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INORGANIC CHEMISTRY

FOR

ADVANCED STUDENTS

ROSCOE AND HARDEN

C. E. Burry

INORGANIC CHEMISTRY

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INORGANIC CHEMISTRY

FOR

ADVANCED STUDENTS

BY

THE RIGHT HON. SIR HENRY ROSCOE
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AND

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SECOND EDITION
(COMPLETELY REVISED)

With Fifty-three Illustrations in the Text

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PREFACE TO SECOND EDITION

THE lapse of time having necessitated a thorough revision of the text, the opportunity has been taken of introducing the system of atomic weights based on the atomic weight of oxygen—16, which is now universally employed.

Two additional lessons have been inserted, one dealing in an elementary manner with the constitution of some of the simpler compounds of carbon, and the other with the radioactive elements.

Additional prominence has been given to various points of chemical theory, and it is hoped that the new edition will meet the requirements of a somewhat wider circle of students than the one which it replaces.

HENRY E. ROSCOE.
ARTHUR HARDEN.

December 1910.

PREFACE

THE present work is intended to supplement the smaller volume of *Inorganic Chemistry for Beginners*, published six years ago. It has been, therefore, prepared for the use of students who have mastered the more elementary portions of the Science. But at the same time, whilst the endeavour of the authors has been to put forward the most important characters of the compounds of those non-metallic elements not treated of in the former work, and to add the properties of the commoner metals and their salts in a clear and concise form, it is to be noted that the volume cannot lay claim to being an advanced treatise on the Science. In addition to the portions describing the properties of chemical compounds, lessons will be found on certain important points of chemical theory, and others on the application of chemistry to the Arts and Industries. These chapters are interspersed through the volume, in order to relieve the student from the somewhat tedious task of working without interruption through a long series of lessons on the metals and their compounds.

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CONTENTS

LESSON I

MOLECULAR AND ATOMIC WEIGHTS

In the *Inorganic Chemistry for Beginners*, which constitutes an introduction to the present work, the student has been familiarised with the laws of chemical combination (Roscoe and Lunt, p. 27), and with Dalton's atomic theory (R. and L., p. 30). The application of this theory to the combination of gases has also been discussed (R. and L., p. 55), together with the experiments and reasoning which have led chemists to the adoption of Avogadro's theory, *that equal volumes of all gases (measured under the same conditions) contain equal numbers of molecules.*

We now pass on to the next important step in chemical theory—the application of Avogadro's theory to the determination of molecular and atomic weights.

The Molecular Weights of Volatile Substances

The first and most direct consequence of the adoption of Avogadro's theory is that if we weigh *equal volumes* of two gases it is obvious that we are weighing *equal numbers of the molecules of both gases.* Thus, since we find by experiment that 1 litre of oxygen weighs 16 times as much as 1 litre of hydrogen, we may conclude that *each molecule of oxygen weighs 16 times as much as each molecule of hydrogen*, since, by Avogadro's theory, there are the same number of molecules in 1 litre of each gas.

It is to be observed that this does not tell us the actual weight of a single molecule of oxygen or hydrogen, but only the relation between the two, so that the ratio, 1:16, represents the relative weight of the molecules of hydrogen and oxygen.

The relative weights of the molecules of all gases may be determined in a similar manner to the above by simply comparing the densities of the gases under the same conditions of temperature and pressure. An account of the experimental methods to be adopted for this purpose is given in Lesson II, pp. 8-14.

For the sake of convenience and uniformity, it is necessary to select some substance as a standard and compare the molecular weights of all substances with that of the standard material. Any substance may be chosen for this purpose, and at one time it was usual to take hydrogen as the standard substance. More recently it has been found convenient, for reasons explained on p. 62, to select oxygen as the standard substance. Now the molecule of oxygen, as we have just seen, is 16 times as heavy as that of hydrogen, and hence the molecular weight of any gaseous substance, compared with that of oxygen, can be ascertained either directly by determining the density of the gas compared with oxygen, or indirectly by comparing the density with that of hydrogen and then calculating. Now the weight of the molecule of any substance must obviously be equal to the sum of the weights of the atoms which are contained in it. Before going any further, therefore, it is necessary to ascertain *how many atoms there are in a molecule of the standard substance.* Taking first the case of hydrogen, this may be done by considering the combination of this gas with chlorine.

1. We know by experiment that 1 *volume* of hydrogen unites with 1 *volume* of chlorine to form 2 *volumes* of hydrochloric acid gas.

2. It follows from this, according to Avogadro's theory, that 1 *molecule* of hydrogen unites with 1 *molecule* of chlorine to form 2 *molecules* of hydrochloric acid gas.

3. Each of these molecules of hydrochloric acid gas must contain at least one atom of hydrogen, because the gas is a compound of hydrogen with chlorine; and hence it follows:—

4. That each molecule of hydrogen has yielded two separate atoms of hydrogen.

This chain of reasoning may be illustrated diagrammatically as follows:—

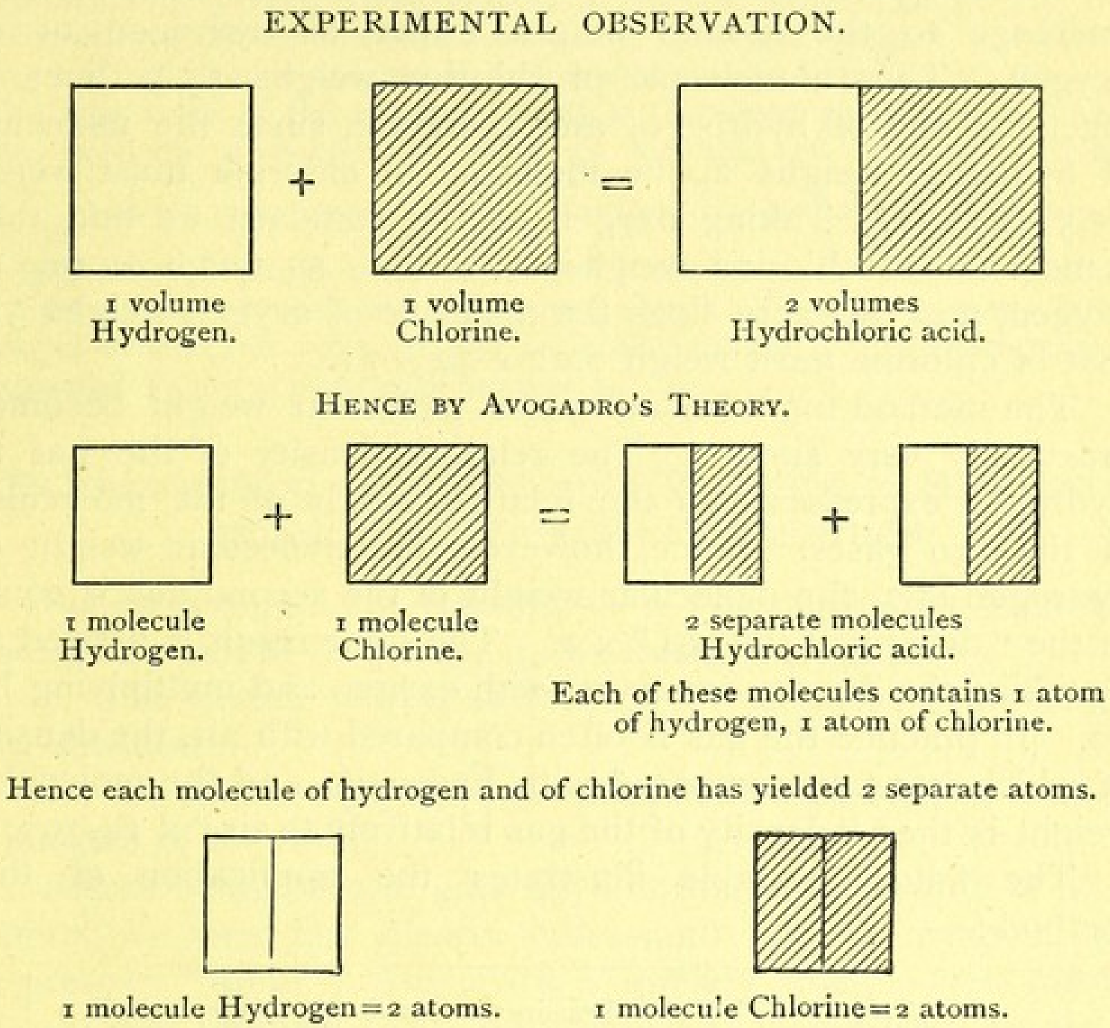


Fig. 1.

It thus appears that *each molecule of hydrogen consists of at least two atoms*, the same being true of the molecule of chlorine. No case has ever yet been found in which a single molecule of hydrogen yields more than two separate atoms of hydrogen, and hence the conclusion is drawn that it only contains two atoms.

When therefore the atomic weight of hydrogen is taken as 1, the molecular weight of hydrogen is 2.

It can be shown in a precisely similar manner that the molecule of oxygen also contains two atoms. Two volumes of hydrogen unite with one of oxygen, forming two volumes of gaseous water. Hence, as above, each molecule of oxygen must have yielded two atoms of oxygen. When, therefore, the atomic weight of oxygen is taken as 16, the molecular weight of oxygen is 32.

We are now able to express all molecular weights with reference to the atomic weight either of hydrogen or of oxygen. Thus a molecule of chlorine weighs 35.5 times as much as one of hydrogen, and therefore, since the molecule of hydrogen weighs 2, the molecule of chlorine must weigh $35.5 \times 2 = 71$. Taking oxygen as the standard we find that a molecule of chlorine weighs 2.22 times as much as one of oxygen, and therefore since the molecule of oxygen weighs 32, that of chlorine must weigh $2.22 \times 32 = 71$.

The method for calculating the molecular weight becomes practically very simple. The relative density of the gas to hydrogen expresses also the relative weight of the molecules of the two gases. Since, however, the molecular weight of hydrogen is 2, the molecular weight of the second gas is equal to the "density of the gas" × 2. The same result is arrived at by taking the density compared with oxygen and multiplying by 32. In practice the gas is often compared with air, the density of which is 14.39 compared with hydrogen and the molecular weight is then "density of the gas relatively to air" × 14.39 × 2.

The following table illustrates the application of this method:—

Substance.	Density compared with Hydrogen.	Approximate Molecular Weight.
Hydrogen	1	2
Oxygen	16	32
Chlorine	35.5	71
Carbonic acid gas	22	44
Carbonic oxide	14	28
Nitrous oxide	22	44
Nitric oxide	15	30
Ammonia	8.5	17
Marsh gas	8	16
Water	9	18

Determinations of molecular weight from the density are not very accurate, unless very elaborate corrections are made. This is owing to the fact that all gases deviate to some degree from the ideal state for which Boyle's law holds exactly. Hence Avogadro's theory is only approximately true, and the molecular weights determined by its aid are also not perfectly accurate. The number 16 given above for the density of oxygen compared with hydrogen is also only approximate and represents the nearest whole number to the true value. As long as it is accepted, no difference exists between the molecular weights expressed in terms of the atomic weights of hydrogen = 1 and of that of oxygen = 16. The true value of the relative density is, however, 15.88, so that when the molecule of oxygen is taken as 32, that of hydrogen becomes $\frac{1}{15.88} \times 32 = 2.016$, instead of 2. As already mentioned the molecular weight of oxygen = 32 is taken as the standard of comparison, and this number must be used for all accurate work. Except in cases where special accuracy is required, the molecular weight of hydrogen may be expressed by the approximate number 2.

Determination of the Atomic Weights of Elements which form Volatile Compounds

Before assigning a formula to a substance of which the molecular weight is known, it is necessary to learn—

1. The atomic weight of each of the elements contained in the substance.

2. The number of atoms of each element present in a single molecule of the body.

Before being able to gain any information on either of these points, we must first clearly understand what is meant by the expression "atom." Atoms are, as already explained (R. and L., p. 30), the ultimate particles of which all substances are made up. What we have to ask is, then, What is the smallest amount of each element which is ever found? This question can be answered by finding out *the smallest amount of an element which ever occurs in a molecule*, and this is taken as the atom.

Let us commence with oxygen. The amount of oxygen contained in a molecular proportion of any substance can be ascertained by determining the molecular weight of the substance, and then finding out by analysis the amount of oxygen present in this quantity of it.

Thus oxygen readily combines with carbon to form carbonic acid gas, which is found by analysis to contain 72.7 per cent of oxygen, whilst its molecular weight is 44.

Since 100 parts of carbonic acid gas contain 72.7 of oxygen, 44 parts contain $\frac{72.7 \times 44}{100} = 32$ of oxygen.

In order to find out whether the number 32 represents the atomic weight of oxygen, it is next necessary to compare the amounts of this element which are contained in the molecules of a number of its compounds. This is done in the following table, the amount of oxygen in the molecule being in each case calculated from the analysis of the substance.

Substance.	Percentage of Oxygen found by Analysis.	Molecular Weight.	Amount of Oxygen in the Molecule.	Number of Atoms of Oxygen in Molecule.
Carbonic acid gas	72.7	44	32	2
Nitrous oxide	36.4	44	16	1
Water	88.9	18	16	1
Carbonic oxide	57.1	28	16	1
Sulphur dioxide	50	64	32	2
Sulphur trioxide	60	80	48	3
Oxygen gas	100	32	32	2
Ozone	100	48	48	3

The least of these numbers is 16, and since no compound of the element is found the molecule of which contains less than 16 of oxygen, the atom of oxygen is said to weigh 16 times as much as the atom of hydrogen.

We thus see that the molecule of carbonic acid gas contains 2 atoms of oxygen, that of water 1 atom, that of oxygen itself 2 atoms, that of ozone 3 atoms, etc.

By exactly similar methods it is found that the atomic weight of chlorine is about 35.5, that of nitrogen 14, that of carbon 12, etc. The numbers obtained by the foregoing methods are only approximately correct, since the determination of the density of gases and vapours is attended by unavoidable errors; and, moreover, the different gases do not behave exactly in the same way when their temperature or pressure is altered.

The numbers which are actually taken to represent the atomic weights of the elements are therefore obtained by very carefully ascertaining the *equivalent* of each element by analysis, and then finding out what multiple of the equivalent is most nearly equal to the atomic weight, as determined by the method given above. Moreover these equivalents are determined by finding the amount equivalent to 8 parts of oxygen (p. 63). Thus strictly speaking 8 parts of oxygen combine with 1.008 of hydrogen, and these are therefore equivalent quantities. Now, as we have seen, when the atomic weight of oxygen is taken as 16, that of hydrogen is approximately 1, and the nearest multiple of 1.008 to this is $1.008 \times 1 = 1.008$. Hence 1.008 is taken as the exact atomic weight of hydrogen, 1 being only used as a convenient whole number when no great exactness is required.

Molecular Volume of Gases.—The volume occupied at N.T.P. by the weight of a gas equal to the molecular weight expressed in grams. is called the molecular volume of the gas, and it follows from Avogadro's theory that this is the same for all gases. The actual value of the molecular volume is determined by ascertaining the volume of 32 grams. of oxygen at N.T.P. and is found to be 22.4 litres.

SUMMARY

1. The molecular weight of a volatile substance is ascertained by determining the density of the vapour of the substance compared with some standard substance, such as oxygen, hydrogen, or air.

2. The molecule of hydrogen contains two atoms, and the molecular weight of hydrogen is (approximately) 2. The molecular weight of any other gas or vapour is therefore (approximately) equal to twice its density compared with hydrogen.

3. The atomic weight of an element is the smallest amount of it which is ever found in a molecule. It is ascertained by comparing the amounts of the element which are contained in the molecules of a number of its compounds.

4. Oxygen is now taken as the standard of comparison instead of hydrogen, the molecular weight being 32, the atomic weight 16, and the equivalent weight 8. The corresponding exact values for hydrogen are, molecular weight 2.016, atomic weight and equivalent weight 1.008. The molecular weight 2 and atomic weight 1 can be used for hydrogen when no great accuracy is desired.

LESSON II

EXPERIMENTAL DETERMINATION OF THE MOLECULAR WEIGHTS OF GASES AND VOLATILE LIQUIDS AND SOLIDS

In order to determine the molecular weight, it is necessary, as we have just seen, to ascertain the density of the substance in the state of gas. It is therefore possible to determine the molecular weight of any substance which can be converted into a gas without undergoing decomposition. The method employed is in principle always the same; the weight of a given volume of the gas or vapour is compared with the weight of an equal volume of air or some other gas of known density, measured under the same conditions of temperature and pressure. Practically somewhat different methods have to be used when the substance is a gas under ordinary conditions, and when it is a liquid or a solid.

1. Permanent Gases

For this purpose it is only necessary to determine the specific gravity of the gas, air being usually taken as the practical unit of comparison. A large glass balloon, capable of holding from 1 to 10 litres of the gas, is employed, and is first of all freed from air as far as is possible by the vacuum pump and weighed. In weighing a body of such large volume, it is essential to make allowance for the buoyancy of the air, since the body to be weighed appears to be lighter than it really is by an amount equal to the weight of the air which it displaces. This is best accomplished (Fig. 2) by suspending a vessel of similar size and shape to the other arm of the balance, by which arrangement the effect of buoyancy is neutralised, each of the vessels being affected in the same manner, and at the same time the uncertainties of calculation, due to the varying temperature, pressure, and moisture of the atmosphere are

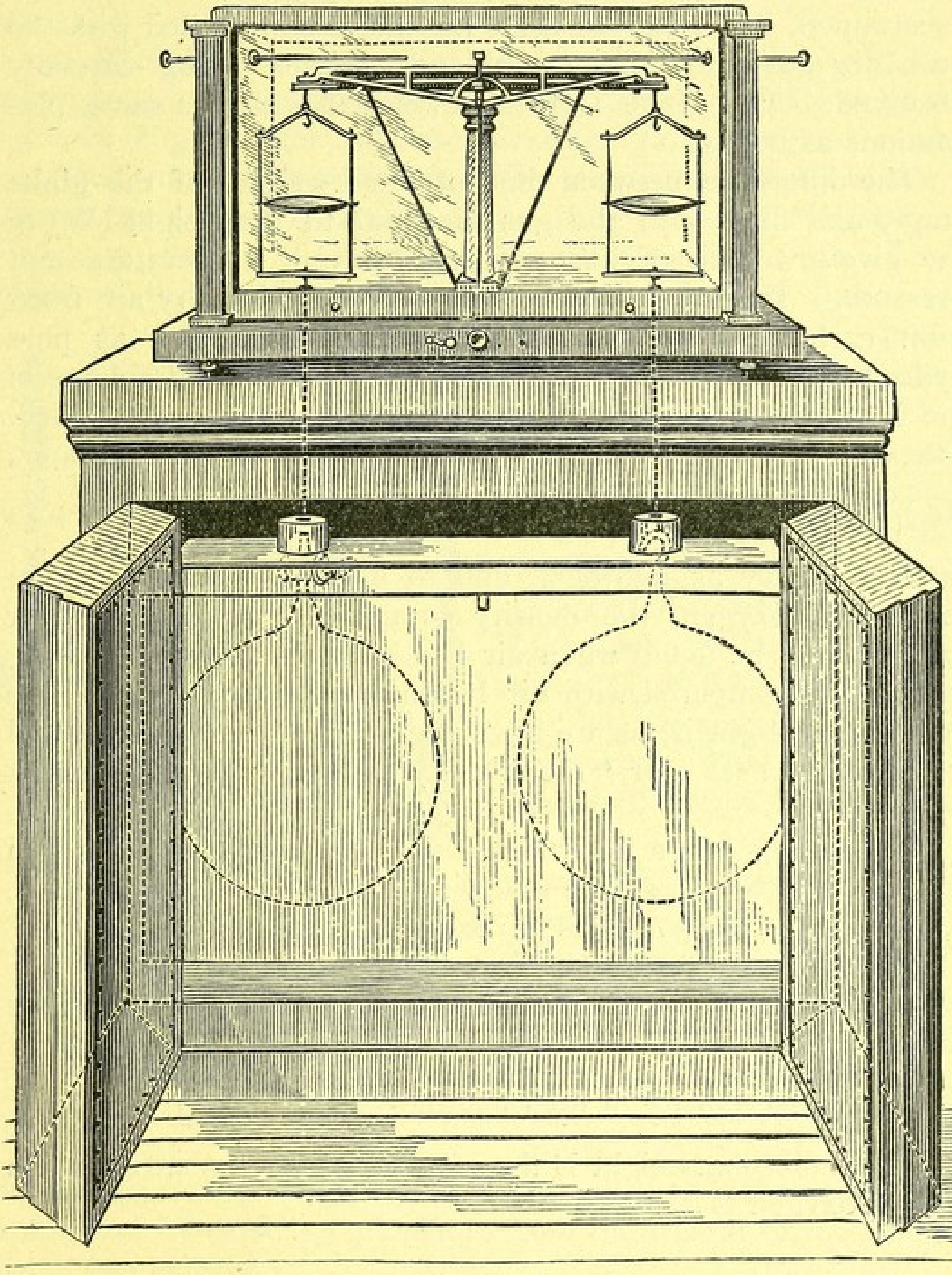


Fig. 2.

avoided, as well as any inaccuracy due to condensation of moisture on the surface of the glass.

As soon as the weight of the empty vessel has been ascertained, it is removed from the balance and filled with the pure dry gas, the temperature and pressure being carefully observed. The globe is then reweighed with the same precautions as before.

The difference between the corrected weights of the globe empty and filled with the gas is equal to the weight (W) of the given volume of gas at the observed temperature and pressure. The same globe is then filled with dry air freed from carbonic acid (or else with some gas, such as pure hydrogen, oxygen, etc.), and the weight of an equal volume of the latter (A), under the same conditions, thus ascertained. The specific gravity of the gas compared with air (or hydrogen, etc.) is then equal to $\frac{W}{A}$. Since air has been found to be 14.39 times as heavy as hydrogen and to have the density 0.9062 relative to oxygen, the density compared with hydrogen or oxygen may be found when air has been used by multiplying the density compared with air by one of these numbers. The molecular weight is, as we have seen, "the density compared with oxygen × 32" or "the density compared with hydrogen × 2."

Example.—In a determination of the density of hydrogen compared with oxygen the following results were obtained:—

Weight of 8.837 litres of oxygen at 0° and 760 mm. = 11.788 grms.

Weight of an equal volume of hydrogen under the same conditions = 0.7423.

Hence the density of hydrogen is $\frac{0.7423}{11.788} = 0.063$.

The molecular weight is therefore $0.063 \times 32 = 2.016$, when that of oxygen is 32.

2. Volatile Liquids and Solids

The specific gravity of the vapour of a liquid or solid can be determined in two ways: either by weighing the vapour which occupies a known volume under given conditions of temperature and pressure (Method of Dumas), or by measuring the volume occupied under given conditions by the vapour of a known weight of the liquid or solid (Method of Victor Meyer).

1. *Method of Dumas.*—For this purpose a thin glass globe is employed of 150-200 cc. capacity, having a finely drawn-out neck (Fig. 3); the exact weight of the globe, weighed in air and filled with dry air at the prevailing temperature and pressure, having been found, a small portion of the substance of which the vapour density is to be determined is brought inside. The globe is then heated by being plunged into a water or oil-bath raised to a temperature at least 30° above the boiling-point of the substance. As soon as the vapour has ceased to issue from the end of the neck, the latter is drawn out and hermetically sealed before a blowpipe, and the exact temperature of the bath as well as the barometric pressure observed. The bulb thus filled with vapour is carefully cleaned, allowed to cool, and accurately weighed. The point of the neck is next broken under water, which rushes into the globe, the vapour having condensed, and, if the experiment has been well conducted, completely fills it with the exception of a small bubble. The bulb is then weighed full of water, and its capacity calculated from the weight of the water which has entered.

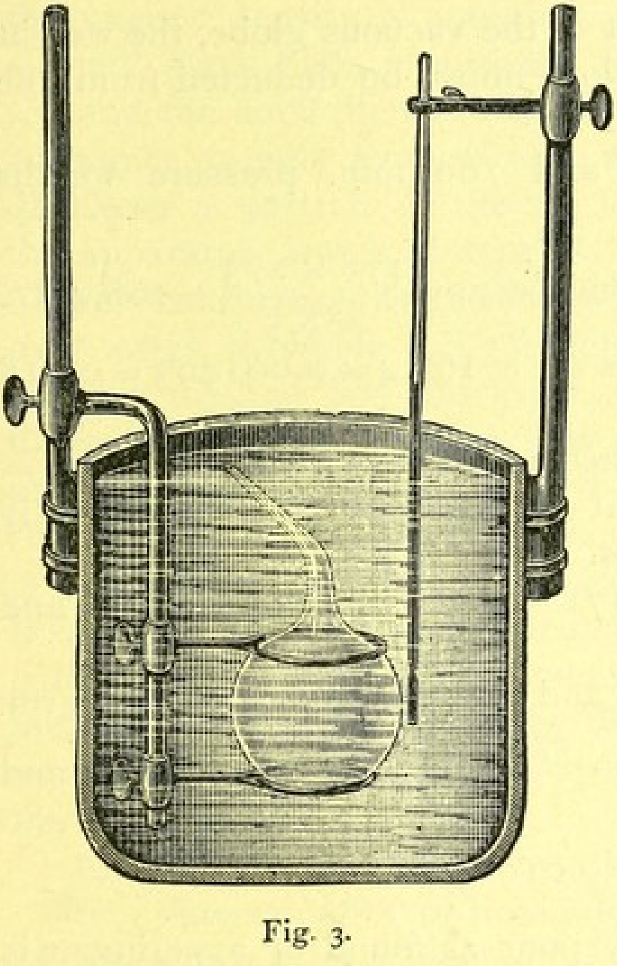


Fig. 3.

We have now all the data necessary for the determination. In the first place, we have to find the weight of the given volume of the vapour under certain conditions of temperature and pressure, and we have then to compare this with the weight of an equal volume of hydrogen or oxygen gas measured under the same circumstances. The following example of the determination of the vapour density of water may serve to illustrate the method of calculation :—

Weight of globe filled with dry air at 15.5° .	23.449 grms.
Weight of globe filled with vapour at 140° .	23.326 ,,
Capacity of the globe . . .	178 cc.

As the barometric column, 760 mm., underwent no change from the beginning to the end of the experiment, no correction for pressure is necessary.

In order to find the weight of the vacuous globe, the weight of the air contained in the globe must be deducted from the weight of the globe.

Now 1 cc. of air at 0° and 760 mm. pressure weighs 0.001293 grms.—

178 cc. of air at 15.5° would occupy $\frac{178 \times 273}{288.5} = 168.4$ cc. at 0°, so that the weight of this air is $168.4 \times 0.001293 = 0.218$ grms.

Hence the weight of the vacuous globe is $23.449 - 0.218 = 23.231$ grms.; and the weight of the vapour is consequently $23.326 - 23.231 = 0.095$ grms.

We must now find what 178 cc. of hydrogen at 140° and 760 mm. will weigh.

1000 cc. of hydrogen at 0° and 760 mm. weigh 0.0899 grm.

178 cc. at 140° contract to $\frac{178 \times 273}{413} = 117.6$ cc. at 0°, and these weigh $\frac{117.6 \times 0.0899}{1000} = 0.0106$ grm.

Hence the density of the vapour as found by experiment is

$$\frac{0.095}{0.0106} = 8.96,$$

and the molecular weight of water is $8.96 \times 2 = 17.92$.

If required the more accurate factor 2.016 may be used, in which case the result becomes $8.96 \times 2.016 = 18.06$.

In this example many minor corrections, such as the expansion of the glass globe, the error of the mercurial thermometer, etc., are not considered, but the above method, carried out as described, gives results which are sufficiently accurate when the object, as in this case, is to control the molecular weight of a compound.

2. *Method of Victor Meyer.*—The glass vessel (*b*, Fig. 4) filled with air is heated by the vapour of water or some other liquid placed in the bulb (*c*), which may if necessary be replaced by an air bath, until no more air is observed to pass out of the gas delivery tube (*a*). The cork (*d*) is then removed and a weighed quantity of the substance of which the vapour density is required, contained in a small glass bulb, is dropped into the tube (*b*), and the cork then quickly inserted. The substance rapidly evaporates and its vapour displaces a portion of the air contained in the apparatus, which is expelled through the delivery tube and collected in a graduated tube over water, in which it is carefully measured.

This method has the great advantage of dispensing with a knowledge of the temperature to which the tube is heated. It is to be borne in mind that what we require to know is the weight of such a quantity of air as is equal in bulk to the vapour under the same conditions. Whether this volume of air be measured at the temperature of the vapour or at that of the atmosphere, it has of course the same weight.

