)} + \overset{\text{Aluminium hydroxide}}{Al_2(HO)_6}$$

Even by this process the production of the metal is slow, for only about one ounce of aluminium is obtainable per E.H.P. per hour.

Properties.—The pure metal is white, with a slight tinge of blue; is very ductile and malleable, and possesses a bright metallic lustre that does not tarnish in air at ordinary temperatures.

The specific gravity of cast aluminium is 2·58, but after hammering or rolling increases to 2·68, and it is the lightest of those metals which are sufficiently permanent in air to allow of their use. For this reason it is employed for purposes for which lightness and tenacity are of value, as in beams of delicate balances, optical instruments, dirigible balloons, etc. The metal itself is extremely sonorous when lightly struck.

Nitric acid has little action on the metal, and sulphuric acid attacks it only when heated. Hydrochloric acid and the alkaline hydroxides readily dissolve it with the evolution of hydrogen.

Aluminium is used to some considerable extent in alloys and in the production of steel as a deoxidiser. It is also finding extensive use in a mixture of metallic oxides with the finely divided metal, under the name of *thermit*. When combustion is started by means of a fuse, a very high temperature is reached, oxygen from the metallic oxide combining with the aluminium. The material has been applied for work which must be done *in situ*, such as welding rails, repairing propeller shafts, etc.

COMPOUNDS OF ALUMINIUM.

Aluminium Oxide (Al_2O_3).—Aluminium forms but one compound with oxygen, called alumina. In the natural crystallised state it constitutes, according to its colour, various precious stones, such as the sapphire, ruby, amethyst, corundum and emery. Combined with silica and silicates of various metals it forms the garnet, emerald, topaz, beryl, and the splendid blue mineral known as lapis lazuli. Alumina combined with silica forms clay.

Hydroxides.—Three of these are known, a monhydrate ($Al_2O_3.H_2O$), a dihydrate ($Al_2O_3.2H_2O$) and a trihydrate ($Al_2O_3.3H_2O$), the latter being easily obtained by adding ammonium hydroxide to a solution of an aluminium salt. It is readily soluble in hydrochloric acid and sodium or potassium hydroxide, forming the aluminates ($Al_2O_3.K_2O$).

The Alums.—One of the most important classes of salts of this metal is the alums. These consist of double sulphates of triad metals such as aluminium with the sulphates of the monads. For instance, potash alum has the formula [$Al_2(SO_4)_3.K_2SO_4.24H_2O$], and can be formed by mixing, in proper proportions, solutions of aluminium sulphate and potassium sulphate and crystallising.

Very frequently ammonium sulphate (from gas liquor) is used instead of the potassium salt, in which case ammonia alum is formed [$(NH_4)_2SO_4.Al_2(SO_4)_3.24H_2O$].

Alum is a white crystalline body, soluble in water, and has an astringent taste. Its solution has an acid reaction. It is largely used as a mordant to fix colouring matters on calico, the aluminium hydroxide combining with certain organic colouring matters to form insoluble "lakes."

GOLD (AURUM, Au = 197).

Gold is found most widely diffused in nature, but in small quantities only. It occurs chiefly in the metallic (native) form, but occasionally combined with other elements, especially tellurium. It is also found mixed with iron, lead, zinc and silver ores. In the native form it is obtained principally from the quartz veins in some of the older rocks or from alluvial deposits. Owing to the simplicity of the metallurgical treatment, it is found profitable to work with rock containing as little as one ounce, or even less, of gold to the ton, and in the case of alluvial deposits as low as a few grains to the ton.

The alluvial deposits may exist as surface gravel beds called "shallow placers," or as "deep leads," which occur at greater depth, and are probably the beds of ancient rivers. In the Transvaal, "banket reefs," or inclined seams of gravel cemented together, have been worked to a considerable depth.

In the metallurgical treatment of the ordinary alluvial deposits, the sand is simply washed away by the action of running water, and the heavier gold remains behind. With the rock or cement, the latter is pulverised to a powder by means of "stamps." The finely divided powder after being passed through a sieve is carried by a current of water over the surface of amalgamated copper plates. By this means any gold that may be in the rock is dissolved by the mercury, and remains behind, whilst the powdered rock is washed away. After a time the mercury is collected, squeezed through a leather bag, and the solid amalgam remaining is heated in a retort. The mercury distils over, and is used again, whilst the gold remains behind.

The extremely valuable nature of the metal naturally makes it essential that with any process the losses shall be as small as possible, and the commercial success of most mines depends upon the care taken in recovering the last traces of the gold. The washings from the amalgamated plates are run into settling tanks, in the first series of which the coarser particles, "tailings," subside, whilst in the last tanks a fine mud, known as "*battery slimes,*" settles out.

One of the most successful methods of recovering the gold from the tailings is the cyanide process largely worked in South Africa. In this the precious metal is dissolved in large vats having a false bottom, to allow the weak solution of potassium cyanide to percolate through slowly. The gold is then recovered from the double cyanide of gold and potassium by means of metallic zinc.

Another process depends on the conversion of the gold into chloride ($AuCl_3$) by the action of chlorine gas. Since sulphides of other metals would also be attacked and pass into solution, pyritic ores must first be roasted to convert them into oxides which are not capable of being attacked by chlorine. The metal is precipitated as a soft brown powder by means of ferrous sulphate solution.

$$\overset{\substack{\text{Ferrous}\\ \text{sulphate}}}{6(FeSO_4)} + \overset{\substack{\text{Gold}\\ \text{chloride}}}{2(AuCl_3)} = \overset{\substack{\text{Ferric}\\ \text{chloride}}}{Fe_2Cl_6} + \overset{\substack{\text{Ferric}\\ \text{sulphate}}}{2Fe_2(SO_4)_3} + \overset{\text{Gold}}{Au_2}$$

The precipitated gold is collected and refined by melting under a mixture of borax and nitre. Gold has little affinity for oxygen, and the oxides of gold can be formed only indirectly. This property of gold of resisting the action of oxygen in the air and not rusting, classes it as one of the noble metals.

Many copper ores contain considerable quantities of silver and small quantities of gold, which however it pays to extract. By suitable treatment most of the copper is extracted, leaving an alloy of silver with a fair quantity of gold and still a little copper. The various methods of separating the gold and silver are known as "parting," and three of these may be briefly referred to :—

(*a*) "Parting" by strong sulphuric acid, with which the granulated ore is heated, the silver and copper being converted into sulphates, the gold being left unattacked. From the solution silver is recovered by precipitation with copper or zinc.

(*b*) By strong nitric acid, whereby the silver is converted into the nitrate, from the solution of which it is precipitated as chloride by the addition of salt, this chloride being further reduced to produce metallic silver by the hydrogen evolved when zinc and sulphuric acid are in contact with the silver chloride.

(*c*) By passing chlorine gas into the molten alloy covered with borax, when the less precious metals are first attacked forming chlorides, the commencement of the attack of the gold being evidenced by the appearance of orange vapours, when the chlorination is stopped. For success with this process, the amount of silver should be small.

Gold is now generally purified by passing chlorine through it when in a molten condition, in the most recent practice the gas being led into the crucible through a tube made of quartz.

Properties.—Gold possesses a bright yellow colour by reflected light, and is the most malleable of all metals; if beaten out into thin sheets it transmits green light. It is not acted on by any single acid (except selenic), but dissolves in the presence of free chlorine, and in nitro-hydrochloric acid. Gold is nearly as soft as lead, so that it cannot be used for coinage in the pure state, the standard gold of our country being an alloy of eleven parts of gold to one of copper. For jewellery, pure gold is regarded as of 24 carats. An 18 carat gold, therefore, contains $\frac{18}{24}$ or three-fourths its weight of gold.

One of the most curious compounds of gold is fulminating gold. This is prepared by acting on the trioxide (Au_2O_3) with aqueous ammonia in excess; a yellow-brown powder is obtained which, when dry, explodes very readily when heated to 100° C. or struck by a hammer. The composition of this substance is not accurately known, but it is no doubt an ammonium compound, in which part of the hydrogen of the ammonium is replaced by gold.

By adding a mixed solution of stannous and stannic chloride to a solution of gold chloride, a purple precipitate is obtained, which is called the "Purple of Cassius." The precipitate dissolves in melted glass, imparting to it a magnificent red tint; it is also used for painting on porcelain.

SILVER (ARGENTUM, $Ag = 108$).

Silver occurs both native and as sulphide in silver glance (Ag_2S), and chloride in horn silver ($AgCl$). Large quantities are obtained from galena, the ore of lead, which contains traces of this metal. Sea water also contains minute traces of silver.

The oldest method of obtaining silver consisted in fusing the ore with lead, when the latter metal dissolved out the silver, which was recovered by " cupellation." In this process advantage is taken of the ready oxidation of lead to litharge at high temperatures, the silver remaining unoxidised. The process is usually carried out in a special type of reverberatory furnace, having an almost elliptical hearth, suitably hollowed, the material employed for lining it being bone-ash. A strong current of air is forced over the molten alloy and the lead slowly oxidised, the melted oxide being driven out of the cupel by the blast. Since in the last stages the litharge carries with it much silver, it is usual to stop the first cupellation before loss of the precious metal takes place, and to subject the much richer alloy to a further cupellation, reserving the litharge so produced for future reduction and recovery of the silver it contains. The amount of silver per ton of lead must exceed 8 ozs. for the cupellation method to be economically carried out.

Recovery of Silver from Commercial Lead.—The first and most important method for de-silverising lead when the quantity is below that suitable for cupellation was due to Pattinson, advantage being taken of the fact that when an alloy of lead-silver is cooled, pure lead crystallises out, leaving as a mother liquor the richer *eutectic alloy* (see " Alloys "). A series of iron pots is employed, each heated by a separate fire, and the lead containing small quantities of silver is melted in the centre pot. On allowing to cool, the mass being repeatedly stirred, crystals of nearly pure lead separate, and are ladled into the next pot with a perforated iron ladle. When a definite fraction has been thus removed, the richer lead-silver alloy is transferred to the pot on the left. Lead containing approximately the same amount of silver as that already transferred is added in each case, in order that the charges operated on may be about the same, when the melting and cooling process is repeated. It will be seen that the lead practically free from silver is being gradually worked in one direction, while the richer alloy, becoming richer and richer in silver at each pot, is being worked in the other direction. In this manner the amount of silver per ton of lead may be raised to several hundred ounces per ton. The eutectic alloy contains about 800 ounces of silver per ton, but in practice it is not usual to work the process beyond 500 ounces to the ton. To recover the silver the rich alloy is then submitted to cupellation.

The Parkes process depends on the superior attraction for silver which molten zinc has over lead. By adding zinc to the lead, on cooling the two metals almost completely separate, the zinc as an upper layer carrying with it nearly all the silver. By distilling the silver-zinc alloy (containing some lead) with lime and coal the zinc is recovered, and the silver is afterwards obtained from the remaining lead by cupellation.

Silver is also extracted by amalgamation with mercury, the latter being afterwards distilled off.

Properties.—Silver is the whitest of all metals, and admits of the highest polish. It is the best conductor of heat and electricity. It is very ductile, and so extremely malleable that it can be beaten out into leaves that transmit a bluish light. Silver melts at 962° C., and possesses the remarkable power of absorbing oxygen from the air while it is liquid, and giving off the gas again when it is solidifying. When a mass of molten silver is allowed to cool, the film of solid metal which is formed upon its surface is burst in several places by the escaping oxygen, forming beautiful cones. This phenomenon is called "spitting," frequently causing a loss of the metal. Silver is rarely used in the pure state, as it is too soft, and is therefore generally alloyed with other metals, chiefly copper. English standard silver is an alloy containing 7·5 parts of copper to 92·5 of silver. A beautiful alloy is produced by adding a small proportion of silver to aluminium. The properties of aluminium silver are similar to those of aluminium, but its hardness and elasticity are considerably increased, while its colour is identical with that of silver. The alloy being capable of taking a high polish and not being liable to oxidation renders it particularly useful for general use in lieu of silver itself.

COMPOUNDS OF SILVER.

Silver is extensively used for coating other metals by electrodeposition; the object to be plated being placed in a bath consisting of silver chloride dissolved in a solution of potassium cyanide, the object is connected with the negative pole of a battery, the positive pole being connected with a silver or platinum plate and immersed in the bath opposite the object to be plated. Silver is also employed for silvering mirrors and reflectors. A flask or globe may be easily silvered by taking a solution of silver nitrate, adding two or three drops of ammonia, then potassium hydroxide, and lastly a solution of grape sugar in alcohol. On warming the contents of the flask gradually, the silver is reduced by the grape sugar, and deposits as a brilliant mirror on the inside of the flask.

Oxides.—Silver does not combine readily with oxygen, and on this account is useful for coating other metals and for coinage, the tarnishing of silver being due to the presence of sulphur compounds in the air, which coat the silver with a film of the sulphide. Two oxides of silver are known; both are, however, very unstable, hence they are powerful oxidising agents. The *monoxide* (Ag_2O) is prepared by precipitating a solution of silver nitrate with alkaline hydroxides; a brown earthy powder is obtained, extremely soluble in ammonia, and this solution evaporated at a gentle heat yields crystals, probably of the composition ($AgNH_2$), which are most violently explosive at the slightest touch.

If silver monoxide be acted on by hydrogen peroxide, oxygen is given off, and metallic silver left.

$$\begin{array}{ccccccccc} \text{Silver monoxide} & & \text{Hydrogen peroxide} & & \text{Silver} & & \text{Water} & & \text{Oxygen} \\ Ag_2O & + & H_2O_2 & = & Ag_2 & + & H_2O & + & O_2 \end{array}$$

Silver Dioxide (Ag_2O_2) is a brown powder produced by the action of ozone on silver.

Nitrate.—*Silver Nitrate* ($AgNO_3$) is one of the most important salts of the metal. It is formed by dissolving silver in nitric acid, the salt crystallising in plates that contain no water. It melts at 193° C. without decomposing, and solidifies to a crystalline mass on cooling, known as lunar caustic. The salt is used as a cautery, also for marking inks and in hair dyes.

Halogen Compounds.—Silver combines with the halogens, chlorine, bromine, and iodine, forming salts having the composition respectively represented by $AgCl$, $AgBr$ and AgI. These are all insoluble in water, but completely soluble in sodium hyposulphite. These salts are easily prepared from silver nitrate by precipitation with the chloride, bromide, or iodide of potassium.

PHOTOGRAPHY.

The three halogen compounds show, in a marked degree, the action of light on silver salts, namely, their instability under the action of white light. Certain parts of the spectrum, the blue end especially, have the power to decompose them, probably with the formation of sub-salts, and for this reason they have been employed most successfully in the processes of photography.

An emulsion of silver bromide is made by dissolving silver nitrate in water, adding a little gelatine, which prevents the silver bromide produced later settling out and maintains it in a finely divided state. Potassium bromide solution is then added to form the silver bromide, at the same time potassium nitrate is produced. To make the mixture sufficiently sensitive it is now heated with ammonia or boiled with hydrochloric acid, then the potassium nitrate is completely washed out with water, the emulsion melted up with a small quantity of alcohol and the glass plate or celluloid film coated and dried.

On exposure to light no visible change takes place, but a "latent" image is formed. The nature of the change is not fully explained by any one of the many theories put forward; from the chemical point it is probable that a sub-salt of silver is the result,

$$\overset{\text{Silver chloride}}{2(AgCl)} = \overset{\text{Silver sub-chloride}}{Ag_2Cl} + \overset{\text{Chlorine}}{Cl}$$

$$\overset{\text{Silver bromide}}{2(AgBr)} = \overset{\text{Silver sub-bromide}}{Ag_2Br} + \overset{\text{Bromine}}{Br}$$

On treating the exposed plate with a developer the latent image becomes changed to a visible image through the deposition of silver, in greater or less degree, where the light has affected the plate. All such developers are strong reducing substances, primarily acting only on those portions where the light has already initiated the series of changes. To confine the action to such parts of the plate, restrainers, such as potassium bromide, are added to the developer.

Those portions of the plate which have received no light still contain the original silver bromide, and this salt is also present unaltered in greater or less degree in the exposed parts. To remove this the developed plate is immersed in a solution of sodium hyposulphite until only the reduced silver image is visible, after which the plate is washed to remove all soluble salts and dried.

The image so formed is a "negative," *i.e.* it is densest and opaque where the action of light has been strongest. To obtain a "positive" print, a paper which has been "sensitised" by a similar coating to that employed for the negative may be exposed to light passing through the negative and the latent image developed by a suitable developer, the print being fixed and washed as usual. A direct and visible print may be obtained by employing a paper coated with an albumen or gelatine emulsion of silver chloride. The reddish image produced by the decomposed silver salts requires "toning." The print is therefore taken, all soluble salts removed by water washing, and the print now immersed in a toning bath containing gold chloride. Pure gold becomes deposited on the silver image produced by the action of the light, and after washing soaking in hyposulphite solution removes the remaining undecomposed silver salts. After further washing the print is dried.

Various other printing processes are also used, *e.g.* platinotype and ferrotype photographs are made by taking advantage of the fact that ferric salts are converted by light into ferrous salts, and that these, when placed in a bath of potassium chloro-platinite, reduce the salt, and platinum is deposited in a fine black powder on the portions of the exposed paper where the ferrous compounds have been formed.

The well known blue prints made from tracings, etc., are produced by exposing a paper which has been treated with ferric chloride and potassium ferricyanide. Where light reaches this paper, the ferric salt is reduced to the ferrous condition. On soaking in water the ferrous salt gives the characteristic blue reaction with potassium ferricyanide.

$$\overset{\substack{\text{Ferrous}\\\text{sulphate}}}{3(FeSO_4)} + \overset{\substack{\text{Potassium}\\\text{ferricyanide}}}{K_6Fe_2(CN)_{12}} = \overset{\substack{\text{Ferrous}\\\text{ferricyanide}}}{Fe_3.Fe_2(CN)_{12}} + \overset{\substack{\text{Potassium}\\\text{sulphate}}}{3(K_2SO_4)}$$

In the so-called carbon process, advantage is taken of the fact that a mixture of gelatine and potassium bichromate becomes insoluble on exposure to light. If then a piece of paper be coated with a film of this mixture (the gelatine being coloured by suspending some pigment such as lampblack in it) and be exposed under a negative, where the light has penetrated, the gelatine will become insoluble, and on immersion in hot water the unacted on portions will dissolve away and leave behind a positive picture composed of gelatine, rendered visible by the colouring matter suspended in it.

PLATINUM (Pt = 194·5).

Platinum is only found native, that is in the metallic condition, but always alloyed with other metals. Its chief sources are the Ural Mountains, but it occurs also in very small quantities in Peru, California, etc.

The present method of working up platinum is to melt the ore in a very powerful furnace, using the oxy-hydrogen blowpipe. In this way an alloy of platinum, iridium and rhodium is formed, the other constituents or impurities of the ore being absorbed by the lime of the crucible, or volatilised by the intense heat. This alloy is more useful than pure platinum, being harder and less easily attacked by acids than the pure metal.

Platinum is a white metal, does not tarnish in the air, is extremely infusible, and can be melted only by means of the oxy-hydrogen blowpipe or electric arc. It also resists the action of any single acid, but dissolves in aqua regia, or chlorine water; for this reason platinum vessels, wire and foil are much used in the laboratory. Caustic alkalies, silicon, phosphorus and carbon, however, attack the metal at high temperatures; also several metals, such as lead and antimony, form fusible alloys with the platinum. Vessels made of this metal should therefore never be brought in contact with these substances at an elevated temperature.

Molten platinum, like silver, has the power of absorbing oxygen and of giving it off again on solidifying. At a red heat the metal is readily permeated by hydrogen, but not by oxygen and the other gases. Another remarkable property this metal has, is the power to condense gases on its surface; this power, however, depends greatly on the physical condition of the metal. In a very finely divided state, as in the form of spongy platinum, or in the form of platinum black, many gases and vapours unite with the oxygen of the air, even at ordinary temperatures.

Platinum is tetravalent and combines with chlorine to form platinum tetrachloride ($PtCl_4$), a brownish red deliquescent salt, soluble in alcohol and ether, and is remarkable for the ease with which it forms double chlorides with the chlorides of the alkalies and alkaline earth metals and with the chlorides of many vegetable alkaloids. For this reason it is used to determine quantitatively the amount of potassium and ammonium present in different compounds. The double chloride of potassium and platinum has the formula ($PtCl_4.2KCl$).

CHAPTER XXX

NICKEL, COBALT, MANGANESE, CHROMIUM, ANTIMONY AND BISMUTH

NICKEL ($Ni = 58{\cdot}5$).

THIS metal is nearly always found associated with cobalt. The most important ore is *nickeline* ($NiAs$), whilst considerable quantities are found as a silicate of nickel and magnesium in New Caledonia. A magnetic pyrites containing nickel is also worked in Pennsylvania. Canada and Norway contribute largely to the supply of nickel, which, since the extensive introduction of nickel steel, has become a metal of great importance.

Metallurgy.—The first step in the production of the metal is the concentration of the metal into a " matte," from which it can afterwards be reduced.

The usual process is to roast the ore and then treat it in a blast furnace, lime and slag being added. The ore usually averages from 2 to 4 per cent. of nickel, and after smelting the amount is between 15 and 30 per cent. The matte is now treated much as iron is in the Bessemer process, when sulphur, arsenic and iron are oxidised.

There are many methods, both wet and dry, by which the matte may be treated, in order to obtain the metal, one of the most recent and successful being that introduced by Mond. When the metal in a fine state of division is heated to about 80° C. in presence of carbon monoxide, nickel carbonyl [$Ni(CO)_4$] is obtained, which is volatile. The stream of carbon monoxide carrying with it nickel carbonyl is then led through a series of tubes heated to 180° C., when the carbonyl is decomposed and pure nickel is deposited.

$$\underset{\text{Nickel carbonyl}}{Ni(CO)_4} = \underset{\text{Nickel}}{Ni} + \underset{\text{Carbon monoxide}}{4(CO)}$$

The carbon monoxide is then available for further use.

Properties.—Nickel is a steel-like metal capable of taking a high polish. It is not oxidised in air at ordinary temperatures, but on heating is slightly attacked. The melting point is somewhat uncertain, but it is slightly lower than that of iron. Acids attack it with fair ease.

The metal is largely employed in steel for armour plates, shells, etc. (see p. 418), and in the form of alloys. Since the metal so well withstands the action of the atmosphere it is extensively used for plating steel for bicycles and other purposes.

Nickel forms at least two definite oxides (NiO) and (Ni_2O_3). From the former all the salts of nickel may be regarded as derived, the chloride ($NiCl_2$) and the sulphate ($NiSO_4$) being the most common. The use of nickel oxides on the plates of the Edison cell is referred to on p. 54.

COBALT ($Co = 59$).

Cobalt occurs in the metallic state in meteoric iron, also is found combined with arsenic as *Speiss cobalt* ($CoAs_2$) and *cobalt glance* ($CoAsS$). This metal resembles iron in colour, but melts at a somewhat lower temperature, and has nearly double the tenacity of iron. It is only slightly malleable, but is very ductile. It is not acted on by dry air, but oxidises rapidly at a red heat. The metal dissolves in acids to form cobaltous salts, which are soluble in water, forming red solutions.

$$\overset{\text{Cobalt}}{Co} + \overset{\text{Hydrochloric acid}}{2(HCl)} = \overset{\text{Cobalt chloride}}{CoCl_2} + \overset{\text{Hydrogen}}{H_2}$$

This salt crystallises in dark red prisms with six molecules of water ($CoCl_2.6H_2O$) which lose part of their water when heated to 120° C. and become blue ($CoCl_2.2H_2O$), finally becoming anhydrous at 140° C. By writing with a dilute solution of cobaltous chloride on paper, the writing after drying at the ordinary temperature is almost totally invisible; on warming the paper the writing becomes dark blue, but fades away on cooling in moist air (sympathetic ink).

Cobalt forms several oxides, but only the cobaltous oxide (CoO), in which the metal is a dyad, yields stable salts. This oxide is extensively used to impart a blue colour to glass. Fused with an acid silicate and ground to a powder it forms the pigment "smalt." The blue colour is not affected by acids or alkalies.

MANGANESE ($Mn = 55$).

Manganese occurs chiefly combined with oxygen as *pyrolusite* or dioxide (MnO_2) ; also as manganese spar or carbonate ($MnCO_3$), as *Braunite* (Mn_2O_3) and *Hausmannite* (Mn_3O_4).

The metal manganese is only obtained in the pure state in small quantities for scientific purposes, but it plays a most important part in the manufacture of steel and in the production of alloys, such as manganese bronze, in each case the source of the metal being either *ferro-manganese* or *spiegeleisen.*

Spanish ores containing iron and manganese can be readily reduced in the blast furnace, alloys containing as much as 70 to 80 per cent. of manganese being produced. Higher percentages entail certain difficulties in working. Ferro-manganese is usually made to contain between 70 and 80 per cent. of manganese, whilst spiegeleisen may be taken to contain anything below 40 per cent., although the usual amount lies between 5 and 20 per cent.

Manganese is a reddish-grey metal, very hard and brittle, scratching glass ; but owing to its rapidly oxidising in moist air, has to be kept under naphtha. The metal combines with oxygen, forming a very complete series of oxides ; the lowest being basic and the highest acid forming, whilst the intermediate ones are neutral.

COMPOUNDS OF MANGANESE.

Oxides.—The most important oxide is the dioxide (MnO_2). This is found tolerably pure, and is largely used in the preparation of chlorine gas (p. 333). The oxide is a powerful oxidising agent in the presence of sulphuric acid ; *e.g.* oxalic acid is completely oxidised by this mixture to carbon dioxide.

$$\overset{\text{Manganese dioxide}}{MnO_2} + \overset{\text{Sulphuric acid}}{H_2SO_4} + \overset{\text{Oxalic acid}}{H_2C_2O_4} = \overset{\text{Manganese sulphate}}{MnSO_4}$$

$$+ \overset{\text{Carbon dioxide}}{2(CO_2)} + \overset{\text{Water}}{2(H_2O)}$$

Manganous oxide (MnO) is a strong base, and dissolves in acids to form pink or white salts in which the manganese is a dyad. The chloride and sulphate are both used in calico printing.

Several other oxides are known.

Hydroxide.—$Mn(OH)_2$ is obtained as a white precipitate when sodium or potassium hydroxide is added to a solution of a manganese salt, but on exposure to air the precipitate quickly turns brown, owing to absorption of oxygen from the air, with the formation in the first place of Mn_3O_4 and finally Mn_2O_3.

Manganese forms two series of salts, manganous salts, such as the chloride ($MnCl_2$) and the sulphate ($MnSO_4$), and manganic salts which are not so well defined ; the chloride (Mn_2Cl_6) has not been isolated but is believed to exist in solution, whilst the sulphate [$Mn_2(SO_4)_3$] is very unstable.

CHROMIUM ($Cr = 52$).

Chromium occurs principally as chrome-ironstone or *chromite* ($FeO.Cr_2O_3$), from which large quantities of chrome-iron are obtained, to be afterwards utilised in the production of chrome steel. The chrome-iron is easily obtained by reduction in the blast furnace, though the consumption of fuel is much greater than for pig-iron.

The pure metal may be obtained by the reduction of chromium sesquioxide (Cr_2O_3) with carbon in the electric furnace, the large amount of carbon accompanying the first product being removed by subsequent fusion with lime, when calcium carbide is formed.

Chromium is a metal harder than glass, and has a very high melting point. It combines with carbon much in the same way as iron does, the resulting body being so hard that it can be cut only by a diamond. In its other properties it closely resembles iron.

COMPOUNDS OF CHROMIUM.

Oxides.—Chromium forms two oxides, the one chromium sequioxide (Cr_2O_3) being *basic* and from which a series of chromium salts are derived, the other chromium trioxide (CrO_3) being *acidic*, yielding an important series of salts, the *chromates*, much resembling the sulphates.

When the sesquioxide is fused with an oxidising substance, such as potassium nitrate, it is converted into a potassium salt of chromic acid (H_2CrO_4). Other powerful oxidising agents can bring about a similar change ; thus if potassium hydroxide be added to a solution of a chromium salt, a chromium hydroxide is precipitated, but dissolves to a green solution in excess of the potassium hydroxide.

$$\overset{\text{Chromium chloride}}{Cr_2Cl_6} + \overset{\text{Potassium hydroxide}}{6(KOH)} = \overset{\text{Chromium hydroxide}}{Cr_2(HO)_6} + \overset{\text{Potassium chloride}}{6(KCl)}$$

On now adding lead peroxide and boiling, the colour of the solution changes from green to yellow, owing to the conversion of chromium hydroxide into the lead salt of chromic acid.

$$\overset{\text{Chromium hydroxide}}{Cr_2(HO)_6} + \overset{\text{Lead peroxide}}{3(PbO_2)} = \overset{\text{Lead chromate}}{2(PbCrO_4)} + \overset{\text{Lead oxide}}{PbO} + \overset{\text{Water}}{3(H_2O)}$$

The converse change of a compound of chromic acid to one of chromium sesquioxide may be brought about by the action of reducing agents; thus sulphuretted hydrogen brings about such reduction with the liberation of the whole of its sulphur.

By treating one molecular proportion of a chromate with half a molecular proportion of sulphuric acid, a *bichromate* is obtained, which may be regarded as a combination of the chromate group with one CrO_3 group, thus :—

$$\overset{\text{Potassium chromate}}{K_2CrO_4} + \overset{\text{Chromium trioxide}}{CrO_3} = \overset{\text{Potassium bichromate}}{K_2Cr_2O_7}$$

An excess of strong sulphuric acid added to a chromate or bichromate in solution, leads to the deposition of fine long red crystals of chromium trioxide (CrO_3) which is an extremely powerful oxidising agent, rapidly attacking organic matter. For this reason a mixture of sulphuric acid and potassium bichromate is frequently employed for cleansing glass apparatus in the laboratory.

ANTIMONY ($Sb = 120$).

Antimony is a very brittle crystalline metal, having a density of 6·7. It is rarely found native, but occurs principally as trisulphide in the ore called *Stibnite* (Sb_2S_3). The metal is obtained on a large scale by heating the trisulphide with half its weight of metallic iron, when ferrous sulphide and metallic antimony are obtained—

$$\overset{\text{Antimony sulphide}}{Sb_2S_3} + \overset{\text{Iron}}{3Fe} = \overset{\text{Ferrous sulphide}}{3(FeS)} + \overset{\text{Antimony}}{Sb_2}$$

The crude metal so obtained is purified by repeated fusion with dry sodium carbonate.

Antimony undergoes no alteration in the air at ordinary temperatures, but if heated up to 450° C. it melts and rapidly oxidises ; if heated more strongly, it takes fire and burns with a white flame, giving off dense white fumes of antimony trioxide. Antimony is not attacked by dilute hydrochloric or sulphuric acids. Nitric acid attacks the metal, dense red fumes of the lower oxides of nitrogen are given off, and a white insoluble powder is left behind, called antimony pentoxide, but this is usually accompanied by lower oxides.

The alloys of antimony are largely used in the arts (p. 519).

COMPOUNDS OF ANTIMONY.

Antimony Hydride (SbH_3) very much resembles arsenic hydride (AsH_3) being obtained as a colourless, odourless gas on treating zinc-antimony alloys with dilute hydrochloric acid. The gas burns with a bluish white flame and, like arseniuretted hydrogen, deposits the metal on any cold surface brought in the flame.

Oxides.—Antimony forms three oxides, Sb_4O_6, Sb_2O_4, and Sb_2O_5.

Antimonious Oxide (Sb_4O_6) is produced when the metal burns in air, and also when steam is passed over the heated metal.

This oxide dissolves when boiled with a solution of cream of tartar (hydrogen potassium tartrate), forming the substance "tartar emetic," employed in medicine.

Antimony Tetroxide (Sb_2O_4, or $Sb_2O_3.Sb_2O_5$) is obtained as a yellowish white residue when the metal is treated with nitric acid. Unlike the above oxide, it is not soluble in cream of tartar.

Antimony Pentoxide (Sb_2O_5) is a light yellow powder, which on heating yields the tetroxide. It may be regarded as the anhydride of antimonic acid ($HSbO_3$), two molecules of which on losing one molecule of water would give Sb_2O_5. Since antimonic acid is obtained when nitric acid of suitable strength acts on the metal, it is often mixed with some of the anhydride.

Antimony Trichloride ($SbCl_3$)—sometimes called butter of antimony—is formed when powdered antimony is thrown into chlorine gas, or by dissolving the trisulphide in hydrochloric acid, evaporating the excess of acid, and then distilling off the antimony chloride.

$$\overset{\text{Antimony trisulphide}}{Sb_2S_3} + \overset{\text{Hydrochloric acid}}{6(HCl)} = \overset{\text{Antimony trichloride}}{2(SbCl_3)} + \overset{\text{Sulphuretted hydrogen}}{3(H_2S)}$$

This method is used for the preparation of sulphuretted hydrogen, when the gas is required free from hydrogen.

If a solution of antimony chloride be mixed with much water, a white precipitate of the oxychloride is obtained.

$$\overset{\text{Antimony trichloride}}{SbCl_3} + \overset{\text{Water}}{H_2O} = \overset{\text{Antimony oxychloride}}{SbOCl} + \overset{\text{Hydrochloric acid}}{2(HCl)}$$

The trichloride is used extensively to produce the brown surface on steel in guns, which prevents rust. *Antimony pentachloride* is prepared by saturating the trichloride with chlorine; it is decomposed easily by water or by heating. It is used as a chlorinator, since it readily gives up a portion of its chlorine.

Antimony Trisulphide (Sb_2S_3) and **Antimony Pentasulphide** (Sb_2S_5) can be precipitated from solutions of corresponding salts by sulphuretted hydrogen. The trisulphide so precipitated is of an orange-red colour, and is employed for vulcanising caoutchouc. If this red sulphide be strongly heated it becomes permanently grey, and resembles the natural black sulphide of antimony. The native sulphide when mixed with chlorate potassium and copper phosphide is employed in the manufacture of electric fuses.

BISMUTH (Bi = 208·5).

Bismuth usually occurs native and in combination with sulphur, as *bismuthite* (Bi_2S_5). To obtain the metal the sulphide is roasted in the air, and the resulting oxide reduced with charcoal. Bismuth is a reddish-white metal of specific gravity 9·9. It is permanent in dry air at ordinary temperatures, but rapidly oxidises at a red heat. It is brittle, and may be easily pulverised. It melts at 268° C., and, like water, expands at the moment of solidification. The solidified metal has a pronounced crystalline structure, taking the form of rhombohedra in shape, closely approximating to cubes. It is very soluble in nitric acid, slowly soluble in sulphuric acid, and practically insoluble in hydrochloric acid.

The metal *per se* is not used in the arts, but is employed as an admixture in various alloys, most of which are remarkable for their low melting points.

COMPOUNDS OF BISMUTH.

Oxides.—Bismuth forms three oxides, Bi_2O_3, Bi_2O_4 and Bi_2O_5.

Bismuth Trioxide (Bi_2O_3) is formed when the metal is strongly heated in air, and when potassium hydroxide or ammonia is added to a solution of a bismuth salt, a hydrated oxide ($Bi_2O_3.H_2O$) is precipitated.

Chlorides.—Two chlorides are known, $BiCl_2$ and $BiCl_3$.

Bismuth Chloride ($BiCl_3$) is formed when bismuth is dissolved in aqua regia, and like the nitrate and other salts, it is decomposed by much water, forming an oxychloride.

$$\overset{\substack{\text{Bismuth}\\\text{chloride}}}{BiCl_3} + \overset{\text{Water}}{H_2O} = \overset{\substack{\text{Bismuth}\\\text{oxychloride}}}{BiOCl} + \overset{\substack{\text{Hydrochloric}\\\text{acid}}}{2(HCl)}$$

This substance is used as the pigment "pearl white."

Bismuth Nitrate $Bi(NO_3)_3$ is formed when bismuth dissolves in nitric acid, and it crystallises with five molecules of water of crystallisation. These crystals are deliquescent. When water is added to the salt a basic nitrate is produced, but this readily dissolves in dilute acids.

Bismuth Sulphide (Bi_2S_3) is obtained as a dark brown powder when sulphuretted hydrogen is passed through solutions of bismuth salts.

CHAPTER XXXI

METALS OF THE ALKALINE EARTHS

The four metals, magnesium, calcium, strontium, and barium constitute the metals of the alkaline earths, and of these the only one which, in the metallic state, is of any importance, is magnesium, the others being oxidised by moist air with such rapidity that they can have no commercial value, and are little more than scientific curiosities. Their numerous compounds, however, are of great importance.

They all form oxides in which one atom of the metal is united with one atom of oxygen, and these oxides dissolve to some extent in water, magnesium oxide but slightly, while the solubility increases until it reaches a maximum with barium oxide. The solutions in every case are alkaline, hence the term "alkaline earths."

Magnesium ($Mg = 24$).

Magnesium occurs widely diffused in nature and in large quantities, especially as carbonate in dolomite and magnesite, as sulphate in Epsom salts, and as silicate in asbestos, meerschaum, talc, steatite or soap-stone, etc. It is found as sulphate and chloride in sea water.

Magnesium has been extracted in any quantity only during the last few years, a considerable demand for it having arisen in consequence of its property of burning in air with a very brilliant flame, rich in actinic or chemical rays, which make it valuable as a source of artificial light in photography. A wire of 0·3 millimeter in diameter in burning produces a light equal to that of seventy-four sperm candles, of which six go to the pound. Magnesium is used to a small extent in alloys, particularly in conjunction with aluminium, magnalium being the best known of these. For signalling purposes a preparation is made by fusing together ten parts of shellac with sixty parts of barium nitrate, grinding and adding two parts powdered magnesium. This mixture when made into torches constitutes the so-called "Bengal lights."

Preparation.—The metal is prepared by heating to redness a mixture of sodium and magnesium chlorides with one-fifth its weight of metallic sodium in an iron vessel. Magnesium is also prepared by the electrolysis of magnesium sodium chloride. The crude magnesium so obtained is then distilled, out of contact with air, at a white heat into an iron receiver placed directly over the crucible.

Magnesium is a white metal resembling silver, but soon tarnishes in moist air owing to the formation of a film of oxide on the surface. It melts at about 800° C., is malleable, and at a temperature of 450° C. can be readily worked and rolled into any form.

COMPOUNDS OF MAGNESIUM.

Oxide (MgO).—Magnesium oxide or magnesia is formed when the metal is burnt in the air, or when the carbonate or nitrate is ignited. It is a white amorphous powder, almost insoluble in water (one part dissolving in about 55,000 parts of water), giving it a feeble alkaline reaction.

Magnesia formed by the prolonged ignition of the carbonate is much used in pharmacy, whilst the commoner kinds are used for the manufacture of crucibles, fire-bricks, etc., on account of their infusibility.

Chloride ($MgCl_2$).—The metal readily dissolves in dilute acids, forming the different salts. Magnesium chloride is present in sea water, and also occurs in large quantities, combined with potassium chloride in the mineral *Carnallite* ($MgCl_2.KCl.6H_2O$) in the Stassfurt deposits. From this compound the magnesium chloride is separated, and is used by the cotton spinners in this country as a thread lubricator.

Carbonate ($MgCO_3$).—Magnesium carbonate, commercially known as *magnesia alba*, is prepared by precipitating a solution of the sulphate or chloride with sodium carbonate. A basic carbonate is thrown down, having the probable formula of $[3MgCO_3.Mg(HO)_2.3H_2O]$. A denser variety having an extra molecule of water may be obtained in the same manner, only using hot and strong solutions.

Sulphate ($MgSO_4$).—Magnesium sulphate is found native in many places, and forms the purgative principle of several spring waters, such as those obtained from Epsom, Seidlitz, and Püllna. The salt is easily soluble in water, and is largely used in the cotton trade as a warp-size, also for medicinal and agricultural purposes.

Nearly all the minerals containing magnesium silicate may be recognised by their peculiar greasy feeling; this is most marked in soap-stone.

CALCIUM ($Ca = 40$).

Calcium forms a very large proportion of the rocks of which the earth is composed, and occurs in considerable quantities, forming whole mountain chains of limestone, chalk, and gypsum. It is also found in all animals and vegetables, being absorbed by means of their food.

The metal itself is of a light yellow colour, of specific gravity 1·58, is harder than lead, and very malleable. In ordinary air it combines slowly with the oxygen, but at a red heat it fuses and burns with a brilliant light, forming calcium monoxide or quicklime.

$$\underset{\text{Calcium}}{Ca} + \underset{\text{Oxygen}}{O} = \underset{\text{Calcium monoxide}}{CaO}$$

COMPOUNDS OF CALCIUM.

Oxides.—Two oxides are known, the monoxide (CaO) or *lime*, and a dioxide (CaO_2).

The former is produced in large quantities wherever limestone rocks are found, since it is extensively used in the production of mortar and bleaching powder, in tanneries, and for agricultural purposes. The limestone ($CaCO_3$) together with coal is thrown into suitable kilns, the type ot which varies in different localities, when the heat resulting from the combustion of the coal breaks up the calcium carbonate, carbon dioxide being driven off and calcium oxide (*quick lime*) settling to the bottom of the kiln, where it is raked out from time to time.

Calcium oxide, when pure, is white, and on strongly heating emits an intense light, and is used in the form of cylinders in the oxy-hydrogen light.

Calcium Hydroxide $Ca(HO)_2$.—On exposing lime to moist air, water is slowly absorbed, forming the hydroxide, which on prolonged exposure further absorbs carbon dioxide. If freshly burnt lime is taken, and water added to it, the formation of the hydroxide takes place with such energy that considerable heat is developed, the mass swells up, and if not too great a quantity of water has been added, the mass breaks up into a dry white powder, calcium hydroxide (*slaked lime*).

$$\underset{\text{Lime}}{CaO} + \underset{\text{Water}}{H_2O} = \underset{\text{Calcium hydroxide}}{Ca(HO)_2}$$

Calcium hydroxide is slightly soluble in water; the clear solution obtained by allowing the excess of the hydroxide to settle is called "lime-water," and is employed medicinally and in the laboratory. It is alkaline to test paper, and on exposure to air absorbs carbon dioxide, forming a white precipitate of calcium carbonate.

$$\underset{\text{Calcium hydroxide}}{Ca(HO)_2} + \underset{\text{Carbon dioxide}}{CO_2} = \underset{\text{Calcium carbonate}}{CaCO_3} + \underset{\text{Water}}{H_2O}$$

Calcium Chloride ($CaCl_2$) can readily be obtained by the action of hydrochloric acid on the carbonate.

It combines with water to form several crystalline salts, which on heating lose water, forming a dry granular mass which is largely employed for drying gases and liquids, since it is very hygroscopic.

Ammonia gas and alcohol both form compounds with calcium chloride, so the material is unsuitable as drying agent in these cases.

Calcium Carbonate ($CaCO_3$).—Calcium occurs principally as the carbonate, and from this all the manufactured compounds of lime are prepared. The forms in which the carbonate are found are very numerous. In the amorphous state it exists as limestone and chalk; the crystalline forms being calc spar or Iceland spar, and arragonite. Marble has also a crystalline form, and sometimes is found coloured or variegated by the presence of oxides of iron and manganese. Black marble owes its colour to the presence of bituminous matter. Calcium carbonate is also the principal constituent of egg shells, the shells of fishes, and coral.

Calcium Sulphate ($CaSO_4$) occurs in nature as "*anhydrite,*" but more generally combined with two molecules of water, as selenite, alabaster and gypsum ($CaSO_4.2H_2O$). From gypsum, the substance called *plaster of Paris* is obtained, by heating the former to a temperature between 110° to 120° C.; it then loses about three-fourths of its water and forms a substance which, on being powdered, has the property of recombining with water, forming a hard mass, which expands at the moment of setting or solidifying, and is therefore much used in taking casts.

In burning the gypsum to form "plaster of Paris" care has to be taken to avoid too high a temperature, in which case it becomes "overburnt" and to a great extent loses the property of recombining with water. An addition of a small percentage of lime to plaster of Paris (not more than 10 per cent.) increases the rapidity of setting and makes it harder; this latter property being also induced by addition of a little solution of alum to the plaster and again burning.

Plaster of Paris must always be kept in a dry place, otherwise it absorbs water, and to a great extent loses its power of setting.

Calcium sulphate is slightly soluble in water (1 part in 400, at 35° C.), and less so in hot water. It is one of the chief causes of the permanent hardness of water, which is not removed by boiling. The presence of other salts, such as sodium and magnesium chlorides, increases its solubility in water.

Calcium Nitrate [$Ca(NO_3)_2$] is an extremely deliquescent and soluble salt, found in many well waters, and often as an efflorescence on the walls of places where there is any organic refuse. It is made artificially on the Continent for the production of nitre, by mixing organic matter, both animal and vegetable, with chalk, old mortar, etc., moistening occasionally with liquid stable manure, and exposing the mass to the air, in the dark, for two or three years. The soluble salts are then dissolved out, and consist largely of calcium nitrate. This is decomposed by adding a solution of potassium sulphate or carbonate, the corresponding calcium salt is precipitated, and the potassium nitrate crystallised out.

Calcium Fluoride (CaF_2) is found in Nature as fluor-spar; it is used as a source of hydrofluoric acid, and as a flux in many smelting operations. Its special value lies in the increased fluidity it imparts to the slags.

✓ **Calcium Carbide** (CaC_2) is a compound which is now produced on an extensive scale for the preparation of acetylene, which it readily yields on treating with water.

$$\overset{\text{Calcium carbide}}{CaC_2} + \overset{\text{Water}}{2(H_2O)} = \overset{\text{Calcium hydroxide}}{Ca(HO)_2} + \overset{\text{Acetylene}}{C_2H_2}$$

For the manufacture, a mixture of finely ground lime and coke is charged into an electric furnace, the bottom of which frequently consists of a carbon plate to form one pole and a large carbon rod, capable of being raised and lowered, forms the other pole. On striking an arc and gradually raising the upper pole, the materials interact, and slowly an ingot of the carbide is built up.

$$\overset{\text{Calcium oxide}}{2(CaO)} + \overset{\text{Carbon}}{6C} = \overset{\text{Calcium carbide}}{2(CaC_2)} + \overset{\text{Carbon monoxide}}{2(CO)}$$

Calcium carbide so prepared is a black crystalline substance. If care be taken in the proper selection of the materials as to their purity, the acetylene generated is very pure.

The salts of calcium impart a yellowish-red colour to flame. The most commercially important compound of calcium is bleaching powder ($CaOCl.Cl$), the preparation and uses of which are described under "Chlorine" (p. 339).

BARIUM (Ba = 137) AND STRONTIUM (Sr = 87).

These metals very much resemble calcium in their properties, and form salts of an exactly similar type. These have a very limited use, being employed mainly in the manufacture of coloured fires—barium salts imparting a green colour to flames and strontium salts a magnificent crimson.

The chloride and nitrate of barium [$BaCl_2$ and $Ba(NO_3)_2$] are used as laboratory reagents, and also to a certain extent the clear solution of the hydroxide [$Ba(HO)_2$], known as "*baryta water*," which serves as a more delicate test than lime-water for carbon dioxide.

Barium dioxide (BaO_2) is used extensively in the production of oxygen by Brin's process (p. 62).

THE ALKALI METALS.

There are five metals included in this group which strongly resemble each other in their properties; they are all silvery white, so soft that they may easily be cut with a knife, but the cut surface almost immediately tarnishes in the air. They all decompose water at ordinary temperatures. Of these five metals the only two of practical importance are potassium and sodium.

POTASSIUM ($K = 39$).

Potassium was not known until 1807, when Sir Humphry Davy succeeded in breaking up potassium hydroxide by a strong galvanic current.

This element exists very widely distributed in nature, both in combination with chlorine as potassium chloride (large deposits of which, together with magnesium chloride, are found in Saxony), and with silica and alumina in the minerals felspar and mica, and it is from these minerals, by the process of disintegration, that it passes into the soil in a soluble state. All plants depend very largely on the supply of potassium salts in the soil, and when any vegetable matter is burnt, the ash is found to contain a considerable percentage of potassium in the form of carbonate.

Preparation.—Davy first obtained the metal by the electrolysis of fused potassium hydroxide, but owing to the difficulty of obtaining sufficient current, the method was not a commercial one. Within recent years, however, the development of electrolytic processes has been very rapid, and now the greater part of this metal is prepared by a method identical with that of Davy, only, of course, adapted for commercial purposes. This will be referred to in greater detail under "Sodium" (p. 482).

Potassium may also be obtained from the hydroxide by fusing it with a mixture of carbon and iron (which may contain some iron carbide, Fe_2C), when the carbon reduces the hydroxide in the following manner :—

$$\overset{\substack{\text{Potassium}\\ \text{hydroxide}}}{6(KOH)} + \overset{\text{Carbon}}{2C} = \overset{\substack{\text{Potassium}\\ \text{carbonate}}}{2(K_2CO_3)} + \overset{\text{Hydrogen}}{3H_2} + \overset{\text{Potassium}}{K_2}$$

COMPOUNDS OF POTASSIUM.

Oxides.—It is probable that potassium forms four oxides, but the only one of importance is the monoxide (K_2O), which is readily obtained when the metal burns in air or oxygen. It is a powerful base which readily dissolves in water, forming potassium hydroxide (KHO).

Potassium Hydroxide is formed from the monoxide by its solution in water, but is prepared on a large scale commercially by boiling together lime and a solution of potassium carbonate.

$$\overset{\substack{\text{Potassium}\\ \text{carbonate}}}{K_2CO_3} + \overset{\substack{\text{Calcium}\\ \text{hydroxide}}}{Ca(HO)_2} = \overset{\substack{\text{Potassium}\\ \text{hydroxide}}}{2(KHO)} + \overset{\substack{\text{Calcium}\\ \text{carbonate}}}{CaCO_3}$$

A certain degree of dilution is necessary, and when the reaction is complete the calcium carbonate is allowed to settle out, the clear liquid being afterwards concentrated in iron pans until on cooling it solidifies.

Potassium hydroxide is largely used commercially and also for laboratory purposes, such as the absorption of carbon dioxide in gas analysis.

The salts of potassium are numerous, and many of them are very important, being largely used in our manufactures. Of these may be mentioned the nitrate, or saltpetre, which has been treated at length under "Gunpowder." The chlorate and iodide have also been previously described. *Potassium sulphate* (K_2SO_4) is found crystallised with magnesium salts in large natural deposits forming the substance called *kainit*. The salt itself is largely used in making potassium alum.

Potassium Carbonate (K_2CO_3) was at one time the main source of potassium salts, being obtained by extraction from the ashes of wood—hence the name "potash." It is now manufactured by processes similar to those employed for the production of sodium carbonate (p. 484).

Nearly all the salts of this metal are very soluble in water.

The compounds of potassium may be recognised by adding a solution of platinum chloride to a strong aqueous solution of the salt, when a yellow crystalline precipitate is obtained on stirring the mixture; also by the violet colour which they impart to flame when a fragment is taken on a clean platinum wire, moistened with hydrochloric acid, and then heated in the inner blowpipe flame. Potassium is one of the lightest of the metallic elements, having a specific gravity of 0·865, and an atomic weight of 39·1.

SODIUM ($Na = 23$).

Sodium very strongly resembles potassium, both in the elementary state and in its compounds, but is far more abundant in Nature, common salt, or sodium chloride, existing in enormous quantities in sea water, and also in very extensive deposits found in many parts of the world.

In warm countries sea water is run into shallow tanks, where it evaporates under the heat of the sun, and on reaching a specific gravity of 1·2 begins to deposit coarse crystals of crude sodium chloride known as " bay salt," which, after being allowed to stand and drain free from the deliquescent magnesium chloride, are ready for use in the manufactures in which it is employed ; whilst the " bittern " or mother liquor which has given birth to the crystals is utilised for the production of bromine.

Preparation.—As in the case of potassium, sodium is now prepared on a large scale by the electrolysis of the hydroxide under suitable conditions, the metal produced being at one time largely employed in the extraction of aluminium and magnesium. The commercial success of the electrolytic method has been due mainly to Castner. In order that the yield of metal shall be good, it is essential that the electrolysis shall take place at about 330° C., therefore means are provided for maintaining this temperature—with low currents gas heating is employed, whilst for heavy currents it is necessary to keep the fused hydroxide down in temperature by circulating water around the iron vessel in which the action takes place. The metal, together with hydrogen, is liberated at the negative pole, and being lighter than the fused hydroxide, rises into an inverted cylinder, from which it can be ladled out with a perforated ladle which allows the fused hydroxide to run back into the furnace.

COMPOUNDS OF SODIUM.

The compounds of sodium are amongst the most important in nature, the chloride being essential to animal life, and being also used to a very large extent for glazing earthenware and for agricultural use, whilst sodium carbonate is of the greatest importance and use in the arts and manufactures, as well as for cleansing purposes.

Oxides.—Two of these are known, and when sodium burns in air a mixture of the two results. The *peroxide* (Na_2O_2) is a yellowish white body which, in contact with water, evolves oxygen (mixed with a certain amount of ozone) and forms sodium hydroxide.

Sodium peroxide		Water		Sodium hydroxide		Oxygen
Na_2O_2	$+$	H_2O	$=$	$2(NaHO)$	$+$	O

Sodium peroxide is frequently employed for oxidising purposes, and has been used for supplying oxygen in closed spaces, such as submarines, for not only does it evolve the necessary oxygen to support life, but the sodium hydroxide produced in the process is capable of absorbing the carbon dioxide evolved during respiration.

The *monoxide*, Na_2O, is an amorphous grey powder which, like the corresponding oxide of potassium, readily forms the hydroxide with water.

Sodium Hydroxide (caustic soda) ($NaHO$).—In a pure condition this may be obtained by the action of sodium on water, the liquor remaining being concentrated in silver vessels.

A crude product is very largely employed technically, and the manufacture is one of very great importance. The solution obtained by treating the "black ash" in the Leblanc process (p. 484), and which contains sodium carbonate and sulphide, is heated and agitated with an excess of lime, when the following reaction takes place :—

Sodium carbonate		Calcium hydroxide		Calcium carbonate		Sodium hydroxide
Na_2CO_3	$+$	$Ca(HO)_2$	$=$	$CaCO_3$	$+$	$2(NaHO)$

The calcium carbonate is allowed to settle out, the clear liquor being concentrated in iron pans, when by means of air which is blown through and the addition of sodium nitrate, the sodium sulphide is oxidised to sulphate which may be crystallised out, the mother liquor being still further concentrated until a fused mass results, which is then cast into cakes or sticks as desired.