An example will make this clear.

In a determination of the molecular weight of chloroform, $CHCl_3$, heated by water vapour, it was found that 0.1008 grm. of substance displaced 20 cc. of air, measured over water at 15° and 770 mm. pressure.

The corrected volume of dry air is, therefore,

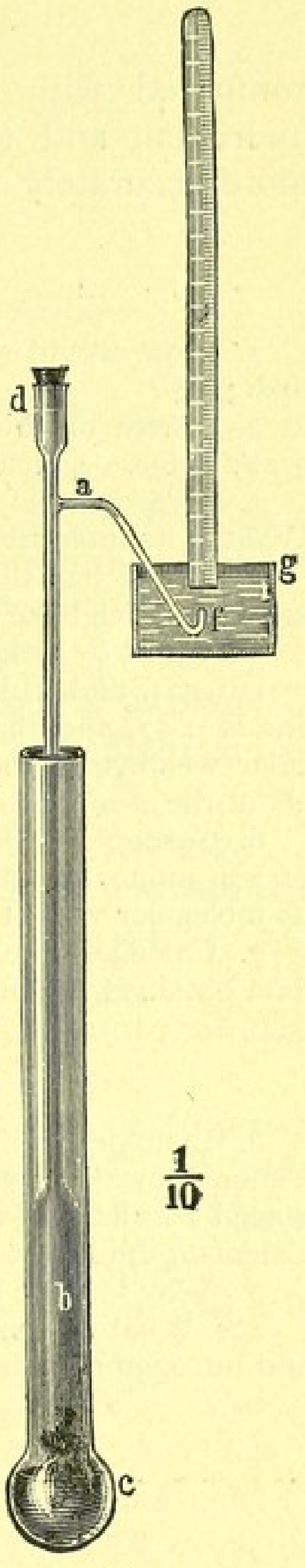


Fig. 4.

$$\frac{20 \times 273 \times (770 - 13)}{288 \times 760} = 18.9 \text{ cc.}$$

(13 is the vapour pressure of water at 15° in mm. of mercury).

The weight of this volume of air is $18.9 \times 0.001293 = 0.0244$ grm. The vapour density of chloroform is, therefore,

$$\frac{0.1008}{0.0244} = 4.13$$

compared with air, or $4.13 \times 14.39 = 59.4$ compared with hydrogen, and the molecular weight is $59.4 \times 2 = 118.8$ (or more accurately $59.4 \times 2.016 = 119.7$).

EXERCISES

1. How would you determine the molecular weight of sulphuretted hydrogen?

2. 1 litre of chlorine measured at 0° and 760 mm. pressure weighs 3.207 grms. Calculate from this the molecular weight of chlorine.

3. Hydrochloric acid gas has the density 1.26 compared with air. What is its molecular weight?

4. Ozone has the density 1.5 compared with oxygen. What is the molecular weight of this gas?

5. 1 part by weight of hydrogen unites with 3 parts of carbon to form marsh gas, and with 6 parts to form olefiant gas. The density of marsh gas is 0.57, and that of olefiant gas 0.97 (air = 1). Calculate the molecular weights of these gases. What information do these facts afford about the atomic weight of carbon?

6. Carbon oxychloride is formed by the union of equal volumes of carbon monoxide and chlorine, and has a density of 3.4. (Air = 1.) Find its molecular weight and formula.

7. Calculate the molecular weight of chloroform from the following data obtained by Dumas' method.

Capacity of bulb = 127 cbc.
Temperature of bath = 136° C.
Weight of vapour = 0.4524.

8. In a determination of the vapour density of carbon disulphide by Victor Meyer's method, it was found that 0.380 grm. of the liquid displaced 12.1 cbc. of air measured over water at 15° and 760 mm. pressure. Calculate the molecular weight of the substance.

9. Why has the atomic weight of 14.01 been assigned to nitrogen?

10. What reasons have we for supposing that the molecules of chlorine and nitrogen contain two atoms?

LESSON III

SOLUTION AND CRYSTALLISATION

It has already been pointed out that many solids dissolve in liquids, and that the amount dissolved in a given weight of the liquid, or, as it is called, the *solubility of the substance*, depends on the temperature, and generally becomes greater as the temperature rises, although this is not always the case (R. and L., p. 116).

A solution of a solid substance in water differs in many of its properties from pure water, some of the most important of these differences being the following :—

I. **Boiling-point and Vapour Pressure.**—A solution of a solid substance in water always boils at a higher temperature than pure water. Thus a saturated solution of common salt boils at 109°, whilst calcium chloride solution boils at 180°; and solutions of this kind are often used for obtaining a constant temperature higher than that of boiling water.

EXPERIMENT 1.—Prepare saturated solutions of common salt, potassium nitrate, and ammonium chloride, and ascertain their boiling-points, taking care that some of the solid salt is present throughout the experiment.

Now the boiling-point of a liquid is simply the temperature at which its vapour pressure is equal to the pressure of the atmosphere to which it is exposed (R. and L., p. 108). Hence it appears that a saturated solution of common salt has a vapour pressure of 1 atmosphere or 760 mm. of mercury at 109°, whilst pure water has the same pressure at 100°, its boiling-point, and at 109° has the greater vapour pressure of about 1.4 atmospheres. When compared at the same temperature therefore *a solution of a salt always has a lower* *vapour pressure than the pure liquid used as the solvent.* This is shown graphically in the curves (Fig. 5), which represent the vapour pressures at different temperatures of pure water and a 20 per cent solution of common salt, NaCl. Thus at 100° when the vapour pressure of water is 760 mm., that of the salt solution is only about 680 mm., whilst at 103° when that of the salt solution is 760 mm., that of the water is about 900 mm. A similar behaviour is shown by all solutions of solid substances in water, even when very dilute.

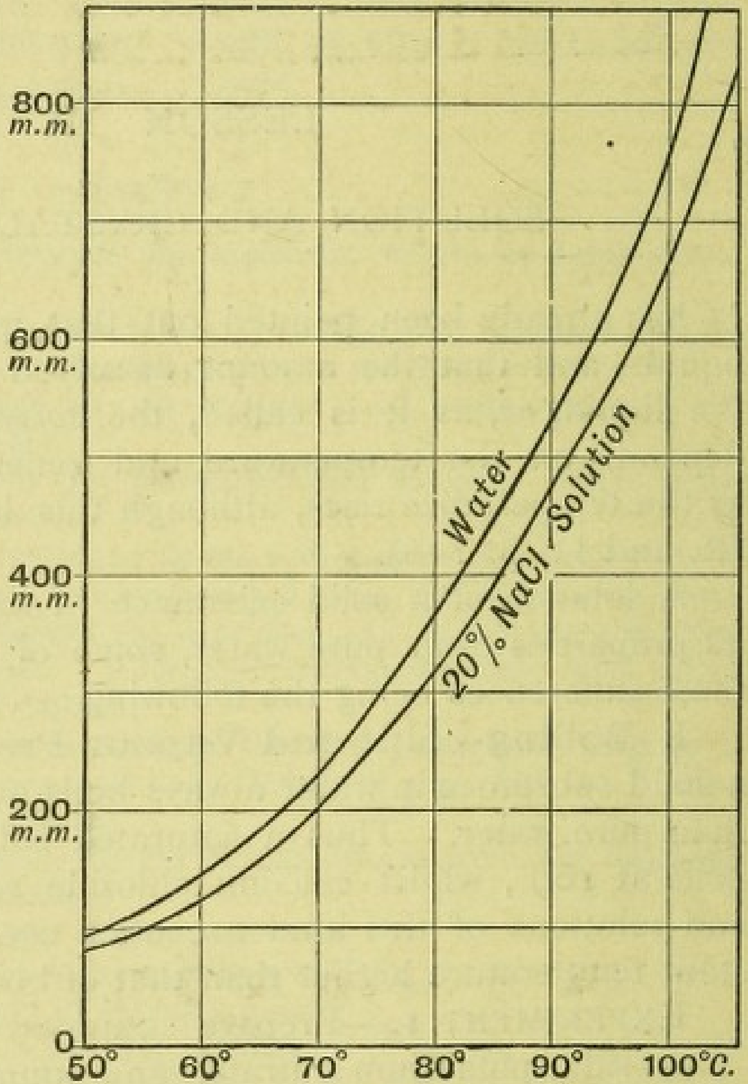


Fig. 5.

II. Behaviour on Cooling.—The freezing-point of a liquid is the temperature at which it becomes solid, and is a perfectly definite property of the liquid. When a pure liquid is cooled, it begins to solidify as soon as this temperature is reached, and the temperature remains constant until the whole has become solid, provided that the mass is well agitated.

When a solution of a salt or other solid is cooled, however, a number of different things may happen. Taking a solution of potassium nitrate, or ammonium chloride as one of the simplest examples, what occurs is as follows:—

1. When a saturated solution of potassium nitrate is cooled, a solid, identical in composition with the original salt, separates out. This is the usual result obtained by cooling a saturated

solution of a solid substance ; but in some cases the substance which separates out is not identical with that which was dissolved but contains water of crystallisation, some of the solvent having combined with the salt. This is the case, for instance, when anhydrous sodium carbonate or anhydrous calcium chloride is dissolved in water.

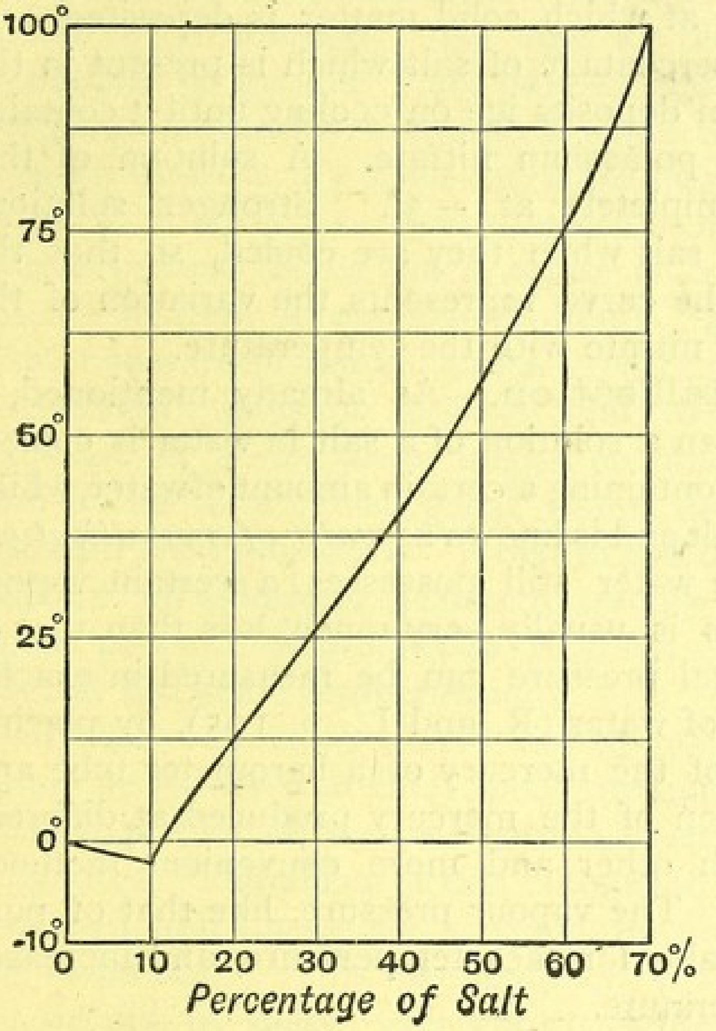


Fig. 6.

EXPERIMENT 2.—Make hot saturated solutions of potassium nitrate and anhydrous sodium carbonate, cool and allow to crystallise. Drain the crystals, and then thoroughly dry with filter paper. Test the original salts and the powders thus obtained by heating in a dry tube, and notice that the potassium nitrate, like the original salt, does not give off any moisture, whereas the crystallised sodium carbonate, unlike the original salt, gives it off freely.

2. When a sufficiently dilute solution of a salt is cooled, it is found that its temperature can be lowered below 0°, the freezing-point of pure water, without any ice being formed, but that at last a temperature is reached at which ice is formed. The solid matter which thus separates out from dilute solutions is pure ice, and does not contain any of the dissolved salt.

3. Whilst strong solutions deposit the *salt* when they are

cooled, and weak solutions deposit *ice*, it is found that there is a solution of intermediate strength which solidifies entirely when cooled to a sufficiently low temperature, a mixture of the salt and ice being formed.

The curve (Fig. 6) represents the behaviour of a solution of potassium nitrate when it is cooled. The horizontal lines show the temperatures at which solid matter is deposited, and the vertical lines the percentage of salt which is present in the solution. This solution deposits ice on cooling until it contains about 10 per cent of potassium nitrate. A solution of this strength solidifies completely at −3°. Stronger solutions than this deposit the salt when they are cooled, so that the ascending portion of the curve represents the variation of the solubility of potassium nitrate with the temperature.

Water of Crystallisation.—As already mentioned, it often happens that when a solution of a salt in water is cooled, crystals are deposited containing a certain amount of water, which is combined with the salt and is known as *water of crystallisation.* In such a crystal the water still possesses a certain vapour pressure, although this is usually very much less than that of pure water. The actual pressure can be measured in exactly the same way as that of water (R. and L., p. 105), by placing the crystal at the top of the mercury of a barometer tube and observing the depression of the mercury produced at different temperatures, although other and more convenient methods are usually employed. The vapour pressure, like that of pure water, has a definite value for each temperature, and increases rapidly with the temperature.

When a crystal containing water of crystallisation is exposed in a vacuum or to dry air, it loses water; the water present, in fact, evaporates, just as pure water or that contained in a solution would do under the same circumstances, but more slowly. The rate at which water is lost from crystals is usually very slow at ordinary temperatures, whereas at 100-200° it is much more rapid. Hence many crystals lose their water of crystallisation when they are heated to 100-200° in the air, or better in a current of dry air. The amount of water of crystallisation contained in the substance is estimated in this way, a weighed amount of the salt being heated at the proper temperature, which varies for different salts, and the weight of the dry residue then ascertained, the difference being due to loss of water.

Efflorescence and Deliquescence.—The behaviour of a crystal when exposed to the air depends on the vapour pressure of the water in the crystal and on the amount of water in the air, and in this respect resembles the behaviour of a solution. As long as the vapour pressure of a solution is greater than that of the moisture in the air, the solution steadily evaporates, since the air is able to take up moisture from it; if, on the other hand, the vapour pressure of the solution is less than that of the moisture in the air, the inverse process takes place, water is condensed from the air and the solution becomes more dilute. As the vapour pressure of the moisture in the air varies greatly in different places and at different times, it follows that a solution which would evaporate in a dry place might, on the other hand, become more dilute in a moist place, where the air was more nearly saturated with moisture. When exposed to air saturated with moisture, all solutions become gradually more dilute, since the vapour pressure of a solution is always less than that of pure water at the same temperature.

Crystals behave in a very similar manner to solutions. If the air be so dry that the vapour pressure of the moisture in it is less than that of the water in the crystal, the latter gradually evaporates. The effect of this is that the crystalline structure is destroyed, and the crystal is converted into an opaque mass or falls to powder. This phenomenon is known as *efflorescence*, and occurs in many well-known substances, among which, perhaps, the most familiar is washing soda, $Na_2CO_3 + 10H_2O$. On the other hand many substances, both such as contain water of crystallisation and such as do not, when exposed to the air actually become liquid, this phenomenon being known as *deliquescence.* An example of this is found in crystallised calcium chloride, $CaCl_2 + 6H_2O$.

In this case the vapour pressure is less than that of the moisture in the air, and the solution formed by the condensation of a very small amount of water vapour also has a low vapour pressure. Hence more vapour is condensed and the whole of the solid dissolves.

Many substances which do not contain water of crystallisation also deliquesce on exposure to the air, examples of this being potassium carbonate, caustic potash, etc.

EXPERIMENT 3.—1. Prepare cold saturated solutions of sodium carbonate, copper sulphate, and potassium carbonate, and expose them to the air for a considerable time in evaporating basins. The solutions of sodium carbonate and copper sulphate dry up, whereas that of potassium carbonate does not.

2. Expose solid potassium carbonate, crystallised copper sulphate, and washing soda to the air. The potassium-carbonate deliquesces, the copper sulphate remains unaltered, and the washing soda effloresces.

3. Expose the same three substances to dry air, either in a desiccator or in a glass tube, through which a current of air dried by sulphuric acid is passed. In this case the potassium carbonate remains unaltered, and both the washing soda and the copper sulphate lose water and become white and opaque.

4. Heat some powdered copper sulphate to 200° in an air bath. The salt, which remains unaltered in the air and only loses water very slowly in dry air at the ordinary temperature, rapidly loses water and becomes white.

Formation and Decomposition of Hydrates.—Many salts are capable of forming several different crystalline hydrates, which are deposited from their solutions at different temperatures. A striking example of this is ordinary calcium chloride. The long needle-shaped crystals deposited at the ordinary temperature have the formula $CaCl_2 + 6H_2O$, whilst the crystals deposited from a hot solution at about 45° have the composition $CaCl_2 + 2H_2O$. A solution of sodium sulphate, on the other hand, deposits crystals of the formula $Na_2SO_4 + 10H_2O$ at the ordinary temperature and at all temperatures up to 33°. Above this point, however, the crystals $Na_2SO_4 + 10H_2O$ can no longer exist, and at all temperatures above this the anhydrous salt, Na_2SO_4, is deposited. Now, an anhydrous salt generally has quite a different solubility from its hydrates, just as though it were an entirely different substance, and sodium sulphate is no exception to this rule. The hydrate, like most other salts, is *more* soluble in hot water than in cold, whereas the anhydrous salt is *less* soluble in hot water than in cold.

The effect of this is that when crystallised sodium sulphate is shaken up with water, the amount of sodium sulphate found in solution increases until the temperature reaches 33°, and then decreases, since above this temperature the solid substance is converted into anhydrous sodium sulphate, the solubility of which, as we have seen, decreases as the temperature rises. This behaviour is illustrated graphically by the curve (Fig. 7), in which the amount of sodium sulphate taken up by 100 parts of water is measured along the vertical lines and the temperature along the horizontal lines.

EXPERIMENT 4.—Make a saturated solution of Na_2SO_4 + $10H_2O$ by adding the powdered salt to about 25 cc. of water, stirring well and keeping the temperature at about 33° until an excess of the solid salt is present. Allow to settle, and pour off the clear solution into a beaker.

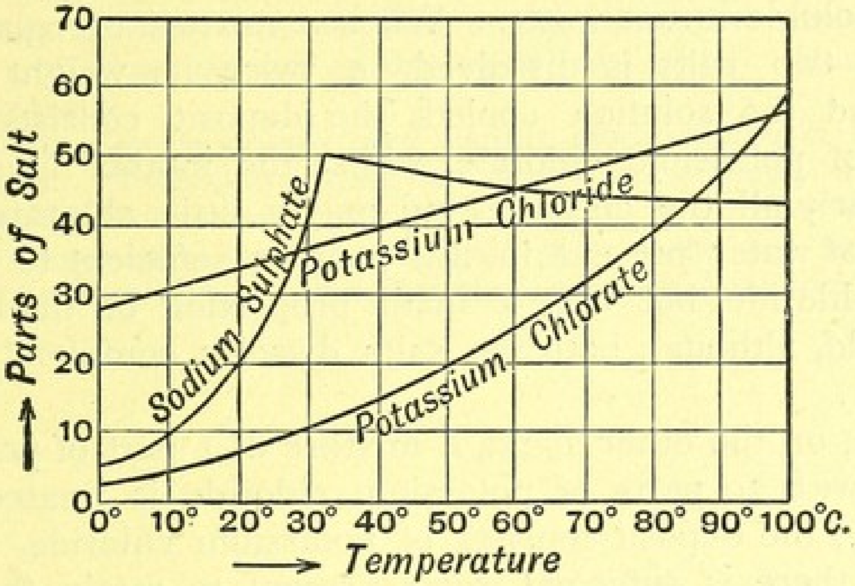


Fig. 7.

1. Heat a portion of this to boiling in a test-tube. Thin flakes or needles of the anhydrous salt immediately separate out.
2. To another portion add a few crystals of the salt and heat to boiling. The transparent crystals do not dissolve but decompose, losing their water and forming a white opaque powder of the anhydrous salt.

Recrystallisation.—When two substances differ much from one another in solubility in water, this property may be used for separating the two. If one of the two be quite insoluble, all that is necessary is to treat the mixture with water, filter and wash the residue. Thus, for example, a mixture of sand and salt could at once be separated into its constituents in this way.

When both the substances dissolve, but one is more soluble than the other in cold water, only a partial separation can be effected, and the method to be adopted depends entirely on the proportions of the two salts and on the difference in solubility. Thus (as shown by the curves in Fig. 7) potassium chlorate is sparingly soluble in cold water, whereas potassium chloride dissolves readily, whilst the two salts are almost equally soluble in hot water. When a mixture of equal parts of these two salts is dissolved in twice its weight of hot water and the solution cooled, the deposit consists almost entirely of potassium chlorate, whilst the mother liquor contains nearly all the chloride and only a little chlorate. The amount of water present in this case is sufficient to dissolve all the chloride, but only a small proportion of the chlorate in the cold, although both the salts dissolve completely in the hot water.

When, on the other hand, a mixture of 1 part of potassium chlorate with 20 parts of potassium chloride is treated in the same way, the deposit consists of potassium chloride, since in this case there is sufficient water present to retain the whole of the potassium chlorate but only part of the potassium chloride in solution in the cold.

EXPERIMENT 5.—Confirm the above statements, using mixtures of potassium chloride and potassium chlorate.

These two examples show how the process of recrystallisation can be used for purifying a salt, and this method is very frequently employed both in the laboratory and on the large scale for the purpose. Salts which are sparingly soluble in water are naturally the most easily obtained pure in this way, since a comparatively large amount of water can be used, in which most of the impurities remain dissolved, whilst the pure salt crystallises out. It is often necessary to repeat the process several times in order to ensure the complete removal of the impurities and the consequent purity of the product.

A knowledge of the facts discussed in this lesson is of great practical importance for the preparation of salts of the metals, and numerous instances will occur which illustrate the various points which have been mentioned.

Exercises on Lesson III

1. Compare the behaviour of a solution of a salt in water with that of pure water ; (*a*) when the two are heated ; (*b*) when they are cooled.

2. How can the vapour pressure of a crystal of washing soda be determined ?

3. Define the terms solubility, saturated solution, water of crystallisation, efflorescence, deliquescence.

4. When powdered copper sulphate is exposed to air saturated with moisture it deliquesces ; when exposed to the atmosphere it remains unchanged, and when exposed to dry air it loses water. How do you account for this ?

5. Sodium chloride is only very slightly more soluble in hot water than in cold. Potassium nitrate has the same solubility as sodium chloride at 25°, but is four times as soluble at 70°. How would you proceed to separate a mixture of equal parts of the two salts by recrystallisation from water ? Is it possible to separate them completely ?

LESSON IV

THE HALOGEN ELEMENTS

FLUORINE. CHLORINE. BROMINE. IODINE

CHLORINE, as we have seen, is distinguished from the other elements which have hitherto been described (Oxygen, Hydrogen, Nitrogen, Sulphur, and Carbon (see R. and L., pp. 67 *et seq.*), by several well-marked chemical properties, the most important of which are the two following :—

1. It combines directly with hydrogen and many of the metals ; producing with hydrogen an acid, and with the metals, salts.
2. It does not combine directly with oxygen, although its oxides can be prepared indirectly.

These properties are to a large extent shared by three other elements, fluorine, bromine, and iodine, so that these four are thus marked out as a *group* or *family* of elements.

It is found by experience that many such groups occur among the elements, the members of which, although they differ from each other in many ways, yet show a general resemblance in their properties and behaviour. Fluorine, chlorine, bromine, and iodine are known as the group of *halogen elements*, this name being derived from two Greek words meaning "salt producing," because they combine directly with the metals to form salts, many of which, such as common salt, fluorspar, potassium iodide, and sodium bromide are well-known substances.

A study of these four elements will clearly show what is meant by the term a group or family of elements.

The chief properties of chlorine and its compound with hydrogen have already been described (R. and L., pp. 170-186), and we therefore pass on to the study of the remaining three members of the family, which will be treated in the order in which they actually came to the knowledge of chemists.

Iodine, I, 126·92

Iodine is the name given to an element discovered in 1812 by the French chemist Courtois in the ash left when seaweed is burned. The name is derived from the Greek word meaning violet, and was applied to this element because of the beautiful violet coloured vapour which it forms.

The chemists who first examined this substance, Humphry Davy in England and Gay-Lussac in France, were at once struck by its remarkable similarity to chlorine, an element which had been known to chemists for many years, and which differed very much from all the other elements then known in its chemical properties.

Iodine occurs in extremely small quantities in sea-water, but is taken up by many seaweeds, so that the ash of these, known by the name of *kelp*, contains as much as 0.1-0.3 per cent of it. It is also found as sodium iodate in the sodium nitrate, or Chili saltpetre (Caliche), which occurs in South America, and is now usually manufactured from this source by a method which will be better understood after the properties of the iodates have been studied (p. 54).

In the kelp the iodine is present in the form of an iodide, mixed with bromides and much larger amounts of chlorides and sulphates. The mass is washed with water and the solution allowed to crystallise, the chlorides and sulphates being first deposited and the mother liquor thus rendered relatively richer in iodine. The liberation of iodine from these liquors may be effected in several different ways, which are illustrated by the following experiments :—

EXPERIMENT 6.—Take 1 cc. of a 10 per cent solution of potassium iodide, dilute it with 10 cc. of water, and add chlorine water drop by drop. A reddish-brown colour is first produced, due to the liberation of free iodine, which dissolves in the potassium iodide solution.

As more of the chlorine water is added, more of the potassium iodide is decomposed, until at last the whole of the iodine is liberated and a black precipitate of iodine is formed.

Allow to settle, and notice that the liquid above the precipitate is only coloured a faint yellow, because iodine only dissolves to a very slight extent in water, the solubility being about 1 part in 3750 parts of water.

Pour off the liquid, gently heat the crystals which are left, and observe the violet fumes produced.

We thus learn that iodine is liberated when chlorine is added to an iodide. The chlorine combines with the metal with which the iodine was formerly united, and the iodine is set free.

$$2KI + Cl_2 = 2KCl + I_2.$$

Experiment 7.—In a small 2-oz. retort place 3 grms. potassium iodide, 1 grm. finely-divided manganese dioxide, and 5 cc. dilute sulphuric acid. Heat gently, and allow the product to pass into a small flask cooled by a stream of water. Violet fumes are evolved, and iodine and a little water pass into the flask. Warm the neck of the retort to drive the condensed iodine into the flask, pour the mass out into a basin and then pour off the liquid, which is a solution of iodine in water, and use the crystals for the experiments described below.

This experiment teaches us that iodine is liberated when an iodide is acted on by sulphuric acid and an oxidising agent, just as is chlorine when a chloride is treated in the same manner (R. and L., p. 172). Hydriodic acid, HI (p. 28), is first formed, and is then oxidised by the oxygen of the oxidising agent to form water and free iodine,—

$$2HI + O = H_2O + I_2.$$

The whole reaction is expressed by the equation,—

$$2KI + 3H_2SO_4 + MnO_2 = 2KHSO_4 + MnSO_4 + 2H_2O + I_2.$$

Iodine was formerly manufactured in this way from kelp.

Experiment 8.—With the crystals of iodine obtained above try the following experiments.

1. Place a few crystals of iodine in each of three test-tubes, and add to the first water, to the second potassium iodide solution, and to the third chloroform. The solution in water is light yellow, that in potassium iodide is reddish-brown and much deeper in shade, and that in chloroform is violet.
2. Heat a little iodine in a dry test-tube. It melts and then vaporises, forming a beautiful violet vapour, which condenses in glittering crystals on the cool part of the tube. Iodine is often purified by this process, which is known as *sublimation*, by which it is separated from all non-volatile impurities.
3. Prepare a solution of starch by grinding a small piece of starch with a little water and pouring the mixture into about 100 cc. of boiling water. To 10 cc. of the cold starch solution add one drop of a solution of iodine in water. A deep-blue coloration is produced due to *iodide of starch*. Heat the liquid, and notice that the blue colour disappears but reappears on cooling. The compound with starch is decomposed when the temperature rises, but is again formed when it falls.