A more modern method consists in electrolysing brine of a suitable strength, when not only can the caustic soda be obtained, but also chlorine for the manufacture of bleaching powder (p. 339).

A divided cell is employed in order that the liberated elements, sodium and chlorine, may be separated as quickly as possible; the cathode is of mercury, the anode being of carbon in order that it may not be attacked by the liberated chlorine. On passing the current, sodium is liberated at the mercury cathode, where it at once forms sodium amalgam, which flows off into a separate vessel containing water. Here the sodium acts on the water, forming a solution of the hydroxide which can be concentrated.

Sodium Carbonate (Na_2CO_3).—This compound is of the greatest importance in the arts and manufactures, being employed in the production of glass, soap, etc., and as ordinary washing soda; the crystals contain 10 molecules of water of crystallisation ($Na_2CO_3.10H_2O$), but in dry air they lose water, assuming a white appearance on the surface (*efflorescence*).

Manufacture.—At one time the manufacture was entirely dependent upon supplies of "barilla," the ash obtained by burning suitable forms of sea-weed, etc. This ash contained about one-fourth its weight of sodium carbonate, and the great scarcity which arose at the time of the French Revolution led to the introduction of methods of preparation from common salt.

In the Leblanc process common salt (sodium chloride) is mixed with an equal weight of sulphuric acid upon the hearth of a reverberatory furnace, which converts it into sodium sulphate, at the same time expelling hydrochloric acid gas, the fumes are passed up towers filled with coke, down which water is allowed to trickle, and as hydrochloric acid gas is intensely soluble in water the acid is dissolved, forming the solution which is commercially known as "Muriatic Acid" or spirits of salt.

$$\underset{\text{Sodium chloride}}{2(NaCl)} + \underset{\text{Sulphuric acid}}{H_2SO_4} = \underset{\text{Sodium sulphate}}{Na_2SO_4} + \underset{\text{Hydrochloric acid}}{2(HCl)}$$

The dried sodium sulphate, called "*salt cake,*" is then mixed with an equal weight of chalk (calcium carbonate) and about one-half its weight of fine coal dust, and is again heated upon the hearth of the furnace, when decomposition takes place; carbon monoxide is evolved, and a mixture of sodium carbonate with lime and calcium sulphide is left. This mass is called "*black ash,*" and it is next treated with water, which dissolves out the sodium carbonate, leaving most of the calcium sulphide behind; the solution then has air blown through it to oxidise any calcium sulphide to sulphate, which being very slightly soluble, settles out, and the clear liquid is evaporated and yields impure sodium carbonate called "*soda ash.*"

$$\overset{\text{Sodium sulphate}}{Na_2SO_4} + \overset{\text{Calcium carbonate}}{CaCO_3} + \overset{\text{Carbon}}{4C} = \overset{\text{Sodium carbonate}}{Na_2CO_3} + \overset{\text{Calcium sulphide}}{CaS} + \overset{\text{Carbon monoxide}}{4(CO)}$$

On dissolving the soda ash in water and evaporating to the necessary strength, crystals of washing soda containing 10 molecules of water separate out.

Several other processes have of late years come into extensive use, one of the most important being the "ammonia-soda or Solvay's process," which consists of passing carbon dioxide through a saturated brine solution, containing one-fifth its own volume of strong ammonia solution, when sodium bicarbonate is thrown down:—

$$\overset{\text{Sodium chloride}}{NaCl} + \overset{\text{Ammonium hydroxide}}{NH_4HO} + \overset{\text{Carbon dioxide}}{CO_2} = \overset{\text{Sodium bicarbonate}}{NaHCO_3} + \overset{\text{Ammonium chloride}}{NH_4Cl}$$

On strongly heating the bicarbonate, it breaks up into the carbonate with evolution of carbon dioxide—

$$\overset{\text{Sodium bicarbonate}}{2(NaHCO_3)} = \overset{\text{Sodium carbonate}}{Na_2CO_3} + \overset{\text{Carbon dioxide}}{CO_2} + \overset{\text{Water}}{H_2O}$$

The ammonia can readily be recovered from its chloride and used for saturating fresh brine, and similarly the carbon dioxide liberated in the second reaction can be re-employed, hence the process is an extremely economical one.

The salts of sodium give no precipitates with the ordinary reagents, but may be recognised by the intense yellow colour which they impart to flame.

Spectrum Analysis.—The preceding metals all impart a particular colour to flame, but when two or more are present at the same time the colours often interfere with or mask each other, but their presence is easily detected by spectrum analysis.

In the spectroscope a narrow beam of light is allowed to pass through a glass prism whereby it becomes refracted, the degree of refraction being dependent upon the wave length of the particular rays, violet rays being deflected most and red rays least. Consequently, white light gives a continuous band of colours, known as the *spectrum* and ranging through violet, indigo, blue, green and orange to red.

By a suitable scale moving with the viewing telescope, the location of the portion of the spectrum due to light of a given wave length may be determined. The salts of a large number of metals impart characteristic colours to a non-luminous Bunsen flame, consequently the refraction of the different rays from compounds of the same elements leads to the appearance of bright coloured bands at fixed and definite positions in the spectroscope. Sodium salts, for example, give two bright yellow bands ; potassium salts a band in the red and another in the violet. The merest traces of salts show their characteristic lines, and the bands from a mixture of different salts are each capable of recognition, so that spectroscopic analysis is an invaluable adjunct to other methods of investigation. The spectrum of metals not volatilised by a Bunsen flame may be examined by sparking between two rods of the metal attached to an induction coil. Gases also have characteristic spectra : to examine these a tube having platinum wire terminals sealed through the glass is employed. The tube is filled with the gas, exhausted by an air pump, and sealed ; on passing the discharge from an induction coil, the highly rarefied residual gas becomes luminous and may be examined spectroscopically.

On viewing direct sunlight in the spectroscope, definitely placed dark lines, known as Fraunhofer lines, are seen, and these correspond to the bright lines of certain metals, iron, magnesium, sodium, etc. The explanation of this coincidence and its meaning are found when an intense white light is passed through a flame coloured with a given salt : instead of the line appearing bright, it is now seen as a black line, because the coloured flame absorbs light of the same wave length which it emits. The Fraunhofer lines therefore are probably due to the presence of the vapour of many terrestrially familiar metals, etc., in a gaseous condition in the atmosphere of the sun, and by absorption of portions of the white light of the sun in passing through its atmosphere manifest their presence. In a similar manner the composition of the atmosphere of many stars has been arrived at.

AMMONIUM COMPOUNDS.

The similarity in behaviour of the radicle (NH_4) to the metals potassium and sodium in the formation of salts has already been pointed out. It is therefore necessary to consider the salts of this radicle with those of the two above-mentioned metals.

Ammonium Chloride (NH_4Cl) is commercially known as *sal-ammoniac*, and has been known from very early times. The Arabs obtained it by heating the soot deposited when camels' dung is burned. When ammonia gas and hydrochloric acid gas are brought together, dense fumes of ammonium chloride are formed. It is manufactured by passing ammonia from gas liquor into hydrochloric acid.

Ammonium chloride is a white solid, which easily volatilises, but the vapour readily dissociates into ammonia and hydrochloric acid, which, however, recombine on cooling.

Sal-ammoniac is extensively employed for use in Leclanché batteries, and in the laboratory is the common source from which ammonia gas is obtained.

Sulphides.—The normal sulphide of ammonium has the composition $(NH_4)_2S$, but this is a very unstable body, which, by the elimination of ammonia, yields the well-known stable *ammonium hydrogen sulphide* (NH_4HS). This is largely prepared for laboratory work by saturating dilute ammonia solution with sulphuretted hydrogen.

Ammonium Sulphate, $(NH_4)_2SO_4$, is a salt of great commercial importance, and it is obtained largely as a by-product in the production of coal-gas and in producer gas practice (p. 200), the material finding a ready sale as a fertiliser, and is much employed as a source of other ammonia salts. The method of preparation consists in passing the ammonia vapours from the ammoniacal liquors into sulphuric acid contained in lead-lined tanks, the crystals of the salt being removed by perforated ladles.

Ammonium Nitrate, NH_4NO_3, is a white crystalline deliquescent substance, readily decomposed by heat into nitrous oxide and water. The substitution of this nitrate for potassium nitrate in certain forms of powder has already been referred to.

When the material is sharply heated up, it undergoes decomposition with explosion.

Carbonate.—Three carbonates of ammonium are known. The *normal ammonium carbonate* $(NH_4)_2CO_3$ is unstable, and when dissolved in water, readily parts with ammonia, forming *ammonium hydrogen carbonate* (NH_4HCO_3). Either of these salts dissolved in ammonia solution yields a *tetrammonium dihydrogen carbonate* or *sesquicarbonate.* The relation between these three substances may be shown thus :—

Ammonium carbonate	Ammonium sequicarbonate	Ammonium hydrogen carbonate
$(NH_4)_4.(CO_3)_2$	$(NH_4)_4.(CO_3)_2.H_2CO_3$	$(NH_4)_4.(CO_3)_2.2H_2CO_3$

CHAPTER XXXII

ALLOYS

Except for scientific purposes the quantity of metal used in the pure condition is very small. For electrical purposes both copper and very pure iron are requisite, but for most other purposes the modifying influence of other elements is utilised to produce the desired qualities. The most valuable form of iron, steel, is, as has been shown, dependent upon carbon for its special characters, although this is not strictly speaking an alloy, the term being better restricted to the permanent mixture of two or more metals, the term " mixture " being used in its wider sense.

An alloy has been defined by a Committee appointed by the Iron and Steel Institute as " a substance possessing the general physical properties of a metal, but consisting of two or more metals, or of metals with non-metallic bodies in intimate mixture, solution, or combination with one another, forming when melted a homogeneous mixture."

The inclusion of non-metals in the above definition is open to question, for there are several compounds of metals and non-metals which are clearly not alloys, yet which exhibit quite as many " metallic properties," and have quite as distinct metallic appearance as some undoubtedly true alloys of the brittle class, in which the metals are united in definite atomic proportions, as for example, $SnCu_3$. Manganese carbide, for example, can be fused in an electric furnace, and certainly might far more readily be taken for an alloy than many of the indisputable alloys of two metals. Many authorities therefore restrict the term to metals " in intimate mixture, solution or combination." Such restriction necessarily excludes the combinations of iron and carbon in steel, the desire to include which possibly influenced the inclusion of non-metals in the first definition.

Although by this definition the mixture is homogeneous when fluid, it by no means follows that when the alloy solidifies the mixture will then have the same composition throughout, indeed, in the majority of cases very important changes take place during the actual freezing, and frequently in the completely solidified alloy.

Alloys containing mercury are frequently liquid or semi-solid, and all mercury alloys are termed *amalgams.*

It is probable that metal was first employed in the form of the alloy "bronze," and the brass of the Old Testament and the brass armour of the Greeks is well known to have been the copper-tin alloy now termed bronze. Iron might also have been employed at very early times, but owing to its rapid rusting, most of the early iron implements, etc., would be lost, which is not the case with bronze, the latter being relatively permanent.

By alloying metals some special and suitable modification of their properties results, in certain cases very small amounts of other elements exercising a most unexpected influence. It may be that a soft metal requires hardening, as in the case of gold, silver and copper for coinage ; these metals in their pure condition being so soft that they would be unable to resist the wear in exchange. Generally speaking, the alloy of any two metals has a lower melting point than that of either constituent, a fact taken advantage of in the preparation of solders. Again, various alloys are made with the object of producing metal of a particular colour, nickel to brass for instance, imparting to it a silvery nature.

It is not possible to get any pair of metals to alloy ; they may in the molten condition form a homogeneous fluid, but on setting may almost entirely separate. A mixture of lead and zinc may, for example, be poured into a cylindrical mould, but on examining the cast rod, almost pure lead will be found in the bottom portion and pure zinc in the upper. Aluminium and bismuth are another pair of metals which cannot be alloyed.

The characteristic property by which chemists classify the elements into non-metals and metals is the ability of the latter to form at least one basic oxide. Some metals form only basic oxides, such as copper, whilst others form in addition oxides which are distinctly acidic. The two oxides of chromium, Cr_2O_3 and CrO_3 (p. 469), may be cited, and tin oxide (SnO_2) may be regarded as the anhydride of stannic acid (H_2SnO_3). Now, it is generally found that metals which form only basic oxides are difficult to alloy together, whilst a metal of this class usually unites readily with a metal which may also produce an acidic oxide. As an example, in the case of bronze, most perfect alloying takes place between the copper and tin.

Methods of Formation of Alloys.—The most general method is that of uniting the constituents whilst in a fused condition. The usual practice is to first melt that metal which has the higher melting point, and then add the requisite amount of the other metals, these being frequently heated but not melted. This is a simple process if neither constituent is volatile, but with volatile metals, such as zinc or antimony, loss is unavoidable, and allowance must be made for this. To minimise the loss the volatile metal, in lumps, is usually plunged well below the surface of the molten metal, so that as much combination takes place as possible before the vapours can escape. Again in remelting old alloys, one constituent being volatile, loss of the latter must occur and is made good by the addition of fresh metal.

One of the most interesting methods by which alloys may be produced is due to Spring, who showed that finely divided metals under great pressure may be caused to " flow " with the production of true alloys, although it was conclusively proved that practically no rise of temperature sufficient to produce fusion had taken place.

Alloys may also be deposited from suitable solutions by electrolysis, although great care is necessary in the adjustment of the current, otherwise one or other of the metals may be deposited in a nearly pure condition. Naturally, as the deposition is slow, the production of a skin of metal of any thickness is a tedious process.

Nature of Alloys.—Whilst analysis alone serves only to ascertain the proportions of the different elements present, valuable information as to the actual constitution of alloys is obtained from a study of the thermal changes taking place during solidification and cooling, combined with the microscopic examination of specimens quenched at different stages.

Cooling Curves are obtained by means of a protected thermojunction of two dissimilar wires, such as pure platinum and an alloy of platinum with 10 per cent. rhodium. Heating of such a junction sets up an electric current proportioned to the temperature, and this may be read off on a galvanometer scale, calibrated at certain fixed temperatures.

Three main types of freezing curves are known ; (*a*) where solidification takes place at a constant temperature, which is the case with pure metals, compounds, and alloys of definite composition, known as *eutectics;* (*b*) where there is progressive separation of some constituents of varying composition; (*c*) where there is first progressive separation ending in the separation of a eutectic at constant temperature. These three types of curves are diagrammatically illustrated in Fig. 57. In each case AB represents the molten alloy cooling; from B to D the metal is solidifying and consists of a mixture of solid and liquid. Solidification is complete at D, and D E represents the cooling of the solid metal.

A freezing-point diagram for the whole of the alloys possible in the case of two metals is constructed from a series of such freezing-point curves by arranging temperatures as ordinates and composition along the abscissæ, and plotting the points B and D for each alloy, when lines drawn through these points respectively will indicate the temperature at which freezing commences and terminates for an alloy of any composition through the series.

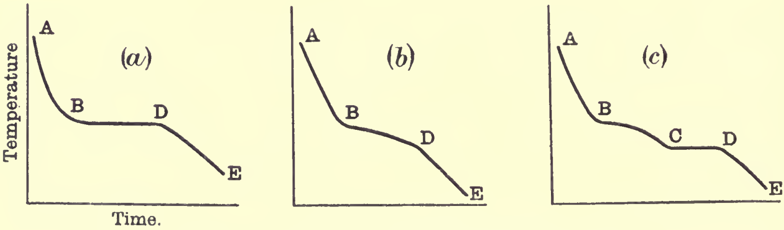


FIG. 57.—Types of freezing-point curves.

Further changes in molecular arrangement frequently occur after solidification is complete, being manifested by irregularities in the cooling of the solid alloy, or may be traced by quenching the alloy at different temperatures and examining the structure existing at the moment of quenching by means of the microscope.

From investigations carried out by the above methods the structure and components of a large number of alloys have been arrived at, and such knowledge is of the utmost importance in explaining their physical behaviour and properties. The alloys of more than two metals (ternary and quarternary alloys) are too complex to be dealt with here, but brief consideration is demanded of the alloys of two metals (binary alloys).

BINARY ALLOYS.

A. *No Chemical Compounds are formed.*

a. On solidification the two metals remain completely soluble in each other forming a solid solution.

The structure under the microscope is seen to be similar for any proportion of the two metals, and practically the proportion of one metal to the other may vary over comparatively wide limits with little variation in the properties of the alloys.

Freezing is usually of the "progressive" type (*b*, Fig. 57), and the freezing-point diagram commonly has the form shown in Fig. 58 for the metals X and Y. The upper line indicates where freezing commences, the lower where it is completed. A 50 per cent. alloy commences to solidify at B, and solidification ends at D. Although perfect uniformity of structure is revealed under the microscope, the crystals separating at B are not of the same composition as those separating at D, otherwise solidification would take place throughout at a constant temperature. With slow cooling, however, there is some diffusion between crystals of slightly differing composition which reduces their differences. The structure is said to consist of "mixed crystals."

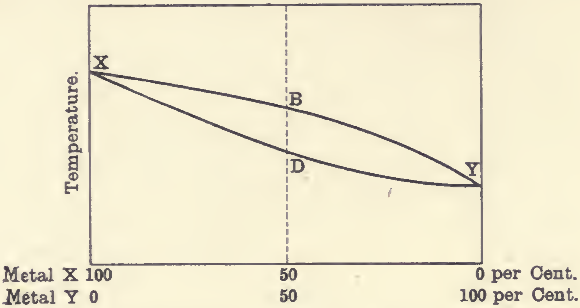


FIG. 58.—Freezing-point diagram—metals completely soluble.

The characteristic structure of all such alloys is similar to that of annealed brass (Fig. 3, Plate III). Alloys of silver and gold are good examples of this complete solubility.

The following pairs of metals give alloys of this type: gold-platinum, gold-silver, gold-copper, copper-nickel, antimony-bismuth.

b. The metals are completely insoluble in each other on solidification.

Although this is probably never actually the case, the metals lead and tin very closely approach it, and this system demands consideration.

The freezing point of a solvent is always lowered by the presence of a dissolved substance, thus the water from brine freezes out as practically pure water, but at a temperature more or less below zero according to the amount of salt present. There will eventually be found a lowest freezing temperature which corresponds to a given quantity of salt. Similarly with metals insoluble in each other on freezing, thus in Fig. 59 X and Y represent the freezing points of the metals X and Y respectively: Addition of Y to X in increasing amounts progressively lowers the freezing point of X, and similarly addition of X to Y lowers its freezing point. A point E must be reached where the two ultimately intersect, and the alloy corresponding will have the lowest freezing point possible in the whole series, and is termed the *eutectic alloy.*

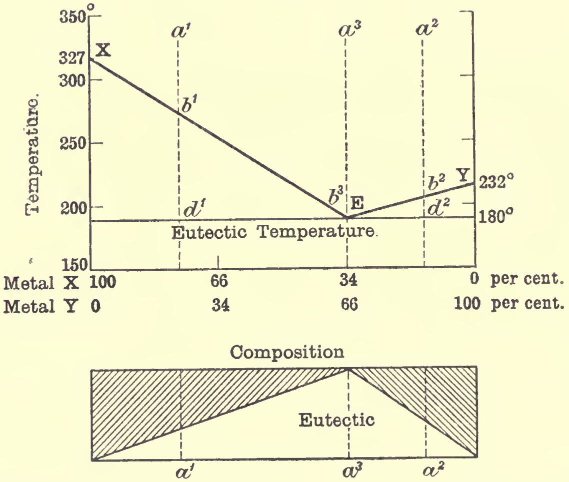


FIG. 59.—Freezing-point diagram—metals completely insoluble; with eutectic.

In considering the actual changes when alloys of different compositions in the series solidify, the alloys of composition represented by the verticals a^1, a^2, and a^3 will be taken. When the temperature falls to b^1 only the metal X will crystallise; this enriches the still fluid portion in Y, and further crystallisation cannot take place until a further fall of temperature, and the separation of the pure metal X goes on during the whole temperature fall from b^1 to d^1. At this point the composition of any remaining liquid will be that corresponding to the eutectic alloy, and the remainder will solidify at a constant temperature. The cooling curve of this alloy a^1 will be of the type *c*, Fig. 57. A similar series of changes will occur with the alloy a^2, only the metal to separate first will be Y, but the same eutectic alloy as before will solidify when the temperature d^2 is reached. Taking the eutectic alloy itself, a^3, its freezing will take place at a constant temperature, the cooling curve being of type *a*, Fig. 57.

The structure of the alloy of any given composition is indicated by the corresponding section in the lower diagram. Alloy a^1 would consist of crystals of X surrounded by the eutectic, alloy a^2 of the metal Y surrounded by the eutectic, and microscopic examination in such cases fully confirms this. Since the eutectic contains both metals, and since they are mutually insoluble, at the moment of solidification they mutually reject each other, and the structure of the eutectic is seen to consist of alternate plates or groupings of the two metals.

In this diagram the metal X is lead and Y tin.

The typical structure of a eutectic alloy is illustrated in the case of bismuth-tin (Fig. 2, Plate I), and the formation of a dendritic crystal of the excess metal—bismuth, from an alloy containing a slight excess over the eutectic proportion, surrounded by the large area of eutectic, is shown in Fig. 1, Plate II.

It will be obvious that the behaviour of an alloy of eutectiferous class is of great practical importance. During the slow cooling of ingots it will allow segregations of eutectics to take place, and these segregates greatly influence the value of the metal. The segregation of the phosphorus-iron eutectic in steel has already been mentioned (p. 416). Where the amount of eutectic is small it may almost completely surround the crystal grains of the pure metal first solidifying. The tenacity and ductility of the metal as a whole will therefore be dependent primarily on the properties of the eutectic. The enormously great influence which a small quantity of impurity, such as arsenic, has on the conductivity of copper is due to its concentration in the eutectic which forms a bad conducting "skin" on the pure copper crystals. The applicability of coarse solder to the making of "wiped" joints is due to the manner of solidification, pure lead first crystallising, leaving a still fluid eutectic which keeps the mass pasty, so enabling the joint to be made. The eutectic alloy, setting at a constant temperature, would be inapplicable, but for a solder to be used with an iron at the lowest temperature; fine solder, which is almost of eutectic composition, is obviously most suitable.

c. The metals are partially soluble in each other and form a eutectic.

Detailed description of the changes on solidification in such alloys need not be considered, but their course may be followed from the diagram (Fig. 60).

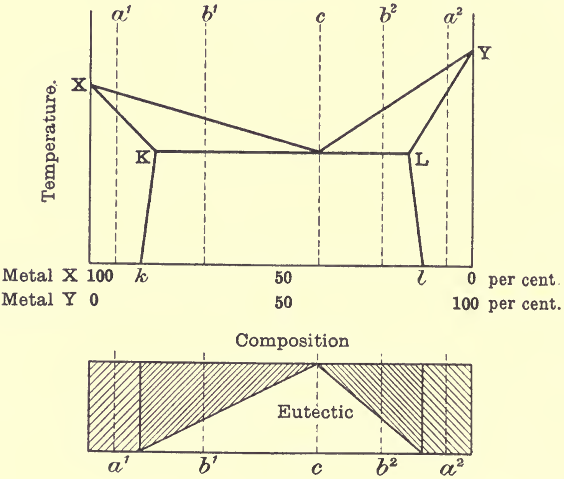


Fig. 60.—Freezing-point diagram—metals partly soluble; with eutectic.

Alloys a^1–a^2 will have freezing curves of the type *b*, Fig. 57.

a^1 will consist of mixed crystals of metal X with more or less of metal Y, in each case below the saturation amount.

a^2 conversely, the metal Y with more or less of metal X.

Alloys b^1–b^2 will have freezing curves of the type *c*, Fig. 57.

b^1 will first separate crystals of the saturated solution of Y in X, finally the eutectic.

b^2 will first separate saturated crystals of X in Y and then the eutectic.

Alloy *c* will have a freezing curve of the type *a*, Fig. 57.

The solid will be wholly eutectic, and this must be built up of alternate layers of the two kinds of crystals, the saturated solid solution of X in Y and Y in X.

The eutectic domain will be only between the limits K and L at the temperature when solidification is completed. Since in practically every case the solubility of one metal in another, even when solid, decreases with temperature, when cold the eutectic domain will be somewhat extended, such as *k* and *l*. The position of these points can be ascertained only by microscopic examination.

The following pairs of common metals alloy with the formation of a eutectic; it is probable that they all belong to type *c*, since no two metals are definitely established as completely insoluble in each other.

Metals.	Eutectic alloy, percentage of metal by weight.	Freezing-point of eutectic alloy.
Aluminium-zinc	6 per cent. Zn	375° C.
Antimony-lead	13 ,, Pb	228° C.
Bismuth-tin	45 ,, Sn	143° C.
Cadmium-zinc	16 ,, Zn	250° C.
Lead-silver	2·25 ,, Ag	305° C.
Lead-tin	33·0 ,, Pb	180° C.
Copper-silver	28 ,, Cu	778° C.

A subsidiary case of limited solubility of each constituent in the other is where no eutectic is formed; though of rare occurrence in a complete form, yet it occurs frequently as one portion of the complete freezing-point diagram of a pair of metals, and since the very important alloys of copper with zinc (brass) and with tin (gun-metal) include such conditions, this case must be briefly considered.

The clearest idea will be gained by the similarity to the behaviour of ether and water solutions. Ether dissolves to a limited extent in water and water in ether. Below the solubility limit only one uniform solution is found. Exceed the limit, and an ether layer separates on the water, and the ether layer is saturated with water and the water layer saturated with ether.

The freezing-point diagram in such a case with metals is shown in Fig. 61.

An alloy of the composition represented by the vertical a^1 will consist of the solid solution of Y in X. Similarly a^2 will consist of the solid solution of X in Y, the limit of solubility at the moment of complete solidification being respectively represented by *a* and *b*. The degree of solubility diminishes somewhat as the solid alloy cools. To these constituents letters from the Greek are usually applied, the first constituting the α constituent, the second the β.

The alloys freezing between *a* and *c* will consist of mixed crystals of the α and β constituents, as shown for b^1.

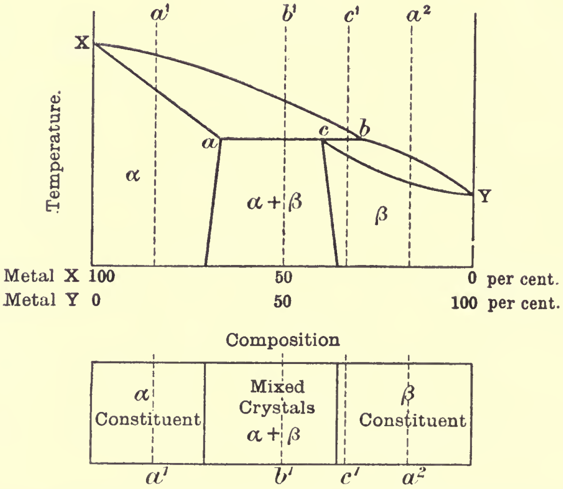


Fig. 61.—Freezing-point diagram—metals partly soluble in eutectic.

The alloy c^1 will, on freezing, separate first the α constituent; for reasons too lengthy to enter upon, when the temperature has fallen to the line *b c*, the α crystals will transform by interaction with the still fluid portions, and the final structure will be entirely that of the β constituent.

The uniformity of a solid solution of the α type is illustrated in Fig. 3, Plate III, for brass, and the mixed $\alpha + \beta$ structure in the case of Muntz metal, Fig. 4, Plate III.

B. *One or more Definite Chemical Compounds are formed.*

The presence of definite compounds in an alloy is not always easy to establish; they are indicated by the perfectly uniform appearance under the microscope, definite crystals often being visible (Fig. 2, Plate III); by the cooling curve of the pure compound being of type *a*, Fig. 57; and finally by the occurrence of one *maximum* point in the freezing-point diagram for each compound. Many of these compounds are totally different from the other alloys of the series; they are frequently so brittle that they may be easily powdered, and are usually hard.

In many white bearing alloys these hard compounds play an important part, embedded as they are in a softer plastic matrix of eutectic. They serve to carry the bearing in a reduced area since the softer surroundings are quickly worn; in the shallow depressions the lubricating oil film is perfectly maintained, and, moreover, owing to the plasticity of the softer parts, there is a certain amount of yield in the metal.

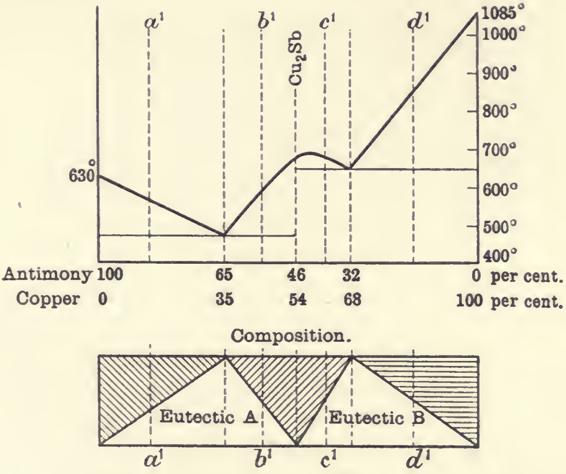


FIG. 62.—Freezing-point diagram—one compound formed; metals and compound mutually insoluble.

The compound (or compounds) present may behave in exactly similar manner to one of the metals as described above; it may be completely soluble, insoluble, or partly soluble in one or other of the metals which is in excess of the atomic proportion for its formation. The conditions where a eutectic exists are the only ones which require further references. A good example is found in the copper antimony series (Fig. 62), where there is the compound Cu_2Sb. There must always be one more eutectic alloy than the number of compounds present; in this case there are two eutectics. One (A) consists of alternate plates of antimony with Cu_2Sb; the other (B) of copper and Cu_2Sb. All alloys other than the two eutectics and the pure compound will consist of either (a^1) excess antimony with eutectic A; (b^1) excess Cu_2Sb with eutectic A; (c^1) excess Cu_2Sb with eutectic B; (d^1) excess copper with eutectic B.

Among the other copper alloys the following compounds have been definitely established: copper-tin, Cu_3Sn; copper-zinc, Cu_2Zn_3; copper-aluminium, Cu_3Al, $CuAl$, $CuAl_2$. The cooling curves are very complicated.

CAST IRON AND STEEL AS ALLOYS.

The important influences which carbon, free and combined, exercises on the properties of cast iron, and as combined carbon on steel, have already been dealt with, but a full understanding of these important matters is only possible when cast iron and steel are considered in the light of our present knowledge of alloys generally.

Certain well-ascertained facts must first be stated. It is established that iron exists in three allotropic forms; that carbon is soluble in pure molten iron to the extent of about 7 per cent., and on solidification under normal conditions much carbon is rejected as graphite; that in steel the carbon is always combined with iron, the amount present being under 2 per cent.; that this retained carbon is in a different condition according to whether the steel is slowly cooled (soft) or is quenched (hard). The definite compound Fe_3C can be readily isolated from soft steels.

The course of solidification of iron-carbon alloys follows exactly one portion of the curves already given, for the case of one metal partially soluble in another where a eutectic occurs (Fig. 60). A diagram for the iron-carbon alloys is given below (Fig. 63).

Pure iron freezes about 1600° C., and its solidification point is lowered by the solution of carbon, reaching a minimum at 4·3 per cent. carbon, shown at point C. This composition represents the eutectic alloy of the iron-carbon series. Up to about 2 per cent. (D) the iron can retain all carbon in solid solution. It may be a solid solution of carbon in iron or of a compound (a true carbide) in iron ; the point is not settled. The degree of solubility is lessened as the temperature falls, but the actual lowering of solubility is uncertain, and is, therefore, indicated by a dotted line. Cast iron may be regarded as commencing with the appearance of the eutectic C, which contains free carbon at about 2 per cent. carbon (*d*), all alloys below this constituting steel.

All alloys (steels) at 1000° C. will consist of crystals of this solid solution approaching saturation at 2 per cent. ; if quenching could be sufficiently rapid to preserve this structure it would be uniform, and to this constituent the name *austenite* is given. The constitution of normal cast iron immediately after solidification will readily be followed from the diagram. Important changes take place in the cast iron on further cooling, the course of these being profoundly modified by other elements, giving white, grey, or mottled irons, but as these are not well understood, it is not proposed to pursue the question.

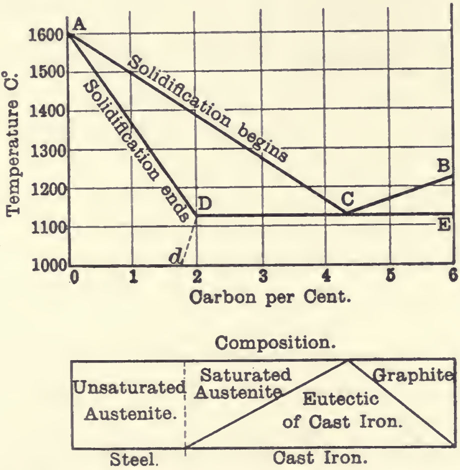


FIG. 63.—Freezing-point curve—iron-carbon alloys.

The further transformations which take place in the solidified steel are, however, generally agreed upon, and are of the utmost practical importance. When pure iron is cooling, say, from 1000° C., it does not do so with complete uniformity, certain well-marked periods occurring, during which the process is much retarded, showing that some internal molecular change evolving heat is taking place. Similar points are observed during heating up, these being denoted by *Ac*, whilst those on cooling (which usually occur some 30 degrees lower) by *Ar* (from *arrêter*). With practically carbon-free iron, the following are the observed temperature checks during cooling :—

*Ar*3	860° C.	Pronounced check.
*Ar*2	750° C.	Slight check.
*Ar*1	660° C.	Almost imperceptible check.

The first two points agree with certain well-marked changes in the physical properties of the iron. At *Ar*3 there is a sudden change in the rate of variation of electric resistance, and at *Ar*2 we have the reappearance of magnetic properties, which above this point have disappeared. Since *Ar*1 is almost unnoticeable with carbonless iron, but rapidly increases in importance with increase of carbon, it is undoubtedly connected with changes in the condition of the carbon.

With low carbon steels, all three points are observed, *Ar*1 being more definite and *Ar*3 less marked. With further increase of carbon *Ar*3 as an individual point disappears, and there are now well-marked checks at *Ar*2 and Ar1. Still further increase in the carbon results in only one big check being observed, corresponding with *Ar*1, so much heat being frequently evolved that the metal visibly heats up again, giving the well-known phenomenon of *recalescence.*

The well-marked checks *Ar*3 and *Ar*2 in the case of pure iron can be due only to molecular change in the metal, and most authorities are agreed that they indicate allotropic conditions; thus below *Ar*2 the iron is said to be in the α condition, between *Ar*2 and *Ar*3 in the β condition, and above *Ar*3 in the γ condition.

From the results of thermal analysis in conjunction with the microstructure of steels of all possible carbon contents quenched at all temperatures, a very complete diagram may be constructed illustrative of the changes involved. Such a diagram is given in Fig. 64, but it must be clearly remembered that, owing to all the transformations taking place in a solid or almost solid mass, they are subject to "lag" and do not occur instantly, but a given change is spread over many degrees. It is for the same reason that the temperature at which a given change takes place during cooling is always noted at a lower temperature than the corresponding change in heating up.

The points Ar^3, Ar^2, Ar^1, are shown for pure iron; up to nearly 0·4 per cent., the three are noted. The temperature at which Ar^3 occurs falls with increase of carbon, because it is associated with the solubility of carbon in γ iron, increasing amounts, therefore, lowering the change point. Ar^2 is associated purely with a transformation of carbonless iron, so it occurs at the constant temperature Ar^2D.

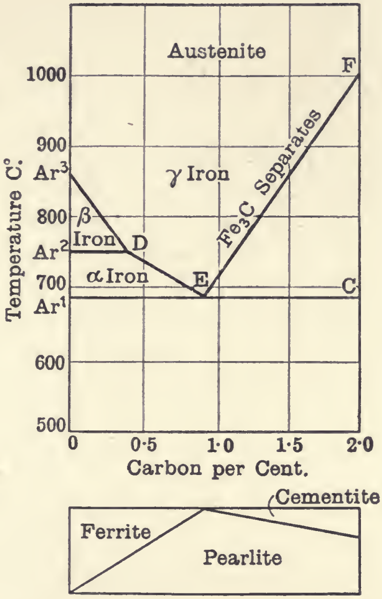


Fig. 64.—Cooling curve diagram of steels below 1000° C.

The line Ar^3 D E F, through the temperatures at which transformations in the solid steel commence, is almost identical in form with the freezing point curve for alloys composed of two metals completely insoluble on freezing and forming a eutectic (see Fig. 59), and the changes in steel are open to the same interpretation :—

Steel containing :—

Below 0·89 *per cent. carbon.*—On cooling to the line Ar^3D E separates pure iron, to which the name *ferrite* is given. This, in an exactly similar manner to the changes in alloys like lead and tin, increases the carbon content of the unchanged part, and further change only takes place as the temperature falls along the line Ar^3D E.

Below about 0·4 *per cent. carbon.*—This separated iron exists as β iron between Ar^3D and Ar^2D. At the latter it changes to α iron.

Between about 0·4 *and* 0·89 *per cent. carbon.*—The γ iron either changes directly to α iron, or if it passes through the intermediate β iron the change is so rapid that it has not been observed.

Above 0·89 *per cent. carbon.*—The line F E is really a continuation of the dotted line D*d*, Fig. 63. It represents the temperatures at which the austenite splits up into free iron and the carbide Fe_3C (*cementite*), and the solubility of Fe_3C decreases as the temperature falls.

The most important changes take place along the line Ar^1 EC. Down to this temperature iron has separated for all steels with less than 0·89 carbon and Fe_3C for all steels above 0·89 per cent. The result is that, in either case, the iron and carbon have reached 0·89 per cent. in the still unchanged part. As soon as the temperature reaches this critical point E, the condition in which the carbon exists is totally changed; above this temperature it was either a solid solution of free carbon in γ iron or a definite carbide in solid solution. At the critical temperature it undoubtedly changes into free iron, *ferrite,* and the carbide Fe_3C, *cementite.* These constituents lie interstratified, and the transformed material has every appearance of a eutectic alloy, and, moreover, the transformation occurs at the mimimum temperature.

This eutectic-like product is known as *pearlite,* from its resemblance to mother-of-pearl in its iridescent character. The close resemblance in its appearance to a true eutectic will be evident by comparing Fig. 2, Plate I, and Fig. 1, Plate IV. Pearlite is termed the *eutectoid of steel.*

Slowly cooled steel will consist entirely of pearlite when there is 0·89 per cent. of carbon. Steels containing less than 0·89 will consist of free iron (*ferrite*) with *pearlite,* the area occupied by the latter increasing proportionately with the carbon. Steels above 0·89 per cent. of carbon will mainly consist of *pearlite,* but bright crystals of *cementite* will be interspersed throughout. Steels are hence termed "saturated" or "eutectoid" when containing

0·89 per cent. carbon; "unsaturated" or "hypo-eutectoid" when below this; "supersaturated" or "hyper-eutectoid" when this amount of carbon is exceeded.

In Fig. 2, Plate IV, a low carbon steel is shown. The light areas are ferrite, the dark patches pearlite. In Fig. 1, Plate V, beautiful crystals of cementite are shown, taken from a high carbon tool steel.

Hard Steel.—Consideration must now be given to the condition in which the iron and carbon exist at temperatures above the critical points since the hardness due to quenching is the result of the preservation, in a more or less unchanged degree, of these conditions.

At the outset it must be remembered that changes are not instantaneous, being frequently spread over a considerable temperature range, and that quenching, however rapid, cannot altogether check changes already initiated.

A high carbon tool steel heated to well above 1100° C., and rapidly quenched in iced brine, shows a mixed structure consisting of bright needles of a constituent (*austenite*) (lighter constituent in Fig. 2, Plate V), interspersed with dark, *very hard* material (*martensite*). A simple high carbon steel, however rapidly quenched, always shows this mixed structure. A low carbon steel can never be quenched sufficiently rapidly to show austenite. Clearly the carbon is responsible for retarding the change from austenite to martensite. High manganese and nickel steels can be quenched so that austenite is the only constituent, that is, these elements, in conjunction with carbon, still further retard the change to martensite. Such steels are quite unmagnetisable.

Steel quenched at lower temperatures, but still well above the line Ar^3D E F, consists of a coarse interlacing needle structure which is extremely hard, and this is the martensite already referred to (Fig. 1, Plate VI). Quenched at temperatures only just above Ar^3D E F the needle-like structure is so fine that the steel appears almost or quite structureless. Martensite is the invariable constituent of all commercially hardened steels.

Austenite is the solid solution of carbon or Fe_3C in γ iron. It is quite non-magnetic. Martensite is supposed to be the first product of a series of decompositions which are set up as the steel cools towards the various critical points. It doubtless contains some β and α iron, as it is capable of magnetisation, though difficult to magnetise. As the steel cools the more will β and α

iron be produced, so that a steel quenched above its critical point contains more or less of the three allotropic forms of free iron according to the temperature and rapidity of quenching. γ iron appears to be the only form of iron capable of dissolving carbon (or a carbide) to yield a solid solution which forms a hard alloy on sudden cooling.

According to the diagram (Fig. 64), in which no account can be taken of overlapping, just above Ar^3D E F the steel consists wholly of the solid solution; in the region Ar^2D EAr^1 of solid solution $+\alpha$ iron; in the region Ar^3DAr^2 of solid solution $+\beta$ iron. In the region F E C of solid solution $+ Fe_3C$.

For the maximum hardness it follows that quenching must take place above the Ar^3D E F line; the most suitable quenching temperature will, therefore, vary with the carbon content. For fine structure, the steel should not be heated too highly above this, but since quenching can never be so instantaneous as to altogether prevent any changes, the steel must, in practice, be quenched at a temperature a little removed from this critical line.

In treating of alloy steels, which include the high speed tool steels, it was shown that such steels maintain their hardness up to a low red heat. This arises from the fact that the introduction of certain other metals to steel separates, by a very wide temperature interval, the point at which hardening carbon passes out of its solution (austenite to ferrite, cementite, etc.) on cooling from the point at which carbon will enter into solution on raising the temperature, to form austenite. In a simple carbon steel it has been mentioned that these two points are separated only by some 30° C.

Thus, with about 20 per cent. of nickel, on cooling down slowly from 1000°, no change is observed until about 100° C.; the steel remains hard on slow cooling. On heating up after it has naturally softened the reverse change does not occur until nearly the normal critical temperature is reached, in this case about 600° C. The steel is quite non-magnetic down to the critical point at about 100° C. A nickel steel, 20 per cent. Ni, 1 per cent. C, 1·4 per cent. Mn, does not alter on cooling until — 188° C.

Manganese again prevents the resolution of austenite, and a slowly cooled manganese steel remains hard and non-magnetisable. It exhibits no critical point on cooling until well below atmospheric temperatures.

Tempering.—In hard steel the solid solution in γ iron is in a state of temporary stability. It maintains this condition only because of the hindrance carbon offers to the allotropic change taking place in the iron. At a temperature but little above 200° C. this hindering effect commences to disappear ; at temperatures well below the recalescent point Ar^1E C it has disappeared altogether. Tempering really consists then in heating to such a temperature that the amount of carbon which passes out of the hardening condition into the condition characteristic of soft steel is just sufficient to impart to the steel the necessary toughness and spring which are requisite. A tempered steel then will consist of a mixture of the constituents of hard steel (martensite), and of those of soft steel (ferrite, cementite, and pearlite), the proportion of the latter being directly related to the temperature and time occupied in the tempering.

The characteristic constituents of different steels may be summarised as follows :—

SATURATED STEEL.

Soft.	*Hard.*
Pearlite { Ferrite. Cementite.	Martensite.

UNSATURATED.

Soft.	*Hard.*
Ferrite. Pearlite.	Martensite.

SUPERSATURATED.

Soft.	*Hard.*
Cementite. Pearlite.	Martensite.

Several other transition forms, to which metallographists have ascribed names, are recognised, but these need not be detailed.

CHAPTER XXXIII

COMMERCIAL ALLOYS

Copper Alloys.

Brass.

This alloy of copper and zinc is one of the most generally employed and important alloys known. The principal advantages gained by the addition of zinc are that the alloy melts at a lower temperature than copper, and is much more fluid when molten, thus allowing sound castings to be produced. Copper again works badly with cutting tools, and its softness gives it little resistance to wear, both disadvantages being overcome by the zinc.

Copper and zinc alloy in all proportions, but the practical limits for the amount of zinc lie between 30 and 43 per cent. The freezing-point diagram for alloys richer in copper is given in Fig. 65.

Within the above limits it will be seen that the alloys will either consist of one constituent (α), zinc forming a solid solution in copper up to 36 per cent., or above this limit, of a mixed structure of the α and β constituents. The first will be of uniform structure, as shown for 70Cu/30Zn brass, Fig. 3, Plate III; the second will exhibit a duplex structure, as in Muntz metal, 60Cu/40Zn, Fig. 4, Plate III.

The properties of the alloy are closely related to the amount of zinc present, and hence great variety is found in the metal as prepared for different purposes. For castings, the metal must be as fluid as possible and set "sound," with a fine grain. Standard brass for casting contains 66·6 per cent. of copper. The mechanical properties of the brass vary greatly with the condition of the metal, since on rolling or beating it becomes hard and increases in tenacity. For many purposes it requires careful annealing, which will be referred to later. The highest tensile strength is obtained with 45 per cent. of zinc, but the highest quality of brass, such as is employed for cartridge cases on account of its great malleability, contains 70 parts of copper and 30 of zinc. Suitable brass may, with careful annealing, be rolled and beaten out to a thickness of less than $\frac{1}{50000}$ of an inch, forming the well-known imitation of gold-leaf, "Dutch metal leaf."

Brass was originally made by smelting an ore which contained both copper and zinc, but later the ore of zinc was reduced in contact with the copper, for brass was employed for ages before the existence of zinc as a metal had been discovered. Soon after the discovery of zinc the production of brass by the direct mixing of the two metals was introduced. About the year 1700 Bristol was the centre of the brass trade, but about 1740 the manufacture was introduced in Birmingham, where it became one of the principal industries.

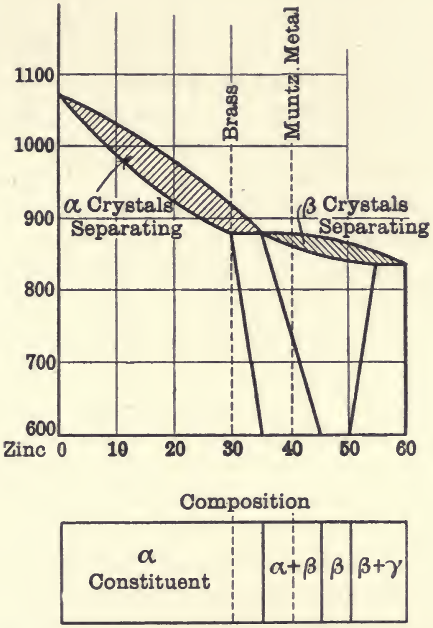


Fig. 65.—Freezing-point diagram of copper-zinc alloys.

Manufacture.—The alloying of the copper and zinc is carried out in two distinct types of furnace. For the production of relatively small quantities of high-class brass the copper is melted down in fireclay pots, heated usually on the regenerative gas principle, and then the addition of zinc is made by means of suitable proportions of scrap brass and metallic zinc, which have been previously heated up. Considerable quantities of zinc become vapourised at the high temperature requisite to maintain the copper fluid, though these losses are reduced by the first addition of scrap metal and also by the careful exclusion of air, the oxygen of which rapidly combines with zinc at the high temperature necessary; however, greater uniformity can be obtained in the product, when made in pots.

Where large quantities of brass, such as Muntz metal, are required, then the alloying is carried out on the hearth of a reverberatory furnace, although the loss of zinc is necessarily much greater, but the zinc fume is led away through suitable condensing chambers, and the metal recovered.

Great care and skill are requisite in pouring the finished metal. If it is to be employed for future castings, then it is poured into ingot moulds, but for rolling and drawing it is cast into plates.

The composition of the brass has a very great influence on its behaviour during rolling. Above 62 per cent. of copper the metal can be rolled cold but not hot, whilst the alloys containing somewhat less than this amount (such as Muntz metal) can be rolled hot, which is desirable from an economical standpoint. During rolling the metal hardens and requires annealing, in which process it becomes black, this blackness, due to the oxides of the metals, being removed by a mixture of dilute sulphuric acid and sand. If hard sheet brass is desired, then the metal is passed again through the rolls two or three times after the final annealing, but if soft brass is wanted the annealed sheets are simply cleaned up.

During annealing the brass may suffer considerable reduction in quality if the temperature employed be too high, though to a great extent this is dependent on the purity of the metal, a good quality, 70 Cu, 30 Zn, brass suffering little nearly up to its melting point. The effect of annealing is shown in Plate III. Cast brass has a distinct dendritic structure, but on rolling naturally the crystals themselves become greatly broken down and distorted, so that hard rolled brass shows only an indefinite minutely crystalline structure. On heating to a bright heat and quenching, distinct polygonal grains are developed, but if the heating be maintained for some time to a temperature of some 800° C., then a large crystalline structure is developed, many of the crystals having characteristic dark bands across them. If the temperature rises to the softening point, the structure is totally changed, becoming that of cast brass. The structure is closely associated with the physical properties, such as malleability and ductility, and much attention is now paid to obtaining suitable temperatures for the annealing of the brass to be employed in cartridge cases at Woolwich, pyrometers having been installed in the annealing ovens, and the progress of the annealing checked by examining the microstructure. If tin or lead be present in the brass, great care is requisite to avoid "burning," which spoils the metal.

For certain special purposes other metals are added to brass. From 1 to 2 per cent. of lead is said to make the metal work better in the lathe or when filed, but many engineers strongly object to its addition. Tin is also added to brass, especially for use by engravers, as the metal cuts out cleaner.

Muntz Metal contains more zinc than ordinary brass, the proportions usually varying between 38 and 40 per cent. The metal specified in a patent (1846) was 56 copper, 40·25 zinc, and 3·75 lead, the latter being added to make the metal roll better. It was introduced as a cheaper metal than brass, both in production and in rolling, since this can be performed hot, thus leading to economical working. The metal was said to resist the action of sea-water better than copper or ordinary brass. With reference to the former, the failure of yellow metal sheathing as compared with copper will be dealt with later, the very resistance which the yellow metal offers to exfoliation preventing it throwing off barnacles, weed, etc., whilst the claim that it resists the action better than ordinary brass has been clearly disproved. The important question of the relative corrosion of copper-zinc alloys is discussed later (p. 527).

Sterro, Aich's, and Delta Metal.—These are all brasses which contain iron, which imparts strength and elasticity, and considerably increases the hardness. The amount of iron which can be introduced in brass is small, and many discordant results have been obtained in practice. In Delta metal a small percentage of phosphorus is found to give great improvement. Such alloys offer special resistance to corrosion.

The approximate composition of the more commonly employed copper-zinc alloys is as follows :—

	Copper	Zinc	Other constituents
Best brass	70	30	—
Common brass	64	36	Composition variable.
Muntz metal	60–63	40–37	Sometimes lead.
Naval brass	70	29	1 tin.
Sterro metal Aich's metal	60	38·5	1·5 iron, sometimes tin.
Hard solder (for iron)	57	43	—
Do. (for brass)	50	50	—

Aluminium Brass may have the following limits of composition :—

Copper	67–71 per cent.
Zinc	25·5–32 ,,
Aluminium	1·25–3·5 ,,

These alloys are tough and of high tensile strength, rendering them suitable for propellers, rudder frame, etc.

BRONZE (*Gun-metal*).

The alloys of copper and tin are known under the general term of *bronze,* and since the mixture in certain well-defined proportions was formerly employed for casting ordnance, the term "gun-metal" came into general use. This alloy consisted originally of copper and tin only, but at the present time it is commonly applied to strong and tough alloys which contain, in addition of copper and tin, other metals, such as zinc. Higher proportions of tin constitute "bell-metal," and with still higher proportions the white brittle alloy, "speculum-metal," is obtained.

As already mentioned, bronze has been known from very early times, its valuable property of being hardened by slow cooling and hammering, in which condition it can take a fine cutting edge, being taken advantage of by the ancients in producing weapons of war and of the chase. Some of the earliest coins are also of bronze.

The addition of tin to copper lowers its melting point and renders the molten alloy very fluid, thus enabling good castings to be made. The proportions found most generally useful are those formerly employed in the best gun-metal, viz. 90 copper, 10 tin, the strongest alloy, however, being that containing 18 per cent. of tin. All the commercial copper tin alloys are subject to "liquation," and therefore variation in the composition of castings is very liable to occur.

That portion of the freezing-point diagram embracing the copper-tin alloys of commercial importance (excluding speculum metal) is given in Fig. 66.

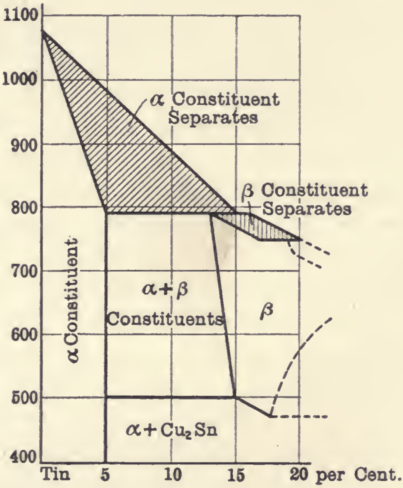


Fig. 66.—Freezing-point diagram—copper-tin alloys.

It will be seen that up to 5 per cent. tin only the α constituent, *i.e.* a solid solution of tin in copper, is found. From 5 to 15 per cent. a duplex structure is found. In this range of composition a critical temperature at 500° C. is noted, and a compound Cu_2Sn appears to be formed. With higher percentages of tin the curves become very complex.

Small quantities of zinc improve the fluidity of the metal, though it is not desirable to add more than 2 per cent. Iron, in small quantities, may also be present in metal intended for bearings, and a little lead is also said to improve the working of the metal.

The composition of the principal copper-tin alloys is as follows :—

	Copper	Tin	Other constituents
Bronze coins ..	95	4	1 zinc
Gun-metal ..	90	10	—
Bell metal ..	78 to 80	24 to 20	—
Speculum metal	67	33	—

Very great improvements have been made in recent years in the production of special bronzes of great strength and malleability, notably manganese, silicon and phosphor bronzes. Many of the latter are found on analysis to contain very little phosphorus, but the introduction of this element during the preparation greatly improves the properties of the bronze, this being due mainly to its action upon the metallic oxides formed during the melting of the metals, the phosphorus combining with the oxygen forming the acidic oxide (P_2O_5), which combines with a further quantity of the basic metallic oxides to form easily fused slags. The alloy is generally more homogeneous than a similar alloy in the preparation of which no phosphorus has been employed. Phosphor bronze does not develop crystalline structure, and, moreover, resists well corrosive action.