Properties of Iodine.—Iodine is an opaque, lustrous, blackish-gray solid, which forms crystals belonging to the rhombic system. It melts at 114° and boils at 184°, forming the characteristic violet vapour, which has a peculiar smell distantly resembling that of chlorine. The solid is a bad conductor of electricity.

Vapour Density and Molecular Weight. — The density of iodine vapour is found experimentally to be about 126 compared with hydrogen. Hence, by Avogadro's theory, its molecule weighs 126 times that of hydrogen. Since the molecular weight of hydrogen is 2, it follows that the molecular weight of iodine is $126 \times 2 = 252$ (or more accurately $126 \times 2.016 = 254$). Since, as we shall learn later, the atomic weight of iodine is 126.9, it appears that the molecule of iodine contains 2 atoms, and the molecular formula is therefore I_2.

At a very high temperature the vapour density of iodine is much lower than this. This phenomenon will be discussed later on in the chapter on Dissociation, p. 209.

Hydriodic Acid, Hydrogen Iodide, HI.

When equal volumes of iodine vapour and hydrogen are mixed, combination does not occur, as in the case of chlorine and hydrogen, when the mixture is exposed to light, or when an electric spark is passed through it or a flame applied. Even when the mixture is heated or passed through a red-hot tube, only a small proportion of it combines (see p. 30). A compound of the two elements can, however, be readily prepared by indirect means, and it is then found that the new substance is a colourless gas, which, like hydrochloric acid gas, forms a strongly acid solution in water. This gas, known as hydriodic acid gas, or hydrogen iodide, is formed by the action of acids on the iodides, just as hydrochloric acid is produced from the chlorides (R. and L., p. 176). Sulphuric acid, however, cannot be employed, because it readily oxidises hydriodic acid, forming water and free iodine, whilst it is itself reduced, sulphuretted hydrogen and sulphurous acid being formed. Nitric acid also acts as an oxidising agent to hydriodic acid gas, and it is therefore necessary to use phosphoric acid, which does not decompose the gas.

EXPERIMENT 9.—1. Place in a test-tube a little powdered potassium iodide, add a few drops of concentrated sulphuric acid and warm gently. A violent evolution of strongly acid fumes, coloured violet by iodine, is produced, accompanied by a smell of sulphur dioxide and sulphuretted hydrogen.

2. Repeat this experiment with concentrated nitric acid, and notice the liberation of iodine and the production of brown fumes by the reduction of the nitric acid.

3. Mix some powdered potassium iodide with a little powdered glacial phosphoric acid, add one drop of water and warm gently. Hydriodic acid gas is evolved, but if the heat applied be too violent, iodine is liberated.

Preparation of Hydriodic Acid.—A more convenient method for the preparation of the gas is to act on water with iodine in the presence of red phosphorus, when the following reaction occurs,—

$$P + 5I + 4H_2O = H_3PO_4 + 5HI.$$

The preparation by this method requires great care, and should only be attempted by experienced workers.

Five grms. of red phosphorus are made into a paste with 10 cc. of water in an 8-oz. flask, and 50 grms. of iodine are then added in small portions, the flask being well cooled after each addition. After standing for some time, the flask is fitted with a delivery tube and gently warmed, the gas being passed through a U-tube containing glass beads and a little red phosphorus to remove the last traces of iodine (Fig. 8). Collect a jar of the gas by downward displacement, and then make a solution in water by directing the stream of gas on to the surface of 25 cc. of water in a beaker, without letting the tube dip into the water, as otherwise water will probably rush back into the apparatus.

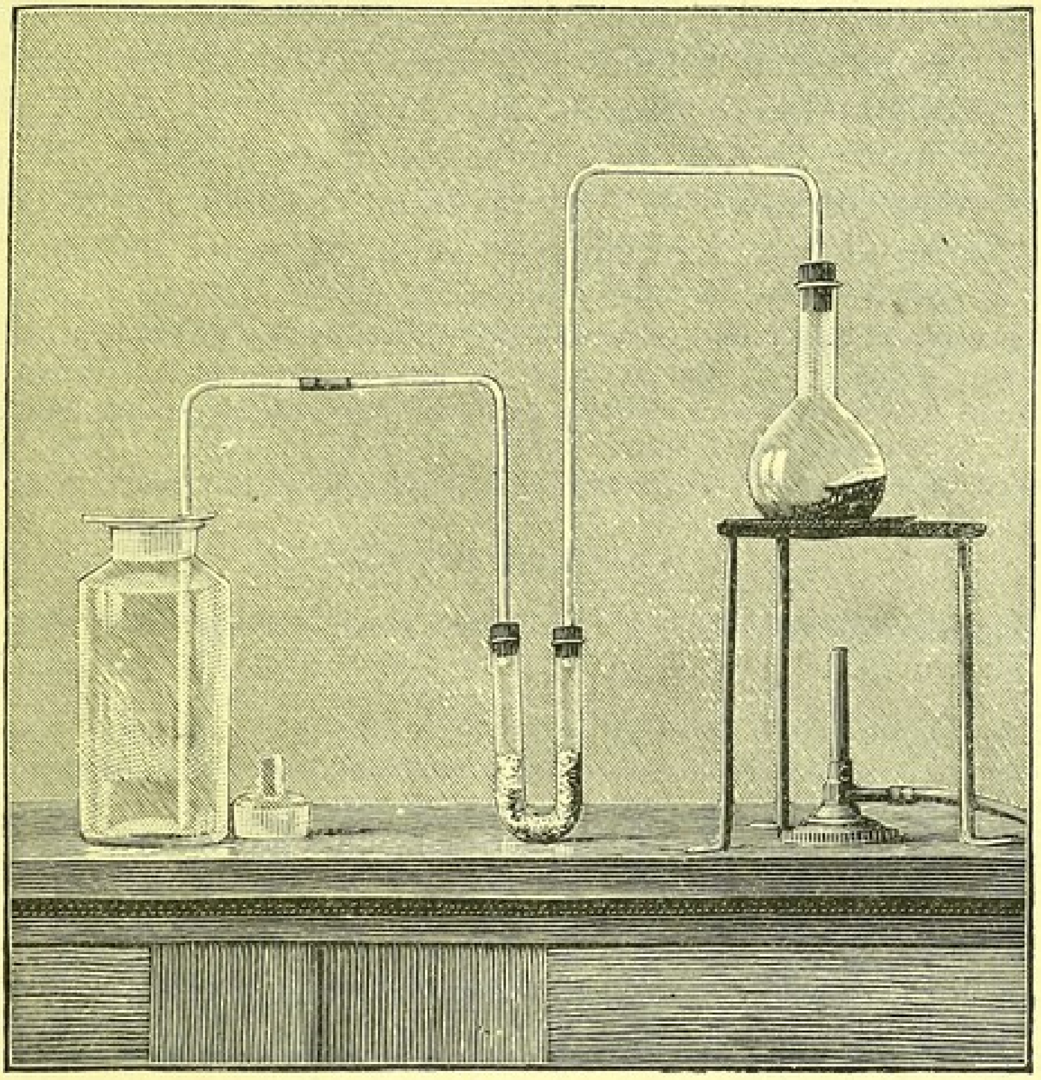


Fig. 8.

A dilute solution of the gas may be made by passing a current of sulphuretted hydrogen into water in which iodine is suspended,—

$$H_2S + I_2 = 2HI + S.$$

EXPERIMENT 10.—Pass a current of sulphuretted hydrogen into 25 cc. of water in which 3 grms. iodine are suspended and stir well. The iodine gradually disappears and a precipitate of sulphur is formed. Boil off the excess of sulphuretted hydrogen, filter, and test the solution as follows: 1. Add to sodium carbonate solution, effervescence occurs. 2. Add to granulated zinc, hydrogen is evolved. 3. Add chlorine water, iodine is liberated.

Reversible reactions.—Only a dilute solution of the acid can be prepared in this way, as it is found that when the concentration of the acid reaches a certain point (50%) the reaction no longer takes place. When concentrated hydriodic acid is treated with sulphur, on the other hand, the acid is decomposed and sulphuretted hydrogen is formed. This is an instance of a *reversible reaction*. The equation of this reaction is best written,—

$$H_2S + I_2 \rightleftharpoons 2HI + S.$$

the sign $\rightleftharpoons$ meaning that the change does not take place completely, but only up to a certain limit of concentration above which the reverse change occurs.

Many, perhaps all, chemical reactions are of this kind, but frequently the change is so nearly complete that the exact limit of concentration at which the reaction ceases cannot be determined.

Another good instance of such a reaction is that between gaseous iodine and hydrogen (p. 28):—

$$H_2 + I_2 \rightleftharpoons 2HI.$$

When iodine and hydrogen are mixed together at a constant temperature a certain proportion of each combines and a mixture of gaseous iodine, hydrogen and hydrogen iodide is produced. Exactly the same mixture is formed if the experiment is commenced with pure hydrogen iodide. Thus at 518° the mixture consists of—

	Per cent by volume.
H_2	12
I_2	12
HI	76
	100

whether the original gas was pure hydrogen iodide or a mixture of equal volumes of iodine vapour and hydrogen. These quantities of the gases are said to be in *chemical equilibrium* with each other at this temperature.

At a higher or lower temperature a new equilibrium is set up, more hydrogen iodide being present at low and less at high temperatures.

The combination between hydrogen and iodine occurs very slowly and hence this is not a practical method for preparing hydrogen iodide. It may be hastened by the presence of platinum which itself undergoes no alteration, but this does not alter the composition of the equilibrium mixture. The platinum in a case like this is termed a *catalytic agent* or *catalyst.*

Properties.—Hydriodic acid gas is colourless and invisible, fumes strongly in the air, and is extremely soluble in water, forming a fuming, strongly-acid liquid, which acts in most ways like hydrochloric acid. Thus it decomposes carbonates with effervescence, and dissolves metallic zinc with evolution of hydrogen. Hydriodic acid gas very readily decomposes into its elements when heated. Thus when a hot platinum wire is plunged into a jar of the gas, violet vapours of free iodine are at once produced. On exposure to air and light the solution very soon becomes dark coloured, because the acid is slowly oxidised, free iodine being liberated,—

$$2HI + O = H_2O + I_2.$$

EXPERIMENT 11.—Make a dilute solution of hydriodic acid by adding sulphuric acid to a solution of potassium iodide. Expose this to sunlight for a few minutes; notice the yellowish colour produced and test for free iodine with starch solution.

Composition of Hydriodic Acid.—Hydriodic acid gas, like hydrochloric acid gas, is decomposed by sodium amalgam, sodium iodide being formed and hydrogen liberated. The volume of this is found to be, as in the case of hydrochloric acid, exactly half that of the original gas (R. and L., p. 183).

One litre of the gas at N.T.P. is found to weigh 5.71 grms. and hence 22.4 litres weigh 128 grms. This quantity of the gas, however, yields half its volume, that is, 11.2 litres, of hydrogen, the weight of which is 1 grm. (or more accurately 1.008 grms.) and the remainder, 127 grms., consists of iodine. The composition of the gas is therefore by weight—

$$\begin{aligned} H &= 1 \\ I &= 127 \\ \hline &\ 128 \end{aligned}$$

Observe that we do not learn from the above the volume of iodine vapour yielded by 1 vol. of hydriodic acid gas. Experiment, however, shows that 127 grms. of iodine occupy the same volume as 1 grm. of hydrogen, when they are compared at the same temperature, and hence we know that hydriodic acid is formed from equal volumes of hydrogen and gaseous iodine.

Molecular Weight and Formula of Hydriodic Acid. Atomic Weight of Iodine.—The density of hydriodic acid gas being 64, its molecule must, by Avogadro's theory, be 64 times as heavy as that of hydrogen. Taking the molecular weight of hydrogen as 2, that of hydriodic acid gas is $64 \times 2 = 128$. This, as we have just seen, contains 1 part of hydrogen and 127 parts of iodine. Hence the atomic weight of iodine must be 127 or some fraction of this number, for the *atomic weight of an element* is the *smallest amount of it which is ever found in the molecule of any substance* (p. 5). As a matter of fact, among the very numerous volatile compounds of iodine, none has been found which contains less than 127 parts of this element in the molecule, and hence the atomic weight of iodine is taken as, approximately, 127, and the formula of hydriodic acid is HI.

The *exact* value of the atomic weight of iodine has been found to be 126.92 by the very careful determination of the composition of silver iodide (p. 64).

The Iodides.—Iodine combines directly with many of the metals forming iodides, most of which are soluble in water.

EXPERIMENT 12.—Heat a drop of mercury with iodine in a test-tube; a brilliant yellow and red sublimate of mercuric iodide is formed.

The salts of silver, lead, and mercury are the least soluble, and are precipitated when soluble salts of these metals are added to potassium iodide.

EXPERIMENT 13.—Add a solution of potassium iodide to—

1. Silver nitrate—yellow precipitate of silver iodide, insoluble in nitric acid and in ammonia,—

$$AgNO_3 + KI = AgI + KNO_3.$$

2. Mercuric chloride—red precipitate of mercuric iodide, soluble in excess of potassium iodide,—

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

3. Lead nitrate—yellow precipitate of lead iodide, which dissolves in hot water, especially in presence of excess of potassium iodide, and crystallises, on cooling, in brilliant golden spangles,—

$$Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3.$$

Exercises on Lesson IV

1. From what sources is iodine obtained, and how can it be prepared in the free state?

2. Describe the chief properties of iodine. How can it be detected in small quantities?

3. How can a solution of hydriodic acid be prepared? What occurs when it is treated with (*a*) sodium carbonate, (*b*) metallic zinc, (*c*) starch paste, (*d*) a drop of chlorine water?

4. What evidence have we that hydriodic acid is a monobasic acid?

5. How can the composition of hydriodic acid be determined?

6. Why is the formula I_2 given to iodine?

LESSON V

THE HALOGEN ELEMENTS (*Cont.*)

Bromine, Br, 79.92

THE name of bromine (from a Greek word meaning stinking) was given in 1826 to a new element discovered by the French chemist Balard, because of the intensely irritating and disagreeable vapour which it forms abundantly, even at the ordinary atmospheric temperature.

It occurs in the form of the bromides of sodium, potassium, and magnesium in very small quantity in all sea-water, which contains only about 0.006 per cent of this element. It is also found in rock-salt, in the vast deposits of potassium salts at Stassfurt (p. 182) and in many mineral waters. The bromides, like the iodides, are, as a rule, more soluble than the chlorides, and hence, when sea-water is concentrated, sodium chloride is first deposited, whilst the bromide remains in solution. When chlorine water is added to this concentrated solution, a similar reaction occurs to that which takes place with a solution of an iodide (p. 25). Bromine is liberated and the solution becomes of a deep-red colour, whilst, if the liquid be very concentrated, heavy red drops separate out. When the liquid is warmed, a deep red-coloured vapour is evolved, the smell of which will be found quite to justify the name chosen by Balard for the element,—

$$2KBr + Cl_2 = 2KCl + Br_2.$$

EXPERIMENT 14.—Pass a slow current of chlorine through a well-cooled solution of 1 grm. potassium bromide in 2 cc. water. Red drops of bromine fall to the bottom of the tube. Warm the liquid, and note the red fumes evolved. The chlorine may be prepared by warming a few crystals of potassium dichromate with concentrated hydrochloric acid in a test-tube provided with a cork and delivery tube.

Bromine is actually manufactured in this way from the potassium salts which occur at Stassfurt (p. 182). Chlorine (from D, Fig. 9) is passed through the concentrated solution (in A) obtained by allowing as much as possible of the potassium chloride to crystallise out. The vapour of bromine is then condensed (in *p*), and the liquid purified by distillation.

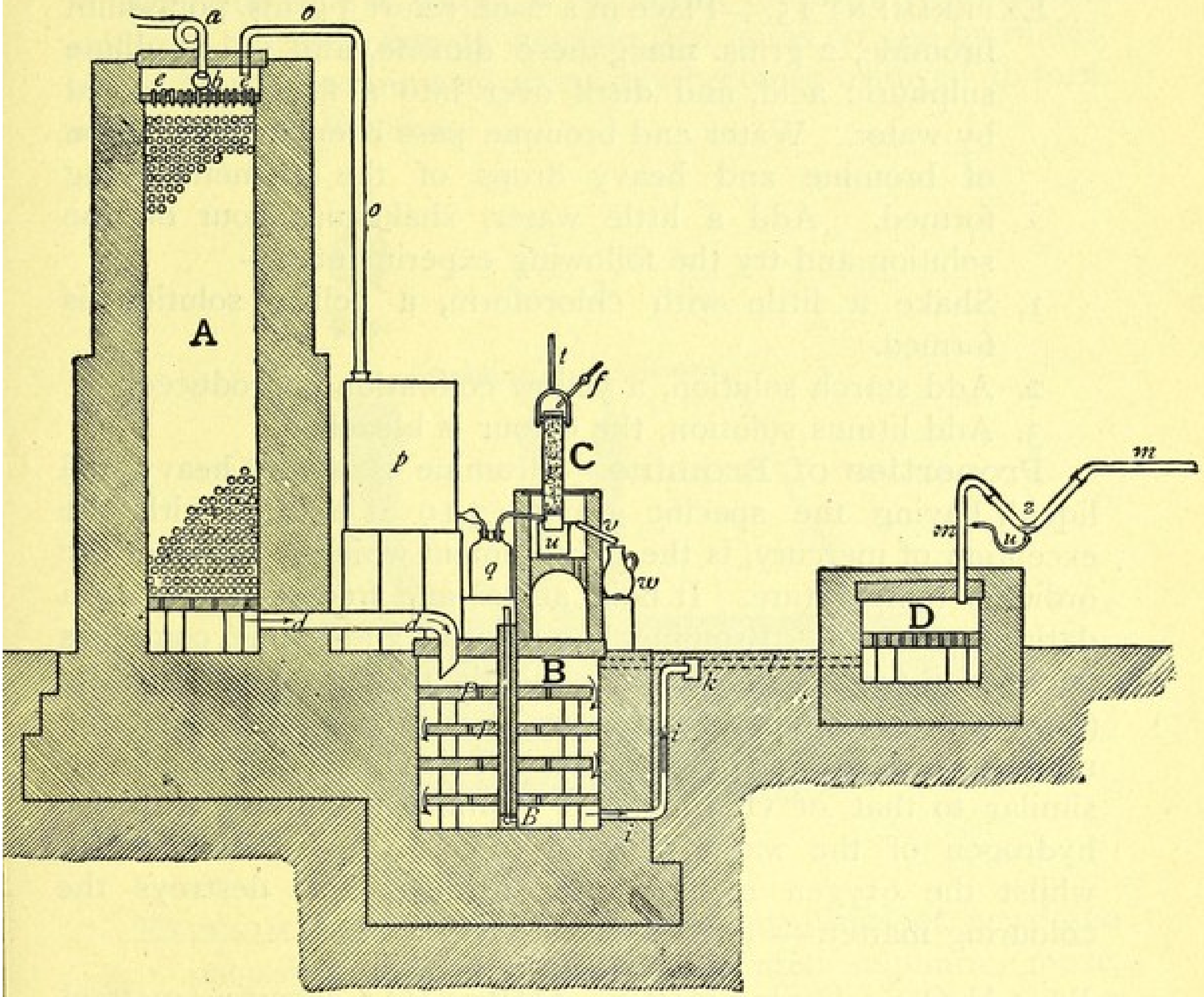


Fig. 9.

In the laboratory, however, bromine is usually prepared in a similar manner to chlorine and iodine. Hydrobromic acid is liberated in presence of an oxidising agent, such as manganese dioxide or potassium dichromate, which converts the hydrogen of the acid into water and sets free bromine,—

$$2KBr + 3H_2SO_4 + MnO_2 = 2KHSO_4 + MnSO_4 + 2H_2O + Br_2.$$

EXPERIMENT 15.—Place in a 2-oz. retort 3 grms. potassium bromide, 2 grms. manganese dioxide, and 10 cc. dilute sulphuric acid, and distil over into a flask well cooled by water. Water and bromine pass over, a red solution of bromine and heavy drops of the element being formed. Add a little water, shake up, pour off the solution and try the following experiments :—

1. Shake a little with chloroform, a yellow solution is formed.
2. Add starch solution, a yellow coloration is produced.
3. Add litmus solution, the colour is bleached.

Properties of Bromine.—Bromine is a very heavy, red liquid, having the specific gravity 3.19 at 0°, and, with the exception of mercury, is the only element which is liquid at the ordinary temperature. It boils at 59° and freezes at $-7°$ to a dark-brown solid. Bromine, like chlorine and iodine, combines very readily with many of the metals to form metallic salts (p. 39). Like chlorine, moreover, it bleaches many colouring matters, but not so vigorously. This bleaching action is similar to that of chlorine, the bromine combining with the hydrogen of the water present to form hydrobromic acid, whilst the oxygen of the water oxidises and destroys the colouring matter,—

$$Br_2 + H_2O + \text{colouring matter} = 2HBr + [O + \text{colouring matter}].$$

The deep red-coloured solution in water is known as bromine water, and is often used as an oxidising agent.

Vapour Density and Molecular Weight.—The density of bromine vapour compared with hydrogen is found to be 80 at a temperature of about 200°. Hence its molecular weight must be approximately $80 \times 2 = 160$. Since its atomic weight is 79.92, it follows that the molecule of bromine contains two atoms, and that it has the molecular formula Br_2.

Hydrobromic Acid, Hydrogen Bromide, HBr

Hydrogen does not combine with bromine nearly so easily as with chlorine. Thus, sunlight has no effect on a mixture of hydrogen with bromine vapour, but unlike hydrogen and iodine the two elements do unite completely when they are heated together.

As in the case of iodine, it is difficult to obtain hydrobromic acid gas by the action of concentrated acids on the bromides, because hydrobromic acid so readily becomes oxidised to form water and free bromine.

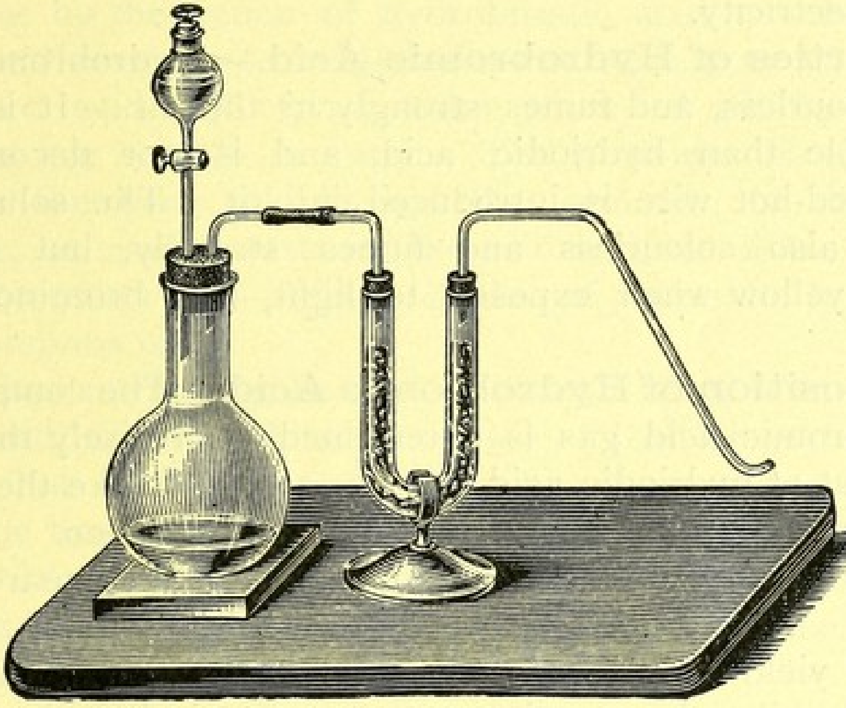


Fig. 10.

Experiment 16.—Treat separate quantities of powdered potassium bromide with concentrated sulphuric, nitric, and phosphoric acids, and compare the results with those obtained with potassium iodide (p. 28).

Preparation of Hydrobromic Acid.—The acid is therefore usually prepared in a similar manner to hydriodic acid by acting on water and red phosphorus with bromine,—

$$P + 5Br + 4H_2O = 5HBr + H_3PO_4.$$

This preparation requires great care, and should only be attempted by experienced workers.

Make a paste of 5 grms. red phosphorus and 10 cc. water in an 8-oz. flask fitted up as shown in Fig. 10, and allow bromine to drop slowly into the mixture. The gas evolved must be passed through a U-tube containing glass beads and a little red phosphorus to remove the last traces of bromine. The gas may be collected and a solution prepared in the manner described under hydriodic acid (p. 29).

A second way of making hydrobromic acid is to prepare it by the direct union of the two elements at a high temperature. This may be effected by passing hydrogen through warm bromine, and then allowing the mixture of gases to pass through a glass tube containing a coil of platinum wire heated to redness by electricity.

Properties of Hydrobromic Acid.—Hydrobromic acid gas is colourless, and fumes strongly in the air. It is much more stable than hydriodic acid, and is not decomposed when a red-hot wire is introduced into it. The solution in water is also colourless and fumes strongly, but rapidly becomes yellow when exposed to light, free bromine being liberated.

Composition of Hydrobromic Acid.—The composition of hydrobromic acid gas is determined in precisely the same way as that of hydriodic acid gas (p. 31), and, like the latter, hydrobromic acid yields half its volume of hydrogen.

The density of the gas is found to be 40.45, compared with hydrogen. Hence (see p. 7) 22.4 litres of it weigh 80.9 grms. and yield 11.2 litres of hydrogen, the weight of which is 1 grm., whilst the remaining 79.9 grms. is bromine. The composition of the gas by weight is, therefore—

H	1
Br	79.9
	80.9

Since the density of bromine vapour is about 80, it also follows that the gas is formed by the union of equal volumes of hydrogen and bromine vapour.

Molecular Weight and Formula of Hydrobromic Acid. Atomic Weight of Bromine.—All these are determined in the manner described under hydriodic acid.

The molecular weight of hydrobromic acid gas is $40.45 \times 2 = 80.9$, and since this contains 1 of hydrogen and 79.9 of bromine, the atomic weight of bromine must be 79.9 or some fraction of this number. No substance is, however, known of which the molecular weight contains less than 79.9 parts of bromine, and hence this is taken as the atomic weight.

The exact atomic weight is 79.92, and has been ascertained by the careful determination of the composition of silver bromide (p. 63).

The Bromides.—The bromides, like the iodides, can be obtained either by the direct union of the element with the metals, or by the action of hydrobromic acid on the metals or their carbonates, etc. Hydrobromic acid acts as a strong monobasic acid and forms salts, most of which, like the chlorides, are soluble in water. The bromides of silver and lead are the least soluble, and the formation of these can, therefore, be used as tests for the acid and its soluble salts.

EXPERIMENT 17.—Add a solution of potassium bromide to solutions of—

1. Silver nitrate—yellow precipitate of silver bromide.
2. Lead nitrate—white precipitate of lead bromide, soluble in hot water.

All the bromides are decomposed by chlorine, with liberation of free bromine and formation of the corresponding chloride, and this affords the best test for the presence of the acid,—

$$2KBr + Cl_2 = 2KCl + Br_2.$$

On the other hand, bromine decomposes all the iodides, free iodine being liberated and the corresponding bromide produced,—

$$2KI + Br_2 = 2KBr + I_2.$$

EXPERIMENT 18.—1. To a solution of potassium bromide add a drop of chlorine water, and shake up with a little chloroform. A yellow solution is obtained.

2. To a solution of potassium iodide add a drop of bromine water, and shake up with a little chloroform. A violet solution of iodine is obtained.

Exercises on Lesson V

1. What compounds of bromine occur in nature? Describe the preparation of the element.

2. What occurs when bromine water is added to solutions of the following substances: (*a*) potassium chloride, (*b*) starch, (*c*) hydriodic acid?

3. Describe the preparation of hydrobromic acid gas; (*a*) from bromine, (*b*) from potassium bromide.

4. Describe a method for showing that hydrobromic acid gas contains half its volume of hydrogen.

5. A solution of hydrobromic acid in water has the specific gravity 1.25, and contains 30 per cent of the acid. How much bromine is present in a litre of the solution?