Manganese Bronze.—Both iron and manganese may be added to copper or its alloys with zinc and tin, producing greater hardness and strength. Of the two metals manganese is in every way preferable, and it can be added in much larger amounts than iron. Bronzes containing manganese are made of widely varying composition. The usual method of producing them consists in first making a rich cupro-manganese alloy by reducing manganese dioxide in presence of granulated copper. In some cases a ferro-manganese alloy is made, and either of the above are added in suitable quantities to bronze containing either tin alone, or both tin and zinc.

One of the most useful alloys is that obtained by the addition of a fair percentage of manganese, together with a little iron, to an alloy of the ordinary gun-metal composition (90/10 Cu, Sn). This manganese bronze gives good sound castings of great strength, and is largely employed for ships' propellers. For this purpose it has many advantages and is now very generally employed. It is claimed for such propellers that they can be made lighter than steel ones ; that they are more true, not having to undergo an annealing process as with steel, they are smoother and less liable to corrosion.

Cases have occurred where such propellers have met with severe blows, with the result that the blade affected has been seriously bent, in one case quite double, but no sign of cracking has been observed.

Silicon Bronze has been employed with much success where wire of great strength and good electric conductivity, as for telegraph and telephone purposes, is required. The presence of even traces of phosphorus on the conductivity of copper is well known, but by using silicon this trouble is overcome, and very strong and elastic wire is obtained. The silicon acts much as does the phosphorus in phosphor bronze, combining with the oxygen of any metallic oxides, whilst any excess enters into the alloy, although in the analysis of such alloys it is unusual to find more than a trace of silicon.

Aluminium Bronze usually contains from 5 to 10 per cent. of aluminium, the remainder being copper. Many of the alloys are of the colour of gold, and much cheap jewellery is made from them, 5 per cent. of aluminium giving the best colour. Considerable heat is evolved when the aluminium is introduced into the molten copper.

The alloy containing 10 per cent. of aluminium can be beaten out with great ease when hot, the metal being very malleable and ductile, possessing tensile strength equal to mild steel (43 tons per sq. in.). This alloy is remarkable in giving as high tensile strength in chill castings as in specimens rolled down to bar from ingots.

Alloys containing from 1 to 10 per cent. aluminium are practically non-corrodible in sea water even when bolted to mild steel plates. In fresh water they are relatively more corrodible than Muntz metal or naval brass.

Aluminium Bronze is largely made by the Cowles process in the electric furnace, alumina, generally in the form of *bauxite*, being reduced in the presence of copper. The process is interesting, as it was employed previous to the electric furnace method of producing pure aluminium (p. 453).

Aluminium bronze sometimes has zinc or ordinary brass added to it in order to produce aluminium brass, the aluminium present ranging from a little over 1 per cent. to some 3·5 per cent. (p. 512).

Speculum metal is an extremely hard, white and brittle alloy, capable of taking a high polish. It is employed chiefly for reflecting purposes in optical instruments. It consists of copper and tin approximately in the ratio of 2 : 1.

The influence of temperature on the tensile strength of copper alloys is of considerable importance, and Professor Unwin carried out numerous experiments for the Admiralty to determine this. Briefly, his results showed with ordinary brass, Muntz metal, and phosphor bronze, the tensile strength steadily diminished up to 260° C., and the metals had still considerable strength up to well over 300°, whilst with gunmetal the decrease in tensile strength became rapid after passing 158°–175°, and in some cases at 260° C. *the metal exhibited no tenacity whatever.*

Machine Brasses, such as are employed in bearings, etc., must have certain general characters, such as resistance to wear, and properties which allow of the metal being readily prepared in the desired form for the variety of purposes for which it may be applied. The composition adopted by different makers for metal for similar purposes is so variable that it is difficult to select typical mixtures, but generally the alloys contain from 75 to 85 per cent. of copper, the remainder being tin and zinc, sometimes one preponderating, sometimes the other. One authority recommends the substitution of lead for zinc in the mixtures.

Plastic bronzes consist essentially of a sponge of hardened copper, the pores being filled with lead. Tin, antimony, or nickel may be added to the copper to harden it. On melting together copper and lead a liquid " emulsion " is formed, from which the constituents separate on cooling, giving the above structure.

TIN ALLOYS.

Next to the alloys containing a large percentage of copper, those of tin with other metals, notably lead, are of the greatest importance. Tin alloys with lead in all proportions, the alloys being generally characterised by low fusibility, hence their general employment as " soft " solders. The freezing-point diagram has already been given (Fig. 59, p. 494) as illustrating the case where two metals alloy in all proportions, but are practically insoluble in each other. Three different ratios of tin to lead are commonly employed; for *fine* solder, melting at 180° C., 2 : 1; for *common* solder, 1 : 1; and for *coarse*, or plumbers' solder, 1 : 2. Fine solder practically agrees in composition with the only eutectic alloy occurring in the lead-tin series, hence it has a very definite setting point, which is lower than for any other proportions. On the other hand, with the ratio of 1 : 2, when the alloy first begins to set, practically pure lead crystallises, the crystals being surrounded with the still fluid eutectic, hence the solder remains pasty for several minutes, depending on the mass of metal. It is owing to this property that such solder can be employed for "wiped" joints, a purpose for which fine solder would be quite inapplicable, owing to its definite setting point.

Pewter originally consisted of tin-lead in the proportions of 80 : 20, but since pewter has again come into vogue, manufacturers have considerably altered its composition, each employing his own special mixture, hence there is great variety both in the metals employed and their proportions.

An alloy consisting mainly of tin and antimony, known as *Britannia metal*, is largely employed for the production of many articles, since it gives excellent castings, can be rolled or stamped, and takes a high polish. From 1 to 2 per cent. of copper is usually present, together with small quantities of zinc, bismuth, or lead.

LEAD ALLOYS.

The principal alloys containing lead, in addition to those already described, are those employed as *type metal*, the essential features requisite for such a purpose being—ready fusibility, sufficient hardness to resist wear, and well-defined castings. The alloys always contain antimony, and frequently in addition tin, whilst where special hardness is required, a small quantity of copper is added.

Shot metal consists of lead to which a small quantity of arsenic (and frequently also antimony) has been added, these additions rendering the otherwise soft lead sufficiently hard for the purpose of shot. The lead is melted at the top of a high tower, and additions of suitable proportions of a richer alloy of lead with arsenic and antimony added, the alloy being then poured through a perforated iron basin, spherical drops being formed as the metal falls down the tower into water placed at the bottom. The different sizes are made by employing basins with holes of varying diameter, and also by mechanically sorting the shot. It is essential that the alloy shall be quite fluid, otherwise the shot does not assume a spherical form.

The "mixed metal" for shrapnel steel contains 4 parts of lead to 1 part antimony.

LEAD-TIN ALLOYS.

	Lead	Tin	Antimony	Other constituents
Fine solder	33·3	66·6	—	—
Common solder ..	50	50	—	—
Plumbers' solder ..	66·6	33·3	—	—
Pewter	20	80	—	—
Britannia metal ..	—	92	6·5	1·5 Cu
Type metal	80	—	20	—
,, ,, ...	70	10	18	2 Cu
,, ,, (stereo) ..	82	3	15	—
Shot metal	99·7	—	—	0·1 to 0·3 As

Fusible Alloys usually contain lead, tin, and bismuth, and they derive their name from their low fusibility, which may be below the boiling point of water. Rose's metal, for example, melts at 94° C., and consists of two parts bismuth, one part tin, and one part lead. Various fusing points may be obtained with different proportions of these metals, and plugs of such alloys are used in water sprinklers for fire prevention and in boilers to minimise the risk of explosions, since as soon as the steam reaches a temperature (owing to increase of pressure) above that desired, the plug of fusible alloy melts, permitting the steam to escape.

Anti-friction Metal.—These alloys forming a "liner" of soft white metal inside the ordinary "brass" of a bearing are a great advantage, since suitable compositions greatly reduce the friction, and the alloys being of low fusibility are easily melted out when worn, and replaced. Microscopic examination in polished specimens generally shows hard crystalline granules embedded in a soft matrix, which polishes away, leaving the harder portions in relief. Charpy has pointed out that the value of these alloys is due mainly to this structure, the harder portions acting as supports, whilst the yielding qualities of the softer portion allow of the metal flowing to suit the bearing.

The microstructure of a tin-antimony alloy is shown in Fig. 2, Plate II. The hard cubical crystals are the compound SbSn, and they are embedded in a eutectic alloy.

The metals usually employed are lead, tin, zinc, antimony, and copper, and examples of different compositions have been collected from various sources and are given below.

Lead	Tin	Zinc	Antimony	Copper
88	—	—	12	—
78[1]	6	—	16	—
14	81	—	—	5
—	81	—	14	5
—	14	80	—	6
—	—	85	10	5
5[2]	19	69	3	4

Although the composition is so varied, yet it is found that quite small amounts of impurity greatly increase the friction with many of these alloys.

There are a large number of other alloys employed for special purposes, but of these only one or two call for mention. An alloy of aluminium with some 10 to 20 per cent. of magnesium, known as *magnalium,* promises to be of considerable value, since it is light, strong, and not easily tarnished.

The alloy of iron with 30 per cent. of nickel, *invar,* is remarkable for the very slight expansion and contraction which it undergoes with change of temperature, hence it is extremely useful for such purposes as clock pendulums, etc.

Some of the most important of the rarer alloys are those which are employed for electrical resistances. The composition of the more generally employed of these is as follows :—

	Copper	Zinc	Nickel	Other constituents
German silver	50 to 60	25 to 15	25 to 15	—
Argentan ..	52	19	24	—
Platinoid ..	50 to 60	25 to 15	25 to 15	1 to 2 per cent. tungsten
Manganin[3] ..	84	—	12	4 Mn.
Rheotan[3] ..	84	4	—	12 Mn.

[1] Magnolia metal (Hiorns). [2] Babbitt's metal (Ledebur). [3] Hiorns.

CHAPTER XXXIV

THE CORROSION OF METALS, PROTECTION FROM CORROSION, FOULING OF SHIPS AND ITS PREVENTION, PIGMENTS

The Rusting of Iron.—When iron is exposed to the action of the atmosphere under normal conditions corrosion rapidly commences, and continues at an increasing rate, until finally the whole of the metal is converted into "iron rust," consisting mainly of a mixture of ferric oxide (Fe_2O_3) and ferric hydroxide $Fe_2(HO)_6$.

The various reactions which lead to corrosion under all the different conditions which arise in practice are by no means fully understood. It has been shown that *pure* iron does not rust in contact with pure oxygen and pure water, but no commercial form of iron will remain unacted on under these conditions. There seems little doubt but that galvanic action set up by differences of potential through differences in constitution is the initial cause of corrosion. The solution of metals in electrolytes has been already dealt with at length in considering galvanic action (see p. 55), and need not be further discussed. In the case of pure iron incipient corrosion may take place if it is admitted that there is always some ionic dissociation of the water, leading to the existence of free hydrogen ions.

In the case of iron such reactions would occur in the following manner :—

$$\mathrm{Fe} + 2\mathrm{H}^+ + 2(\mathrm{OH})^- = \underset{\substack{\text{Ferrous}\\ \text{hydroxide}}}{\mathrm{Fe(OH)_2}} + \mathrm{H_2}\ \text{(atomic)}$$

Polarisation due to the hydrogen would soon take place and stop further action so that the presence of oxygen or some oxidising agent is essential if the reaction is to proceed further, when the ferrous hydroxide would become ferric hydroxide.

$$2\mathrm{Fe(OH)_2} + \mathrm{H_2O} + \mathrm{O} = 2\mathrm{Fe(OH)_3}$$

The presence of traces of free acid, such as carbonic acid, or traces of many salts in solution will greatly stimulate the action of the electrolyte upon the metal. Acid is not essential to corrosion with commercial iron and steel. It has been shown that it takes place in faintly alkaline solutions of salts such as sodium and potassium nitrates, sulphates, etc.

Although carbonic acid is not essential to corrosion, in the large majority of cases where iron is exposed to the action of water, either submerged or in a damp atmosphere, carbon dioxide and free oxygen are invariably present, and, allowing that primarily the initial cause of reaction is difference of potential in the presence of an active electrolyte, the actual chemical changes are of the following character.

If the dissolved oxygen is eliminated from water, and the solution is saturated with carbon dioxide at ordinary pressure, and kept from contact with the air, the carbonic acid present will act directly upon iron or steel forming ferrous carbonate and liberating hydrogen gas :—

$$\overset{\text{Iron}}{Fe} + \overset{\text{Carbonic acid}}{H_2CO_3} = \overset{\text{Ferrous carbonate}}{FeCO_3} + \overset{\text{Hydrogen}}{H_2}$$

This ferrous carbonate being soluble in the excess of carbonic acid present, the solution remains perfectly clear until air is admitted, when the ferrous salt at once is oxidised, and the liquid turns brown, throws down a brown precipitate, and a brown pellicle forms on its surface.

The reactions involved in the rusting of iron in ordinary circumstances may therefore consist in, first, the direct action of carbonic acid (H_2CO_3) on the metal ; secondly, the oxidation of the ferrous carbonate formed, into probably first of all basic carbonates and finally ferric oxide.

$$\overset{\text{Ferrous carbonate}}{4(FeCO_3)} + \overset{\text{Oxygen}}{O_2} = \overset{\text{Ferric oxide}}{2(Fe_2O_3)} + \overset{\text{Carbon dioxide}}{4(CO_2)}$$

If moisture be present in any quantity ferric hydroxide is formed :—

$$\overset{\text{Ferric oxide}}{Fe_2O_3} + \overset{\text{Water}}{3(H_2O)} = \overset{\text{Ferric hydroxide}}{Fe_2(HO)_6}$$

During these reactions the carbon dioxide is liberated in the moist metal and reacting with more oxygen from the air, carries on the process of corrosion, which is now further accelerated by the fact that the hydrated oxide on the surface of the metal is electro-negative to the metal itself, and excited by the presence of moisture and carbon dioxide creates a galvanic current at the expense of the metal, so that the mass of rust formed being porous, the action continues until all the metal is destroyed and has returned to its natural condition of hydrated oxide.

Analyses of *fresh* iron rust show it to consist mainly of ferric oxide more or less as the hydroxide $Fe_2(HO)_6$, together with ferrous oxide and ferrous carbonate. On exposure to air the two latter compounds readily undergo oxidation, with the formation of more ferric oxide and the liberation of carbon dioxide, so that it frequently happens that analyses of rust, which has been removed from the iron undergoing corrosion, show but little iron to be present in the ferrous condition.

The conditions which are favourable to rapid action are : lack of uniformity in the metal, easy access of carbon dioxide and air, differences in temperature, and the action of light.

Electrolytic action due to differences of potential in the same piece of metal through differences of constitution is probably by far the most important factor. Impurities may be present, such as slag inclusions, sulphide segregates, mill-scale (Fe_3O_4), or even with the highest class material in which these impurities are absent, steel will probably have a mixed structure, the nature of which has already been discussed, and these different steel constituents will give rise to galvanic action. Many of the contradictory results noted are doubtless to be ascribed to actual differences in constitution, as distinct from composition, which have been overlooked. Working the metal in parts, such as in hammering and riveting, will lead to hardening of that part and promote a difference of potential, the strained metal becoming electro-positive.

Easy access of carbon dioxide and air is particularly promoted where an iron structure is alternately wet and dry, as in the case of piers, etc., and corrosion is markedly greater in portions periodically submerged. Similarly it is greatest along the water line in a floating structure, or on a structure always immersed to a uniform depth.

The corrosive action near the surface of the water is further promoted by the effect of light and by the higher temperature of the water at the surface.

Factors which tend to minimise the action will be the condition of the surface, its freedom from scale and other impurities and its closeness of texture. A rough surface is far more easily attacked than a smooth surface; a coarse grained iron is more porous and open to the attacking solution.

Action of Sea Water and Acid Waters.—In the case of many natural waters the corrosion is greatly accelerated by the presence of dissolved salts, free acids, etc. The action of sea water is of special importance. Iron articles which have been recovered after submersion for many years are frequently of a soft spongy character and consist largely of ferrous oxide (FeO). On exposure to air the absorption of oxygen is so rapid that they heat up considerably and become harder.

The highly corrosive action of sea water is due mainly to magnesium chloride, which can act in the absence of oxygen. Solutions of sodium chloride and potassium chloride usually accelerate the action, but in both cases oxygen must also be present, and as the concentration is increased their action is reduced to a minimum. Strong solutions actually hinder corrosion, and cases are known where boilers fed with a mixture of fresh and sea water have had the corrosion materially reduced by increasing the proportion of sea water.

Exposed iron work in a large city is subjected to the action of rain water containing sulphur acids washed from the smoke-laden air, and these seriously increase the rate of corrosion. Again, a ship with her protective composition abraded in places by contact with chains, etc., cruises on the West Coast of Africa, where the rivers sweep down large quantities of vegetable and animal organic matter to the sea, which decompose the sulphates present in the sea water and charge the water with sulphuretted hydrogen, which attacks the exposed metal with great rapidity.

These local causes of corrosion, however, have only to be taken into consideration where they occur, and do not affect the general question.

Relative Corrosion of Iron and Steel.—A very large amount of work has been done with a view to settling this important question and results sometimes in favour of iron and sometimes of steel have been obtained. It has never been proved that a good quality steel is inferior to a good iron, and there seems little reason to assume that one is less liable to corrosion than the other, if both are reasonably free from such impurities as would set up powerful galvanic action.

It has been shown that steel is by no means uniform in composition, mild rolled steels will contain much free ferrite associated with more or less pearlite, so that here is a possible source of galvanic action, even in the total absence of any of the impurities, such as traces of sulphur, phosphorus, etc. Practically nothing is known as to the potential differences between the different steel constituents recognised by the microscopist, but the effect of common impurities is fairly well established.

Sulphur segregates set up active corrosion, the sulphur being converted into free sulphuric acid which greatly aggravates the action.

Silicon, although present in most steels in negligible quantities, confers upon iron great power of resisting corrosion. The amount of silicon which passes into the surface of an iron casting from sand of the mould probably accounts for the noteworthy resistance which cast iron gas and water pipes, etc., offer to corrosion. Chromium and nickel both increase the resistance of steel to corrosion.

Manganese has generally been regarded as promoting corrosion. This is probably due to the bad company (sulphur) in which it is generally found in steel. In the absence of manganese-iron-sulphide segregates there seems no reason for believing manganese acts injuriously.

Whilst isolated plates of good iron and steel corrode at about the same rate under the same conditions, as for example in sea water, when coupled up the total corrosion is very much greater. It depends greatly on circumstances which actually corrodes most quickly. It is clearly not desirable that iron and steel shall be in electrical contact in the same structure ; where steel plates have been fastened together with iron bolts, serious corrosion round the bolts has resulted. Patches of different steel plate on a ship's hull have given trouble.

Corrosion and Pitting in Boilers.—In the Navy the most important cases of corrosion are those which affect the plates and tubes of marine boilers and the plates of the bottom of vessels, and inasmuch as the causes at work in these two cases are not identical, it is better to discuss them separately.

In the marine boilers at present in use, working at pressures of from 50 to 250 lbs., serious pitting and in some cases puncturing of the plates and tubes take place, a result which, before the introduction of hydrocarbon lubricators, was attributed largely to the corrosive action of the fatty acids liberated by superheated steam from the oils and fats used for the lubrication of the cylinders, but as the corrosion and pitting has continued since these lubricants have been discarded, and as the trouble increases with the increase in the pressures employed, it is evident that some other solution of the difficulty must be sought.

The pitting and corrosion are due not to one cause only, but to several acting together.

1. Ordinary corrosion due to the carbon dioxide and oxygen dissolved in all natural water, which act but little when the boiler is in use, the gases being driven off by the steam, but which act rapidly when a boiler is out of use more especially when, as used to be the case in the Navy, the water is partially blown off and the boiler left wet and exposed to air.

The simplest cure for this is, when a boiler is at rest, to fill it quite full with boiled water to which a little lime or other caustic alkali has been added.

2. One of the causes of pitting in a boiler is the formation of spots of rust from the previous cause, which, being electro-negative to the metal, rapidly cause it to corrode, and it is this action, and also the galvanic action of traces of metallic impurities, which is to a certain extent prevented by zinc protectors, zinc being electro-positive to both iron and iron oxide, but for the protectors to be of any use they must be in metallic contact with the metal of the boiler.

3. The solvent action of distilled water upon metals, which, in modern marine boilers fed with condenser water and specially distilled water, rapidly attacks the plates in places where the presence of a trace of slag or other impurity renders the metal less dense or gives it a tendency to lamination. This can be avoided by using a saline solution such as the prepared sea water advocated at page 132 for the prevention of incrustation and avoiding too frequent blowing off, the action of water on iron rapidly decreasing with an increase in its density.

Segregates of iron-manganese sulphide have caused serious pitting. On opening some of the rust cones formed over such places the fluid contained ferrous sulphate and free sulphuric acid. It is evident that an acid fluid of this character would quickly perforate the plate.

4. The fact that at a high temperature water is directly decomposed by iron with formation of black magnetic oxide and liberation of hydrogen :—

$$\overset{\text{Water}}{4(H_2O)} + \overset{\text{Iron}}{3Fe} = \overset{\substack{\text{Black magnetic}\\ \text{oxide of iron}}}{Fe_3O_4} + \overset{\text{Hydrogen}}{4H_2}$$

This action, which is the cheapest method of obtaining the gas, takes place at a dull red heat, and more slowly at temperatures considerably below dull red heat, about 350° C., which are often approached, if not reached, on the surface of tubes coated with incrustation, where the moisture present acts rapidly on the metal and ultimately pierces it.

This latter cause of pitting can be avoided only by keeping the boiler free from all incrustation by using either distilled water or prepared sea water.

Burgess has shown that with a boiler filled with a dilute soda solution (1 in 1000) the heated flue tube became the cathode and was but slightly corroded, but that the cooler shell, being the anode, was far more rapidly attacked.

Corrosion of Plates.—On the outer skin of an iron vessel two processes of rusting are going on, the one simple corrosion on exposed surfaces of the metal, due to the presence of moisture, carbon dioxide and free oxygen, which forms a fairly uniform coating of rust on the metal, and the more local corrosion due to galvanic action, which results in pitting and uneven eating away of the plates.

Rust cones are due to the most local form of galvanic action, caused by the presence of a speck of deposited copper, lead, or other foreign metal, or even a small particle of rust or mill scale left on the surface of the iron, and covered by the compositions used as protectives and anti-foulers ; as soon as the sea water penetrates these, galvanic action is set up, water is decomposed, rust formed, and the escaping hydrogen pushes up the composition, forming a blister ; the hydrogen escapes and water leaks in, the action becoming more and more rapid, and the blister gradually filling with the result of the action—rust. The blister bursts, but the cone of rust has by this time set fairly hard, and continues to grow from the base, the layers of rust being easily distinguished in a well-formed cone, and when the rust cone is detached, the pitting of the metal at the base of the cone is, as a rule, found to be of considerable depth.

The speck of foreign matter which has caused this destructive action generally clings to the surface of the iron, and being at the bottom of the pitting, escapes detection and removal; and when the vessel, newly coated with fresh composition, again goes to sea, fresh corrosion will probably be set up in the same spot.

The corrosion of the plates in the interior of a vessel is a subject quite equal in importance to the external action of sea water and dissolved gases on the metal; and from the fact that certain portions of the interior plates, from their position, escape the frequent examination and attention bestowed upon the exterior, it becomes a still greater source of danger.

Corrosion, like all other forms of chemical action, is much accelerated by increase of temperature; and in the bottom of a ship, near the furnace room and boilers, this has a considerable effect in increasing the rapidity of rusting. Also in the coal bunkers, the mere contact of moist coal with the iron plates sets up galvanic action, carbon being electro-negative to iron, and the coal dust which sifts down into the double bottoms lends its aid to the destruction of the plates; whilst if the coal contains any "pyrites," which is nearly always the case, these double sulphides of iron and copper are gradually oxidised into soluble sulphates of the metals; these, washing down into the bilge water, would at once cause most serious corrosion should they come in contact with any bare portion of the plates. Repairs to any portion of the inside plates will loosen rust and mill scale, which, finding its way into the bottom, tends to set up galvanic action; whilst the scale of copper oxide from copper and brass fittings and pipes is another great cause of danger, as the bilge water would gradually convert it into soluble salts, which will deposit their copper upon the iron wherever a crack or abrasion enables them to come in contact with it; and finally, leakages from stores and cargo are in many cases of a character highly injurious to iron.

In addition to all these sources of danger, it must be remembered that the interior of a vessel is the part most liable to abrasion from shifting and moving of cargo, coals, etc.

CORROSION OF COPPER AND ITS ALLOYS.

In the presence of sea water, corrosion of copper readily takes place, owing to the direct action of the saline constituents of the water, aided by carbon dioxide. This results in the formation of a green coating consisting of the carbonate and oxychloride. The formation of this coating gave the value to copper sheathing, which it undoubtedly possessed over all other sheathings, of remaining " clean " when used on a ship, but in such cases as copper fire-mains on a ship, charged as they are with salt water under pressure, the corrosion becomes a serious matter. A coating of one of the asphaltum compositions is then frequently employed for protection.

With copper-zinc alloys there may be (*a*) corrosion uniformly over the whole surface, (*b*) dezincification, where the zinc is partly and sometimes completely removed leaving a soft mass of copper, (*c*) pitting, which is most serious, frequently leading to perforation in the case of condenser tubes.

The cause of the removal of zinc is to be found in the mixed structure of alloys, containing over 67 per cent. of copper, have been shown to be homogeneous throughout, but with less copper, as in Muntz metal, two distinct constituents are present (Plate III), one relatively richer in zinc than the other. When exposed to an exciting liquid, this richer zinc alloy is attacked, the two forming a galvanic couple. Slowly the zinc is removed, this alloy becoming richer in copper. Ultimately the alloy previously richer in copper will contain more zinc than the residue from the primary attack, when it will then become the positive element in the numerous couples, and zinc will pass out of it. The ultimate result will be the almost complete removal of zinc from the alloy.

The greater the uniformity therefore which can be attained in such alloys, the less likely are they to undergo corrosion. This is frequently seen to be the case with brazed joints in tubes, the brazing, containing a higher proportion of zinc, undergoing much more rapid corrosion than the main portion of the tube.

Local pitting is the result of galvanic action set up between some impurity in the metal, or a deposit on the tube, which forms a couple with the surrounding metal. Probably one frequent cause is due to " spills " in pouring the metal in the first place, resulting in a mechanical defect in which water may be held, or the inclusion of some metallic oxide. Ferric hydroxide may reach the tubes in a condenser and give rise to serious troubles.

The introduction of a third metal exercises an important influence on the liability of copper-zinc alloys to corrosion.

The addition of a small quantity of tin lessens the liability to corrosion, and hence the Admiralty introduced naval brass, consisting of copper 70 per cent., zinc 29 per cent., tin 1 per cent., for all fittings exposed to the action of sea water. Aluminium is also effective in preventing corrosion. The action of tin in preventing corrosion is ascribed by Brühl to the inertness of the tin oxide produced.