LESSON VI

THE HALOGEN ELEMENTS (*Cont.*)

Hydrofluoric Acid, Hydrogen Fluoride, HF

FLUORINE derives its name from the mineral fluorspar, which is a compound of this element with calcium, and is of very common occurrence. When this mineral is powdered and heated with strong sulphuric acid, a fuming gas is given off, which has the remarkable property of attacking glass and rendering it opaque. (See p. 349 for an explanation of this action.) On this account it is necessary to prepare the gas in vessels of some substance which is not rapidly attacked, lead or platinum being the most convenient. The reaction is precisely similar to that by which hydrochloric acid is prepared from common salt,—

$$CaF_2 + H_2SO_4 = 2HF + CaSO_4.$$

EXPERIMENT 19.—Place in a shallow leaden dish 3 grms. powdered fluorspar, add 3 cc. concentrated sulphuric acid and warm gently. Copious acid fumes are evolved. Place over the dish a glass plate coated with bees' wax, on which a word has been written or a design sketched with a pin point. After about five minutes remove the plate, warm it gently, and remove the wax with a cloth. The exposed parts of the plate will be found to be etched.

The gas is very soluble in water, yielding a fuming, strongly-acid liquid, which also attacks glass and is therefore preserved in bottles of gutta-percha. It is manufactured by acting on fluorspar with sulphuric acid in a leaden retort, and conducting the gas by a leaden tube on to the surface of water contained in a platinum basin.

The strong solution of the acid does not act on metals so violently as does hydrochloric acid, but decomposes carbonates, liberating carbon dioxide and forming fluorides.

The acid gas is easily condensed to a fuming liquid, which boils at 19°, and is extremely dangerous to handle, since its vapour attacks the membrane of the lungs very violently, and the liquid produces serious wounds if it comes in contact with the skin, as does also the solution in water. The pure acid is prepared in an apparatus consisting entirely of platinum, by heating anhydrous acid potassium fluoride, $KF \cdot HF$, which decomposes into hydrofluoric acid gas and potassium fluoride.

Both the acid and its salts are used commercially for etching glass.

Composition of Hydrofluoric Acid. — It is very difficult to make experiments with this gas, because it so readily attacks glass and thus becomes decomposed. Hence its composition cannot be determined so simply as that of hydrochloric acid, etc., but must be ascertained in a less direct manner.

When hydrogen is passed over heated silver fluoride in a platinum tube, metallic silver is left and hydrofluoric acid gas produced. By weighing the silver fluoride taken and the silver left, the weight of the fluorine removed by the hydrogen is ascertained, whilst the weight of the hydrogen itself can be calculated from its measured volume. It has thus been found that 1 part of hydrogen by weight unites with 19 parts of fluorine.

Molecular Weight and Formula of Hydrofluoric Acid—Atomic Weight of Fluorine.—The density of the gaseous acid has been determined in an apparatus made of platinum, and has been found to be about 10 between the temperatures of 60°-90°. Hence the molecular weight of the gas is $10 \times 2 = 20$, and this is made up of 1 part of hydrogen and 19 parts of fluorine. Hence the atomic weight of fluorine must be 19 or some fraction of this number; and since no compound is known which contains less than 19 parts of fluorine in its molecular weight, this number is taken as the atomic weight, and the formula of the acid is HF. The accurate atomic weight, 19, has been determined by carefully ascertaining the composition of calcium fluoride (p. 67).

The determination of the atomic weight of fluorine strikingly illustrates the fact that the atomic weight of an element which forms volatile compounds is determined by a study of the compounds of the element and not of the element itself (see p. 5). Fluorine itself was not isolated until 1887, whilst its atomic weight was known as early as 1812.

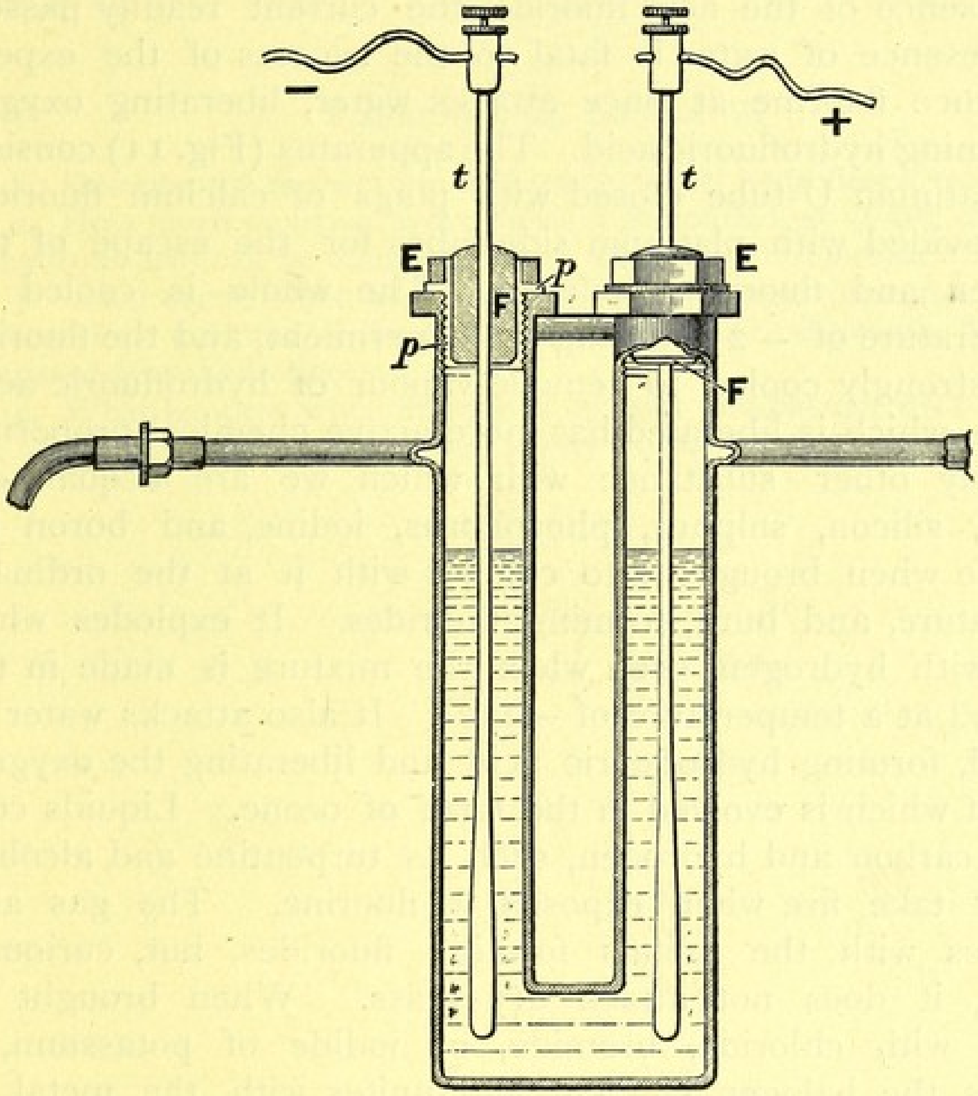


Fig. 11.

Fluorine, F, 19

The preparation of fluorine in the free state is of exceptional difficulty, and remained for many years an unsolved problem, in spite of the numerous attempts of chemists. In

1887, however, the French chemist Moissan succeeded in isolating it, and bringing to light its very remarkable properties.

Fluorine is prepared by passing an electric current through anhydrous hydrofluoric acid containing a little acid potassium fluoride (KF.HF) dissolved in it. The anhydrous acid itself is practically a non-conductor of electricity, like water, whilst in the presence of the acid fluoride the current readily passes. The presence of water is fatal to the success of the experiment, since fluorine at once attacks water, liberating oxygen and forming hydrofluoric acid. The apparatus (Fig. 11) consists of a platinum U-tube closed with plugs of calcium fluoride, and provided with platinum side-tubes for the escape of the hydrogen and fluorine produced. The whole is cooled to a temperature of $-23°$ during the experiment, and the fluorine is also strongly cooled to remove vapour of hydrofluoric acid. The gas which is liberated has more active chemical properties than any other substance with which we are acquainted. Carbon, silicon, sulphur, phosphorus, iodine, and boron all take fire when brought into contact with it at the ordinary temperature, and burn, forming fluorides. It explodes when mixed with hydrogen, even when the mixture is made in the dark and at a temperature of $-252°$. It also attacks water in the cold, forming hydrofluoric acid and liberating the oxygen, much of which is evolved in the form of ozone. Liquids containing carbon and hydrogen, such as turpentine and alcohol, at once take fire when exposed to fluorine. The gas also combines with the metals forming fluorides, but, curiously enough, it does not attack dry glass. When brought in contact with chloride, bromide, or iodide of potassium, it liberates the halogen element and unites with the metal to form potassium fluoride.

The gas has a faint, greenish-yellow colour, less green than that of chlorine, and can be liquefied at a temperature of $-187°$, forming a pale yellow liquid of specific gravity about 1.14. A very remarkable peculiarity of the element is that it cannot be made to unite either directly or indirectly with oxygen to form an oxide or oxy-salt, and this distinguishes it from all other known elements with the exception of helium, argon, and some other similar substances which appear not to enter into chemical combination of any kind.

Density and Molecular Formula of Fluorine.—The density of the gas has been roughly determined by weighing it in a small platinum vessel of known capacity. It was thus found to be about 19 times as heavy as hydrogen, and hence its molecular weight must be $19 \times 2 = 38$. Since, as we have seen, the atomic weight is 19, the molecular formula of the gas is F_2.

EXERCISES ON LESSON VI

1. Describe the preparation and properties of hydrofluoric acid.
2. How much aqueous hydrofluoric acid containing 36 per cent of the anhydrous acid can be obtained from 1 kilogram. of fluorspar?
3. What occurs when an electric current is passed through solutions of hydrochloric acid and hydrofluoric acid in water? How can fluorine be prepared from hydrofluoric acid?
4. What happens when fluorine is brought into contact with (*a*) water, (*b*) potassium chloride, (*c*) iodine, (*d*) hydrogen?

LESSON VII

THE ACTION OF ALKALIS ON THE HALOGENS—OXIDES AND OXY-ACIDS OF THE HALOGENS

WHEN chlorine is passed into a concentrated solution of caustic potash, the gas is rapidly absorbed, the liquid becomes hot, and after a time a white crystalline precipitate is formed, and when this is collected and purified by crystallisation from water it is found to be a new compound, quite distinct from potassium chloride. Thus it is only sparingly soluble in water, and its solution does not give a precipitate with silver nitrate. When the solid salt is heated it gives off oxygen abundantly, and the residue is then found to be easily soluble in water, to give a precipitate with silver nitrate, and to be in every respect identical with potassium chloride, KCl. Reducing agents such as zinc and sulphuric acid and sulphurous acid also convert the new salt into potassium chloride.

EXPERIMENT 20.—Set up an apparatus for the preparation of chlorine as shown in Fig. 12. Place about 50 grms. of lump manganese dioxide in the 12 oz. flask, pour on about 250 cc. of concentrated hydrochloric acid and warm gently, washing the chlorine through a little water placed in the small flask. The delivery tube leaving the small washing flask must be attached to a small inverted funnel, since a narrow tube might easily be stopped up by the separation of crystals. Pass the gas into a solution of 20 grms. caustic potash in 40 cc. water placed in a small beaker, and continue the operation until the liquid smells strongly of chlorine. Cool, pour off the clear liquid, wash the residue by decantation with a little water and recrystallise from hot water.

Filter off the crystals obtained, using a water-pump if possible, wash two or three times with small quantities of cold water and allow to dry.

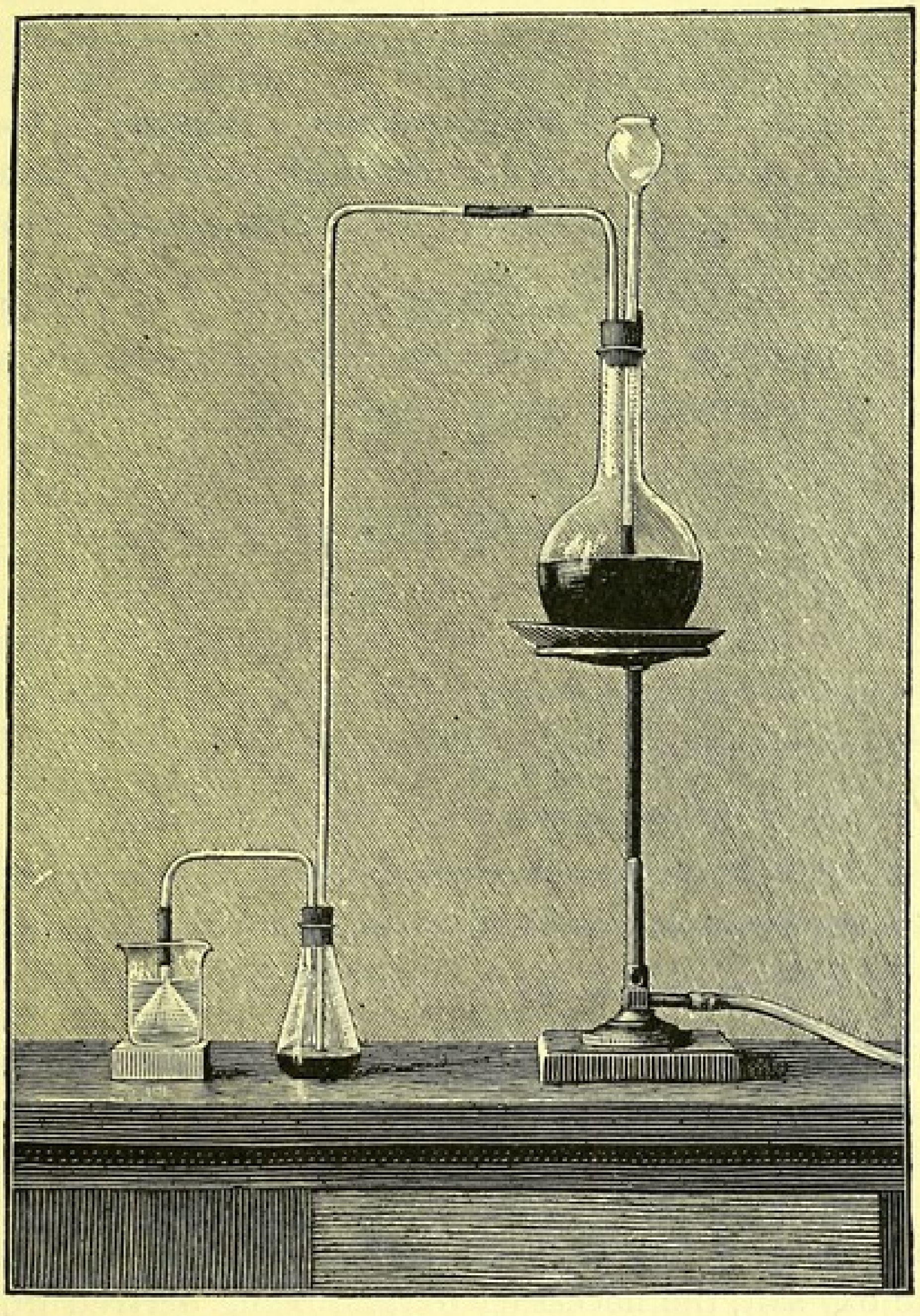


Fig. 12.

1. Dissolve some of the crystals in water and add a solution of silver nitrate,—no precipitate is produced.
2. Heat the dry salt in a test-tube and show, by means of a glowing splint, that oxygen is evolved. Dissolve the residue in water and add silver nitrate,—a white precipitate is now produced.

3. To a solution of the salt add dilute sulphuric acid and a piece of zinc. After a few minutes pour off the clear liquid and add silver nitrate,—a white precipitate of silver chloride is produced.
4. Boil a little of the solution with dilute sulphuric acid and a crystal of sodium sulphite, add nitric acid and silver nitrate,—a white precipitate of silver chloride is produced.

Evaporate the clear liquor obtained in the original preparation and obtain the white readily soluble crystals of potassium chloride.

A quantitative experiment shows that each grm. of the salt yields 0.61 grm. of potassium chloride and 274 cc. of oxygen weighing 0.39 grm.—

	Per Cent.		Ratio.
Potassium chloride	61 ÷ 74.2	= .82	1
Oxygen . .	39 ÷ 16	= 2.44	3
	100		

From these data the formula can be calculated in the ordinary way, and is found to be $KClO_3$. This salt has received the name of *potassium chlorate.*

The filtrate from the potassium chlorate contains potassium chloride, which can be isolated by evaporation, and experiment shows that exactly five times as much chlorine is present in the form of potassium chloride as in the form of potassium chlorate. These facts enable us to construct the following equation to represent the course of the reaction,—

$$3Cl_2 + 6KHO = 5KCl + KClO_3 + 3H_2O.$$

It is thus seen that one-sixth of the chlorine is oxidised to form the oxy-salt, the necessary oxygen being derived from the caustic potash.

When the action of chlorine on a solution of caustic potash is more carefully examined it is found to vary with the strength and temperature of the solution and particularly with the amount of chlorine used. In a hot solution, or in a concentrated solution with excess of chlorine, the change described above occurs, and potassium chlorate is produced. In a cold dilute solution, and when some free alkali is allowed to remain however, the action is different, an unstable salt, known as *potassium hypochlorite*, being formed, which contains only one atom of oxygen for each atom of chlorine, and has the formula $KClO$. The general nature of the reaction is the same as of that by which the chlorate is produced, but in this case one-half of the chlorine is oxidised instead of only one-sixth,—

$$Cl_2 + 2KOH = KCl + KClO + H_2O.$$

The new salt is very soluble in water, and hence is not precipitated like the chlorate. Moreover, it is very unstable, and when its solution is evaporated it is converted into a mixture of the chloride and chlorate,—

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

The salt is, moreover, decomposed by the carbonic acid of the air, and hence it is difficult to obtain it in the pure state. It readily gives up its oxygen to other substances, and thus acts as an oxidising agent.

EXPERIMENT 21.—To a solution of manganese sulphate add caustic soda and potassium or sodium hypochlorite solution. A dark coloured precipitate of the higher oxide of manganese is at once produced.

An alkaline solution of potassium chlorate, on the other hand, produces the same white precipitate of manganous hydroxide as is produced by caustic soda alone.

The action of caustic potash on bromine and iodine is similar to that which it has on chlorine. In both cases an oxidising solution is first obtained, which contains a salt corresponding with a hypochlorite and yields a black precipitate with a manganese salt. Potassium hypobromite, $KBrO$, and potassium hypoiodite, KIO, are, however, even less stable than the hypochlorite, and soon change into potassium bromate, $KBrO_3$, and potassium iodate, KIO_3, which correspond in composition with potassium chlorate.

EXPERIMENT 22.—Dissolve a few crystals of iodine in 10 per cent caustic potash. (*a*) Immediately add a few drops of the solution to manganese sulphate solution,—a dark brown precipitate is at once formed, showing the presence of hypoiodite. (*b*) Boil the caustic potash solution of iodine and then add as before to manganese sulphate solution,—a white precipitate of manganous hydroxide is formed, showing that the hypoiodite is no longer present, but has changed into iodate.

Similar results can be obtained with a hypobromite and hypochlorite, but a much more prolonged boiling is necessary.

No similar compounds of fluorine are known, since this element combines so vigorously with hydrogen that it at once decomposes the water present and liberates the oxygen.

Hypochlorous Acid, HClO.—When an excess of acid is added to the solution obtained by passing chlorine into dilute caustic potash, the whole of the chlorine is liberated. Hydrochloric acid and hypochlorous acid are first set free, and these immediately react, forming free chlorine and water,—

$$HCl + HClO = H_2O + Cl_2.$$

When, however, only a small amount of acid is added, the hypochlorous acid alone is set free and may then be distilled, a dilute solution of the acid passing over into the receiver. This is best carried out by adding dilute nitric acid to a solution of bleaching powder and then distilling.

\ EXPERIMENT 23.—Slake 10 grms. lime with water, and stir the mass up with about 50 cc. water. Through this pass chlorine until the liquid smells strongly of the gas. The solution then contains calcium hypochlorite and calcium chloride.

1. To a portion of this solution add excess of nitric acid—chlorine is evolved with effervescence, a *yellow* solution being formed.
2. To the remainder add nitric acid drop by drop, stirring after each addition until the liquid has a decidedly acid reaction to test paper. Place it in a small retort and distil into a small flask. A *colourless* solution of hypochlorous acid passes over, which may be recognised by its smell and by the fact that it bleaches litmus solution.

6 mins/

This acid, like chlorine, is a strong bleaching agent. The acid gives up its oxygen to the colouring matter, which is thereby converted into colourless substances, and is itself converted into hydrochloric acid,—

$$HClO + [\text{colouring matter}] = HCl + [O + \text{colouring matter}].$$

Chlorine Monoxide, Cl_2O.—When chlorine is passed over precipitated mercuric oxide a brownish-yellow gas is formed, which may be condensed at a low temperature to an orange coloured liquid,—

$$HgO + 2Cl_2 = HgCl_2 + Cl_2O\ ;$$

whilst in the presence of water hypochlorous acid is formed,—

$$HgO + H_2O + 2Cl_2 = 2HClO + HgCl_2.$$

The gas is a powerful oxidising agent, and is readily soluble in water, forming hypochlorous acid,—

$$Cl_2O + H_2O = 2HClO.$$

The liquefied gas explodes violently when shaken or heated. The gas has a molecular weight of 87, and decomposes when heated, two volumes of it yielding three volumes of decomposition products, one-third of which is oxygen and the remainder chlorine,—

$$2Cl_2O = 2Cl_2 + O_2.$$

Chloric Acid, $HClO_3$.—This monobasic acid, like hypochlorous acid, cannot be obtained quite pure, since its solution decomposes when it is concentrated. A dilute solution is obtained by adding sulphuric acid to a solution of barium chlorate,—

$$Ba(ClO_3)_2 + H_2SO_4 = 2HClO_3 + BaSO_4.$$

All the salts, called chlorates, are soluble in water, and are powerful oxidising agents, as is also the concentrated solution of the acid. All the salts decompose when heated, yielding oxygen and the chloride of the metal. The preparation of potassium chlorate on the large scale is described on p. 179.

Chlorine Peroxide, ClO_2, is a dark yellow gas, which is prepared by gently warming a solution of potassium chlorate in sulphuric acid,—

$$3HClO_3 = HClO_4 + 2ClO_2 + H_2O.$$

The gas explodes when heated, and is a powerful oxidising agent, setting fire to any organic matter with which it comes in contact.

\ EXPERIMENT 24.—1. Place *one small crystal* of potassium chlorate in a test-tube, add three drops of concentrated sulphuric acid and heat gently. A violent crackling is produced, due to the formation and explosion of chlorine peroxide.

2. Powder 1 grm. potassium chlorate and mix it carefully *by means of a feather* with 1 grm. sugar. *This mixture must not be ground in a mortar or shaken, as it is highly explosive.* Place it on an iron sand tray in a draught chamber and allow a single drop of concentrated sulphuric acid to fall upon it from the end of a glass rod. Chlorine peroxide is liberated, which instantly sets fire to the sugar, and this then burns completely at the expense of the oxygen of the chlorate.

Before the invention of friction matches this reaction was made use of for obtaining a light. A piece of wood was coated at one end with sulphur, covered with a thick paste of sugar, potassium chlorate, and a little gum, after which it was carefully dried. In order to obtain a light it was plunged into a small bottle containing sulphuric acid.

When potassium chlorate is heated with hydrochloric acid a mixture of chlorine with chlorine peroxide is evolved, which was formerly known as euchlorine. Potassium chlorate and hydrochloric acid are therefore frequently used to produce oxidation, and the gas evolved is often employed as a disinfectant.

Iodic Acid, HIO_3.—This acid is much more stable than chloric acid, and can readily be obtained by the action of an oxidising agent on iodine. For this purpose iodine is treated with highly concentrated nitric acid. A copious evolution of brown fumes occurs, and when the resulting solution is evaporated, iodic acid is left as a white powder, which is easily soluble in water,—

$$3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O.$$

The acid is also formed when chlorine is passed into water in which iodine is suspended,—

$$I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl.$$

Advantage is taken of this reaction in testing for bromine in the presence of an iodide. The iodide can readily be detected by adding chlorine water and starch paste. To detect the bromide, chloroform is added to the solution and then chlorine water drop by drop *is gradually added.* The whole of the iodine and bromine are liberated and dissolve in the chloroform, forming a purple solution. The excess of chlorine then converts the iodine into iodic acid, so that it is removed from the chloroform solution and leaves behind a brown solution of bromine. If no bromine be present, the chloroform is left colourless as soon as all the iodine has been removed.

EXPERIMENT 25.—Mix equal volumes of potassium iodide and potassium bromide solutions, and carry out the process described above.

When it is heated, iodic acid first loses water, forming iodine pentoxide,—

$$2HIO_3 = I_2O_5 + H_2O;$$

and this decomposes at a higher temperature into iodine and oxygen, no residue being finally left,—

$$2I_2O_5 = 2I_2 + 5O_2.$$

Potassium Iodate, KIO_3, can be prepared in a similar manner to the chlorate by dissolving iodine in caustic potash,—

$$3I_2 + 6KHO = KIO_3 + 5KI + 3H_2O.$$

It is only sparingly soluble in water, and when heated decomposes in a similar manner to potassium chlorate,—

$$2KIO_3 = 2KI + 3O_2$$

EXPERIMENT 26.—Dissolve 5 grms. iodine in as small a quantity as possible of 50 per cent potash solution, cool, filter, and drain the crystals. Recrystallise from hot water, and wash with a little cold water.

1. Heat some of the salt in a dry tube,—oxygen is evolved, a little iodine being also liberated towards the end of the reaction. Dissolve the residue in water and add silver nitrate,—a *yellow* precipitate of silver iodide is formed, insoluble in nitric acid.
2. To a solution of the salt add silver nitrate,—a *white* precipitate of silver iodate, soluble in nitric acid, is formed.

The salt can also be prepared by heating potassium chlorate with iodine,—

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2.$$

The iodine displaces the chlorine, and the latter combines with the excess of iodine to form *iodine monochloride*, ICl, a dark brown liquid. This reaction is of great interest, since chlorine displaces iodine from all compounds with hydrogen and the metals, whilst the inverse change occurs in the case just described.

Iodic acid rapidly oxidises hydriodic acid, water being formed and iodine liberated,—

$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

The effect of this is that when iodine is dissolved in an alkali and the solution then acidified, the whole of the iodine is liberated.

EXPERIMENT 27.—Dissolve a few crystals of iodine in 10 per cent solution of caustic potash and acidify with dilute sulphuric acid. The iodine is at once reprecipitated.

This property is utilised as a means of testing an iodide for a small amount of iodate. If the addition of dilute sulphuric acid liberates iodine, the oxy-acid is known to be present. A similar reaction occurs between hydrochloric acid and chloric acid, but in this case (p. 52), the reaction is not complete, and a mixture of chlorine and chlorine peroxide is evolved.

When iodic acid or an iodate is treated with sulphurous acid reduction takes place, and free iodine separates out,—

$$2HIO_3 + 5H_2SO_3 = I_2 + H_2O + 5H_2SO_4.$$

This reaction is employed for the manufacture of iodine from Caliche (p. 25). The concentrated mother-liquors obtained after the crystallisation of the sodium nitrate are simply treated with the necessary amount of sodium bisulphite, and the iodine then filtered off.

If, however, an excess of sulphurous acid be present, the iodine is finally converted into hydriodic acid,—

$$2HIO_3 + 6H_2SO_3 = 2HI + 6H_2SO_4.$$

Bromic Acid, $HBrO_3$, closely resembles chloric acid in its properties, but cannot be obtained in the pure state.

Potassium Bromate, $KBrO_3$, possesses very similar properties to the iodate, and may be prepared by dissolving bromine in concentrated caustic potash.

EXPERIMENT 28.—Add bromine drop by drop to 5 cc. of

50 per cent potash solution until the colour is permanent. White crystals of the bromate separate out. Recrystallise and test in the same way as potassium iodate (p. 53).

To a portion of the mother-liquor add dilute sulphuric acid in excess. The whole of the bromine is set free, just as in the case of a solution of iodine in caustic potash.

No oxide of bromine has ever been obtained, so that this element differs from both chlorine and iodine in this respect.

Perchloric Acid, $HClO_4$, and its Salts.—When potassium chlorate is heated the salt first melts to a thin liquid and rapidly gives off oxygen; after a time the liquid becomes thick and pasty, and it is then found to contain a new salt, potassium perchlorate, $KClO_4$, in addition to potassium chloride and unaltered chlorate. A portion of the chlorate, in fact, has been oxidised at the expense of some of the oxygen of the rest. The equation representing the change is somewhat complicated,—

$$10KClO_3 = 6KClO_4 + 3O_2 + 4KCl.$$

10 gms.

mall Scale

EXPERIMENT 29.—Heat 25 grms. of potassium chlorate in a porcelain basin (3 in. diameter) until the liquid becomes thick. Cool and grind the mass with cold water in a mortar, drain the crystals and wash with a little cold water. Place the washed crystals in a beaker and boil with concentrated hydrochloric acid until no more chlorine is evolved. Add water, filter, wash twice with cold water, and recrystallise from hot water. The cold water removes potassium chloride, whilst the hydrochloric acid decomposes the unaltered chlorate.

1. Heat some of the crystals in a tube. Oxygen is evolved and potassium chloride formed.
2. A solution of the salt gives no precipitate with silver nitrate.
3. Zinc and sulphuric acid reduce the salt to potassium chloride.
4. Boil a solution of the salt with sulphurous acid and then add nitric acid and silver nitrate. No precipitate is produced (compare potassium chlorate, p. 48).

The new salt is one of the least soluble of the salts of potassium. In its chemical properties it resembles potassium chlorate in many respects; thus it yields oxygen and potassium chloride when it is heated, and is reduced to potassium chloride by zinc and sulphuric acid. It is not, however, reduced by sulphurous acid, and is not decomposed by hydrochloric acid, and can thus be distinguished from a chlorate. When it is treated with strong sulphuric acid free perchloric acid, $HClO_4$, is formed, which is a stable substance and can readily be distilled. The acid is a fuming liquid and is a very powerful oxidising agent, which sets fire to wood and paper, and explodes violently when dropped on to freshly prepared charcoal.

Periodic Acid, HIO_4, and its Salts.—Barium periodate can be prepared from the iodate in a similar manner to that by which potassium perchlorate is obtained from the chlorate, and from this the other salts can be prepared by double decomposition. Periodates are also produced when an iodate is treated with chlorine in alkaline solution, the chlorine acting as an oxidising agent,—

$$NaIO_3 + Cl_2 + 2NaOH = NaIO_4 + H_2O + 2NaCl.$$

A large number of salts are known which differ in the amount of water they contain.

The free acid can be prepared by the decomposition of the barium salt with sulphuric acid, and it can also be obtained by the action of free iodine on perchloric acid,—

$$2HClO_4 + I_2 = 2HIO_4 + Cl_2.$$

This corresponds exactly to the formation of potassium iodate by the action of iodine on potassium chlorate (p. 53).

The acid is a white crystalline solid which decomposes when heated into water, oxygen, and iodine pentoxide,—

$$2HIO_4 = H_2O + I_2O_5 + O_2.$$

No corresponding salts or acid have been obtained from bromine.

SUMMARY

The action of caustic potash and other alkalis on the halogen elements takes place in two ways.

1. In a cold dilute solution it yields an unstable hypo-salt, which acts as an oxidising agent, and passes more or less rapidly into the corresponding chlorate, bromate or iodate.

2. When chlorine is passed in excess into a hot or concentrated solution, and when the solutions of bromine and iodine in an alkali are allowed to stand, a more stable salt containing three atoms of oxygen is produced, which loses oxygen when it is heated and also gives up its oxygen when it is treated with zinc and sulphuric acid, sulphur dioxide, and other reducing agents.

EXERCISES ON LESSON VII

1. What occurs when chlorine is passed into the following solutions: (*a*) cold caustic potash, (*b*) hot caustic potash, (*c*) alkaline potassium iodate, (*d*) potassium iodide?

2. Describe the preparation of iodine from Caliche. Give the reactions of hydriodic acid with (*a*) chlorine, (*b*) iodic acid; and those of iodine with (*a*) sulphuretted hydrogen, (*b*) sulphurous acid.

3. What is the action of chlorine on hydrogen, mercuric oxide and hypochlorous acid respectively in the presence of water?

4. Describe some of the chief compounds formed by iodine and contrast them with the corresponding compounds of chlorine and bromine.

5. How is potassium iodate prepared? How can the iodine contained in this salt be liberated?

6. Describe the preparation and properties of the oxides of chlorine.

7. 4 volumes of a mixture of chlorine and chlorine monoxide when decomposed by heat yielded 5 volumes of gas. What was the composition of the original mixture?

8. Describe the preparation of potassium perchlorate.

9. What is the effect of strong sulphuric acid on (*a*) potassium perchlorate, (*b*) potassium iodide, (*c*) potassium chlorate, (*d*) bromine, (*e*) potassium chloride?

LESSON VIII

THE GENERAL PROPERTIES OF THE HALOGEN ELEMENTS

THE four elements, chlorine, iodine, bromine and fluorine have now been described in the order of their discovery, and it remains to group together the various likenesses and differences which characterise their physical properties and chemical behaviour.

The first noticeable feature about these elements is that the formulæ both of the gaseous elements themselves and of their various classes of compounds are similar in form, or, as it is sometimes expressed, are of the same type, whilst the properties of these compounds are also closely analogous. If instead of writing F, Cl, Br, I, we use the letter R to express any one of these four elements, we have the following list of formulæ which may stand for any of them.

R_2	The gaseous element.
RH	A colourless gas which fumes in the air and dissolves in water, forming a strong monobasic acid.

In addition to these two, we have a number of oxy-compounds which are formed by chlorine, bromine and iodine, but not by fluorine.

KRO	A hypo-salt, unstable and easily decomposed.
KRO_3	A much more stable salt, sparingly soluble in water, decomposed by heat with evolution of oxygen, and readily reduced.
KRO_4	A still more stable per-salt (not formed by bromine).

Thus each of the four elements combines with hydrogen to form a monobasic acid, and unites directly with many metals to form salts. With the exception of fluorine they agree in forming similar series of oxy-salts, such as the hypochlorites, chlorates and perchlorates.

If we now compare the various compounds which they form, a very interesting gradation in properties is observed. Taking the compounds with hydrogen and the metals, we find that fluorine combines most energetically with both hydrogen and the metals, and that it is followed by the others in the order chlorine, bromine, iodine. This is proved by many facts. Thus fluorine explodes with hydrogen, even when the mixture is made in the dark and at a very low temperature; chlorine explodes with hydrogen when the mixture is heated, and also when it is exposed to direct sunlight or to a powerful artificial light; bromine cannot be made to explode with hydrogen by sunlight, but unites with it at a red heat almost completely; finally, iodine only combines slowly and incompletely with hydrogen, even when heated. The same gradation is shown by the fact that fluorine displaces chlorine, bromine and iodine from all their compounds with hydrogen and the metals; chlorine displaces both bromine and iodine, and bromine displaces iodine.

The order of intensity of chemical activity with respect to hydrogen and the metals is, therefore,—

	Fluorine.	Chlorine.	Bromine.	Iodine.
Atomic weight	19	35.5	79.9	126.9

It will be noticed that the atomic weights of these elements also exhibit a similar gradation, so that when the elements are arranged in the order of their atomic weights they are also found to be in the order of their chemical activities towards hydrogen and the metals.

A similar gradation is also noticed when the physical properties of the elements, such as their colour, boiling-point, specific gravity, etc., are compared.

	Atomic Weight.	Specific Gravity of Liquid or Solid.	Boiling-Point.		Colour of Vapour.
			Temperature Centigrade.	Absolute Temperature.	
Fluorine .	19	1.14	– 187°	86	Pale yellow.
Chlorine .	35.5	1.44	– 34°	239	Greenish-yellow.
Bromine .	79.9	3.19	59°	332	Red.
Iodine .	126.9	4.94	184°	457	Violet or blue.

Thus fluorine is a pale yellow gas, boiling at – 187° C. or 86° absolute temperature. The absolute temperature is obtained by taking – 273° C. as the zero and calculating the temperatures from this point. The specific gravity of fluorine in the liquid state is about 1.14. Chlorine is a greenish-yellow gas of much deeper colour than fluorine; it boils at – 34° C. (239° absolute), and has the specific gravity 1.44 in the liquid state. Bromine is a deep red liquid of specific gravity 3.19, and boils at 59° C. (332° absolute) forming a deep red vapour. Iodine at the ordinary temperature is a black-gray solid of specific gravity 4.94, and boils at 184° C. (457° absolute), forming a violet, or when very pure, a blue vapour. It will be noticed that the gradation of properties is most regular in the three elements, chlorine, bromine and iodine. Thus the atomic weight, boiling-point and specific gravity of bromine are numerically almost exactly the means of those of chlorine and iodine, whilst bromine is also intermediate between these two elements in colour, physical state and activity towards hydrogen and the metals. Fluorine, on the other hand, differs from the other three elements more than these do from one another, although, as we have seen, a strong general resemblance exists.

In their oxy-compounds, the relations of these elements are not quite so regular, although a certain gradual variation of properties is still to be observed. Fluorine forms no compounds whatever of this class. The compounds of chlorine and bromine are unstable, whilst those of iodine are, on the whole, more stable than the others. The order of chemical activity with regard to oxygen seems to be almost exactly the reverse of that towards hydrogen. Moreover, although chlorine displaces iodine from its compounds with hydrogen and the metals, the very opposite is the case with the oxy-salts and oxy-acids. As we have seen, iodine so readily displaces chlorine from potassium chlorate, that potassium iodate can be prepared conveniently by heating potassium chlorate with iodine.

SUMMARY

We have to notice *in the first place* that a striking general resemblance exists between the chemical properties of fluorine, chlorine, bromine and iodine. This shows itself in the formation of compounds of analogous composition, which can be prepared in a similar manner, and also resemble one another in general properties. *In the second place*, however, we see that this general resemblance is modified by a graduated variation in the properties, both of the elements themselves and of their compounds, which appears to correspond with the change of atomic weight as we pass from one element to the other. These two relations are found to hold in many of the families into which the elements are divided, and, as we shall see later, form the basis of the system of the classification of the elements.

EXERCISES ON LESSON VIII

1. Explain the reasons which have led chemists to classify fluorine, chlorine, bromine, and iodine in the same family of elements.
2. Compare the physical properties of the halogen elements.
3. How can the hydracids of the halogen elements be prepared? Compare the most important properties of these acids and their salts.
4. How do the oxides and oxy-acids derived from iodine differ from those derived from chlorine and bromine?

LESSON IX

EQUIVALENTS — DIRECT DETERMINATION OF THE EQUIVALENTS OF THE HALOGEN ELEMENTS AND SILVER — THE FOUNDATION OF QUANTITATIVE ANALYSIS—INDIRECT DETERMINATION OF EQUIVALENTS

Equivalents.—Those amounts of two elements which combine with, or replace each other chemically, are said to be *equivalent quantities*, or, more shortly, *equivalents* of the elements. Thus the equivalent of chlorine to hydrogen is 35.5 to 1, because 35.5 parts by weight of chlorine unite with 1 part of hydrogen ; again, the equivalent of sodium to hydrogen is 23 to 1, because 23 parts of sodium replace 1 part of hydrogen in its compounds with other elements, such, for example, as the halogens. In the same way the equivalent of copper to magnesium is 2.6 to 1, because 1 part of magnesium replaces 2.6 parts of copper in the sulphate, nitrate, and other salts of that metal.

It is possible to express these equivalents in many different ways. The simplest is to assume hydrogen as the standard and take as the equivalents of all the other elements those quantities which combine with or replace 1 part of hydrogen. For the reasons explained below, however, oxygen is chosen as the standard substance, and *the equivalents of all the other elements are those quantities which combine with or replace 8 parts of oxygen.*

Although the choice of one part of hydrogen as the standard of equivalents is in many ways very convenient, it has certain practical disadvantages. The determination of the equivalents of two elements is best carried out by the direct analysis or synthesis of a compound of the two. Hydrogen, however, either does not unite with a very large number of the elements, or forms compounds which from their properties are unsuitable for accurate analysis. Oxygen on the other hand forms compounds which, as a rule, are admirably adapted for this purpose. For this practical reason (among others) oxygen has been chosen as the standard substance in terms of which equivalents, atomic weights, and molecular weights are all expressed. In order, however, to avoid atomic weights less than one, the value for the atomic weight of oxygen has been fixed at 16, so that the equivalent is 8 and the molecular weight 32. When the atomic weight of hydrogen is taken as 1, the equivalent of oxygen is 7.94, and its atomic weight 15.88, so that when the atomic weight of oxygen is taken as 16, and the equivalent as 8, that of hydrogen becomes 1.008. For most purposes the atomic weight of hydrogen may be taken as 1 without any serious error being involved, and as a rule, in the present work, this is done, attention being called to the fact when the more accurate number is required. It must, however, be understood that strictly the value for hydrogen is 1.008, and that the real standard of comparison is not hydrogen, but oxygen, with the atomic weight 16, the equivalent 8 and the molecular weight 32.

Thus, since 8 parts of oxygen unite with 1 part of hydrogen, or 20 parts of calcium, or 107.88 parts of silver, all these quantities are equivalent.

When an element unites with another in two or more different proportions, it is said to have two or more different equivalents. Thus chlorine has the equivalent 35.5 in chlorine monoxide Cl_2O and 8.875 in chlorine peroxide, ClO_2.

Determination of the Equivalents of the Halogen Elements and Silver.—The most direct way by which the equivalent of two elements can be determined is to allow the two substances to unite and to weigh the quantities which are employed. In order that such a process may give accurate results it is necessary, in the first place, that the substances be perfectly pure, and in the second place that the weighed substances enter completely into combination. This method cannot be applied in every case because of the difficulty in fulfilling these conditions, but when possible it affords by far the most accurate results.

One of the most important instances of the use of this process is the determination of the equivalents of the halogen elements, chlorine, bromine and iodine, and silver, which was carried out with great care by the Belgian chemist Stas, and has since been repeated even more accurately in America by Richards. We will only here consider the cases of iodine and silver, since the other determinations were made in a somewhat similar manner.

In this experiment the first things required were pure silver and pure iodine, and great care was taken to obtain these. The silver was rendered as pure as possible by the ordinary methods, and was then distilled by means of the oxy-hydrogen flame in a cavity hollowed out of a block of quicklime. The iodine was dissolved in potassium iodide solution in order to remove all traces of bromine and chlorine, which decompose potassium iodide with liberation of iodine (p. 39), and was then precipitated by water, distilled and carefully dried.

A weighed amount of the pure silver was dissolved in nitric acid and thus converted into the nitrate, the action of the acid being similar to that which it has on metallic copper (R. and L., p. 156). This was then heated with sulphuric acid, which converted it into the sulphate. On the other hand the pure iodine was weighed and converted by the action of sulphurous acid into hydriodic acid.

The solutions of silver sulphate and hydriodic acid were then mixed, and the silver iodide which was formed allowed to settle.

Several preliminary experiments were first made in order to obtain an approximate value for the equivalent. The quantities were then so chosen that a slight excess of hydriodic acid remained in the clear liquid, and the amount of this was ascertained by adding a very weak solution of silver sulphate containing a known amount of the metal, until no further precipitate of silver iodide was formed, this method being one of extreme delicacy. The whole of the silver iodide was then washed with pure water to remove the sulphuric acid, and was finally dried and weighed. All these operations were carried out with great care and remarkably accurate results were obtained, as is shown by the following numbers, which give in grams. the total results of five experiments :—

Amounts taken.			
Iodine.	Silver.	Total.	Silver iodide obtained.
381.1262 +	324.2575 =	705.3837	705.3718

The total weight of silver iodide obtained was therefore only 0.0119 gram. less than the sum of the weights of the silver and iodine which were taken, or 1 part in 70,000, whereas if the experiment were conducted with perfect accuracy we should expect the two weights to be equal (R. and L., p. 17). This small difference represents the *experimental error* of the process. As a matter of experience it is found that operations such as those described above cannot be carried out without some slight loss of the material, so that in every such experiment a slight unavoidable error is introduced.

According to this experiment, therefore, 324.2575 parts of silver unite with 381.1262 parts of iodine, or 1 part of silver unites with, and is equivalent to, $\frac{381.1262}{324.2575} = 1.1754$ part of iodine.

The most accurate result, the average of several experiments, is that 1 part of silver is equivalent to 1.1765 parts of iodine.

The final step is to determine the equivalent of silver to oxygen, since, when this is known, the equivalent of iodine to oxygen can readily be calculated from the data obtained in the experiment just described. It is necessary to do this by an indirect method, since silver oxide is not a compound which can be obtained pure enough for accurate analysis, and the method which was chosen was that of determining the amount of silver which *replaces* the hydrogen equivalent to 8 parts of oxygen (*i.e.* 1.008 parts of hydrogen, see p. 62) in an acid. For this purpose iodic acid was chosen, which is known to contain 6 times as much oxygen as is necessary to convert its hydrogen into water. This acid was converted into the silver salt, and the silver iodate analysed in order to find out how much silver had replaced 1.008 part of hydrogen, and was therefore present in the salt along with $6 \times 8 = 48$ parts of oxygen. A weighed amount of the salt was heated, or reduced with an excess of sulphurous acid (p. 54), and the amount of silver iodide which was obtained carefully weighed. It was thus found that 282.8 parts of silver iodate yield 48 parts of oxygen and 234.8 parts of silver iodide. We know, however, from the previous experiments that 2.1765 parts of silver iodide contain 1 of silver and 1.1765 of iodine. Hence 234.8 parts contain $\frac{1.1765 \times 234.8}{2.1765} = 126.92$ parts of iodine and

$\frac{1 \times 234.8}{2.1765} = 107.88$ parts of silver. Hence 107.88 parts of silver are the chemical equivalent of 8 of oxygen. Moreover since 107.88 parts of silver unite with 126.92 parts of iodine, the latter number represents the equivalent of iodine.

The corresponding numbers for chlorine and bromine were obtained in a similar manner, the final result being as follows:—

Silver	107.88
Chlorine	35.46
Bromine	79.92
Iodine	126.92

The Foundation of Gravimetric Analysis.—The numbers given above express the composition of the chloride, bromide, and iodide of silver, and this information is of great practical value, because by making use of it a rapid and accurate method can be devised for analysing any salt of hydrochloric, hydrobromic, or hydriodic acid. We know that when any chloride is dissolved in water or dilute nitric acid, and a solution of silver nitrate is added to it, the whole of the chlorine unites with silver and forms insoluble silver chloride, which can be filtered off, dried, and weighed. Since we are acquainted with the composition of silver chloride we can calculate from this weight the amount of chlorine present, all of which has of course been derived from the original substance. An example will make this clear.

1.5 gram. of a salt, when treated in the way described above, yields 1.922 gram. of silver chloride. Required the percentage of chlorine in the salt.

We learn from the numbers given above that 107.88 parts of silver unite with 35.46 parts of chlorine to form 143.34 parts of silver chloride.

Hence, by reduction to unity,

1 part of silver chloride contains $\frac{35.46}{143.34}$ parts of chlorine,

and $\therefore$

1.922 part of silver chloride contains $\frac{1.922 \times 35.46}{143.34}$ parts of chlorine.

This amount of chlorine was furnished by 1.5 gram. of the salt, and hence 100 grams. of the latter contain—

$$\frac{1.922 \times 35.46 \times 100}{143.34 \times 1.5} = 31.7 \text{ grams.}$$

This is an instance of the method generally adopted for the gravimetric determination of chlorine in hydrochloric acid and its salts, and it must be remembered that in every such case use is made of our knowledge of the composition of silver chloride. The analysis of bromides and iodides is carried out on precisely the same principles.

Indirect Determination of Equivalents.—Every such analysis of a pure chloride can be used to calculate the equivalent of the metal present in the salt. The analysis of potassium chloride, for example, shows that this salt contains 47.56 per cent of chlorine, and therefore $100 - 47.56 = 52.44$ per cent of potassium. Hence it follows that 35.46 parts of chlorine are combined with $\frac{52.44 \times 35.46}{47.56} = 39.1$ parts of potassium, and this is therefore the equivalent of potassium. Numerous instances of the application of this indirect method of determining equivalents will be met with in the course of the following chapters. The method is indirect because it involves a knowledge of the composition of silver chloride, any error in which would of course cause a corresponding error in the equivalent of potassium.

The equivalent can be determined not only from the analysis of the *chloride* of the metal, but from that of *any salt*, provided that the composition of the substance into which it is converted is accurately known. Thus, for example, the equivalent of fluorine, an element which does not form an insoluble compound with silver, has been determined by converting calcium fluoride into calcium sulphate, 1 part of which is obtained from 0.573 part of the fluoride. It is known from other experiments that 1 part of calcium sulphate contains 0.294 of calcium, and therefore this amount of calcium is present in 0.573 part of calcium fluoride, the remainder, $0.573 - 0.294 = 0.279$, being fluorine. Hence, the equivalent of calcium being 20.05, that of fluorine is $\frac{0.279 \times 20.05}{0.294} = 19.$

Exercises on Lesson IX

1. Define the terms *equivalent* and *atomic weight*.

2. 1 gram. of a certain metal was found to yield 1.246 gram. of the oxide. Calculate the equivalent of the metal.

3. 2 grams. of metallic silver when heated in sulphur vapour yielded 2.2965 grams. of silver sulphide. Calculate the equivalent of sulphur. The equivalent of silver is 107.88.

4. 6.4406 grams. of diamond yielded on combustion 23.6114 grams. of carbonic acid gas. Calculate the equivalent of carbon.

5. 3.352 grams. of a certain metal when dissolved in caustic soda yielded 4161.6 cc. of gaseous hydrogen at N.T.P. What is the equivalent of the metal?

6. 1 gram. of silver was converted into the nitrate, and it was then found that 1.5380 gram. of potassium iodide was just sufficient to precipitate the whole of this as silver iodide. Calculate the equivalent of potassium. The equivalent of silver is 107.88, and that of iodine is 126.92.

7. 4.9474 grams. of the bromide of a metal exactly precipitated 6 grams. of silver in the form of silver bromide from a solution of silver nitrate. Calculate the equivalent of the metal.

8. 1 gram. of calcium carbonate when treated with sulphuric acid yields 1.3605 gram. of calcium sulphate. How can the equivalent of calcium be calculated from these numbers, and what other equivalents does the calculation involve?

9. 4.258 grams. of the chloride of a metal yielded with silver nitrate a precipitate of 5.869 grams. of silver chloride. Calculate the equivalent of the metal.

LESSON X

METALS AND NON-METALS

FROM the earliest times the bright and shining metals were distinguished from all other kinds of matter by a special name, and were regarded as a class apart. Only seven metals—gold, silver, mercury, copper, tin, iron, and lead—were known to the early alchemists who lived and worked in Alexandria. The endeavours of these ancient workers were nearly all vainly directed towards converting the last four of these metals into the noble metals, gold and silver, and the attempt was generally made by means of mercury or quicksilver, the liquid condition of which, joined to its great density and bright lustre, rendered it specially remarkable. These seven metals all agree in being heavy and possessing a peculiar lustre, which we now call a metallic lustre, and, with the exception of mercury, which is liquid, they are all malleable, that is to say, can be beaten out by the hammer into plates without breaking up into fragments, as do such substances as glass and pottery, which are said to be brittle.

As time went on other substances were discovered, which, like the seven metals, were bright and heavy, but, unlike them, were brittle. These were such substances as zinc, bismuth, and antimony, and for a long time many workers at chemistry refused to recognise them as metals, but called them semi-metals or bastard metals.

The further progress of chemistry, however, has revealed the fact that the seven metals of the ancients and the semi-metals discovered by their successors are not only alike in outward appearance, but also in chemical properties, and this was fully recognised at the close of the eighteenth century.

All these metals unite, directly or indirectly, with oxygen to form *basic* oxides, that is, oxides which react with acids to form salts. Thus copper oxide is converted by hydrochloric acid into copper chloride; litharge or oxide of lead, when treated with nitric acid, yields lead nitrate; zinc oxide when dissolved in sulphuric acid yields zinc sulphate; and so on for the others.

Most of the so-called non-metallic elements then known presented a complete contrast to these metals, both in their physical and chemical properties. They were either gases, such as hydrogen, oxygen, nitrogen, and chlorine, or substances like carbon and sulphur, quite devoid of any similarity to the metals in appearance. Their oxides, moreover, were either indifferent substances (nitric oxide, carbonic oxide, etc.), or yielded strong acids when brought into contact with water.

To sum up the chief properties of the two classes into which the elements were divided.

The Metals were characterised by—

1. Metallic lustre.
2. Opacity.
3. High density.
4. Great conductivity for heat and electricity.
5. The formation of basic oxides, which reacted with acids to form salts.

The Non-Metals, on the other hand, were devoid of these qualities.

1. They had no metallic lustre.
2. Many of them were transparent.
3. They had comparatively low densities.
4. They were bad conductors of heat and electricity.
5. They formed oxides which united with water to produce acids.

An entirely new class of substances was brought to light in 1807, when Davy succeeded in decomposing the alkalis, which had long been regarded as elementary bodies. He thus obtained the elements known as sodium and potassium, about which he himself said: "These both agree with metals in opacity, lustre, malleability, conductive powers as to electricity, and in their qualities of chemical combination." In one important respect, however, they differ from all the metals which had up to that time been discovered. They are both lighter than water, and hence many chemists refused for some time to consider them as true metals. In the end, however, it has been admitted that they are as truly metals as copper or zinc, since like these they form basic oxides and displace the hydrogen of acids, forming salts.

The opacity of the metals was another property, which, as we have seen, was at one time thought to distinguish them from the non-metals, many of which are transparent. It has, however, been found that many of the metals are also transparent when a very thin layer is examined. Thus gold-leaf, which appears *yellow* by reflected light, transmits *green* light, whilst silver allows blue light to pass through it.

The final conclusion is that neither the chemical nor the physical properties of the elements are of such a nature as to divide them *sharply* into two classes, the metals and the non-metals. Many elements, for example, are now known which yield oxides which are not exclusively either basic or acid forming. Thus oxide of aluminium dissolves in hydrochloric acid, a strong acid, to form aluminium chloride, and with equal readiness dissolves in caustic potash, a strong base, to produce potassium aluminate, in the formation of which it plays the part of an acid-forming oxide.

It has thus been found impossible to fix on any one property or even a series of properties by means of which any particular element may be classed as a metal or a non-metal, and this classification is now only made use of as a convenient way of roughly grouping the elements into two divisions.

It may still, however, be said that most of the metals have a bright metallic lustre, conduct heat and electricity well, and form basic oxides, whereas most of the non-metals have not a metallic lustre, do not conduct electricity well, and yield acid-forming oxides.

It is easy thus to distinguish a well-marked metal, such as silver, from a well-marked non-metal like chlorine. On the other hand, it is possible in some cases to group together in a single family a number of elements which all resemble each other in somewhat the same way as the halogen elements, whilst the member of lowest atomic weight is a well-marked non-metal, and that of highest atomic weight a characteristic metal, the members of intermediate atomic weight being also intermediate in chemical properties. This is, for example, the case in the nitrogen group of elements among which nitrogen and phosphorus are well-marked non-metals, arsenic and antimony are intermediate in character, and bismuth is a well-marked metal.

We shall, therefore, proceed to the study of this gradual passage from a non-metal to a metal in the nitrogen group, and then pass on to the consideration of the properties of the typical metals.

SUMMARY

The metals, as a rule, have a bright metallic lustre, conduct heat and electricity well, and form basic oxides, whereas the non-metals, as a rule, do not have a metallic lustre, conduct heat and electricity badly, and yield acid-forming oxides. It is, however, impossible to divide the elements sharply into these two classes, since many of them behave in some respects as metals, in others as non-metals. In many of the families of the elements the members of low atomic weight are non-metals and those of high atomic weight are metals, whilst those of intermediate atomic weight are also intermediate in properties between the metals and non-metals.

LESSON XI

THE ELEMENTS OF THE NITROGEN GROUP

NITROGEN. PHOSPHORUS. ARSENIC. ANTIMONY. BISMUTH.

THE properties of nitrogen and some of its chief compounds have already been described (R. and L., pp. 129-169).

In addition to these the following important compounds are formed by nitrogen with hydrogen, oxygen, and the halogen elements.

Hydrazine, N_2H_4.—This substance can be prepared by a complicated process from ammonium thiocyanate, NH_4CNS. It is also formed by the action of sodium hypochlorite on excess of ammonia, the reaction proceeding in two stages. In the first, the ammonia is converted into a chlorine derivative, *monochloramine*, NH_2Cl, which has not been isolated, and this then reacts with a second molecule of ammonia forming hydrazine hydrochloride :—

$$(1)\ NH_3 + NaOCl = NH_2Cl + NaOH.$$
$$(2)\ NH_2Cl + NH_3 = NH_2{\cdot}NH_2{\cdot}HCl.$$

The best yield is obtained in the presence of some substance such as gelatine.