It has been shown in the case of brass that where the metal has been bent or distorted, there the action takes place first, and with much greater vigour than elsewhere.

Water containing decaying organic matter, such as marsh waters and bilge waters, have a rapid action on brass.

It is more in connection with the use of these alloys for condenser tubes that trouble has arisen and this has been particularly noticeable in the Mercantile Marine where Muntz metal tubes have been employed. The use of 70Cu/30Zn metal of uniform structure has reduced this difficulty, which is further minimised by the use of naval brass containing tin. One large mail line is employing tubes of the composition 78Cu, 21Zn, 1Sn.

Pitting of condenser tubes of really good composition occasionally takes place, in many cases it being difficult to satisfactorily account for. It must be due to some purely local cause, possibly the deposition of a small speck of foreign material, or it may be segregation of some constituent of the alloy employed.

Bronze resists corrosion much better than brass, but where it has been employed in connection with copper sheathing, etc., then it is slowly corroded. Bronze, however, is very permanent when in contact with iron.

Copper-Aluminium Alloys.—Alloys containing from 1 to 10 per cent. aluminium are practically incorrodible in sea water, even when bolted to mild steel. In fresh water they are more corrodible than Muntz metal.

PROTECTION OF IRON FROM CORROSION.

The protection of iron and steel from corrosion has been attempted in two ways: either by covering the surface with some other metal not easily corroded, or which is attacked in preference to the iron; and by the application of various paints, varnishes, and the like which prevent access of the agents causing corrosion.

Metallic Coatings.—Of these the principal are zinc, tin, nickel and copper. Zinc is far preferable to the others for the reason that it maintains the iron in the electro-negative condition, itself undergoing any corrosion, hence frequently the coating lasts a comparatively short time. In the case of the other metals, so long as their surface remains intact, the protected iron will undergo no corrosion, but once the surface becomes abraded, then corrosion of the iron will take place locally at a greater rate than it would if uncoated, since it now becomes the positive metal in a galvanic couple.

Galvanising consists in covering the iron with a thin coating of metallic zinc, the name originating from the galvanic couple so obtained.

The plates which are to be coated must first be thoroughly cleaned by pickling in either dilute sulphuric or hydrochloric acid. The commercial zinc (*spelter*) is maintained at a temperature of about 450° C. in a special tank having a "flux" box containing ammonium chloride at either end. The tank is fitted with rollers which carry the sheets through the bath of molten metal, the sheets entering and leaving through the flux boxes. The zinc readily adheres to the clean iron surface, together with a certain amount of the flux, to remove which the galvanised plates are passed through two tanks of water. The plates are finally cleaned up with sawdust and dried.

Made up articles, such as cisterns, buckets, etc., are simply dipped in the zinc bath after suitable pickling.

Zinc may also be deposited by the electrolytic method, and this is employed for certain Admiralty work, such as the framing, etc., of torpedo boats. The metal surface to be coated is first cleaned and immersed in a solution of either the sulphate or chloride of zinc. Zinc anodes are employed, but since these do not dissolve with sufficient rapidity to keep up the strength of the bath, the liquid is made to circulate through vats containing zinc dust. The Admiralty require a coating of about 0·86 of an ounce to the square foot.

Instead of using a bath, a current at fairly high voltage is sometimes passed through suitable brushes saturated with the electrolyte.

Another process of considerable interest recently introduced, consists in heating the articles when they are surrounded by finely divided zinc, to a temperature below the actual melting point of the zinc. Penetration of the latter takes place, and a firm adherent coating is obtained. The process is known as *Sherardising.*

Zinc is practically the only metal which could be used to preserve the iron plates of a ship from corrosion, since it places them in an electro-negative position, and it is therefore to zinc that inventors have turned from time to time, the chief novelties introduced being the method of attachment. As far back as the year 1835, Mr. Peacock tried zinc plates on the bottom of H.M.S. *Medea,* and in 1867 Mr. T. B. Daft again brought the subject forward; Sir Nathaniel Barnaby, Mr. M'Intyre, and others, also suggesting various plans of attachment, whilst more recently Mr. C. F. Henwood read a paper at the United Service Institute again strongly advocating zinc sheathing as attached by his system.

There is no doubt that if a surface of iron is kept in galvanic contact with zinc, and the surface of zinc exposed be of sufficient size relatively to the iron surface to be protected, it will act as a perfect protection against the more active forms of galvanic corrosion, but it will not entirely prevent the ordinary oxidation due to the dissolved gases in sea water; and it must also be remembered that the salts in sea water have a fairly rapid action upon the zinc, which, when it is increased by the galvanic action set up by the enormous surface of iron present, would destroy the zinc sheathing too rapidly to render it a practical method, several cases having occurred in which an iron ship coated with zinc plates has returned from a voyage minus a considerable portion of her sheathing. If no galvanic contact exists the zinc sheathing will last fairly well, but does not afford any protection to the iron.

Attempts have been made to galvanise the iron before the building of the ship, but Mr. Mallet showed as early as 1843 that this coating was absolutely useless in sea water, as in from two to three months the whole of the zinc was converted into chloride and oxide; but used as a foundation over which the ordinary protective and anti-fouling compositions are to be painted, galvanising acts as a perfect protective, the only trouble being that it affords but little hold for the compositions which have to be put on over it, so that a galvanised torpedo boat quaking along at twenty knots requires a very adhesive composition to stick on. This objection could, however, be easily got over by a slight roughening of the galvanised surface so as to give the paints a "grip."

Tinning.—The protection of iron by coating it with tin is a very old process, and was introduced into South Wales, the centre of this important industry, as early as 1665.

At one time a specially prepared sheet iron was alone employed, but at the present time what is practically an extra mild steel is used. The success of the process depends on a thorough cleansing of the plate and the production of a fine surface by means of special rolls. The plates are first cleaned by pickling in B.O.V. sulphuric acid (p. 330), they are then annealed and rolled, afterwards undergoing a further annealing and pickling.

In the old process the plates were kept in a bath of melted tallow, and on withdrawing them from this, they were dipped in a bath of melted tin, the surface of which was protected from oxidation by a layer of fat ; after taking out and brushing over quickly to remove any excess of tin, they were dipped in a second pot of the metal kept at a higher temperature than the first, being placed finally in a bath of highly heated tallow, when the excess of tin ran to the lower edge and was detached by a sharp blow. Such a procedure led to very uneven covering, and was, moreover, somewhat slow.

In the modern method, the plates are lowered into the tin bath, through a flux of zinc chloride containing a little ammonium chloride, and are then raised until they engage in the first of several pairs of rollers placed above each other and running in grease. These rollers have below them small troughs in which the tin squeezed off the plate collects. The speed at which the rollers travel determines the amount of metal left on each plate. By the old dipping process, about 8 lbs. of tin was required for every 1 cwt. of plates, but with the modern method the usual practice is to employ but a few ounces over 2 lbs. for the same quantity.

The tinned plates are polished up with sheepskin rubbers and bran. For certain purposes a cheaper grade of plate is made by dipping in a lead-tin bath, such plates being termed "*terne plates.*"

As long as the tin surface remains unimpaired, the iron beneath is adequately protected, but if abrasion occurs, so that the iron is exposed, local rusting is very rapid, since iron is electro-positive to the tin.

Non-metallic Coatings.—The coatings of this type which are intended to do away with corrosion, are very numerous. In addition to those still holding a place in the market, the patent list for several decades shows an enormous number which were practically still-born.

They may be divided for convenience into—

(*a*) Oil paints.
(*b*) Pitch, asphalt, or tar.
(*c*) Varnishes, consisting of resins and gums dissolved in volatile solvents.
(*d*) Varnishes containing substances to give them body.
(*e*) Coatings of cement.

Before going into these in detail it is necessary to consider the condition of the surfaces to which they will have to be applied, and the effect this will have upon them.

Air has the power of holding water vapour in suspension, the amount so held being regulated by the temperature; the higher the temperature the more vapour can the air hold, whilst when the air, saturated at a particular temperature, is cooled the surplus moisture is deposited. When a ship is scraped down to the bare iron in the dry dock, there is a large surface of metal which varies in temperature much more rapidly than the surrounding air, and cools much more rapidly than the stone walls of the dock; as it cools so it chills the layer of air in immediate contact with it, and causes a deposition of the surplus moisture on its surface—a phenomenon known as the "sweating of iron"—and on to this moist surface the protective composition has to be painted. If now a quickly drying varnish is put on, the rapid evaporation of the volatile solvent causes another sudden fall of temperature—evaporation being always accompanied by loss of heat—and this fall of temperature again causes a deposition of moisture, this time on the surface of the protective, so that the coating is sandwiched between two layers of moisture, both of them probably acting deleteriously upon the resin or gum in the varnish, whilst the moisture on the iron also prevents adherence of the varnish to the metal. If, instead of a quick-drying varnish, the old-fashioned red lead and linseed oil protector had been used, the second deposition would not have taken place, but the sweating of the iron would have prevented adhesion, and, when dry, any rubbing of the coating would bring it off in strips.

The condition of the outer skin of a ship, when she is being coated with her protective composition, is one of the prime factors in the discrepancies found in the way in which compositions act;

it being a very usual thing for a composition to give most satisfactory results on several occasions, and then, apparently under exactly similar circumstances, to utterly break down, and to refuse even to keep on. Too much stress cannot be laid upon the condition of the plates at the time of coating, and it is absolutely essential either to have a perfectly dry ship, or else a composition which is not affected by water.

Oil Paints.—When an old ship is broken up, the numbers are often seen on the backs of the plates, having been painted on them with white lead and linseed oil before the ship was built, and under the paint the iron is in a perfect state of preservation, the reason being that the paint was put on while the plates were hot and dry.

Boiled linseed oil, mixed with red or white lead, is amongst the oldest of the protective compositions in use, but of late years has been but little employed, since it was proved by M. Jouvin of the French Navy, and also in this country, that compounds of lead, when exposed by the wasting of the linseed oil to the action of the sea water, are converted into lead chloride, and this is rapidly acted on by the iron, depositing metallic lead and forming iron chloride, the deposited lead carrying on the corrosion of the iron by rapid galvanic action. The drying of boiled linseed oil is due to the fact that it has in it a certain quantity of an organic compound of lead, and the drying properties are given to it by boiling it with litharge (lead oxide), so that even when red or white lead is not mixed with it, still lead compounds are present, and this action will go on to a smaller extent.

When the boiled oil dries, it does so by absorbing oxygen from the air and becomes converted into a sort of resin, the acid properties of which also have a bad effect upon iron, so that the protectives containing boiled oil are open to objection. A good example of the action of sea water on the bottom of an iron ship, coated with red lead, was afforded by H.M.S. *Nile*, which, after being painted over with coats of red lead, was allowed to remain for some months in Milford Haven, with the result that her bottom was very seriously corroded, and, on examination of specimens of rust taken from her, the crystals of metallic lead were in many cases easily identified.

If red lead is used, it can only form a ground work for an anti-fouling composition which has to protect the red lead as well as the iron of the ship from the action of sea water, and when the anti-fouling composition perishes, then serious corrosion must ensue.

Pitch, Asphalt, etc.—The second class of protectives, consisting of tar and tar products, such as pitch, black varnish, and asphalt, are amongst the best protectives, not being affected by the sweating of the plates, and forming admirable coatings. Certain precautions, however, must be taken in the case of tar and tar products, both of which are liable to contain small quantities of acid and of ammonium salts ; but if care be taken to eliminate these, and if it could be managed to apply this class of protectives hot to warm plates, the question of protection would be practically solved, bituminous and asphaltic substances forming an enamel on the surface of the iron which is free from the objections to be raised against all other protectives, that is, that being microscopically porous they are pervious to sea water. Coverings of this class are commonly employed for protecting water and gas mains, which have to be buried in the earth, and with proper care in selecting a composition, and in its application, very good results are obtained.

Simple Varnishes.—The third class of protectives consists of varnishes formed by dissolving gums or resins in volatile solvents, such as spirit, turpentine, naphtha, fusel oil, etc., and such varnishes are open to several objections—in the first place, they are acted upon by moisture, which causes a deposition of the resins or gums as a non-coherent powder, and destroys the tenacity of the varnish. The amount of action which moisture has on such a spirit varnish, depends to a considerable extent upon the proportion of resin or gum to spirit. When the solvent is present in large quantities, and the resin in comparatively small, then the moisture has apparently little action ; but it must be remembered that the drying of such protectives means the rapid evaporation of the solvent and concentration of the resin or gum, whilst the rapid volatilisation which is going on cools the hull of the ship, and causes deposition of moisture on the drying varnish with most disastrous results.

Another point which must be borne in mind is that no such varnish is impervious to gases and liquids. A coating of varnish is generally regarded as being perfectly homogeneous ; but on examining it through a microscope, it is seen to be full of minute capillary tubes, which become gradually enlarged by the action of water, and finally result in the destruction of the varnish, whilst moisture and dissolved gases find their way to the metal and carry on corrosion. The application of several coats of varnish tends to diminish this evil, as in many cases the holes in the first coat will not correspond with the holes in the second, and so each succeeding coat will tend to make the protective more and more impervious. In using such varnishes, they must only be applied in favourable weather, and must be allowed to thoroughly harden before being brought in contact with the water.

Varnishes with Mineral Additions.—In the fourth class we have varnishes of this kind to which body has been given by the addition of foreign constituents, generally mineral oxides; and this class is far preferable to the last, if the solvent used is not too rapid in its evaporation, and if care has been taken to select substances which do not themselves act injuriously upon iron or upon the gums or resins which are to bind them together, and are also free from any impurities which could do so.

At present the favourite substance used to give colour and body to such varnishes is red oxide of iron, the colour of which effectually cloaks any rusting which may be going on under it. In using the red oxide for this purpose, care should be taken that it contains no free sulphuric acid or soluble sulphates, as these are common impurities and are extremely injurious, tending to greatly increase the rate of corrosion. The finest coloured oxides are, as a rule, the worst offenders in this respect, as they are made by heating green vitriol (ferrous sulphate), and in most cases the whole of the sulphuric acid is not driven off, as the heat necessary for this impairs the colour.

The best form of iron oxide to use for this purpose is obtained by calcining a good specimen of hæmatite iron ore at a high temperature. When prepared in this way, it contains no sulphates, but from 8 to 40 per cent. of clay; if the percentage does not, however, exceed 12 to 18 per cent. it is unobjectionable.

A far better substance to use for this purpose would be the mixture of finely-divided metallic zinc and zinc oxide, which can be obtained as an impalpable powder from the cones used to close the nozzles of the retorts in the Belgian process of distilling zinc (p. 447). If a good sound shellac varnish had body given to it by this mixture, which usually contains about 80 per cent. of zinc, no action would take place until the varnish had perished, and when this took place the zinc would set up galvanic action with the iron and afford the plates a further period of protection, leaving a spongy coating of zinc oxide behind on the metal, which would again tend to protect it.

The United States Naval authorities have adopted an anti-corrosive paint of the composition advocated above, and find it much cheaper than other similar paints on the market, and it has given excellent results on their battle-ships.

Cement Coatings.—In the fifth class of protectives we have cement coatings; but these, together with such schemes as covering the hull of the vessels with vitreous glazes, glass, etc., have of late years been entirely abandoned. The action of cement on iron, however, must be discussed later in its important bearing on the protection of the interior portions of the hull, for which it is largely employed, its weight and the difficulty of attachment rendering it unfitted for outside work.

In selecting a protective composition for the bottom of a vessel, one of the second or fourth class should be chosen, attention being given to the points indicated, which are that in the bituminous and asphaltic compositions all the original acids must be eliminated, and that in the varnishes of the fourth group quickly evaporating solvents should be avoided, and, if possible, zinc substituted for iron oxide.

The vessels should have her plates as dry as possible during the application of the protective, and, if feasible, days on which the air is fairly dry, and a brisk breeze blowing, should be chosen. The protective should not be too thick as, if it is, it does not readily fill into inequalities in the plates; and, if in this way any air is enclosed, change of temperature will cause it to expand or contract, thus causing a blister to form, which will fill with sea water and set up rapid corrosion. The composition must either be elastic or else have the same rate of expansion and contraction as the iron; for, if not, the change of temperature will cause cracking and tearing of the composition with disastrous results. The vessel, if she has to be scraped down to the bare metal, must be scrubbed free from all traces of rust, and where a well-adhering coating of composition exists, it should be painted over and not disturbed. In the case of a new ship, she must be cleaned with dilute acid to get rid of every trace of mill scale, and then washed down with some slightly alkaline liquid to neutralise every trace of acidity, the alkali in turn being removed by clean water. Under these conditions, and given a composition with good adhering properties, but little apprehension need be felt as to the ravages of corrosion on the metal of a ship's bottom, the chief risk being from abrasion and other mechanical injury to the composition, coupled with improper constituents in the anti-fouling composition.

The protection of the interior portion of the vessel, where the plates are exposed to the corrosive action of bilge water, rendered more active by a high temperature, leakage from cargo, acids and sulphates from wet coals, and the presence of such electro-negative bodies as coal dust, scale and rust, is a matter of quite as great importance as the external protection; whilst the great risk of mechanical abrasion during coaling and shifting of cargo, as well as the difficulty of getting at the lower portions of the hold to examine the condition of the plates, renders adequate protection absolutely necessary. The corrosion found in the portions underneath the engine seats, the bunkers, and the water ballast chambers, especially near the engine room, is often very serious, and needs most careful watching, which, from the position of these parts of the vessel, it is very hard to bestow upon it.

It must also be remembered that the bilge water in a vessel is in constant motion, and that the air in these parts of the vessel may be expected to be exceptionally rich in carbon dioxide, which is the most important factor in corrosion. Under these conditions any abraded portion would probably be continually washed over, and then exposed to the foul air, a condition of things most conducive to rapid rusting. There are three main classes of protectives for the interior of a ship—

(1) Cements.
(2) Bituminous coatings.
(3) Paints.

The first of these, the cement coatings, have many good points to recommend them, but they also have many serious drawbacks.

The rigidity, firmness of adherence and endurance, are all of them points of the greatest importance, and there is no doubt but that the silicates present in the cement in time not only bind the cement into a mass of great hardness, but also bind the cement to the iron. A thin coating of Portland cement, however, is highly porous, and can be permeated by liquids and gases. Suppose, now, that the oxidation of copper pyrites in the coal bunkers had given rise to some soluble copper sulphate which had washed down into the bilge water, this solution would soak through the capillary orifices in the cement until it came in contact with the iron below, when the copper would be deposited on the iron, and rapid galvanic action set up, the cement being loosened, and to a certain extent lifted, by the formation of rust, whilst corrosion would gradually extend under the cement, giving on the outside of the coating but little sign of the damage taking place below it.

That this is a real danger is proved by the fact that on several occasions a deposit of metallic copper has been found under the cement and in contact with the iron.

Also, the hardness and rigidity of the cement give it a tendency to crack away from the metal when any strain is thrown on the plates, or during any expansion or contraction of the metal; whilst any repairs on the outside of the ship, such as making a boring to test the thickness of plate, replacement of rivets, etc., would undoubtedly cause a loosening of the cement coating within, and, wherever a loosening takes place the space between the cement and the plate will quickly become a starting point for corrosion, which rapidly spreads and loosens the cement, and will only be discovered by chance.

It is for this reason that bituminous or asphaltic varnishes, freed from any trace of acid and applied hot, or sound tough paint, are preferable to cement; as, although they are not so hard, yet if serious corrosion should be set up, it is easily discovered and stopped before much damage results, whilst being impervious to moisture, deleterious solutions, either from the coal bunkers or cargo, would be prevented from acting upon the skin of the ship.

FOULING AND ANTI-FOULING COMPOSITIONS.

In approaching the subject of fouling, one is impressed with the apparent hopelessness of obtaining any reliable information from the successes or failures registered by the bottoms of the vessels in the Service, or in the Mercantile Marine. Hundreds of ships may be examined, and their condition and the nature of the compositions used upon them registered, and just as one begins to feel that the key to the mystery is within one's grasp, a whole series of results so abnormal suddenly comes to light that it seems impossible to reconcile them with previous experience. A ship may sail half a dozen times to the same waters, coated with the same composition—on four occasions she will come home clean and in good condition, whilst on the other two voyages she may accumulate an amount of weed and animal life sufficient to reduce her speed from nine knots to five. Moreover, if the compositions with which she was coated be examined, and scrapings taken from her on her return, no cause will present itself that can in any way explain the great difference in her condition. After several years' close observation, however, certain factors begin to make themselves apparent. Some seasons of the year give rise to more fouling than others, according to the waters in which the ship has been; one also begins to realise that the amount of fouling increases enormously if the ship has been long at anchor. Ships which have been lying at the mouths of rivers, although quite clean in the brackish water, foul much more rapidly on going to sea than vessels which have been cruising, or even at anchor for the same time in salt water; and finally, certain ports and certain seas seem to exercise a deleterious effect, both as regards corrosion and fouling, which is not to be found elsewhere.

Turning back to the naval history of the past, it is found that fouling is no new trouble arising from the advent of the modern iron ship, but that it has been the one trouble that the combined engineering and scientific skill of many centuries have been unable to overcome.

Copper Sheathing.—With our wooden ships, metallic copper sheathing, if it were of the best kind, answered the purpose fairly well; but then the copper wasted so fast that inferior kinds and alloys were substituted to prevent the rapid loss, and, with the slowing down of the destruction of the copper, at once the trouble of fouling returned.

A sheet of pure copper is unacted on by any of the salts present in sea water or by sea water itself providing dissolved oxygen is absent. From quite pure salt solutions copper cannot replace the necessary hydrogen ion unless there is some depolariser, such as oxygen, present. Moreover, it is found that with copper the most rapid action takes place with the chlorides of sodium and potassium; magnesium chloride is not nearly so active, whilst with iron it is the most active agent in promoting corrosion.

In the presence of sea water containing dissolved oxygen a basic oxychloride of copper, in which two (OH) groups of the normal copper hydroxide have been replaced by chlorine, is formed, thus—

$$4[Cu(OH)_2] \rightarrow Cu_4(OH)_6.Cl_2.H_2O$$

The value of copper sheathing as a preventive of fouling lay in the ease with which this greenish-blue film of basic oxychloride became detached from the metal, carrying with it any vegetable or animal germs and organisms which may have attached themselves to it, a process called "exfoliation." Sir Humphry Davy, who first investigated this action, also found that the presence of even very small proportions of metals electro-positive to it prevented this action and slowed down the wasting of the copper, but that this at once allowed fouling to take place.

If the purest copper also is not used, the scale of oxychloride is more adherent; and setting up galvanic action with the still exposed metallic portions of the plate, after a short time causes it to be unevenly eaten away at these points.

It is noteworthy that, in the opinion of most engineers, the purest electrolytic copper is far more liable to corrosion than copper refined by the usual process of poling. This at first appears contradictory to the usual theories on corrosion, but it most probably arises either from the fact that electrolytic copper contains occluded or dissolved hydrogen which increases its solution pressure, or that fire-refined copper contains traces of impurities which greatly lessen its solution pressure.

When iron ships began to replace the wooden ones, as was only natural, attempts were made to utilise the metal which had before given relief; but it was quickly found that the effect of the galvanic action set up by the copper was fatal to the iron plates of the ship, and attempts were then made to sheathe the ship with copper plates in such a way that they should be insulated from the iron of the vessel. This idea has been revived from time to time down to the present day, and, indeed, is in considerable use in some foreign Services; but the difficulty of ensuring complete insulation, and the great risk of serious damage which must ensue to the iron of the hull if any injury happened to the insulating sheathing, make it a most undesirable method if any other means can be adopted to fulfil the same purpose as that for which the copper is used.

ANTI-FOULING COMPOSITIONS.

Compositions.—Early in the history of iron shipbuilding the idea was conceived of using coatings of paint, so prepared as to fulfil the same function as the copper plates had done ; but from 1840, when the first paint of this kind was patented, down to the present day, when there are upwards of thirty-two different compositions in the market, very little progress has been made in their manufacture, and the best of the present compounds cannot be relied upon for keeping a ship's bottom even fairly free from fouling for periods extending over nine months.

The idea which originally led to the present class of anti-fouling compositions was that the copper salts formed by the action of the sea water on the metallic sheathing owed a considerable portion of their value as anti-foulers to the poisonous action they exerted upon marine animal and vegetable growths ; but when an observer comes to study the natural history of these lower forms of animal life and vegetation, it is gradually forced upon him that it is only in the early stages of their growth—the germ period—that metallic poisons can affect them. Seaweeds do not take in the constituents they require for their growth by means of their roots, as is, to a certain extent, the case with ordinary plants, but absorb them by means of their pores from the water itself, the root only serving to attach them to the solid they choose for their resting place ; and it is also well known that when once a marine plant which has passed the first stages of existence is dislodged or torn from its support, it cannot again attach itself to anything else, whilst most of the mineral poisons have little or no effect upon their life and growth.

In the same way we find that, with the animal life found on a ship's bottom, the under-side is used to cling on with only, and not as an extractor of nourishment ; and that, therefore, after the seeds and germs have once obtained a foothold on the side of the vessel, no amount of poison which can be put into a composition will have any effect upon them. Metallic poisons undoubtedly do exert an influence upon the germs in their earliest stages ; but after that, they are perfectly useless as anti-foulers, and only imperil the plates of the vessel.

The germs of both kinds of growth are of necessity more abundant in the surface water near shore than in deep water, and, therefore, the period when the ship is in port is the time when the germs are most likely to make good their attachment, after which their further development is, unless other methods of getting rid of them are employed, merely a matter of time.

On examining the conditions under which a vessel is placed when coated with a composition which relies for its anti-fouling powers on metallic poisons only, we at once see the reasons which must make such a coating of little or no avail. In the composition we have drastic mineral poisons, probably salts of copper, mercury, or arsenic, which have been worked into a paint by admixture with varnishes of varying composition, and each particle of poison is protected from the action of the sea water by being entirely coated by this vehicle ; that this must be so is evident, or the composition would not have sufficient cohesive power to stick on the ship. As a rule, care is taken to select fairly good varnishes which will resist the action of sea water, for, perhaps, two or three months before they get sufficiently disintegrated to allow the sea water to dissolve any of the poison ; whilst, even with the accidental or intentional use of inferior varnishes, three or four weeks will pass before any solution can take place, and any poison be liberated to attack the germs. A ship is dry docked, cleaned, and her anti-fouling composition having been put on, she goes probably into the basin to take in cargo. Here she is at rest, and, with no skin friction or other disturbing causes to prevent it, a slimy deposit of dirt from the water takes place, and this, as a rule, is rich in the ova and germs of all kinds of growth, whilst the poisons in her coating are locked up in their restraining varnish, and are rendered inactive at the only period during which they could be of any use. After a more or less protracted period, the ship puts to sea, and the perishing of the varnish being aided by the friction of the water, the poisonous salts begin to dissolve or wash out of the composition ; but the germs have already got a foothold, and with a vessel sweeping at a rate of, say ten to twelve knots through the water, the amount of poison which can come in contact with their breathing and absorbing organs is evidently so infinitesimally minute that it would be impossible to imagine it having any effect whatever upon their growth. If the poison is soluble, it is at once washed away as it dissolves ; if it is insoluble, then it is also washed away, but there is just a chance that a grain or two may become entangled in the organs of some of the forms of life, and cause them discomfort. As the surface varnish perishes, the impact of the water during the rapid passage of the vessels through the water quickly dissolves or washes out the poisonous salts, and leaves a perished and porous, but still cohesive coating of resinous matter, which forms an admirable lodgment for anything which can cling to it. By the time the vessel lays-to in foreign waters, teeming with every kind of life, the poison which would now again have been of some use is probably all washed away, and a fresh crop of germs is acquired, to be developed on the homeward voyage, and a " bad ship " is reported by the person who looks after her docking. It is evident that a poison, even if it has the power of killing animal and vegetable life in all stages, could act only with the vessel at rest, unless it were of so actively corrosive a nature as to burn off the roots and attachments of the life rooted to it ; and if it did this, what would become of the protective composition and the plates of the vessel ? Any poison so used must be under conditions in which it is very unlikely to be in a position to act when it might do good.