In the free state it is a colourless liquid boiling at 113°, and having the specific gravity 1.0114. Like ammonia it readily combines with acids to form salts. Unlike ammonia it can, however, unite with either one or two molecules of a monobasic acid, so that two series of salts are formed ; and it is therefore termed a diacid base,—

Hydrazine Monohydrochloride.	Hydrazine Dihydrochloride.
$N_2H_4 . HCl.$	$N_2H_4 . 2HCl.$

Hydrazine combines much more vigorously than ammonia with water. The hydrate of ammonia, ammonium hydroxide, NH_4HO, is decomposed when a solution of ammonia in water is boiled, whereas hydrazine hydrate, N_2H_5HO, can be distilled without undergoing decomposition. It is, however, decomposed when heated for some time with anhydrous baryta, free hydrazine being produced. Hydrazine has the constitutional formula $NH_2 . NH_2$, and very readily undergoes oxidation with formation of water and gaseous nitrogen.

Hydrazoic Acid or Azoimide, N_3H. When ammonia is passed over heated sodium, a compound known as sodamide, NH_2Na, is produced,—

$$2NH_3 + 2Na = 2NH_2Na + H_2.$$

This substance is converted by nitrous oxide into the sodium salt of hydrazoic acid,—

$$NH_2Na + N_2O = N_3Na + H_2O.$$

When the sodium salt is dissolved in water and distilled with dilute sulphuric acid, a solution of hydrazoic acid, N_3H, passes over. The pure substance, when freed from water, is a colourless liquid which has an unpleasant smell and boils at 37°. It is extremely unstable and explodes with great violence when suddenly heated. This substance acts as a strong monobasic acid and dissolves metals with evolution of hydrogen. It also forms salts with sodium and potassium, which are not explosive, but decompose when carefully heated, nitrogen being evolved and the metal left in the free state,—

$$2N_3Na = 3N_2 + 2Na.$$

It is remarkable that this compound is a strong acid, and forms salts with metals and basic oxides, whilst ammonia, NH_3, and hydrazine, N_2H_4, are bases and yield salts with acids.

Hydroxylamine, NH_3O.—When nitric oxide is treated with tin and hydrochloric acid, it becomes reduced and hydroxylamine is formed,—

$$2NO + 6H = 2NH_3O.$$

It is manufactured by electrolysing a mixture of nitric and sulphuric acids, the nitric acid undergoing reduction.

This substance is very difficult to prepare in the free state. It is a white solid which melts at 33° and explodes when strongly heated. Like ammonia it unites with acids to form stable salts.

It is very easily oxidised and therefore acts as a strong reducing agent, precipitating many metals from solutions of their salts.

Hydroxylamine Hydrochloride NH_3O,HCl, crystallises well and is very soluble in water. The reactions of hydroxylamine show that it has the formula $NH_2.OH$, one of the hydrogen atoms of ammonia having been replaced by the group $-OH$ (hydroxyl, see p. 198), and it was on this account that it received its name.

Nitrogen Trichloride, NCl_3.—Nitrogen unites with chlorine to form a very unstable compound, which explodes very violently when it is heated or when brought into contact with grease or turpentine. It is prepared by the action of chlorine on a warm solution of ammonium chloride, when oily drops of the above compound are formed,—

$$NH_4Cl + 3Cl_2 = NCl_3 + 4HCl.$$

Nitrogen Iodide.—When iodine is brought into strong ammonia it is converted into a black powder, which explodes violently when dried and heated, or even touched. This substance is obtained in the pure state by the action of ammonia on a freshly prepared dilute solution of iodine in caustic potash, and has the formula, $N_2H_3I_3$.

The characteristics which distinguish nitrogen from the other elements, which have so far been described, may be summarised as follows :—

1. It forms a large number of oxides, the highest of which has the formula N_2O_5, and unites with water to form a strong monobasic acid known as nitric acid, HNO_3. The trioxide N_2O_3 is very unstable, and forms the unstable weak acid known as nitrous acid, HNO_2.

2. It unites with hydrogen under special conditions to form the gaseous compound ammonia, NH_3, which combines with acids to form salts, such as ammonium chloride, NH_4Cl.

3. Its compound with chlorine is so unstable that it explodes violently when gently heated.

4. Free nitrogen is a colourless gas which only liquefies at − 194°, and solidifies at − 214°.

These properties must be borne in mind whilst the remaining members of the group are being studied, since they serve as a standard of comparison by which the progressive change in the character of these elements may be measured.

Phosphorus, P, 31

Phosphorus differs very sharply from nitrogen in combining so readily with oxygen that it takes fire when exposed in large pieces to the air. A small piece does not take fire, but gradually oxidises, emitting a greenish light during the process, which is easily visible in a dark room. The name of phosphorus (Greek, light bearer) was given to the element on account of this remarkable property, which is known as phosphorescence. This property of shining in the dark is possessed by a great many substances, and is not always due to chemical change, but can be produced by exposing the substance to light, or in other ways. "Luminous paint," for example, which, as we shall see, consists of calcium sulphide, is luminous in the dark after it has been exposed to the light, but undergoes no change in composition, whilst fluorspar becomes luminous when it is gently heated, and sugar when it is rubbed or broken.

Phosphorus does not occur in nature in the free state, but usually in the form of a phosphate or salt of phosphoric acid, the most important of these phosphates being two salts of calcium, phosphorite, $Ca_3(PO_4)_2$, and apatite, $3Ca_3(PO_4)_2 + CaF_2$, both of which occur very largely, especially in Canada.

All vegetable fruits and seeds also contain phosphorus, this element being essential for their proper development. The plants obtain their phosphorus from the phosphates of the soil, and hence when heavy crops of grain are grown in succession on a piece of land, compounds of phosphorus must be added in some form of fertiliser to ensure a good yield. Calcium phosphate, moreover, forms the mineral part of bones, and various compounds of phosphorus are also found in almost all parts of the animal body.

Manufacture of Phosphorus.—Free phosphorus is almost always prepared from calcium phosphate, either the natural mineral or bone ash prepared by calcining bones, and thus burning away all the organic matter, being employed. This is treated with sulphuric acid, which converts it into calcium sulphate and phosphoric acid,—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The insoluble sulphate is filtered off, and the phosphoric acid evaporated down, mixed with charcoal, and strongly heated in earthenware retorts.

The phosphorus distils over, and is condensed in water.

$$H_3PO_4 = HPO_3 + H_2O,$$
$$2HPO_3 + 6C = H_2 + 6CO + 2P.$$

Another process consists in mixing the calcium phosphate with charcoal and silica and submitting the mixture to the very high temperature produced in the electric furnace.

In both processes the reaction is one of reduction, the oxygen of the phosphoric acid or calcium phosphate being removed by the carbon.

The crude phosphorus is then remelted, pressed through chamois leather, and cast in sticks.

Allotropic Forms of Phosphorus.—Like oxygen, carbon, and sulphur, phosphorus exists in two allotropic forms. These are known as—(1) ordinary or yellow phosphorus; (2) red phosphorus.

1. The phosphorus obtained in the way just described is known as ordinary or yellow phosphorus, and is a slightly yellow, transparent, wax-like substance of specific gravity 1.83. It melts at 44.3°, boils at 290°, and can readily be distilled, the operation being carried out in an apparatus from which the oxygen of the air has been removed, or replaced by coal gas or carbon dioxide. It dissolves in carbon disulphide, forming a solution which, on evaporation, leaves a residue of phosphorus in so finely divided a condition that it at once takes fire in the air. Ordinary phosphorus takes fire when it is plunged into chlorine, unites with many of the metals, and is slowly acted on by caustic soda solution, phosphine being produced (p. 87). It must be preserved and handled under water, since, as already mentioned, it takes fire readily when exposed to the air, and this process is greatly aided

by friction or a blow. The vapour density is about 62 compared with hydrogen, and hence the molecular weight is 124. Since, as we shall see (p. 91), the atomic weight is 31, it follows that the molecule of phosphorus vapour contains 4 atoms, its formula therefore being P_4.

2. Red phosphorus is formed when ordinary phosphorus is heated for some time to about 250° in an atmosphere free from oxygen. The change takes place much more rapidly and at a lower temperature when a trace of iodine is added. It is a red powder which is made up of crystals, although it was long thought to be amorphous, and has the specific gravity 2.106. It is much less chemically active than ordinary phosphorus. Thus it does not take fire on exposure to the air or when plunged into chlorine. It is, moreover, insoluble in carbon disulphide, and is not acted on by caustic soda solution, so that it can easily be freed from ordinary phosphorus by treatment with this latter reagent. When heated in the air to about 350° it changes back into yellow phosphorus and then takes fire.

EXPERIMENT 30.—Place a small piece of ordinary phosphorus at one edge of an iron sand tray, and an equal amount of red phosphorus at the opposite edge, and heat the tray by a flame placed at its centre. The ordinary phosphorus takes fire long before the red phosphorus.

A form of red phosphorus known as scarlet phosphorus which is much more active than that obtained in the usual way is produced when a solution of yellow phosphorus in phosphorus tribromide is boiled. It is bright scarlet in colour and is in a very finely divided state. Although it does not oxidise in the air, it is much more chemically active than the usual form and dissolves rapidly in caustic soda solution, and is at once oxidised by nitric acid. Moreover it can be used instead of ordinary yellow phosphorus for the production of matches which can be struck on any surface (p. 79).

Another variety of phosphorus is also known which closely resembles red phosphorus in everything but its appearance. It is prepared by heating phosphorus with metallic lead. The molten lead dissolves the phosphorus, which is again deposited in crystals on cooling. When the mass is treated with dilute nitric acid, the lead dissolves and the phosphorus is left behind as a black mass.

Lucifer-matches—Phosphorus is chiefly used for making lucifer-matches. The old way of producing a flame artificially was to strike a piece of steel against a flint and allow the sparks, which consist of burning fragments of steel, to fall on charred linen, called tinder. A match of wood coated at one end with sulphur was then thrust into the smouldering tinder and a flame thus obtained.

The first chemical matches produced were tipped with sulphur coated with a mixture of potassium chlorate, sugar, or other organic matter, and gum, and were ignited by being thrust into a bottle containing sulphuric acid (p. 52). These were very inconvenient, and were soon superseded by friction-matches, known as "Congreves," which were first introduced in 1827 by J. Walker of Stockton-on-Tees, and were sold at the rate of one shilling and twopence for a tin box containing 100 matches and a piece of glass paper. These matches were tipped with sulphur coated with a mixture of antimony sulphide, potassium chlorate, and a little gum, and were ignited by being drawn between two folds of glass paper. The oxygen of the potassium chlorate combines with the elements of the antimony sulphide, and the heat produced by this union ignites the sulphur with which the match is tipped.

Much more convenient than these are phosphorus matches, tipped with a mixture of potassium chlorate, ordinary phosphorus, chalk, and gum, which ignite much more readily than the old matches containing no phosphorus. Unfortunately the fumes given off during the manufacture of these matches are extremely poisonous, and sometimes, unless proper precautions as to ventilation, etc. are taken, cause decay of the bones of the jaw, known commonly as "phossy jaw," among the workers engaged in their production. A sulphide of phosphorus, P_4S_3, or the scarlet form of red phosphorus, is now generally substituted for ordinary phosphorus in matches, as these substances are not dangerous to the workers and yet enable the matches to be struck on any surface. "Safety-matches" have also been introduced, which contain no phosphorus, but are tipped with potassium chlorate or some other oxidising agent, antimony sulphide, and gum. They are caused to ignite by being rubbed on a surface covered with red phosphorus, the use of which is not attended by any ill results to the work-people. These matches, moreover, are not so liable to accidental ignition as those containing ordinary phosphorus. The wooden stem of the match is now generally impregnated with paraffin in place of sulphur.

It will be noticed that the head of the safety-match has a similar composition to that of the first friction-match, and as a matter of fact, these safety-matches ignite when they are rapidly drawn along an extended smooth surface of non-conducting material, such as glass, paper, etc.

The Oxides and Oxy-acids of Phosphorus

When phosphorus is burned in a plentiful supply of air it is almost completely converted into phosphorus pentoxide, a white, very deliquescent substance. This compound has the empirical formula, P_2O_5, and therefore corresponds in composition with nitrogen pentoxide, N_2O_5.

When the air supplied to burning phosphorus is limited in quantity lower oxides are formed, the chief of which is the trioxide, which has the empirical formula P_2O_3, corresponding with nitrogen trioxide, N_2O_3.

Each of these oxides forms an acid, and these are known respectively as phosphoric acid and phosphorous acid, just as the acids derived from the pentoxide and trioxide of nitrogen are termed nitric acid and nitrous acid.

Phosphorus Pentoxide or Phosphoric Anhydride, P_4O_{10}

Phosphoric anhydride is usually prepared by burning phosphorus in a free supply of air. The product is not quite pure, but contains a small amount of the lower oxides of phosphorus, from which it can be freed by sublimation in a stream of oxygen over heated spongy platinum. It is a pure white powder, which combines with water with great evolution of heat, and rapidly takes up water and becomes liquid when exposed to the air. Since it combines so readily with water vapour, it forms a very valuable drying agent for gases. It is also able to decompose many compounds containing hydrogen and oxygen combined with other elements, and is therefore sometimes used for preparing acid-forming oxides from the corresponding acids, for example, nitrogen pentoxide from nitric acid—

$$2HNO_3 + P_2O_5 = 2HPO_3 + N_2O_5.$$

The empirical formula of the oxide is P_2O_5, but determinations of the vapour density show that even at high temperatures the molecular formula is P_4O_{10}.

The Phosphoric Acids

Phosphoric anhydride is capable of producing no less than three different acids with water :—

When it is allowed to deliquesce in the air or is dissolved in cold water it reacts with one molecule of water and produces an acid of the formula HPO_3, which is known as metaphosphoric acid, and corresponds in composition with nitric acid, HNO_3,—

$$P_2O_5 + H_2O = 2HPO_3.$$

2. When, on the other hand, it is dissolved in boiling water, or when its solution in cold water is boiled or allowed to stand for some time, it reacts with no less than three molecules of water, and forms an acid known as orthophosphoric acid, which has the formula H_3PO_4. No corresponding acid derived from nitrogen pentoxide is known.

$$P_2O_5 + 3H_2O = 2H_3PO_4.$$

3. The third acid, known as pyrophosphoric acid, $H_4P_2O_7$, is formed when orthophosphoric acid is carefully heated, but cannot be obtained by the direct union of phosphoric anhydride with water,—

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

These three acids only differ in composition by the amount of water they contain, as is seen from the following list :—

	Composition.	Empirical Formula.
Metaphosphoric acid . .	$P_2O_5 + H_2O$	HPO_3
Pyrophosphoric acid . .	$P_2O_5 + 2H_2O$	$H_4P_2O_7$
Orthophosphoric acid . .	$P_2O_5 + 3H_2O$	H_3PO_4

They nevertheless form different series of salts with alkalis and show different reactions, so that, although they are all derived from phosphoric anhydride, they must be considered as three distinct and different acids.

Orthophosphoric Acid, H_3PO_4

This acid is not usually prepared by the method referred to above, since it can be more readily obtained by other means. On the small scale it is best prepared by the action of nitric acid on phosphorus, the latter being thereby completely oxidised, whilst the nitric acid is reduced. Oxides of nitrogen are evolved, and the phosphorus in the presence of water converted into phosphoric acid. Like all the oxidising effects of nitric acid, this cannot accurately be represented by any simple equation, because a mixture of oxides of nitrogen is formed, the composition of which depends on the strength of the acid and the temperature.

EXPERIMENT 31.—Place 50 cc. of concentrated nitric acid in an evaporating basin in a draught chamber, and bring into it in small portions at a time 5 grams. of red phosphorus. Start the reaction by warming, and then withdraw the flame until the evolution of nitrous fumes has almost ceased. If any phosphorus is left add another 25 cc. of the acid, and in any case evaporate down until a syrup of phosphoric acid is left. Dissolve in water, dilute to 150 cc. and reserve the solution for the preparation of the sodium salts.

On the large scale the acid is made, as already mentioned (p. 77), from bone ash, which is largely composed of calcium phosphate, by the action of dilute sulphuric acid,—

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The calcium sulphate which is formed is only sparingly soluble in the liquid and is filtered off, the clear solution being then evaporated.

When quite pure the acid forms colourless crystals, which melt at 38.6°. It can be heated to 160° without undergoing any change, but above that temperature it loses water, yielding pyrophosphoric acid as a first product, and is finally converted at a red heat into metaphosphoric acid,—

$$H_3PO_4 = H_2O + HPO_3.$$

The Orthophosphates.—Three series of salts containing a single metal can be prepared from orthophosphoric acid, which is therefore a tribasic acid. The sodium salts may be taken as a typical example of the salts of this acid.

When sodium carbonate is added to orthophosphoric acid until effervescence no longer occurs, and the solution is evaporated, the salt which crystallises out is not the normal salt Na_3PO_4, but the disodium salt Na_2HPO_4. It has a slightly alkaline reaction towards litmus in spite of the fact that, according to its composition, it must be classed as an acid salt (see p. 152). The monosodium salt NaH_2PO_4 contains only half as much sodium as this, whilst the normal or trisodium salt contains one and a half times as much.

EXPERIMENT 32.—1. To 50 cc. of the solution of phosphoric acid prepared in Experiment 31, add dilute caustic soda solution from a burette until the solution is faintly alkaline to litmus paper and note the number of cc. added. Evaporate the solution and allow to crystallise.

2. To a second 50 cc. add half the above quantity of caustic soda, evaporate to a small bulk and allow to crystallise.

3. To the remaining 50 cc. add one and a half times the first quantity of caustic soda and proceed as before.

The concentrated solutions must be allowed to stand for some time and occasionally well stirred with a glass rod to promote crystallisation.

In all three cases, drain the crystals which are finally obtained and dry them between folds of filter paper.

Disodium Hydrogen Phosphate, $Na_2HPO_4 + 12H_2O$, is usually known as ordinary sodium phosphate, and forms efflorescent crystals. When it is heated it first loses the water of crystallisation and then at a higher temperature loses a further quantity of water and is converted into sodium pyrophosphate (p. 86).

Normal Sodium Phosphate, $Na_3PO_4 + 12H_2O$, forms a strongly alkaline solution, and is decomposed by carbonic acid, the ordinary phosphate being formed along with sodium bicarbonate,—

$$Na_3PO_4 + CO_2 + H_2O = Na_2HPO_4 + NaHCO_3.$$

The reaction, however, does not come to an end at this point. The carbonic acid also acts upon the disodium hydrogen phosphate, forming sodium dihydrogen phosphate and sodium bicarbonate. The change in this case, however, is not complete, and affords another instance of a reversible reaction (p. 30),—

$$Na_2HPO_4 + H_2CO_3 \rightleftharpoons NaH_2PO_4 + NaHCO_3.$$

When sodium bicarbonate and sodium dihydrogen phosphate in equivalent quantities are dissolved in a small quantity of water, some carbon dioxide is evolved, the reaction proceeding in this way until the condition of equilibrium is reached

Sodium Dihydrogen Phosphate, $NaH_2PO_4 + H_2O$, yields a solution which has an acid reaction. When the salt is heated it loses water and forms sodium metaphosphate (p. 85).

All these three salts give a yellow precipitate of normal silver phosphate with silver nitrate. In the case of the normal salt, the alkaline solution becomes neutral,—

$$Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3,$$

whilst the solutions of the other two become acid, owing to the liberation of nitric acid,—

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3,$$
$$NaH_2PO_4 + 3AgNO_3 = Ag_3PO_4 + NaNO_3 + 2HNO_3,$$

These two reactions, again, are not complete, but are reversible, a certain amount of the phosphate remaining in solution. In order, therefore, to obtain complete precipitation, sufficient alkali must be added to neutralise the acid liberated according to the equations given above. The reactions for complete precipitation would thus be,—

$$Na_2HPO_4 + 3AgNO_3 + NaOH = Ag_3PO_4 + 3NaNO_3 + H_2O,$$
$$NaH_2PO_4 + 3AgNO_3 + 2NaOH = Ag_3PO_4 + 3NaNO_3 + 2H_2O.$$

EXPERIMENT 33.—Make a solution of a small quantity of each of the three salts prepared in Experiment 32, test their reaction to litmus paper, and then to each solution add *excess* of silver nitrate solution. Again test the solutions with litmus paper and ascertain that their reactions are in accordance with the statement made above.

All orthophosphates may be detected by the two following reactions in addition to those which have been already mentioned.

EXPERIMENT 34.—1. To a solution of sodium phosphate add ammonia, ammonium chloride and magnesium chloride,—a white precipitate of magnesium ammonium phosphate is produced, which rapidly becomes crystalline.

2. To a solution of sodium phosphate add half its volume of nitric acid and then a solution of ammonium molybdate, and warm,—a thick yellow precipitate of complex composition is produced.

Metaphosphoric Acid, HPO_3, is formed, as already described, when phosphoric anhydride is dissolved in cold water, and also when orthophosphoric acid is heated. The material sold as glacial phosphoric acid is solid metaphosphoric acid. It slowly changes into the ortho-acid when its solution is allowed to stand, rapidly when it is boiled.

Sodium Metaphosphate, $NaPO_3$, can be obtained by neutralising the acid with sodium carbonate or by heating sodium dihydrogen phosphate,—

$$NaH_2PO_4 = NaPO_3 + H_2O.$$

It can also be prepared conveniently by heating microcosmic salt (sodium ammonium hydrogen phosphate),—

$$NaHNH_4PO_4 = NaPO_3 + NH_3 + H_2O.$$

The glassy mass thus obtained dissolves in water, forming a solution which gives a white gelatinous precipitate of silver metaphosphate, $AgPO_3$, with silver nitrate, and produces a white precipitate in a solution of albumin. When the solid salt is heated with sodium carbonate, and when the solution is boiled with nitric acid, a salt of orthophosphoric acid is formed.

EXPERIMENT 35.—Heat a little microcosmic salt in a crucible until a glassy mass is left. Dissolve in hot water and—

1. Add silver nitrate,—white gelatinous precipitate.
2. Add a solution of albumin (white of egg),—white precipitate.
3. Boil for a few minutes with a few drops of strong nitric acid, neutralise with sodium carbonate, and add silver nitrate,—a yellow precipitate of silver orthophosphate is formed, whilst albumin forms no precipitate.

Pyrophosphoric Acid, $H_4P_2O_7$, is formed when orthophosphoric acid is heated at 215°,—

$$2H_3PO_4 = H_4P_2O_7 + H_2O.$$

It is a glassy mass and passes into the ortho-acid when its solution is boiled.

Sodium Pyrophosphate, $Na_4P_2O_7$, is obtained by heating ordinary sodium phosphate,—

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O.$$

The pyrophosphates give a white curdy precipitate with silver nitrate, but do not give a precipitate with albumin. When boiled with nitric acid or fused with sodium carbonate they are converted into orthophosphates.

EXPERIMENT 36.—Heat some ordinary phosphate of sodium in a crucible over a Bunsen flame. Dissolve the white mass thus obtained in water.

1. Add silver nitrate,—white curdy precipitate.
2. Add a solution of albumin,—no precipitate.
3. Boil the solution with a little strong nitric acid, neutralise with sodium carbonate and add silver nitrate,—a yellow precipitate of silver orthophosphate is formed.

Phosphorus Trioxide and Phosphorous Acid.

Phosphorus Trioxide or Phosphorous Anhydride.—This oxide has the empirical formula P_2O_3, and is formed when phosphorus is burned in a slow current of air; the oxide volatilises and is condensed by means of a freezing mixture. It is a wax-like mass which melts at 22° and boils at 173.1°. Its vapour density is 110, thus showing that its molecular weight is about 220, and its molecular formula P_4O_6. When heated in the air it burns brilliantly, forming the higher oxide, P_4O_{10}, and oxidises slowly even at the ordinary temperature.

Cold water converts it slowly into phosphorous acid, whilst a complicated decomposition occurs with hot water, phosphine, PH_3, being evolved.

Phosphorous Acid, H_3PO_3, is formed when phosphorus trichloride is treated with water,—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl,$$

and is best prepared by passing chlorine into melted phosphorus under water. The acid is left on evaporation as a crystalline mass which deliquesces in the air. It slowly combines with the oxygen of the air and forms phosphoric acid. It also readily takes up oxygen from many other compounds, and therefore acts as a strong reducing agent. Thus, when it is added to a solution of mercuric chloride a white precipitate of calomel is produced, which is further reduced to the metal if an excess of the phosphorous acid be present,—

$$H_3PO_3 + 2HgCl_2 + H_2O = H_3PO_4 + 2HgCl + 2HCl,$$
$$2HgCl + H_3PO_3 + H_2O = H_3PO_4 + 2Hg + 2HCl.$$

Phosphorous acid is tribasic, but the normal salts are very difficult to obtain, whereas the acid salts are more stable.

Phosphine and Hypophosphorous Acid

Phosphine or Phosphuretted Hydrogen, PH_3.—When ordinary phosphorus is warmed with an alkali a vigorous action takes place and a colourless gas is evolved which has the remarkable property of taking fire when it comes in contact with air or oxygen.

Preparation of Phosphine.—A few small pieces of yellow phosphorus are warmed with a strong solution of caustic soda (30-40 per cent) in a small flask, through which a current of hydrogen or coal gas is first passed to remove the air (Fig. 13). Each bubble of the gas takes fire as it comes to the surface of the water in the pneumatic trough, and gives rise to a very perfect vortex ring of finely divided phosphoric anhydride.

The gas which is evolved is phosphine, PH_3, but contains a small amount of another compound of phosphorus and hydrogen, P_2H_4, and it is this second compound which is spontaneously inflammable in the air, whereas pure phosphine has not this property, although it readily burns when a flame is applied. If the gas prepared by the method just described be passed through a tube cooled by a freezing mixture, the second compound condenses to a liquid and the resulting gas is no longer spontaneously inflammable.

The reaction by which phosphine is produced is a somewhat complicated one, hypophosphorous acid being also formed,—

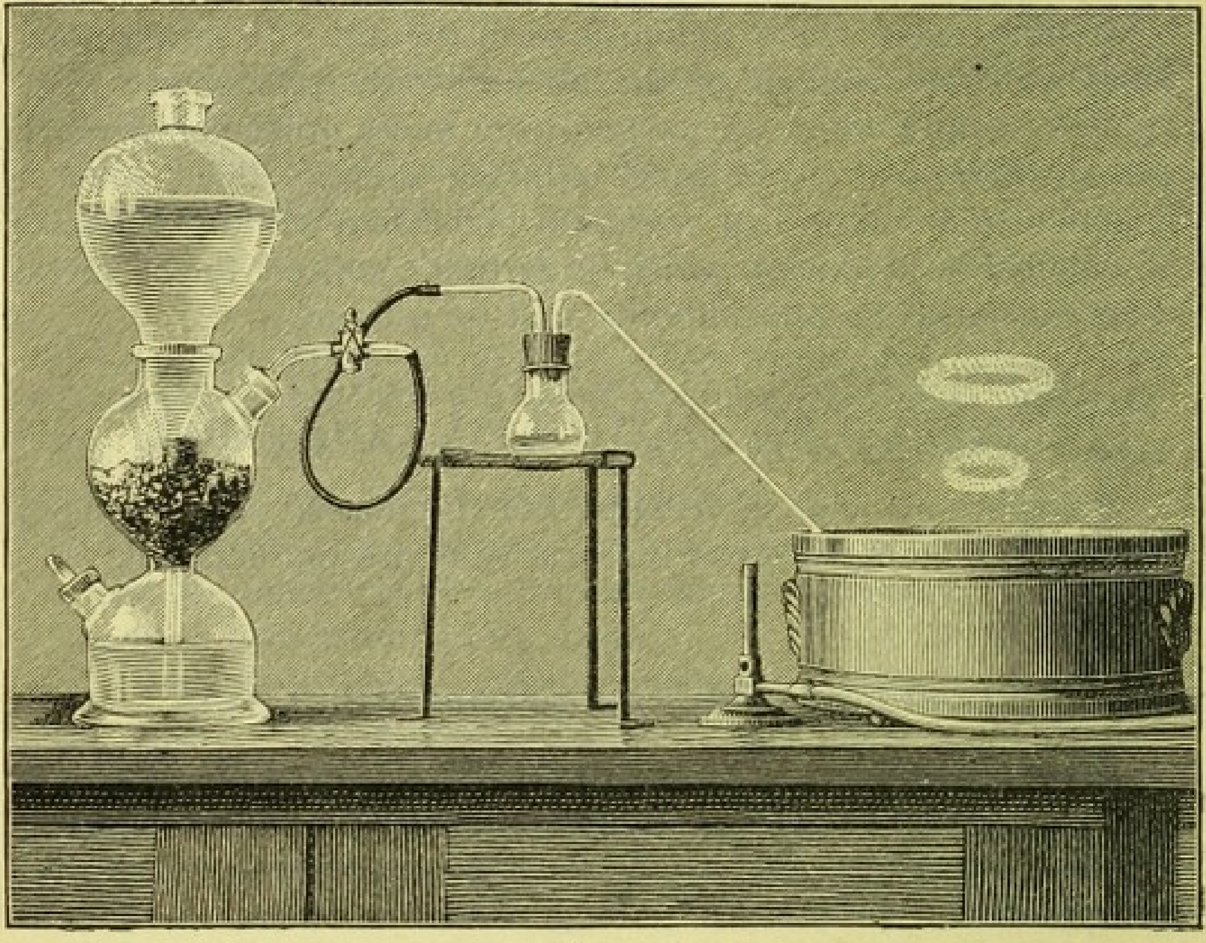


FIG. 13.

$$4P + 3NaOH + 3H_2O = PH_3 + 3NaH_2PO_2.$$

Phosphine has a very powerful unpleasant odour of rotten fish and is very poisonous. When electric sparks are passed through the gas it decomposes into phosphorus, which is deposited in the solid state, and hydrogen, 2 volumes of phosphine yielding 3 volumes of hydrogen. This is precisely similar to the decomposition of ammonia (R. and L., p. 166), except that in the latter case the nitrogen is liberated in the state of gas.