The lamentable failure of composition after composition of this kind has gradually reduced them in number to some ten or twelve in general use, and in most cases it is low price alone which keeps them in the market.

The practical proof, given by experience, that poisons alone are unable to secure a clean bottom soon led many inquirers to the conviction that it was the exfoliation in the case of copper which had acted in giving fairly good results ; and in many compositions the attempt has been made to provide a coating which shall slowly wash off, and, by losing its original surface, shall at the same time clear away germs and partly developed growths, and so expose a continually renewed surface—in this way keeping the bottom of the vessel free from life. There is no doubt that when this is successfully done, a most valuable composition will result, but the practical difficulties which beset this class of anti-foulers must not be overlooked. In order to secure success the composition must waste at a fairly uniform rate when the ship is at rest, and also when she is rushing through the water ; and this is the more important in the case of Service vessels, as in many cases they spend a large percentage of their existence at anchor, or in the basins of the big dockyards. If a composition is made to waste so rapidly that it will keep a vessel clean for months in a basin, then it is a good composition *for that purpose ;* but send the vessel to sea, and under conditions where the water has a higher temperature, and the enormous friction caused by her passage through the water exerting its influence upon the composition, it will be found that the coating, which did its work well for six months at rest in the basin, will, in the course of one month under the altered conditions, be all washed away, and fouling will be set up. Noting this result, the manufacturer renders his composition more insoluble—less wasting—and so obtains a coating which, when the vessel is in motion, scales just fast enough to prevent fouling, and good results at once follow ; the composition is then put on the same or other vessels, and they take a spell of rest in the basin, and bereft of the aid of the higher temperatures and the friction of the water, the composition ceases to waste fast enough, and bad results at once have to be recorded.

There is no doubt that this is the true explanation of the wide discrepancies which are found between the compositions in the Navy and the Mercantile Marine. Take any of the big lines, their steamers are running at a fairly uniform rate of speed, and the periods of inaction are as short as the desire not to waste charge on the capital they represent can make them ; and under these conditions, by varying the constituents in the varnishes used for anti-fouling purposes, it is fairly easy, given the necessary data, to so constitute a composition as to secure admirable results ; but when this same coating is applied to an ironclad, running at various speeds, and as often at rest as in motion, then it is found at once that the composition previously imagined to be all that could be desired fails just as lamentably as the tribe of anti-foulers which preceded it.

Another factor which is often overlooked, and which tends to give misleading results, is the action of brackish water which, in many cases, seems to exert a special action in keeping the bottom of a vessel clean ; the fresh water having a tendency to disagree with certain forms of marine growth, whilst the salt water is apparently equally unpalatable to the fresh water forms of fouling.

In most of the compositions now in use attempts are made to combine strongly poisonous substances with exfoliating and wasting coatings, and this is done either by using metallic soaps, the basis of which is, as a rule, copper, or else by charging a perishable and easily washed off varnish with poisonous salts, consisting as usual of compounds of either copper, mercury, or arsenic, and in some cases all three.

As before pointed out, the presence of these substances does not exert any deterrent action upon the fouling, save perhaps when the vessel is at rest; but they exert undoubtedly an important influence upon the rate of exfoliation, as when the perishing of the varnish exposes them they dissolve, or are washed out, and in this way tend to disintegrate and clear away the surface more rapidly, an important and decidedly useful function, but one which might be more cheaply performed by substances other than high-priced metallic poisons.

The use of metallic poisons of the character indicated throws an increased burden upon the protective composition, as should the latter become abraded by friction of chain cables, barges alongside, or any other cause, the iron of the vessel will be attacked by the metallic salts, either present in the soluble form in the anti-fouling composition, or rendered so by the solvent action of the saline constituents of the sea water, the action of the metallic salts being to dissolve portions of the iron rapidly, and to deposit the metal which they contain upon the surface of the plates, and these deposits, exciting energetic galvanic action, cause corrosion and pitting to go on with alarming rapidity. Both mercury and copper salts are offenders in this way, but copper is by far the most objectionable, from the fact that the salts formed by the action of the sea water upon some of the compounds used in the composition are more soluble than the corresponding salts of mercury, and are, therefore, liable to be present in larger quantity, and so exert comparatively a much more injurious action on the plates.

All the time the ship is in motion the wash of the sea water will prevent the metallic poisons doing the plates or the marine growths much harm, but there is one phase of this question which has been overlooked. In certain ports there is a fashion in compositions, and most of the homes of the Mercantile Marine have some pet local composition which is largely used at the particular port. If, now, many ships are lying in a basin, taking in and discharging cargo, and if the prevalent compositions contain soluble salts of copper, it is evident that a certain quantity will go into solution in the water, which often does not undergo frequent or rapid change, and under these conditions every ship in the basin will be exposed to the same danger, and wherever an abrasion has taken place in the protectives, there copper will be deposited on the iron, causing corrosion and destruction of the plates; and it must be remembered that when the vessel is next docked and coated no amount of scraping will remove the fine particles of copper deposited in the pitted and corroded portions of the plate, and so finely divided as to be invisible to the eye, but that it will remain and carry on its destructive work under the new coatings of protective.

It is a well-recognised fact that when a vessel coated with a copper compound has become corroded from failure of her protective, or from abrasion, even an entire change of composition does little or no good in stemming the tide of corrosion, until after some considerable period has elapsed, a result which is due to the same cause.

At the present time, many of the principal compositions rely upon copper in some form or other as the basis of their anti-fouling composition, and in one which has enjoyed considerable favour finely divided metallic copper itself is used, and should a vessel coated with it, after the varnishes have commenced to disintegrate, be moored alongside an iron ship by a chain cable, or even by a wet hawser, a big galvanic couple would be formed at the expense of serious damage to any exposed iron.

Glazed Surfaces.—In the history of anti-fouling many attempts have been made to obtain highly glazed and glass-like surfaces, which it was hoped would withstand the action of sea water and afford no lodgment to marine growths; but even glass itself is slowly acted upon by sea water, and, when once roughened on the surface, will foul, while the rigidity of such coatings, and the straining and cracking consequent on unequal expansion and contraction of the plates and their coating, offers a serious obstacle to any such scheme.

Grease Paints.—Many compositions have been tried which do not appreciably harden in use but form a soft grease paint. The usual anti-corrosive composition is put on first and then the anti-fouling grease, which generally consists of a copper soap containing a small quantity of copper oxide. Should the poisons not prevent the initial stages of growth, and a plant or organism develop with such plastic material as a bed, the frictional resistance to its passage through the water would detach the growth.

The protective composition is the important composition, and care must be taken to obtain the best in the market, as if the protection is good, the plates remain uninjured even if fouling take place. The anti-fouling composition to be used with it must either be elastic, or have the same rate of contraction and expansion as the protective, and must—at any rate in the Navy—be chosen to suit the work to be done, such as contain soluble copper compounds being carefully rejected, whilst preference should be given to those which rely on exfoliation rather than mineral poisons. If a vessel is to remain at rest for a considerable period, an anti-fouling composition which exfoliates rapidly, and which also contains poisons known to act on germ life, must be used, the amount of such poison depending on the seasons and the waters in which the ship is to be; whilst if a vessel is to be continually running, then a slowly exfoliating composition must be employed, and a very small percentage of poison is all that is required, as skin friction and the comparative absence of the germs and spores in deep water will do the rest.

PIGMENTS.

The question of colours is so closely allied to that of the various compositions and paints in use, that a few words on the nature of colour and the composition of the pigments employed will not be out of place.

All natural objects are distinguished by particular colours and when it is desired to imitate these colours, strongly coloured bodies, called pigments, must be employed.

Theory of Colour.—When a beam of light falls on any substance, some of the coloured rays of which the beam is composed are absorbed and taken up by the substance, whilst the remaining rays are reflected back to the eye, and give the sensation of colour; for instance, a poppy looks red, because its petals have the power of absorbing all the rays, with the exception of the red rays, and these are reflected back to the eye.

A body which reflects all the rays of the spectrum in equal proportion will appear of the same colour as the light that falls upon it, that is to say white. But the majority of bodies reflect some rays in larger proportion than others, and are therefore coloured, their colour being that which arises from the mixture of rays which they reflect.

A body reflecting no light would be perfectly black.

That this is true may be seen by taking a source of light yielding only one kind of ray—called a monochromatic light; and all colours that have not the power of reflecting this particular ray appear black.

When light falls upon an opaque body, it is all either reflected or absorbed, but when it falls upon a transparent body, some of these rays are absorbed, whilst others pass through, and these are said to be transmitted.

A transparent body seen by transmitted light is coloured, if it is more transparent to some rays than to others, its colour being that which results from the mixture of the transmitted rays. Hence, a piece of blue glass appears blue, because it allows the blue rays to pass through.

The condition or state of division of a substance has a great influence upon its colour; for instance, gold is yellow by reflected light, brown in a state of fine powder, and when beaten out into very thin leaf, by transmitted light it is green; in a still finer state, as when precipitated from dilute solutions of gold, it appears blue or purple.

Temperature also, in many cases, affects the tints of colours, and often the colour itself; for instance, if scarlet mercury iodide be heated, it becomes yellow.

But besides these influences, others of even greater importance are always at work, such as oxidation of the oil with which the colour is mixed, light, and the action of impure air; whilst in very many cases the colours used by the artist chemically act upon one another in the course of time, and entirely destroy the effect which he intended to convey.

In order to avoid as much as possible the deterioration of paintings from these and similar causes, it is of great importance that anyone using colours should have an idea of the composition and properties of the substances employed.

WHITES.

White Lead or **Flake White** is a basic lead carbonate [$2PbCO_3.Pb(HO)_2$]. The Dutch method of preparation is to expose gratings of lead (as pure as possible and free from silver, which, even in small quantities, greatly impairs the good colour of white lead) to the action of the mixed vapours of vinegar (acetic acid) and carbon dioxide gas. The carbon dioxide is generated from a covering of spent tan and stable manure, the decomposition of which causes the requisite increase of temperature. The vapours of acetic acid attack the lead and form a basic acetate, which in its turn is converted into basic lead carbonate, acetic acid being liberated, and this attacks a fresh portion of lead. After these actions have gone on for some time, the layers of basic carbonate are scraped off the gratings and ground to a fine powder. This rather clumsy process has been of late somewhat superseded by more rapid methods, in which tribasic lead acetate, formed by boiling an excess of litharge with acetic acid, is decomposed by passing carbon dioxide through it. The white lead produced in this way has a crystalline structure and does not cover so well as that obtained by the Dutch method, hence very considerable quantities are still made by the older process. White lead is very poisonous, and being a cumulative poison, painters and others often suffer from lead colic. In white lead manufactories the workmen drink water containing dilute sulphuric acid, so as to convert the lead into non-poisonous lead sulphate.

The great drawback to white lead as a pigment is that in foul air it gradually darkens. This is due to the fact that the air contains traces of sulphuretted hydrogen, which combines with the lead, forming lead sulphide—a black compound.

$$\overset{\substack{\text{Lead}\\\text{carbonate}}}{PbCO_3} + \overset{\substack{\text{Sulphuretted}\\\text{hydrogen}}}{H_2S} = \overset{\substack{\text{Lead}\\\text{sulphide}}}{PbS} + \overset{\substack{\text{Carbon}\\\text{dioxide}}}{CO_2} + \overset{\text{Water}}{H_2O}$$

Pictures so blackened may be partially restored by washing the surface with a solution of hydrogen peroxide, which converts the black sulphide into white lead sulphate.

$$\overset{\text{Lead sulphide}}{PbS} + \overset{\text{Hydrogen peroxide}}{4(H_2O_2)} = \overset{\text{Lead sulphate}}{PbSO_4} + \overset{\text{Water}}{4(H_2O)}$$

A little lead sulphide or Berlin blue is sometimes added to the commercial white lead to give it a bluish tint.

Lead Sulphate ($PbSO_4$) is used as a constituent of many white paints, but alone it has poor covering power, hence is generally mixed with zinc white, baryta, etc. Since lead sulphate is very insoluble, it is far less poisonous than ordinary white lead, and is commercially known as "non-poisonous white lead."

Lead sulphate is commonly prepared by the addition of dilute sulphuric acid to the basic carbonate. Owing to the crystalline nature of the body as thus prepared, it is greatly improved by grinding.

Sublimed White Lead is composed mainly of the sulphate, but is of very variable composition. It is prepared from the "fume" given off in the smelting of lead (p. 440), and is but little inferior to ordinary white lead, whilst it has the advantage of not turning appreciably darker when exposed to traces of sulphuretted hydrogen.

Zinc or **Chinese White** consists of zinc oxide (ZnO). It is most generally prepared by volatilising zinc from fireclay retorts and admitting air for the combustion of the zinc. The fumes of the oxide are condensed in suitable chambers.

Zinc white is an excellent pigment, mixing readily with oils and water. It is quite unacted on by the impurities likely to be present in air, being therefore very permanent. It is, however, deficient in body, and for ordinary oil-paints cannot be used alone. Generally a mixture of two parts of white lead with one part of zinc white is found most satisfactory.

Zinc Sulphide (ZnS) is also employed as a pigment. It has good body, but considerable difficulty is experienced in obtaining it as a pure white; for this reason it is usual to employ it in mixtures, as, for example, with barium sulphate.

Baryta, or **Permanent White,** is barium sulphate ($BaSO_4$); it is deficient in body, but is of great use in fresco and siliceous painting. It is perfectly permanent under all conditions, and is not affected by sulphuretted hydrogen, since the barium sulphide which might be formed is also white.

BLACKS.

Most of the blacks consist of carbon in a very fine state of division.

Ivory Black is practically animal charcoal, obtained by carbonising ivory cuttings.

Vine Black is a vegetable charcoal, obtained from the twigs of vines, and is given a blue-black tint by mixing it with some Prussian blue.

Lampblack is a very finely divided soot, made by burning resinous oils in an insufficient quantity of air, and condensing the smoke.

Indian ink and Chinese ink consist of lampblack, mixed with gum, shellac, a little borax and water.

All these blacks are good and permanent, and may be mixed with other pigments without fear ; it is better, however, not to mix ivory black with vegetable colours.

Mineral Black (which is very little used) is black manganese oxide ; it does fairly well in oils, but always has a brown tint.

REDS.

These are of two kinds :—(1) Mineral reds, like vermilion, and (2) Organic reds, like carmine, etc.

MINERAL REDS.

Indian Red, Venetian Red, Light Red, consist chiefly of ferric oxide (Fe_2O_3), with an admixture of basic iron sulphates. They are directly prepared by heating ferrous sulphate (the green vitriol of commerce) with a small trace of nitric acid.

$$\overset{\text{Ferrous sulphate}}{2(FeSO_4)} = \overset{\text{Ferric oxide}}{Fe_2O_3} + \overset{\text{Sulphur dioxide}}{SO_2} + \overset{\text{Sulphur trioxide}}{SO_3}$$

Much of the oxide now employed is obtained as a bye-product from liquors containing iron salts, such as the acid used for pickling iron plates before tinning. By the addition of alkalies to the liquors, hydrated ferric oxide ($Fe_2(HO)_6$) is precipitated, which may then be calcined.

The peroxide is permanent under all ordinary conditions, but it must be carefully freed from all traces of acid before being applied as a paint to the surface of iron. It is much used in the protective coating for ships.

Red Ochre is a soft variety of the iron ore, hæmatite (Fe_2O_3), containing a little clay.

Red Lead or **Minium** (Pb_3O_4). This may be regarded as a compound of lead monoxide (PbO) and dioxide (PbO_2), but there is reason for believing that a portion of the monoxide exists in the free condition.

It is prepared by first calcining lead at a moderate heat, in order that whilst the lead may melt, yet the monoxide formed remains as a solid "dross." The lead monoxide first formed is of a yellow colour.

$$\underset{\text{Lead}}{Pb} + \underset{\text{Oxygen}}{O} = \underset{\text{Lead monoxide}}{PbO}$$

This product is now "coloured" by heating in another furnace, with free air supply, when more oxygen is absorbed and red lead produced.

$$\underset{\text{Lead monoxide}}{3(PbO)} + \underset{\text{Oxygen}}{O} = \underset{\text{Triplumbic tetroxide}}{Pb_3O_4}$$

Red lead, although much used, is very unsuitable, as it is open to all the objections of white lead, and also when mixed with oils forms with them a kind of soap, which causes the colour to lose its opacity.

When linseed oil is boiled for some time with lead oxide, it forms and dissolves some of this lead soap, and acquires the property of rapidly drying. Such oil is technically called "driers," and is much used to mix with oil paints to cause them to quickly dry; but as it contains lead, all colours mixed with it are liable to darken in the presence of sulphuretted hydrogen.

Vermilion is the most brilliant of the mineral reds. It is mercury sulphide (HgS) and is found native as *cinnabar*. It may be artificially prepared by precipitating the black mercury sulphide from a solution of mercuric chloride. This black sulphide on being sublimed and finely ground changes to the red variety without altering its composition. The most brilliant colour is obtained by the wet process, which consists of triturating mercury and sulphur together for some hours, and treating the black product formed with a warm solution of potassium hydroxide and water. The colour is not destroyed by any single acid or alkali. When used as a water colour it is apt to turn black in sunlight.

Chrome Red.—This pigment is a basic lead chromate [$PbCrO_4.Pb(HO)_2$], known also as Austrian cinnabar. It is best prepared by fusing the nitrates of sodium and potassium together at a low red heat, and adding gradually yellow lead chromate. After cooling, the insoluble chrome red is well washed and dried.

ORGANIC REDS.

Madder Lake, Rose Madder, Pink Madder, Carmine Madder, are made by treating madder, the root of the "*Rubia Tinctorum,*" which has been previously washed with water, with a boiling solution of alum, filtering the red liquid, and adding some sodium carbonate, when a red precipitate of the colouring matter and alumina, which is the madder lake, separates.

Carmine derives its colour from cochineal, which contains carminic acid, and this is split up by acids into carmine red and glucose.

The common carmine is obtained by treating an aluminous solution of cochineal with sodium carbonate, the lake being precipitated.

Crimson Lake contains more aluminous base than carmine, and consequently has not such a fine colour.

Scarlet Lake is crimson lake with an admixture of vermilion.

Indian Lake and **Dragon's Blood** are obtained from certain resins.

YELLOWS.

Aureolin Yellow is made by warming a solution of cobalt with potassium nitrite in presence of acetic acid, when the yellow is precipitated; it is a rich colour, and mixes well with other pigments, but is not permanent.

Cadmium Yellow is cadmium sulphide (CdS), and is a very stable and valuable colour, being unaffected by sulphuretted hydrogen. It is best prepared by precipitating a solution of cadmium sulphate with sodium sulphide, and thoroughly washing and drying the precipitate.

Lemon Chrome, or **Baryta Yellow,** is barium chromate ($BaCrO_4$); it is difficult to prepare, and the stability and beauty of colour depend on the method of manufacture. The colour is very permanent.

Chrome Yellow is a neutral lead chromate ($PbCrO_4$), and can be obtained by adding potassium chromate to a solution of lead acetate. The pigments known as *chrome orange* are mixtures of chrome yellow and the basic chromate, or *chrome red,* and are prepared by boiling chrome yellow with milk of lime.

King's Yellow, or **Orpiment,** is the highly poisonous arsenious sulphide (As_2S_3), and Naples Yellow contains both lead and antimony as oxides.

The Ochres are native earths consisting chiefly of alumina and silica coloured by hydrated ferric oxide [$Fe_2(HO)_6$]. They are very permanent and can be used with great safety. When heated they become brown, and are then called *sienna.*

Gamboge is a gum resin which exudes from the young shoots of the gokathu tree in Ceylon and Siam.

Yellow Carmine and **Yellow Lake** are prepared from quercitrin, a colouring matter existing in the bark of the quercitron. It is precipitated by means of alum.

Indian Yellow or **Purree** consists of an organic compound of magnesia, and is obtained from the urine of the camel.

GREENS.

Among the many pigments that owe their green colour essentially to copper, the following are important :—

Bremen Green is copper hydroxide [$Cu(HO)_2$], obtained in various hues by mixing with barium sulphate.

Casselman's Green.—A basic compound formed by mixing together boiling solutions of copper sulphate and an alkaline acetate. This salt is, next to the arsenic compounds, the finest of all the colours obtained from copper.

Mineral Green, or **Scheele's Green,** is copper arsenite ($CuHAsO_3$).

Schweinfurt Green or **Emerald Green.**—This is the most beautiful, but also most poisonous of all the copper pigments. It is really an aceto-arsenite of copper, and may be made by adding sodium acetate and arsenious acid to a solution of copper sulphate. It is a well-known fact that paperhangings containing this pigment, and pasted on damp walls, cause the inmates of the rooms to suffer from headaches, due probably to volatile arsenical compounds being formed.

Verdigris is a subacetate of copper. As a water-colour it is very unstable.

Chrome Green, Viridian Green, are usually chromium oxides (Cr_2O_3), prepared by adding sodium hydroxide or carbonate to a solution of chromic chloride. Chrome greens, however, vary much in composition, in some cases consisting of the phosphate [$Cr_2(PO_4)_2$]. They have good body, and do not affect other colours with which they may be mixed.

Terre Vert, as indicated by its name, is found as a green earth, which is a very permanent green, consisting mainly of an oxide and silicate of iron.

Other greens are compounded from yellows and blues; if such mixtures (*e.g.* as Prussian blue mixed with raw or burnt sienna or Vandyke brown) be exposed to light, the green colour gives place to brown, on account of the Prussian blue fading. If the faded colour be then kept for some time in the dark, the colour returns.

BLUES.

Ultramarine.—This is a double silicate of alumina and soda, and contains sulphur in the form of sulphide, but no definite formula has been found for it. It occurs native as "lapis lazuli." The commercial product is obtained by heating together soda, clay, sulphur and charcoal in various proportions. It is first white, but quickly turns green (green ultramarine), and when this is heated with sulphur in presence of air it becomes blue without change of composition. Ultramarine is unacted on by alkalies, but is readily decomposed by acids with evolution of sulphuretted hydrogen.

Cobalt and **Smalt Blues** are exceedingly permanent under all ordinary conditions. They are prepared by dissolving cobaltous oxide in a fused acid silicate, which yields a glass of magnificent blue colour, which is ground to a fine powder.

Cærulean Blue is a stannate of cobalt used for scene-painting.

Prussian Blue is ferrocyanide of iron [$Fe_4(FeC_6N_6)_3$]; it is made by adding a ferric salt to potassium ferrocyanide, when Prussian blue is precipitated. It is readily destroyed by alkalies. The pigment is soluble in oxalic acid and molybdic acid.

Antwerp Blue is a compound of Prussian blue and alumina, but it has been almost completely superseded by *Brunswick blue,* which is a mixture of Prussian blue and bartya.

Indigo is the blue colouring matter obtained from several species of *indigofera.* The leaves are macerated in water, when they undergo oxidation, forming a yellow solution, which, on exposure to the air, deposits indigo in the form of a dark blue powder. The pigment is soluble in Nordhausen sulphuric acid, forming a deep blue solution. For dyeing purposes the cloth is dipped in a vat containing one part of indigo, two parts of ferrous sulphate, and three parts of slaked lime, to about 200 parts of water. On exposure to air the cloth becomes permanently blue by the deposition of insoluble blue indigo. Indigo has also been prepared synthetically.

BROWNS.

Raw and **Burnt Umber** consists of a native ore of iron, containing a little manganese. The pigments are permanent.

Sepia is extracted from cuttlefish, and consists of carbonaceous matter and animal gelatine.

Madder Brown is extracted from the madder root, and is very apt to fade, whilst *Vandyke Brown* and the *Brown Ochres* are oxides of iron, and are quite permanent.

From a series of experiments made on the action of light on water colours, the following notes may be of interest.[1]

Paper painted with simple colours and mixtures was exposed to light under different conditions, with the following results.

Mineral colours are far more stable than vegetable colours.

The presence of moisture and oxygen is in most cases essential for a change to be effected, even in the vegetable colours. It may be said that every pigment is permanent when exposed to light "in vacuo."

The effect of light on a mixture of colours which have no direct chemical action on one another, is that the unstable colour disappears, and leaves the stable colours unaltered appreciably.

Experiments also show that the rays which produce by far

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[1] "Report of the Action of Light on Water Colours," by Russell and Abney.

the greatest change in a pigment are the blue and violet components of white light, and that these for equal illumination predominate in light from the sky, whilst they are less in sunlight and in diffused cloud light, and are present in comparatively small proportion in the artificial light usually employed in lighting a room or gallery.

Experiments have also shown that about a century of exposure would have to be given to water-colour drawings in galleries lighted as are those at South Kensington, before any very marked deterioration would be visible in them, if painted with any but the more fugitive colours ; and that when the illumination is of the same quality as that of gaslight, or of the electric glowlight, rendered normally incandescent, and of the same intensity as that employed in those galleries, an exposure to be reckoned by thousands of years would be necessary to produce the same results.

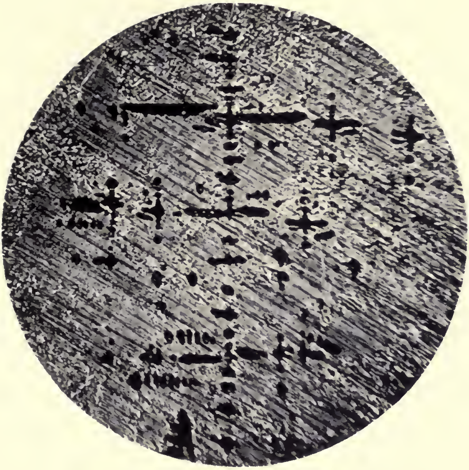

FIG. 1. EUTECTIC ALLOY, BISMUTH-TIN, WITH EXCESS METAL.

FIG. 2. ANTIMONY-TIN ALLOY WITH CRYSTALS OF Sb-Sn.

FIG. 1. HARD ROLLED BRASS.

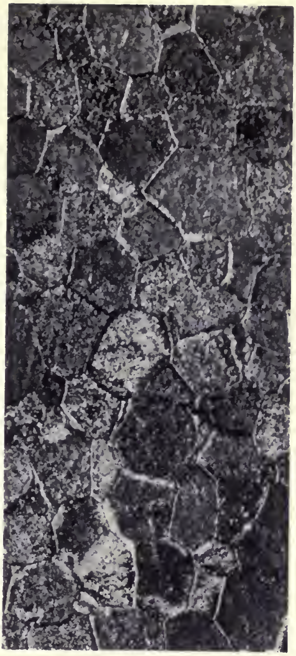

FIG. 2. ANNEALED BRASS—POLYHEDRAL STRUCTURE.

FIG. 3. ANNEALED BRASS—CRYSTALLINE STRUCTURE.

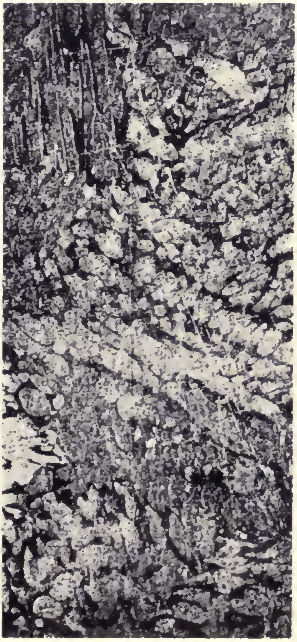

FIG. 4. MUNTZ METAL (ANNEALED).

FIG. 1. PEARLITE.

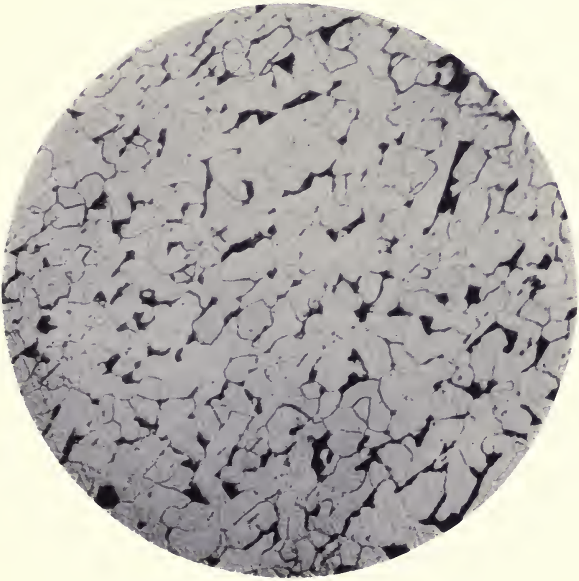

FIG. 2. LOW CARBON STEEL—FERRITE (LIGHT) WITH PEARLITE.

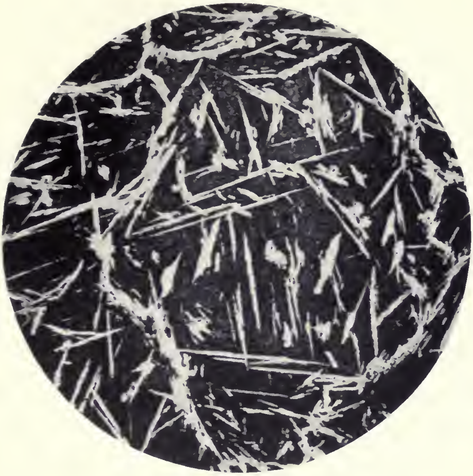

FIG. 1. HIGH CARBON STEEL – CEMENTITE (NEEDLES) WITH PEARLITE.

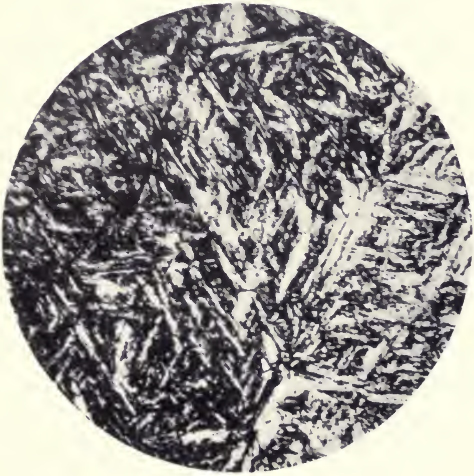

FIG. 2. AUSTENITE (LIGHT) AND MARTENSITE (DARK).

FIG. 1. QUENCHED STEEL—MARTENSITE.

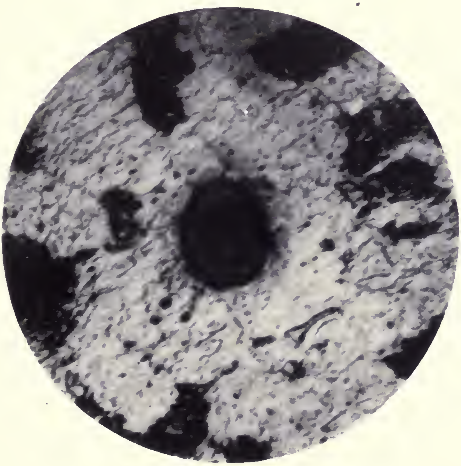

FIG. 2. SULPHUR SEGREGATE (IN CENTRE).

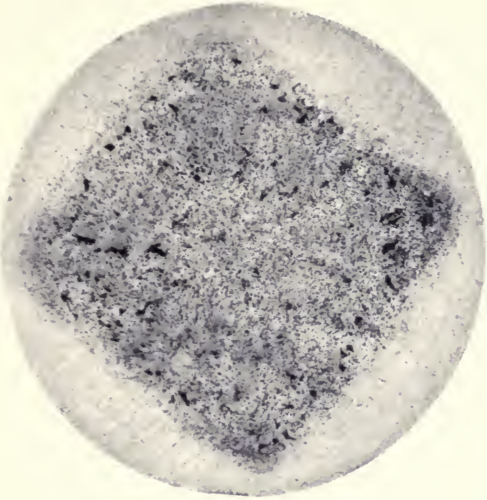

FIG. 1. SULPHUR PRINT OF ROLLED STEEL BAR.

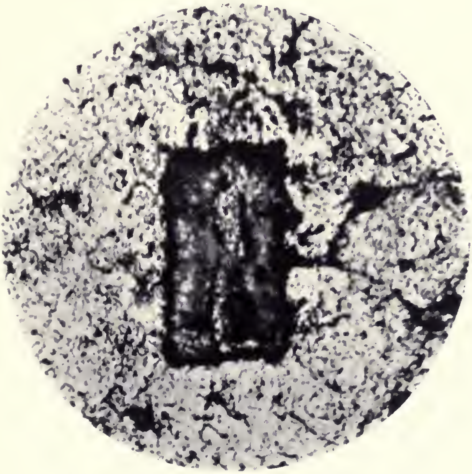

FIG. 2. SEGREGATE IN STEEL.

APPENDIX

WEIGHTS AND MEASURES.

AVOIRDUPOIS WEIGHT.

Drachms.	oz.	lbs.	qrs.	cwts.	ton.	French grammes.
1	0·0625	0·0039	0·000139	0·000035	0·00000174	1·771846
16	1	0·0625	0·00223	0·000558	0·000028	28·34954
256	16	1	0·0357	0·00893	0·000447	453·59
7,168	448	28	1	0·25	0·0125	12,700
28,672	1,792	112	40	1	0·05	50,802
573,440	35,840	2,240	80	20	1	1,016,048

LONG MEASURE.

Ins.	feet.	yards.	fath.	poles.	furl.	mile.	French metres.
1	0·083	0·02778	0·0139	0·005	0·000126	0·0000158	0·0254
12	1	0·333	0·1667	0·0606	0·00151	0·0001894	0·3048
36	3	1	0·5	0·182	0·00454	0·000568	0·9144
72	6	2	1	0·364	0·0091	0·001136	1·8287
198	16½	5½	2¾	1	0·025	0·003125	5·0291
7,920	660	220	110	40	1	0·125	201·16
63,360	5,280	1,760	880	320	8	1	1,609·315

MEASURE OF CAPACITY.

Pints.	galls.	cubic ft.	litres.
1	0·125	0·02	0·5676
8	1	0·1604	4·541
16	2	0·3208	9·082
64	8	1·283	36·32816
512	64	10·264	290·625
2,560	320	51·319	1,453·126
5,120	640	102·64	2,906·25

1 gallon = 277¼ cubic in. = 0·16 cubic ft. = 10 lbs. dist. water = 4·543458 litres.

1 cubic ft. × 6·2355 = gallons.

1 cubic metre = 35·317 cubic ft.

1 grain = 0·064799 gram.

1 lb. avoir. = 0·453593 kilogram.

USEFUL DATA.

1 lb. avoir. = 16 oz. = 7,000 grains = 453·59 grammes = 1·21527 lb. troy.
1 lb. troy = 12 ,, = 5,760 ,, = 373·242 ,, = 0·82285704 lb. avoir.
1 oz. avoir. = 437·5 grains = 28·35 grammes = 0·9114583 oz. troy.
1 cubic cent. = 0·061113 cubic in. = 0·282 fl. drms. = 0·00176 pint = 0·0352 fl. oz.
1 cubic ft. = 28315·3 c.c. = 6·2321 gallons = 28·3153 litres = 997·1364 fl. oz. = 49·8568 pints
1 gallon = 0·16046 cubic feet = 277·274 cubic in. = 4·54346 litres.
1 cubic in. = 16·386 c.c. = 0·577 fl. oz = 0·0164 litre = 0·02885 pint.
1 litre = 0·035316 cubic ft. = 0·220096 gallon = 61·0270 cubic in. = 1·761 pint.
1 fl. oz. = 28·396 c.c. = 1·7329 cubic in.
1 pint = 567·919 c.c. = 0·020057 cubic ft. = 34·659 cubic in. = 0·567920 litre.
1 gramme = 0·002204 lb. = 0·03527 oz. = 15·432348 grains.
1 cubic ft. air (at 0° C. and 760 mm.) = 0·0807 lbs.
1 lb. air (,, ,,) = 12·35 cubic ft.

TABLE OF THE CORRESPONDING HEIGHTS OF THE BAROMETER IN MILLIMETERS AND ENGLISH INCHES.

Milli-meters	=	English inches	Milli-meters	=	English inches	Milli-meters	=	English inches
720	=	28·347	739	=	29·095	758	=	29·843
721	=	28·386	740	=	29·134	759	=	29·882
722	=	28·425	741	=	29·174	760	=	29·922
723	=	28·465	742	=	29·213	761	=	29·961
724	=	28·504	743	=	29·252	762	=	30·000
725	=	28·543	744	=	29·292	763	=	30·039
726	=	28·583	745	=	29·331	764	=	30·079
727	=	28·622	746	=	29·370	765	=	30·118
728	=	28·662	747	=	29·410	766	=	30·158
729	=	28·701	748	=	29·449	767	=	30·197
730	=	28·740	749	=	29·488	768	=	30·236
731	=	28·780	750	=	29·528	769	=	30·276
732	=	28·819	751	=	29·567	770	=	30·315
733	=	28·858	752	=	29·606	771	=	30·355
734	=	28·898	753	=	29·645	772	=	30·394
735	=	28·937	754	=	29·685	773	=	30·433
736	=	28·976	755	=	29·724	774	=	30·473
737	=	29·016	756	=	29·764	775	=	30·512
738	=	29·055	757	=	29·803			

DENSITY OF SEA WATER ON VARIOUS SCALES.

Density or specific gravity 1·025 at 0° C. = $\frac{1}{32}$ salinometer = 10° densimeter.
,, ,, 1·05 ,, = $\frac{2}{32}$,, = 20° ,,
,, ,, 1·09 ,, = $\frac{3}{32}$,, = 30° ,,
,, ,, 1·2 ,, = $\frac{7}{32}$,, = 70° ,,

Table for Converting Degrees of the Centigrade Thermometer into Degrees of Fahrenheit's Scale.

Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.	Centigrade.	Fahrenheit.
—90°	—130°	40°	104	170	338°
85	121	45	113	175	347
80	112	50	122	180	356
75	103	55	131	185	365
70	94	60	140	190	374
65	85	65	149	195	383
60	76	70	158	200	392
55	67	75	167	205	401
50	58	80	176	210	410
45	49	85	185	215	419
40	40	90	194	220	428
35	31	95	203	225	437
30	22	100	212	230	446
25	13	105	221	235	455
20	—4	110	230	240	464
15	+5	115	239	245	473
10	14	120	248	250	482
—5	23	125	257	255	491
0	32	130	266	260	500
+5	41	135	275	265	509
10	50	140	284	270	518
15	59	145	293	275	527
20	68	150	302	280	536
25	77	155	311	285	545
30	86	160	330	290	554
35	95	165	329	295	563

To convert °F. to °C. $\frac{(^\circ\text{F.} - 32) \times 5}{9} = {}^\circ\text{C.}$

To convert °C. to °F. $\frac{^\circ\text{C.} \times 9}{5} + 32 = {}^\circ\text{F.}$

TABLE OF ELEMENTS.

Elements.	Symbol.	Atomic weight.	Specific heat.
		O = 16	
Aluminium	Al	27·1	0·219
Antimony	Sb	120·2	0·049
Argon	A	39·88	—
Arsenic	As	74·96	0·083
Barium	Ba	137·37	—
Bismuth	Bi	208·0	0·030
Boron	B	11·0	0·254
Bromine	Br	79·92	—
Cadmium	Cd	112·40	0·054
Cæsium	Cs	132·81	0·048
Calcium	Ca	40·07	0·180
Carbon	C	12·00	variable
Cerium	Ce	140·25	0·044
Chlorine	Cl	35·46	—
Chromium	Cr	52·0	0·104
Cobalt	Co	58·97	0·103
Columbium	Cb	93·5	—
Copper	Cu	63·57	0·093
Dysprosium	Dy	162·5	—
Erbium	Er	167·7	—
Europium	Eu	152·0	—
Fluorine	F	19·0	—
Gadolinium	Gd	157·3	—
Gallium	Ga	69·9	0·079
Germanium	Ge	72·5	0·074
Glucinum	Gl	9·1	—
Gold	Au	197·2	0·032
Helium	He	3·99	—
Holmium	Ho	163·5	—
Hydrogen	H	1·008	—
Indium	In	114·8	—
Iodine	I	126·92	0·054
Iridium	Ir	193·1	0·032
Iron	Fe	55·84	0·112
Krypton	Kr	82·92	—
Lanthanum	La	139·0	0·045
Lead	Pb	207·10	0·031
Lithium	Li	6·94	0·940
Lutecium	Lu	174·0	—
Magnesium	Mg	24·32	0·245
Manganese	Mn	54·93	0·122
Mercury	Hg	200·6	0·033
Molybdenum	Mo	96·0	0·066
Neodymium	Nd	144·3	—

Elements.	Symbol.	Atomic weight.	Specific heat.
		O = 16	
Neon	Ne	20·2	—
Nickel	Ni	58·68	0·109
Niton (radium emanation)	Nt	222·4	—
Nitrogen	N	14·01	—
Osmium	Os	190·9	0·031
Oxygen	O	16·00	—
Palladium	Pd	106·7	0·059
Phosphorus	P	31·04	0·202
Platinum	Pt	195·2	0·032
Potassium	K	39·10	0·166
Praseodymium	Pr	140·6	—
Radium	Ra	226·4	—
Rhodium	Rh	102·9	0·058
Rubidium	Rb	85·45	—
Ruthenium	Ru	101·7	0·061
Samarium	Sa	150·4	—
Scandium	Sc	44·1	—
Selenium	Se	79·2	0·084
Silicon	Si	28·3	0·165
Silver	Ag	107·88	0·056
Sodium	Na	23·00	0·293
Strontium	Sr	87·63	—
Sulphur	S	32·07	—
Tantalum	Ta	181·5	—
Tellurium	Te	127·5	0·048
Terbium	Tb	159·2	—
Thallium	Tl	204·0	0·032
Thorium	Th	232·4	0·027
Thulium	Tm	168·5	—
Tin	Sn	119·0	0·052
Titanium	Ti	48·1	0·112
Tungsten	W	184·0	0·034
Uranium	U	238·5	—
Vanadium	V	51·0	0·115
Xenon	Xe	130·2	—
Ytterbium (Neoytterbium)	Yb	172·0	—
Yttrium	Yt	89·0	—
Zinc	Zn	65·37	0·093
Zirconium	Zr	90·6	0·066

Arrangement of the Elements on the Periodic System.

Period.	Group. I.	II.	III.	IV.	V.	VI.	VII.	VIII.			O.
1st	Li 7	Gl 9·1	B 11	C 12	**N 14**	**O 16**	H 1 **F 19**				He 4 Ne 20
2nd	Na 23	Mg 24·4	Al 27·1	Si 28·4	**P 31**	**S 32**	**Cl 35·5**				Ar 40
3rd	K 39 **Cu 63·6**	Ca 40 **Zn 65·4**	Sc 44·1 **Ga 70**	Ti 48·1 **Ge 72·5**	V 51·0 **As 75**	Cr 52 **Se 79**	Mn 55 **Br 80**	Fe 56	Co 59	Ni 58·7	Kr 83·0
4th	Rb 85·4 **Ag 108**	Sr 87·6 **Cd 112·4**	Yt 89 **In 115**	Zr 90·7 **Sn 119**	Cb 93·5 **Sb 120**	Mo 96 **Te 127**	**I 127**	Ru 102	Rh 103	Pd 106·5	Xe 130
	Cs 133 **Au 197·2**	Ba 137·4 **Hg 200·5**	La 139 Yb 172 **Tl 204**	Ce 140 **Er 168** **Pb 207**	Pr 140·5 Ta 181·5 **Bi 208**	W 184	Sa 150	Os 191	Ir 193	Pt 195	
				Th 232·5		U 238·5					
Hydrogen or Halogen Compound	MX	MX_2	MX_3	MX_4	MX_3	MX_2	MX				
Highest Oxygen Compound	M_2O	MO	M_2O_3	MO_2	M_2O_5	MO_3	M_2O_7				

TABLE FOR CORRECTION OF VOLUMES OF GASES FOR TEMPERATURE, GIVING THE DIVISOR FOR THE FORMULA.

$$V^1 = \frac{V \times B}{760 \times (1 + \delta t)}$$

$\delta = 0{\cdot}003665$ = co-efficient of expansion for gases.

t °C.	760 × (1 + δt)	Log [760 × (1 + δt)]	t °C.	760 × (1 + δt)	Log [760 × (1 + δt)]	t °C.	760 × (1 + δt)	Log [760 × (1 + δt)]
14·0	798·99	2·9025	18·0	810·13	2·9085	22·0	821·27	2·9144
2	799·55	8	2	810·69	8	2	821·88	7
4	800·10	2·9031	4	811·25	2·9091	4	822·39	2·9150
6	800·66	4	6	811·80	4	6	822·95	3
8	801·22	7	8	812·36	7	8	823.50	6
15·0	801·78	2·9040	19·0	812·92	2.9100	23·0	824·06	9
2	802·33	3	2	813·47	3	2	824·62	2·9162
4	802·89	6	4	814·03	6	4	825·17	5
6	803·45	9	6	814·59	9	6	825·73	8
8	804·00	2·9052	8	815·15	2·9112	8	826·29	2·9171
16·0	804·56	5	20·0	815·70	5	24·0	826·84	4
2	805·12	8	2	816·26	8	2	827·40	7
4	805·68	2·9061	4	816·82	2·9121	4	827·96	2·9180
6	806·23	4	6	817·37	4	6	828·52	3
8	806·79	7	8	817·93	7	8	829·07	6
17·0	807·35	2·9070	21·0	818·49	2·9130	25·0	829·63	9
2	807·90	3	2	819·05	3	2	830·19	2·9191
4	808·46	6	4	819·60	6	4	830·74	4
6	809·02	9	6	820·16	9	6	831·30	7
8	809·58	2·9082	8	820·72	2·9141	8	831·86	2·2900

TABLE OF GASEOUS VOLUMES, COMPOSITION OF GASES, TEMPERATURE, &C., FOR MODERN SMOKELESS EXPLOSIVES.

Name of Explosive.	Calories per gram.	Gases evolved in c.c. per gram, calculated at 0°C. and 760 mm.			Percentage Composition of Permanent Gases.					Co-efficient of potential energy.	Density of loading.	Pressure, tons.
		Permanent.	Water vapour.	Total volume.	CO_2.	CO.	H.	CH_4.	N.			
Nitroglycerin	1652	464	257	741	63·0	(yields	4·0 of	oxygen	)33·0	1224	0·017	—
Nitrocellulose (13·3 N.)	1061	673	203	876	22·3	45·4	14·9	0·5	16·9	929	0·017	—
,, (strand)	1068	689	163	852	29·1	32·9	20·1	0·75	17·5	910	—	3
,, (pellet)	1037	725	162	887	25·7	39·3	18·7	—	16·2	919	—	3
Nitrocellulose powders—												
R. R. Rottweil, German	896	815	178	993	17·9	43·45	24·4	0·6	13·6	890	0·05	3·3
,, ,,	931	759	163	922	25·1	36·55	20·2	4·7	13·4	859	0·22	16·5
,, ,,	1037	681	135	816	35·0	27·8	12·6	11·1	13·4	846	0·45	40·5
Troisdorf, German	943	700	195	895	18·7	47·9	17·4	0·8	15·2	844	0·017	—
Walsrode	1014	669	206	875	21·3	48·2	10·1	0·4	14·8	887	0·008	—
Nitrocellulose with metallic nitrates—												
B. N., French	833	738	168	906	13·2	53·1	19·4	0·7	13·6	755	0·017	—
,,	1003	616	206	822	28·1	32·4	21·9	0·8	16·8	824	—	6
E. C., English	800	420	154	574	22·9	40·6	15·5	0·5	20·5	459	0·017	—
,,	762	718	158	876	11·9	52·1	23·9	0·5	11·6	667	0·008	—
Schultze	786	576	160	736	15·5	46·7	23·0	0·8	14·0	578	0·008	—
Imperial Schultze	742	763	152	915	8·9	52·7	27·0	1·0	10·4	679	0·008	—
Amberite	745	635	156	791	12·0	50·0	25·5	0·4	12·1	589	0·008	—
Cannonite	845	725	146	871	14·6	49·9	22·2	0·6	12·7	736	0·008	—

Nitrocellulose with organic nitro-compounds—												
S. S.	799	584	150	734	18·2	45·4	20·0	0·7	15·7	586	0·017	—
,,	755	695	131	816	11·8	51·3	23·7	0·8	12·4	616	0·008	—
Rifleite, English	864	766	159	925	14·2	50·1	20·5	0·3	14·9	799	0·017	—
Shot gun rifleite	896	705	169	874	19·0	45·3	21·5	0·8	13·4	783	0·008	—
Kynoch's smokeless	807	600	126	726	14·8	49·5	18·8	0·7	16·2	586	0·008	—
Nitrocellulose with nitroglycerin—												
Cordite, nitroglycerin, 60% insol. nitrocellulose, 35%	1280	627	236	863	26·7	39·8	12·8	0·5	20·2	1105	0·017	—
,, nitroglycerin, 58% insol. nitrocellulose, 37%	1253	647	235	882	24·9	40·3	14·8	0·7	19·8	1105	0·017	—
,, ,, ,,	1272	678	200	878	27·1	34·3	17·5	0·3	20·7	1117	0·05	3
,, ,, ,,	1242	692	179	871	31·7	28·9	18·9	1·6	18·8	1082	0·25	21
,, ,, ,,	1360	624	175	799	41·9	19·1	12·1	7·05	19·85	1086	0·5	53
,, ,, ,, (size 0·255)	1284	692	194	886	27·0	34·2	26·9	trace	12·0	1137	—	10
Ballistite nitroglycerin, 50%, English sol. nitrocell., 50 %	1349	568	249	817	36·5	32·5	8·4	0·2	22·4	1102	0·017	—
,, ,, German	1291	591	231	822	33·1	35·4	10·1	0·5	20·9	1061	0·017	—
,, ,, Italian	1317	581	245	826	35·9	32·6	9·0	0·3	22·2	1088	0·017	—
,, ,,	1365	610	197	807	37·3	27·8	19·1	trace	15·8	—	—	6
,, nitroglycerin, 50% insol. nitrocell., 50%	1410	550	247	797	41·8	27·5	6·0	—	24·7	1124	0·017	—
,, sporting	1286	591	234	825	32·2	37·1	10·1	0·4	20·2	1061	0·008	—
Cordite M.D., nitroglycerin, 30% insol. nitrocell., 65%	1031	726	215	941	16·3	50·4	19·7	—	13·6	970	0·008	—
,, ,,	1036	782	173	955	18·15	42·6	23·15	0·35	15·75	989	0·05	2·7
,, ,,	1041	745	143	888	26·75	33·65	19·8	4·65	15·15	924	0·25	21
,, ,,	1190	676	134	810	36·6	24·8	11·9	10·7	16·0	964	0·45	43
Experimental—												
Nitroglycerin, 20% Insol. nitrocell., 80%	1159	637	227	864	26·6	40·8	12·0	0·1	20·5	1001	0·017	—
Nitroglycerin, 20% Sol. nitrocell., 80%	1062	675	226	901	21·7	45·4	15·7	0·1	17·1	957	0·017	—

Note.—Where pressure in tons is given, the figures are from Sir Andrew Noble's experiments. In other cases, from the work of M'Nab and Ristori.

TABLE OF THE TENSION OF AQUEOUS VAPOUR EXPRESSED IN INCHES OF MERCURY, AT 32° F., FOR EACH DEGREE F., BETWEEN 0° AND 100°.

Temp. °F.	Inches of Mercury.	Temp. °F.	Inches of Mercury.	Temp. °F.	Inches of Mercury.	Temp. °F.	Inches of Mercury.
0	0·0439	26	0·1395	51	0·3742	76	0·8964
1	0·0459	27	0·1457	52	0·3882	77	0·9266
2	0·0481	28	0·1522	53	0·4026	78	0·9577
3	0·0503	29	0·1589	54	0·4175	79	0·9898
4	0·0526	30	0·1660	55	0·4329	80	1·0227
5	0·0551	31	0·1733	56	0·4488	81	1·0566
6	0·0576	32	0·1810	57	0·4653	82	1·0915
7	0·0603	33	0·1883	58	0·4822	83	1·1274
8	0·0630	34	0·1959	59	0·4997	84	1·1643
9	0·0659	35	0·2038	60	0·5178	85	1·2023
10	0·0689	36	0·2119	61	0·5364	86	1·2413
11	0·0721	37	0·2204	62	0·5556	87	1·2815
12	0·0753	38	0·2291	63	0·5755	88	1·3228
13	0·0788	39	0·2381	64	0·5959	89	1·3652
14	0·0823	40	0·2475	65	0·6170	90	1·4088
15	0·0861	41	0·2571	66	0·6388	91	1·4537
16	0·0899	42	0·2672	67	0·6612	92	1·4998
17	0·0940	43	0·2775	68	0·6843	93	1·5471
18	0·0982	44	0·2882	69	0·7081	94	1·5958
19	0·1027	45	0·2993	70	0·7327	95	1·6457
20	0·1073	46	0·3108	71	0·7580	96	1·6971
21	0·1121	47	0·3226	72	0·7841	97	1·7498
22	0·1171	48	0·3349	73	0·8109	98	1·8039
23	0·1223	49	0·3476	74	0·8386	99	1·8595
24	0·1278	50	0·3607	75	0·8671	100	1·9170
25	0·1335						

BOILING POINT AND LATENT HEAT OF WATER UNDER VARYING PRESSURES.

Pressure.	Boiling Point.	Latent Heat.
1 atmosphere	212° Fahr.	966 thermal units.
2 ,,	249° ,,	940 ,,
3 ,,	273° ,,	923 ,,
4 ,,	291° ,,	910 ,,
5 ,,	306° ,,	900 ,,
6 ,,	319° ,,	891 ,,

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