The density of pure phosphine is about 17, and hence its molecular weight is 34, and 34 grams. of it occupy 22.4 litres. This volume, as we have just seen, yields 33.6 litres or 3 grams. of hydrogen. The composition of the gas is, therefore—

$$\begin{array}{lr} \mathrm{P} & 31 \\ \mathrm{H} & 3 \\ \cline{2-2} & \underline{\underline{34}} \end{array}$$

and its molecular formula PH_3. Phosphine, moreover, resembles ammonia chemically in one very important respect. It unites with hydriodic acid to form a compound, PH_4I, which is called *phosphonium iodide*, and corresponds exactly in composition with ammonium iodide, NH_4I. This compound is best prepared by acting on iodide of phosphorus with a small quantity of water, and is at once decomposed by warm water, forming hydriodic acid and phosphine; the latter is free from P_2H_4, and is therefore not spontaneously inflammable.

Hypophosphorous Acid, H_3PO_2.—The solution produced by the action of alkalis on phosphorus contains a hypophosphite. The free acid is prepared from the barium salt by adding sulphuric acid and evaporating. It is very readily oxidised to phosphoric acid, and is, like phosphorous acid, a strong reducing agent. Its action on mercuric chloride exactly resembles that of phosphorous acid,

$$2HgCl_2 + H_3PO_2 + 2H_2O = H_3PO_4 + 4HCl + 2Hg.$$

Phosphides of the Metals

Many of the metals combine with phosphorus to form dark coloured compounds known as phosphides, and these can also be obtained in some cases by the action of phosphorus on the oxide of the metal, or of the metal on a phosphate. Thus when phosphorus is added to lime heated to redness in a crucible calcium phosphide is formed.

This compound, like many of the phosphides, is decomposed by dilute acids or water, spontaneously inflammable phosphine being evolved. Again, when any phosphate is heated with metallic magnesium, a portion of the latter combines with the oxygen of the phosphate, forming magnesia, whilst the phosphorus unites with the excess of metal, forming magnesium phosphide. This is decomposed by moist air, and hence phosphine is evolved when the fused mass is powdered and breathed upon. The gas can easily be recognised by its smell, and hence this reaction affords a very delicate test for the presence of phosphates in solid substances.

EXPERIMENT 37.—Make a small tube from narrow thin-walled glass tubing, place in it a mixture of magnesium powder with a little calcium phosphate and heat strongly. Break the tube in a mortar and breathe on the powdered mass. A smell of phosphine is at once perceived.

Compounds of Phosphorus with the Halogens

Phosphorus forms two series of compounds with the elements of the chlorine group, uniting with either 3 or 5 atoms of these elements. All the compounds containing 5 atoms of halogen decompose when heated, with the single exception of the pentafluoride.

Phosphorus Trichloride, PCl_3.—When ordinary phosphorus is brought into chlorine it takes fire spontaneously and burns, forming the trichloride. This compound is best prepared by placing red phosphorus in a retort, heating, and passing dry chlorine over it. It is a colourless liquid which boils at 76°, and therefore distils over and may be collected in a cooled receiver. It is at once decomposed by water, hydrochloric acid and phosphorous acid being produced,—

$$PCl_3 + 3H_2O = H_3PO_3 + 3HCl.$$

When exposed to the air it is decomposed by the atmospheric moisture and forms white fumes.

Its vapour density is 68.75, and hence its molecular weight is 137.5, agreeing with the molecular formula PCl_3.

Phosphorus Pentachloride, PCl_5, is formed when chlorine is passed over the surface of the trichloride, which must be well cooled, as a considerable amount of heat is evolved. The gas is rapidly absorbed and the whole solidifies to a crystalline mass. Like the trichloride it is at once decomposed by water, but in this case phosphoric acid is produced, in addition to hydrochloric acid,—

$$PCl_5 + 4H_2O = H_3PO_4 + 5HCl.$$

When the crystals are heated they volatilise without melting, forming a colourless vapour. This vapour does not consist of unaltered molecules of phosphorus pentachloride but to a large extent of phosphorus trichloride and free chlorine, but on cooling these recombine, forming crystals of the pentachloride. This is an instance of a phenomenon known as dissociation, which is more fully described under ammonium chloride (p. 208).

Phosphorus Oxychloride, $POCl_3$.—When only a small quantity of water is added to the pentachloride the decomposition is not complete, but phosphorus oxychloride, $POCl_3$, is produced,—

$$PCl_5 + H_2O = POCl_3 + 2HCl.$$

This substance can be prepared by the action of the pentachloride on oxalic acid or by that of the trichloride on potassium chlorate. It is a colourless fuming liquid, which boils at 107°, and is decomposed by water, forming phosphoric and hydrochloric acids,—

$$POCl_3 + 3H_2O = H_3PO_4 + 3HCl.$$

Phosphorus Pentafluoride, PF_5, is prepared by the action of phosphorus pentachloride on arsenic tri-fluoride, AsF_3. It is a colourless gas, and has the vapour density 63, corresponding with the molecular formula PF_5.

The Atomic Weight of Phosphorus.—The equivalent of phosphorus has been determined by converting pure red phosphorus into the pentoxide by combustion, and it has thus been found that 8 parts of oxygen (one equivalent) unite with 6.2 parts of phosphorus.

Many volatile substances containing phosphorus are known, several of which have been described, and it is found from their molecular composition that the smallest amount of phosphorus ever present in a molecule is about 31 parts. Since $6.2 \times 5 = 31$ is that multiple of the equivalent which is nearest to 31, it is taken as the exact atomic weight.

SUMMARY

A comparison of the properties of phosphorus with those of nitrogen shows that—

1. Phosphorus is a solid at the ordinary temperature, and like nitrogen, non-metallic in character.

2. The oxides and chlorides of phosphorus are much more stable than the corresponding compounds of nitrogen. Thus phosphoric anhydride is much more stable than nitrogen pentoxide, phosphorus trichloride than chloride of nitrogen, etc.

3. Phosphine is much less stable than ammonia and does not so readily unite with acids.

4. Metaphosphoric acid, HPO_3, is a much weaker acid than nitric acid, HNO_3, with which it corresponds in composition.

EXERCISES ON LESSON XI

1. What are the chief sources of phosphorus, and how is the element prepared on the large scale?

2. Compare the physical and chemical properties of red and yellow phosphorus.

3. How would you prepare sodium metaphosphate and sodium pyrophosphate from ordinary sodium phosphate?

4. Describe the preparation of phosphorus trichloride from phosphorus. How can this substance be converted into (*a*) phosphorous acid, (*b*) phosphoric acid?

5. 11.454 grams. of phosphorus trichloride were found to be exactly sufficient to precipitate 26.978 grams. of silver in the form of silver chloride. Calculate the equivalent of phosphorus from these numbers. What considerations would guide you in deciding the atomic weight of the element?

6. Describe the general course of the chemical change which occurs when a match is struck.

7. Calculate the molecular weight of phosphorous oxide from the following numbers: 137.5 cc. of the vapour measured at 132° C., and at the pressure of 156 mm. of mercury weigh 0.1887 gram.

8. Give three methods by which the presence of phosphorus in bone may be detected.

9. Compare the properties of hydrazine with those of ammonia.

10. Contrast the properties of the compounds formed by nitrogen and phosphorus with chlorine.

LESSON XII

THE ELEMENTS OF THE NITROGEN GROUP (*Cont.*)

Arsenic, As, 74.96

ARSENIC resembles phosphorus very closely in all its chemical properties, but is decidedly more closely allied to the metals. This is particularly to be noticed in the appearance and properties of the element itself, and in the properties of the oxides, which produce weaker acids than do those of phosphorus, and moreover act to some extent as basic oxides. We shall find that all these characteristics are intensified in the two remaining elements of this group, antimony and bismuth.

Arsenic occurs free in many localities in central Europe in kidney-shaped masses, and is found very widely combined with iron as arsenical iron, $FeAs_2$, or with iron and sulphur in the form of arsenical iron pyrites or mispickel, Fe_2AsS_2, as well as in the form of sulphide, as realgar, As_2S_2, and orpiment, As_2S_3.

Preparation of Arsenic.—Commercial arsenic is prepared from mispickel by simply heating it in an earthenware tube, into the mouth of which a roll of sheet-iron is put, to act as a condenser. The arsenic sublimes into this sheet-iron and is removed at the close of the operation, iron sulphide being left behind in the earthenware tube,—

$$Fe_2AsS_2 = 2FeS + As.$$

In order to obtain arsenic from its other compounds, it is necessary first of all to roast these in a current of air by which the arsenic is converted into the volatile arsenious oxide or white arsenic, As_4O_6, which is condensed in long flues,—

$$4FeAs_2 + 9O_2 = 2Fe_2O_3 + 2As_4O_6.$$

This product is then mixed with coal and heated in a crucible covered with an iron cap into which the arsenic sublimes,—

$$As_4O_6 + 6C = 4As + 6CO.$$

Precisely this method is used for the detection of arsenic in solid substances. The solid is mixed with a little sodium carbonate and potassium cyanide to act as a reducing agent, and is then carefully heated in a bulb tube. Arsenic is set free and sublimes into the cold stem of the bulb tube.

EXPERIMENT 38.—1. Draw out a piece of wide glass tubing, about 40 cm. long, so as to form a constriction near one end. Just above the narrow part place a little sulphide of arsenic, and support the tube by a clamp at an angle of about 30° to the bench. Heat the sulphide by the flame of a Bunsen burner. A current of air is produced, the arsenic sulphide is oxidised and a white deposit of arsenious oxide is formed on the cool part of the tube.

2. Blow a *small* bulb on the end of a piece of quill tubing. *Half* fill the bulb with a mixture of arsenious oxide and "fusion mixture," which is a mixture of potassium cyanide and carbonate. Fill the rest of the bulb with pure fusion mixture and heat gently in the flame. A black mirror of arsenic is produced on the cool part of the tube.

Properties of Arsenic.—Arsenic has a specific gravity of 5.7, and when pure has a bright metallic lustre, and is so brittle that it can easily be powdered in a mortar. When it is heated in absence of oxygen it sublimes without melting, forming a black shining mirror, but when heated in a current of air it is oxidised, and burns with an almost colourless flame, forming arsenious oxide, which sublimes in brilliant octahedral crystals, a peculiar smell like that of garlic being produced. Arsenic burns brightly in oxygen, forming arsenious oxide, As_4O_6, and also takes fire when brought into chlorine, producing the trichloride $AsCl_3$. It does not dissolve in dilute hydrochloric acid or sulphuric acid, but is oxidised by strong sulphuric acid, sulphur dioxide being evolved,—

$$2As + 3H_2SO_4 = 2H_3AsO_3 + 3SO_2.$$

Nitric acid at once converts it into arsenic acid, brown nitrous fumes being evolved. Arsenic also readily combines with many of the metals forming arsenides, and in this respect resembles phosphorus and many other non-metals, such as sulphur, iodine, etc. Thus when heated with zinc it forms a mass of zinc arsenide, which is decomposed by acids yielding arseniuretted hydrogen (p. 100), just as zinc sulphide reacts with acids to form sulphuretted hydrogen.

EXPERIMENT 39.—1. Heat a few centigrams. of powdered metallic arsenic in a current of air in a wide glass tube (see Expt. 38, 1, p. 94). The arsenic burns with an almost colourless flame, and a white deposit of arsenious oxide is produced.

2. Heat small portions of powdered arsenic in separate test-tubes, with—

(*a*) Strong nitric acid,—violent action.
(*b*) Dilute hydrochloric acid,—no action.
(*c*) Concentrated sulphuric acid, — sulphur dioxide is evolved.

Arsenic also exists in a yellow crystalline allotropic modification, which is formed when ordinary arsenic is sublimed in a current of carbon dioxide. It is soluble in carbon bisulphide and readily changes back to the ordinary form.

Arsenic is precipitated by metallic copper from acid solutions, and this reaction is used for the detection of arsenic, under the name of *Reinsch's test.*

EXPERIMENT 40.—Dissolve a few milligrams. of arsenious oxide in dilute hydrochloric acid ; add a few fragments of bright copper and warm gently. A dull gray deposit of arsenic is at once produced. If the copper be removed from the solution, dried, and heated in an open test-tube, a crystalline deposit of arsenious oxide is produced on the walls of the tube.

Molecular Weight of Arsenic.—The vapour density of arsenic at a temperature of about 860° (bright red-heat) is 150, so that under these conditions its molecular weight is about 300. As we shall see later on, the atomic weight is 74.96, and the formula of the element under these conditions is therefore As_4, corresponding exactly with that of phosphorus vapour. At still higher temperatures (1700°), however, the molecule undergoes dissociation (p. 209), and the vapour density becomes nearly half of its former value, so that at high temperatures the molecule only contains two atoms and has the formula As_2.

Arsenious Oxide, As_4O_6, and Arsenious Acid, H_3AsO_3.

When arsenic is heated in air or oxygen, the oxide which is produced has the empirical formula As_2O_3, and does not directly combine with any further quantity of oxygen. This constitutes an important difference between this element and phosphorus, which, it will be remembered, burns to form the pentoxide.

Arsenious Oxide or **White Arsenic** is prepared, as already described (p. 94), by heating arsenical ores in a current of air and is then purified by sublimation. It is thus obtained either as a white crystalline powder or as a transparent, glassy mass known as vitreous arsenic, which, however, becomes opaque and crystalline when preserved. When gently heated, the oxide sublimes in bright octahedral crystals, without previously melting.

Arsenious oxide dissolves in water forming arsenious acid, H_3AsO_3, and is therefore an acid-forming oxide. On the other hand it is converted by hydrochloric acid into arsenious chloride, $AsCl_3$, a fuming liquid which is partially decomposed by water. Hence the oxide also acts as a weak basic oxide.

Arsenious oxide acts as a violent poison when administered in large doses (p. 105), but in smaller quantities is a valuable medicine and is much used in skin diseases and nervous complaints. "Fowler's solution" (Liquor arsenicalis) is a solution of the oxide and an equal weight of potassium carbonate, containing 4 grains of the oxide per fluid ounce (8.3 grams. per litre).

Formula of Arsenious Oxide.—The oxide contains 75.8 per cent of arsenic and 24.2 per cent of oxygen, so that its empirical formula is As_2O_3. Its vapour, however, has the density 198, so that its molecular weight is 396, and its molecular formula, therefore, As_4O_6.

Arsenious Acid, H_3AsO_3.—Although the solution of arsenious oxide in water has acid properties, the free acid has never been obtained in the pure state, but many of its salts can readily be prepared, and these show that the acid is tribasic. The sodium salt is formed when the oxide is dissolved in sodium carbonate or caustic soda. A neutral solution of this salt gives, with silver nitrate, a canary-yellow precipitate of silver arsenite, which is easily soluble in acids or ammonia,—

$$Na_3AsO_3 + 3AgNO_3 = Ag_3AsO_3 + 3NaNO_3.$$

When copper sulphate is added to a solution of the salt, Na_2HAsO_3, a green precipitate of copper hydrogen arsenite, $CuHAsO_3$, is formed, which was formerly used as a paint, under the name of Scheele's green,—

$$Na_2HAsO_3 + CuSO_4 = CuHAsO_3 + Na_2SO_4.$$

EXPERIMENT 41.—Dissolve 1 gram. arsenious oxide in hot sodium carbonate solution. Make the liquid exactly neutral by the cautious addition of nitric acid, and try the following tests :—

1. Silver nitrate solution produces a canary-yellow precipitate, readily soluble in ammonia and acids.
2. Copper sulphate produces a light green precipitate.
3. Magnesia mixture produces no precipitate. (As the arsenites are readily converted by oxidising agents into arsenates, a slight white precipitate is sometimes obtained.)
4. Acidify with hydrochloric acid, warm and pass in sulphuretted hydrogen, an immediate yellow precipitate of arsenic trisulphide is produced.

Nearly all the tribasic acids derived from phosphorus, arsenic and antimony, as well as many other polybasic acids, such as silicic acid, H_4SiO_4, etc., show the same peculiarity as phosphoric acid ; that is, they yield several series of salts which are related to one another in the same way as the meta-, ortho-, and pyro-phosphates, and are derived from acids of corresponding composition, although in many cases these have not been obtained in the free state. Hence the names of these salts are distinguished by the same prefixes as are used for the different phosphates, as shown in the following table :—

	ACIDS.			SALTS.		
	Ortho-	Meta-	Pyro-	Ortho-	Meta-	Pyro-
Phosphate	H_3PO_4	HPO_3	$H_4P_2O_7$	Na_3PO_4	$NaPO_3$	$Na_4P_2O_7$
Arsenate .	H_3AsO_4	$HAsO_3$	$H_4As_2O_7$	N_3AsO_4	$NaAsO_3$	$Na_4As_2O_7$
Arsenite .	H_3AsO_3	$HAsO_2$	$H_4As_2O_5$	Na_3AsO_3	$NaAsO_2$	$Na_4As_2O_5$
Silicate .	H_4SiO_4	H_2SiO_3	..	Na_4SiO_4	Na_2SiO_3	..

Arsenic Pentoxide, As_2O_5, and Arsenic Acid, H_3AsO_4

When arsenious oxide is warmed with nitric acid, oxides of nitrogen are evolved and arsenic acid is formed,—

$$As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + NO + NO_2.$$

When the acid solution is evaporated it leaves a residue of arsenic acid, which decomposes at a higher temperature into water and arsenic pentoxide,—

$$2H_3AsO_4 = As_2O_5 + 3H_2O.$$

The oxide is deliquescent and easily soluble in water, forming ortho-arsenic acid (compare the behaviour of phosphorus pentoxide, p. 80).

EXPERIMENT 42.—Place 3 grams. arsenious oxide in an evaporating basin, add 10 cc. of concentrated nitric acid and heat on the water bath until no more brown fumes are evolved. Evaporate down as far as possible to remove the excess of nitric acid, neutralise the arsenic acid which remains with caustic soda and evaporate the solution until crystals begin to separate out. Allow to cool, filter and drain the crystals of sodium arsenate. Use these for the reactions of arsenic acid (p. 99).

Arsenic acid is a white crystalline solid, which loses water when heated ; free pyro-arsenic acid, $H_4As_2O_7$, and meta-arsenic acid, $HAsO_3$, are not known.

The arsenates correspond in their properties and composition with the phosphates and also crystallise in the same forms as these, so that the two series of salts are isomorphous (p. 143).

Sodium Arsenate, Na_3AsO_4, is prepared by dissolving arsenious oxide in caustic soda solution, adding sodium nitrate, evaporating to dryness and fusing the residue. It closely resembles the corresponding phosphate in appearance, and is largely used in calico printing.

Owing to the great similarity of the arsenates and phosphates the reactions given by these two acids in many respects agree closely. Thus both give a yellow precipitate when heated with an acid solution of ammonium molybdate, and a white crystalline precipitate with magnesia mixture. Silver nitrate, however, gives a brick red precipitate with neutral solutions of an arsenate. Moreover, it is possible to distinguish arsenic acid from phosphoric acid by acidifying the hot solution and then passing in sulphuretted hydrogen, which slowly produces a yellow precipitate of arsenic sulphide.

EXPERIMENT 43.—Try the following tests with a neutral solution of sodium arsenate.

1. Add nitric acid and ammonium molybdate and warm gently. A yellow precipitate is produced.
2. Add magnesia mixture. A white precipitate of magnesium ammonium arsenate is formed. Examine the crystals under the microscope, compare them with those of magnesium ammonium phosphate, and ascertain that both salts crystallise in precisely the same form.
3. Add silver nitrate. A brick red precipitate of silver arsenate is produced, which readily dissolves in nitric acid.
4. Add hydrochloric acid, warm and pass in sulphuretted hydrogen. A yellow precipitate is *gradually* produced.

Arsenic acid is easily converted into arsenious acid by mild reducing agents such as sulphur dioxide,—

$$H_3AsO_4 + H_2O + SO_2 = H_3AsO_3 + H_2SO_4.$$

EXPERIMENT 44.—Boil a solution of sodium arsenate with sulphurous acid, or with a crystal of sodium sulphite and some dilute sulphuric acid. Continue boiling until the vapour no longer smells of sulphur dioxide, and then pass in sulphuretted hydrogen. A yellow precipitate of the trisulphide is at once produced.

On the other hand, arsenious acid is readily converted by oxidising agents into arsenic acid. This change is brought about very easily by free chlorine, bromine and iodine in the presence of water, and hence a standard solution (p. 157) of an arsenite is used in volumetric analysis for the estimation of these elements,—

$$H_3AsO_3 + Cl_2 + H_2O = H_3AsO_4 + 2HCl.$$

EXPERIMENT 45.—To a solution of sodium arsenite add a solution of iodine in potassium iodide drop by drop. The colour of the iodine disappears until the whole of the arsenite has been converted into arsenate. Test the resulting solution for an arsenate by ammonium molybdate or magnesia mixture.

Arsine or Arseniuretted Hydrogen, AsH_3

Arsenic forms a volatile compound with hydrogen which corresponds in composition and formula with ammonia and phosphine.

It is prepared in the pure state by acting on zinc arsenide with dilute sulphuric acid, just as sulphuretted hydrogen is prepared by acting in the same way on zinc sulphide,—

$$As_2Zn_3 + 3H_2SO_4 = 2AsH_3 + 3ZnSO_4.$$

The pure gas is *extremely poisonous*, a single bubble having been known to produce death.

A mixture of a small amount of this gas with a large amount of hydrogen is formed when any solution containing arsenic is added to zinc and dilute sulphuric acid. Thus, if arsenious acid be added, the reaction is as follows,—

$$H_3AsO_3 + 6H = AsH_3 + 3H_2O.$$

The reaction is a very delicate one, and is employed in testing for arsenic, under the name of *Marsh's test*.

The gas decomposes into its elements when it is heated to 230°, arsenic being deposited and hydrogen liberated,—

$$2AsH_3 = 2As + 3H_2.$$

It burns in the air with a bluish white flame forming arsenious oxide and water,—

$$2AsH_3 + 3O_2 = As_2O_3 + 3H_2O.$$

If, however, the flame be cooled by being directed against a piece of porcelain, free arsenic is deposited as a metallic stain on the porcelain. When the gas is passed into dilute silver nitrate solution it is oxidised to arsenious acid, which remains in solution, whilst metallic silver is deposited,—

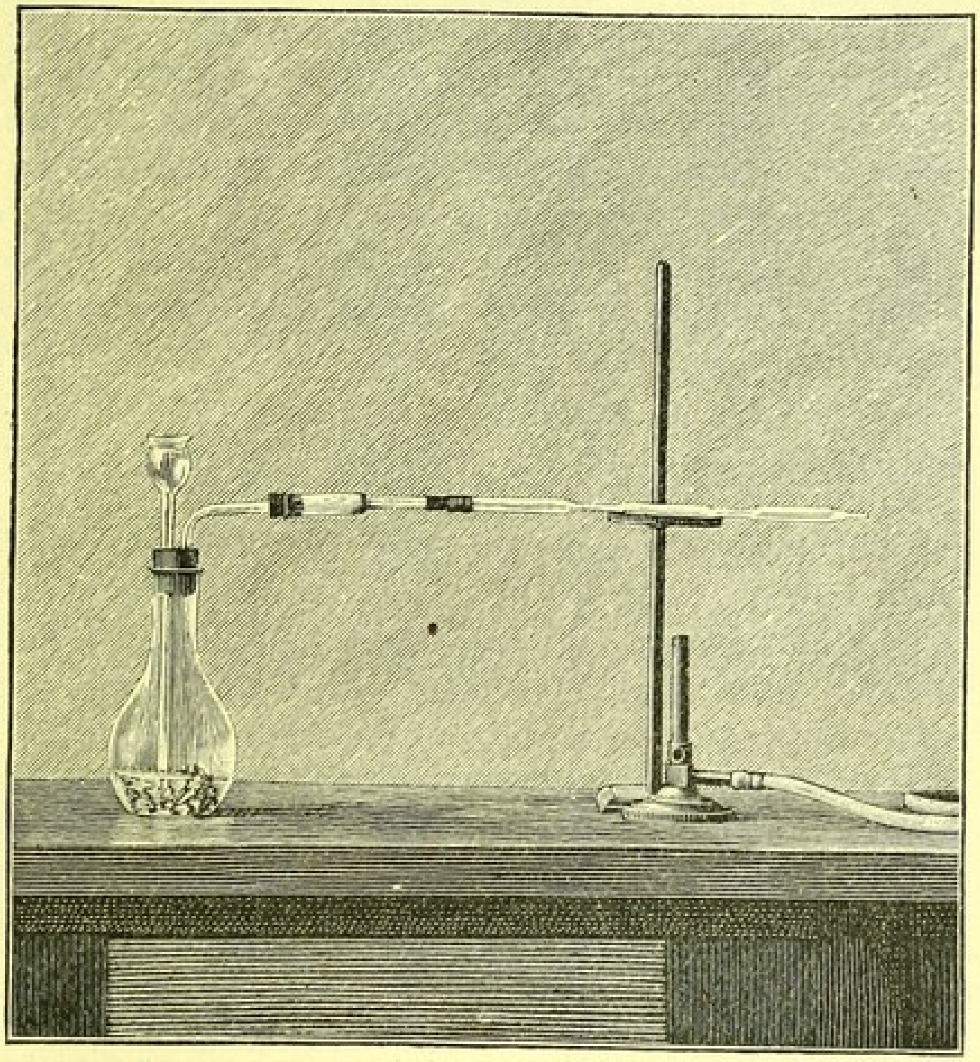


Fig. 14.

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6Ag + 6HNO_3.$$

All these properties are made use of for the identification of the gas produced in Marsh's test.

Experiment 46.—Set up an apparatus for the generation of hydrogen like that shown in Fig. 14. A small wide tube containing a little cotton wool to retain acid spray is fitted by a cork on to the conducting tube, and to this is fastened a tube of hard glass drawn out in several places, and also drawn out at the end so as to form a jet. In the flask place some granulated zinc and add dilute sulphuric acid. After a short time test the gas which is evolved by collecting some in a test-tube held over the jet, removing the test-tube mouth downwards, and bringing it to a flame. When the gas in the test-tube burns quietly, the air has all been displaced from the apparatus and a light may now be applied to the gas issuing from the jet. *In no case must a light be applied to the jet until the absence of air from the apparatus has been proved in the manner described, as otherwise a dangerous explosion may occur.* If the zinc and sulphuric acid are free from arsenic, a common impurity in both of these materials, the flame of burning hydrogen will give no stain on porcelain. Add now a *few drops* of a solution of arsenious acid or of sodium arsenite through the tube-funnel. The flame almost immediately becomes bluish-white and deposits a metallic stain on a piece of porcelain held in it. This stain of arsenic dissolves at once in sodium hypochlorite solution, sodium arsenate being formed. Next heat the tube just behind one of the narrow portions and notice that a metallic mirror of arsenic is deposited in the tube at a little distance from the flame. Disconnect the tube, and substitute another bent once at right angles, and by means of this pass the gas into some silver nitrate solution contained in a test-tube. A black precipitate of metallic silver is formed, whilst the solution becomes acid. When the clear solution is carefully neutralised with ammonia, and (if necessary) silver nitrate added—a yellow precipitate of silver arsenite is formed.

When arsine is decomposed by heat, the hydrogen produced occupies $1\frac{1}{2}$ times the volume of the original gas, and this shows its similarity in composition to ammonia and phosphine,—

$$2AsH_3 = 2As + 3H_2.$$

Arsine does not combine with acids and hence no arsenic compounds are known which correspond in composition with the ammonium and phosphonium compounds (p. 89).

Arsenic and the Halogens

Arsenious Chloride or **Arsenic Trichloride, $AsCl_3$**, is formed when arsenic burns in chlorine, and when arsenious oxide is heated with sulphuric acid and common salt,—

$$As_2O_3 + 6HCl = 2AsCl_3 + 3H_2O.$$

It is a very poisonous oily liquid which fumes in the air and boils at 130°. When it is boiled with water it passes off with the steam ; hence hydrochloric acid solutions of arsenious acid cannot be evaporated without loss, but must first be converted by some oxidising agent, such as potassium chlorate and hydrochloric acid, chlorine, etc., into derivatives of arsenic acid which are non-volatile.

No pentachloride of arsenic is known.

Arsenic Tri-iodide, AsI_3, is formed when the two elements are brought together and is a red solid, which is used in medicine.

Sulphides of Arsenic

Arsenic forms several sulphides, two of which, realgar, As_2S_2, and orpiment, As_2S_3, occur as minerals.

Arsenic Trisulphide, As_2S_3, is formed as a yellow precipitate, insoluble in acids when sulphuretted hydrogen is passed through an acid solution of an arsenite.

The sulphide behaves in many respects like arsenious oxide. Thus, just as the oxide dissolves in alkalis forming the metarsenites, so the sulphide dissolves in the alkali sulphides forming salts, which may be regarded as metarsenites in which the oxygen has been replaced by sulphur,—

$$As_2O_3 + 2NaHO = 2NaAsO_2 + H_2O,$$
$$As_2S_3 + 2NaHS = 2NaAsS_2 + H_2S.$$

These salts are known as the thiarsenites (from the Greek word *theion*, sulphur), and are at once decomposed by acids, the sulphide being reprecipitated,—

$$2NaAsS_2 + 2HCl = 2NaCl + H_2S + As_2S_3.$$

The sulphide also dissolves in caustic soda, a mixture of arsenite and thiarsenite being formed,—

$$2As_2S_3 + 4NaOH = NaAsO_2 + 3NaAsS_2 + 2H_2O.$$

It is also soluble in ammonium carbonate solution.

EXPERIMENT 47.—Acidify a solution of sodium arsenite with hydrochloric acid, warm and pass in sulphuretted hydrogen; filter and wash the precipitate produced. Test separate portions of the precipitate as follows:—

1. Heat with concentrated hydrochloric acid,—no action occurs.
2. Warm gently with dilute ammonium sulphide,—the arsenic sulphide dissolves but is reprecipitated when the liquid is acidified.
3. Treat with dilute caustic soda solution,—the precipitate again dissolves but is reprecipitated when an excess of acid is added.
4. Warm gently with ammonium carbonate solution,—the precipitate dissolves.

These properties of the sulphide are utilised in the separation of arsenic, together with antimony and tin, from those metals whose sulphides are insoluble both in acids, and in alkalis and alkali sulphides, viz. copper, lead, mercury, bismuth and cadium.

Arsenic Pentasulphide, As_2S_5.—When sulphuretted hydrogen is passed into an acid solution of an arsenate, the pentasulphide is slowly precipitated (p. 99). It resembles the trisulphide, and like it dissolves in alkalis and alkali sulphides. For analytical purposes it is best to reduce the arsenate to arsenite by means of sulphur dioxide, and then precipitate with sulphuretted hydrogen as already described.

Atomic Weight of Arsenic.—The equivalent of arsenic has been determined by the analysis of the chloride, from which it appears that 24.987 parts of arsenic unite with 35.46 parts of chlorine. A comparison of the numerous volatile compounds of arsenic shows that the atomic weight of the element is about 75, since this is the least amount of it which is ever found in a molecule. The exact atomic weight is therefore taken as $24.987 \times 3 = 74.96$.

Detection of Arsenic.—All the arsenic compounds are extremely poisonous, especially arsenious acid and its salts. Less than 0.2 gram. of arsenious oxide is a fatal dose, and this substance has often been used for criminal purposes. Arsenic poisoning is sometimes occasioned by the presence of arsenical compounds in colouring matters used for wall-papers, articles of clothing, food, beer, etc.

In testing such materials it is necessary to destroy the greater part of the organic matter present by heating it with potassium chlorate and hydrochloric acid, by which it is oxidised. The liquid is then evaporated and is either examined directly by Reinsch's or Marsh's test, or is first treated with sulphuretted hydrogen and the precipitated sulphide tested for arsenic in the usual way.

Exercises on Lesson XII

1. A specimen of arsenical iron contains 63.21 per cent of arsenic. Calculate what weight of arsenious oxide can be obtained from one ton of the ore.
2. Describe the preparation of arsenious oxide from mispickel. How can arsenic acid and arsenic trichloride be prepared from this compound?
3. Describe the preparation of sodium arsenate from sodium arsenite. How can the arsenate be reconverted into arsenite?
4. 4.858 grams. of arsenious oxide require exactly 2 grams. of potassium chlorate to convert them into arsenic acid, the potassium chlorate being reduced to potassium chloride. Calculate the equivalent of arsenic.
5. Compare the reactions of arsenic and phosphoric acids. How can these two acids be detected in a solution containing both of them?
6. What evidence is there for the statement that arsenious and arsenic acids are tribasic?
7. Describe a method of testing for a small quantity of arsenic in beer.

LESSON XIII

THE ELEMENTS OF THE NITROGEN GROUP (*Cont.*)

Antimony, Sb, 120.2

THE symbol for antimony, Sb, is derived from the name *stibium*, which was formerly applied to antimony sulphide, Sb_2S_3, the chief ore of the metal, which is now known as *stibnite*, and occurs very largely in Japan, Hungary, and Borneo.

In its chemical and physical properties antimony resembles arsenic very closely indeed, forming similar compounds with hydrogen, the halogens, oxygen, and sulphur. It has, however, a somewhat more pronounced metallic character, this being especially marked in the nature of the salts derived from the trioxide.

Preparation of Antimony.—Antimony is usually prepared by simply heating the sulphide with metallic iron which unites with the sulphur, forming sulphide of iron, whilst the antimony is liberated,—

$$Sb_2S_3 + 3Fe = 3FeS + 2Sb.$$

Sometimes, however, it is prepared in a similar manner to arsenic by roasting the antimony sulphide in a current of air and then reducing the resulting oxide, Sb_4O_6, with coal or charcoal,—

$$Sb_4O_6 + 6C = 4Sb + 6CO.$$

Antimony, unlike phosphorus and arsenic, is not volatile below a red-heat, and cannot be prepared or purified by distillation.

EXPERIMENT 48.—1. Heat a little antimony sulphide in a current of air, as described under arsenic (Expt. 38, p. 94). Observe that the oxide is deposited as an amorphous mass and that it is much less volatile than arsenious oxide, and is deposited nearer to the flame.

2. Mix some antimony oxide with sodium carbonate and potassium cyanide, and heat in the reducing flame of the blowpipe on charcoal. Brittle metallic beads of antimony are produced.

Properties of Antimony.—Antimony is a silver white substance of metallic appearance, and has a coarsely crystalline structure. When the fused metal is allowed to cool slowly in the form of a plate or slab, the surface is marked with a peculiar star-like formation, due to the crystallisation of the metal. It is very brittle, melts at 630.5°, and volatilises at a bright red-heat. Although it remains unaltered in the air at the ordinary temperature, it rapidly becomes converted into antimonious oxide, Sb_4O_6, when heated in the air. Metallic antimony is insoluble in dilute hydrochloric and sulphuric acids, but dissolves in boiling concentrated hydrochloric acid, whilst nitric acid converts it into a white powder, which is a hydrated form of the pentoxide, Sb_2O_5. The powdered metal takes fire spontaneously in chlorine and burns, forming the chloride, $SbCl_3$.

EXPERIMENT 49.—Try the following experiments with finely-powdered antimony.

1. Heat a little in a test-tube with dilute hydrochloric acid, —no action occurs.
2. Heat another portion of the metal with concentrated nitric acid,—a vigorous evolution of brown fumes takes place and the antimony is converted into a white powder.
3. Scatter a little powdered antimony into a jar of chlorine. The metal takes fire and burns, producing the chloride.

Antimony is precipitated from solutions of the chloride by metallic zinc,—

$$2SbCl_3 + 3Zn = 3ZnCl_2 + 2Sb.$$

If a piece of platinum be placed in the solution so as to touch the piece of zinc, the whole of the antimony is precipitated on the platinum.

EXPERIMENT 50.—1. In a solution of antimony chloride contained in an evaporating basin place a bright piece of metallic zinc,—antimony is at once deposited as a dull gray layer on the surface of the zinc.

2. Place a piece of platinum foil in a solution of antimony chloride and then a piece of zinc touching the platinum,—metallic antimony is at once deposited on the platinum.

The Atomic Weight of Antimony and **the Formulæ of the Antimony Compounds.**—The atomic weight of antimony has been ascertained in a precisely similar manner to that of arsenic. The analysis of the chloride and bromide shows that the equivalent is 40.07. The atomic weight derived from a study of the numerous volatile compounds of the element is about 120. Hence the number 40.07 × 3 = 120.2 is taken as the correct atomic weight. The formula of the chloride is therefore $SbCl_3$. Like arsenic, phosphorus and nitrogen, it also forms compounds in which a single atom of the element replaces five atoms of hydrogen. Such are the pentoxide, Sb_2O_5, the pentachloride, $SbCl_5$, etc.

Antimonious Oxide or **Antimony Trioxide, Sb_4O_6.**—This oxide is formed when antimony trichloride is decomposed by sodium carbonate solution, and when antimony is gently heated in the air. When the oxide is submitted to a somewhat higher temperature it combines with a further quantity of oxygen and forms a new oxide, Sb_2O_4, which is also formed when the pentoxide is heated in the air, and acts as a very weak acid-forming oxide.

Antimonious oxide is a pale buff-coloured crystalline powder which melts at a dark red-heat and volatilises at about 1500°, yielding a vapour the density of which corresponds with the molecular formula Sb_4O_6, resembling in this respect arsenious oxide, As_4O_6.

Antimonious oxide itself also acts as a weak acid-forming oxide. It does not dissolve in water, but is dissolved by caustic soda, forming sodium metantimonite, $NaSbO_2$. Antimonious oxide also acts, however, as a basic oxide forming salts with many acids,—

$$Sb_4O_6 + 12HCl = 4SbCl_3 + 6H_2O.$$

Like arsenious oxide it is converted by oxidising agents, such as iodine, chlorine, etc., into the higher oxide, antimony pentoxide, Sb_2O_5, and antimonic acid, H_3SbO_4.

Antimony Pentoxide, Sb_2O_5, is formed as already mentioned when the metal is treated with nitric acid and the residue gently heated. It is a light yellow powder, and is insoluble in water.

Antimonic Acid, H_3SbO_4, is a white powder obtained by adding an acid to the potassium salt.

The Antimonates. — The potassium salt, potassium metantimonate, $KSbO_3$, is obtained by fusing antimony with potassium nitrate. It dissolves in water and has the remarkable property of giving a white precipitate with sodium salts, sodium antimonate being the least soluble of the more common salts of sodium.

EXPERIMENT 51.—Fuse 3 grams. potassium nitrate in a small porcelain basin and to the fused mass add gradually 1 gram. powdered antimony. The metal takes fire and glows, a solid mass of potassium antimonate being formed. Extract with hot water, filter, and to a portion of the filtrate add a solution of sodium chloride. A heavy white precipitate is slowly produced, the formation of which is assisted by stirring the liquid and scratching the walls of the tube with a glass rod.

A solution of potassium antimonate may therefore be used as a reagent for sodium salts, but can only be applied after the removal of all other metals except potassium and ammonium, since the antimonates of all these other metals are also insoluble.

The Sulphides of Antimony

These compounds correspond in composition with the oxides, and in their properties closely correspond with the sulphides of arsenic.

Antimony Trisulphide, Sb_2S_3, which is the chief ore of antimony, exists in two forms. When sulphuretted hydrogen is passed into an acid solution of the chloride or some other salt, an orange-coloured amorphous form is precipitated. This orange sulphide becomes crystalline and black when it is heated, whilst the mineral stibnite is always found in this latter form.

Like the sulphide of arsenic it is insoluble in dilute hydrochloric acid, but dissolves in alkalis and their sulphides, thio-salts, known as thio-antimonites, being formed, and these are at once decomposed by acids,—

$$Sb_2S_3 + 2NaHS = 2NaSbS_2 + H_2S,$$
$$2Sb_2S_3 + 4NaHO = 3NaSbS_2 + NaSbO_2 + 2H_2O,$$
$$2NaSbS_2 + 2HCl = 2NaCl + H_2S + Sb_2S_3.$$

It is insoluble in ammonium carbonate solution, in which arsenic sulphide dissolves, and the sulphides can thus be separated.

It readily dissolves in hot concentrated hydrochloric acid, producing sulphuretted hydrogen and antimony chloride, and is often used for the preparation of pure sulphuretted hydrogen, free from hydrogen, the latter being a constant impurity in the gas prepared from ferrous sulphide, a substance which always contains free iron,—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S.$$

Experiment 52.—Pass sulphuretted hydrogen into an acid solution of antimony chloride. Filter, wash, and examine the behaviour of the precipitate to caustic soda, ammonium sulphide, and ammonium carbonate.

Antimony Pentasulphide, Sb_2S_5, closely resembles the trisulphide, and is precipitated when excess of sulphuretted hydrogen water is added to a solution containing antimonic acid. It dissolves in alkali sulphides forming thio-antimonates, such as NH_4SbS_3, ammonium thio-antimonate,—

$$2NH_4HS + Sb_2S_5 = 2NH_4SbS_3 + H_2S.$$

Antimony Trichloride, $SbCl_3$, is formed, as already mentioned, when the metal burns in chlorine. It may be prepared by heating an excess of the metal in a current of chlorine. The chloride distils over as a soft buttery colourless mass, and was hence formerly known as butter of antimony. It can also be obtained by dissolving the oxide or sulphide in hydrochloric acid and distilling. The density of the vapour is 113.3, and the molecular weight is therefore 226.6, and the formula $SbCl_3$.

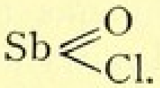
Experiment 53.—Dissolve 10 grams. antimonious oxide in an evaporating basin in 30 cc. concentrated hydrochloric acid, and evaporate as far as possible on the water bath. Place the residue in a small 2 oz. retort and distil in a draught chamber. As soon as the liquid begins to boil quietly, place a small basin to receive the distillate, which solidifies on cooling to a crystalline mass of the chloride.

Antimony chloride is at once decomposed by water with formation of the *oxychloride*, which is insoluble in water,—

$$SbCl_3 + H_2O = SbOCl + 2HCl.$$

EXPERIMENT 54.—Dissolve 5 grams. of the chloride obtained above in a few cc. of warm concentrated hydrochloric acid and pour the solution into 500 cc. of cold water. Allow to settle, decant and collect the precipitated oxychloride on a filter paper. Wash well and dry in the air.

Basic Salts.—This oxychloride is an excellent example of a basic salt. This name is given to salts which are derived from a basic oxide or hydroxide by the replacement of only a part of the oxygen or hydroxyl-groups.

Oxide.	Hydroxide.	Normal Salt.	Basic Salt.
ZnO	$Zn(OH)_2$	$ZnCl_2$	 $Zn\begin{smallmatrix}\diagup OH\\ \diagdown Cl.\end{smallmatrix}$
$(Sb_2O_3)_2$	$Sb(OH)_3$	$SbCl_3$	 $Sb\begin{smallmatrix}\diagup\!\!\diagup O\\ \diagdown Cl.\end{smallmatrix}$

Such salts are often formed in a similar manner to antimony oxychloride by the action of water on the normal salt. They are also often produced when a solution of a normal salt is treated with the corresponding hydroxide or oxide,—

$$ZnCl_2 + Zn(OH)_2 = 2ZnCl(OH).$$

The oxychloride readily dissolves in strong hydrochloric acid, antimony trichloride being reproduced,—

$$SbOCl + 2HCl = SbCl_3 + H_2O.$$

It is also soluble in tartaric acid.

When it is boiled with water or dilute sodium carbonate solution, it is converted into the oxide, Sb_4O_6,—

$$4SbOCl + 2H_2O = Sb_4O_6 + 4HCl.$$

Antimony Pentachloride, $SbCl_5$, is prepared in a similar manner to phosphorus pentachloride by passing chlorine into antimony trichloride. It is a yellow fuming liquid which decomposes when it is distilled at the ordinary atmospheric pressure. It can, however, be distilled without undergoing decomposition if the pressure be lowered, since the liquid then boils at a temperature which is below that at which it begins to decompose. This method of distilling unstable liquids at a low pressure is frequently adopted for the purification of such substances. Antimony pentachloride is decomposed by hot water, antimonic acid being formed,—

$$SbCl_5 + 4H_2O = H_3SbO_4 + 5HCl.$$

It will be remembered that phosphorus pentachloride undergoes a precisely similar decomposition when treated with water even in the cold (p. 91).

Stibine or **Antimoniuretted Hydrogen, SbH_3.**—This gas is prepared in a similar manner to arsine, which it resembles in most of its properties. The gas, however, when prepared in the usual way is always mixed with a large proportion of hydrogen, and is not nearly so poisonous as arsine.

It has been obtained quite pure by cooling the dry mixture of the gas and hydrogen by means of liquid air. A white solid mass of pure stibine is deposited which melts at $-88°$ and boils at $-11°$ forming pure gaseous stibine. It slowly decomposes into hydrogen and antimony and occasionally explodes spontaneously (p. 293).

EXPERIMENT 55.—Fit up the apparatus for Marsh's test as described under arsenic (p. 101), but introduce a few drops of antimony chloride solution instead of an arsenic compound. Proceed in the same manner as with arsenic and obtain a stain on porcelain as well as a mirror in the heated glass tube. The mirror is deposited much nearer to the flame than that of arsenic, metallic antimony being much less readily volatile than arsenic. When heated in a dry test-tube the mirror is converted into a white film of oxide, which does not easily volatilise. The stain on porcelain does not dissolve in sodium hypochlorite solution.

Stibine decomposes at a lower temperature than arsine, but burns in the air in the same manner,—

$$4SbH_3 + 6O_2 = Sb_4O_6 + 6H_2O.$$

It also differs from arsine in its action on silver nitrate solution, a black precipitate of silver antimonide being formed, mixed with a small amount of metallic silver,—

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3.$$

Alloys of Antimony.—The substances formed by the union of antimony with other metals retain the metallic appearance of their constituents, and in every way resemble metallic alloys (p. 116), whereas the compounds of phosphorus and, to a less extent, those of arsenic with the metals more closely resemble such compounds as the sulphides, etc. The most important alloys of antimony are type metal, Britannia metal and pewter. They will be more fully considered under lead and tin.

Medicinal Use of the Antimony Compounds.

The compounds of antimony act as powerful poisons in a similar manner to those of arsenic, although not so violently. They are employed in medicine as emetics, the chief compound used for the purpose being tartar emetic. This substance is prepared by boiling cream of tartar (potassium hydrogen tartrate) with antimonious oxide and water, and forms efflorescent crystals.

Exercises on Lesson XIII

1. Contrast the physical and chemical properties of antimony with those of arsenic.

2. What occurs when metallic antimony is treated with (*a*) nitric acid; (*b*) hydrochloric acid; (*c*) chlorine; (*d*) potassium nitrate?

3. What is meant by a basic salt? Describe the preparation of antimony oxychloride. What is the action of hydrochloric acid on this substance?

4. How can stibine be prepared, and how can it be distinguished from arsine?

5. How can antimonious oxide be converted into antimonic oxide? How can the latter be reconverted into the lower oxide?

6. Why is the formula Sb_4O_6 given to antimonious oxide?

7. 6.0548 grams. of antimony tribromide yielded 9.4858 grams. of silver bromide when precipitated with silver nitrate. Calculate the equivalent of antimony. (The equivalent of silver = 107.88, that of bromine = 79.92.)

LESSON XIV

THE ELEMENTS OF THE NITROGEN GROUP (*Cont.*)

Bismuth, Bi, 208

BISMUTH, the element of the nitrogen group which possesses the highest atomic weight, differs from antimony in its chemical properties much in the same way as antimony differs from arsenic. The trioxide, Bi_2O_3, is no longer acid-forming, but acts solely as a basic oxide, dissolving readily in acids to form salts, but being insoluble in alkalis. The pentoxide, Bi_2O_5, possesses an acid-forming character, but the corresponding bismuthic acid is a much weaker acid than antimonic acid, and its salts are very unstable. No volatile compound of bismuth with hydrogen is known.

Properties of Bismuth.—Bismuth itself possesses all the characteristic properties of a metal. It has the specific gravity 9.7, and possesses a peculiar reddish colour and bright metallic lustre, whilst like antimony it is brittle. It melts at 264° and expands on solidification, like water in the formation of ice. When a mass of the fused metal is allowed to cool partially, the crust then broken and the still fluid metal poured out, hollow crystals are formed which are almost cubical in shape but belong to the hexagonal system. These soon become covered with an iridescent film of oxide, and then present a beautiful appearance.

Bismuth does not dissolve in dilute hydrochloric or sulphuric acid, but is readily dissolved by nitric acid. It also combines directly with chlorine and sulphur and slowly oxidises when heated in the air, the trioxide being formed.

EXPERIMENT 56.—Powder a little bismuth in a mortar and try the following experiments with small portions of it.

1. Warm with dilute hydrochloric acid,—no action.
2. Warm with dilute sulphuric acid,—no action.
3. Warm with concentrated nitric acid,—the metal is rapidly dissolved and brown fumes are evolved.

Atomic Weight of Bismuth and Formulæ of the Bismuth Salts.—The equivalent of bismuth has been determined by converting the metal into the trioxide by acting on it with nitric acid and heating the resulting nitrate, which decomposes, forming the trioxide, whilst oxides of nitrogen and oxygen are liberated,—

$$4Bi(NO_3)_3 = 2Bi_2O_3 + 12NO_2 + 3O_2.$$

It has thus been found that the equivalent is 69.33, since this amount combines with 8 parts of oxygen. Bismuth forms a number of volatile compounds, so that the atomic weight can be settled from a study of their molecular weights and composition. It has been found in this way to be rather more than 200. Hence $69.33 \times 3 = 208$ is taken as the atomic weight of bismuth, and the formula of the oxide is Bi_2O_3. In this compound therefore, 1 atom of bismuth replaces 3 atoms of hydrogen, and the same is true of the chloride, $BiCl_3$, and the other salts derived from the trioxide.

Preparation of Metallic Bismuth.—Bismuth usually occurs in the metallic state mixed with various other minerals, and is often prepared by simply heating the ore in an inclined iron tube. The metallic bismuth melts and drains away from the unfused residue. When other ores, such as bismuth trioxide (bismuth ochre) or the sulphide (bismuthite) or other minerals are used, these are roasted and the resulting oxide then reduced by heating with carbon,—

$$Bi_2O_3 + 3C = 2Bi + 3CO.$$

A little lead is almost invariably found in the commercial metal.

EXPERIMENT 57.—Mix a little bismuth oxide with fusion mixture and heat it on charcoal in the reducing flame of the blowpipe. Beads of bismuth are formed, which are brittle and dissolve readily in nitric acid, forming bismuth nitrate.

Alloys

Bismuth and antimony show their metallic character by forming alloys with other metals. Many metals when melted together mix and form a uniform liquid, which solidifies on cooling to a mass of metallic appearance. The substances thus formed are known as *alloys* and are of immense industrial importance, because they often possess properties which do not belong to the original metals, and which fit them to be used for many purposes to which the pure metals could not possibly be applied.

The alloys formed by bismuth with lead, tin and cadmium form an excellent example of this, since they melt at much lower temperatures than any of their constituents. There are several alloys of this kind, all of which contain half their weight of bismuth alloyed with varying quantities of lead, tin, and sometimes cadmium. Two of the most important of these are the following—

Rose's Metal,
Melting-point, 94°.

Bismuth	2 parts
Lead	1 part
Tin	1 ,,

Wood's Metal,
Melting-point, 60.5°.

Bismuth	4 parts
Lead	2 ,,
Tin	1 part
Cadmium	1 ,,

Bismuth itself melts at 264°, lead at 326°, tin at 232°, and cadmium at 322°.

The most striking properties in which alloys usually differ from the average of their constituents are the melting-point, specific gravity, hardness and tensile strength. The specific heat of an alloy, on the other hand, is the mean of the specific heats of the constituent metals.

The question as to the nature of alloys, that is, whether they are to be considered as compounds or mixtures of their constituents, is a very difficult one, and cannot be discussed in detail here. In some cases crystalline alloys containing the metals in the proportions of their atomic weights have been obtained, whilst in other cases they have not. It seems, therefore, that the substances known as alloys are in some cases true compounds and in others merely mixtures (or solutions) of the original metals with each other or with these compounds.

Numerous instances of the variation in the properties of a metal produced by the addition of a second metal will be found in the following lessons.

These alloys of bismuth, known as fusible metals, not only possess the useful property of melting at low temperatures, but also that of expanding on solidification, and hence they are used for stereotyping. The "sprinklers" employed for the automatic extinction of fires contain plugs of fusible metal, which melt when heated above a certain temperature and release a supply of water.

Bismuth Trioxide, Bi_2O_3.—This oxide is slowly formed when the metal is heated in the air and is prepared by heating the hydroxide, carbonate or nitrate, all of which decompose and yield the oxide,—

$$2Bi(OH)_3 = Bi_2O_3 + 3H_2O,$$
$$4Bi(NO_3)_3 = 2Bi_2O_3 + 12NO_2 + 3O_2.$$

The oxide is a yellow powder, which becomes much darker in colour when heated.

EXPERIMENT 58.—Heat a few crystals of bismuth nitrate in a test-tube—brown fumes are evolved, and a mass left which is dark brown when hot, pale yellow when cold.

The oxide is not volatile, and hence only its empirical formula is known, whereas we are acquainted with the molecular formulæ of the corresponding volatile oxides of phosphorus, arsenic and antimony.

Bismuth Hydroxide, $Bi(OH)_3$, is a white powder obtained by adding caustic soda or ammonia to a bismuth salt,—

$$Bi(NO_3)_3 + 3NH_4HO = 3NH_4NO_3 + Bi(OH)_3.$$

Neither the oxide nor the hydroxide dissolves in alkalis, but they both dissolve in acids forming salts. These, like the salts of antimony, are easily decomposed by water with the formation of basic salts.

The hydroxide is readily converted by reducing agents into a fine black powder of the metal. Thus when caustic soda is added to a solution of a bismuth salt, together with an excess of stannous chloride solution, $SnCl_2$, and the liquid warmed, a black precipitate of metallic bismuth is produced. The stannous chloride is converted by the alkali into stannous hydrate, which takes up oxygen from the bismuth hydroxide and is converted into stannic hydrate,—

$$2Bi(OH)_3 + 3Sn(OH)_2 = 2Bi + 3Sn(OH)_4.$$

This reaction forms an excellent test for small quantities of bismuth.

Experiment 59.—To a solution of bismuth chloride add a solution of stannous chloride, and then caustic soda in excess, and warm gently. A black precipitate of metallic bismuth is formed.

The reduction of bismuth hydroxide to metallic bismuth takes place in two stages. In the first stage an unstable *monoxide of bismuth*, BiO, is formed,—

$$2Bi(OH)_3 + Sn(OH)_2 = 2BiO + Sn(OH)_4 + 2H_2O$$

This oxide is then reduced by excess of stannous hydrate to metallic bismuth.

Corresponding with this monoxide, an unstable chloride, $BiCl_2$ and sulphide BiS are known, in all of which bismuth acts as a bivalent element.

Bismuth Chloride, $BiCl_3$, is obtained by dissolving the oxide in hydrochloric acid or heating the metal in chlorine.

It is a white granular mass, which, like antimony chloride, is volatile and can be distilled. Its vapour has the density agreeing with the molecular formula $BiCl_3$. The chloride dissolves in hydrochloric acid, but, like antimony trichloride, it is decomposed by water, forming the white oxychloride BiOCl, which is insoluble in water but soluble in hydrochloric acid, whilst it is insoluble in tartaric acid,—

$$BiCl_3 + H_2O = BiOCl + 2HCl.$$

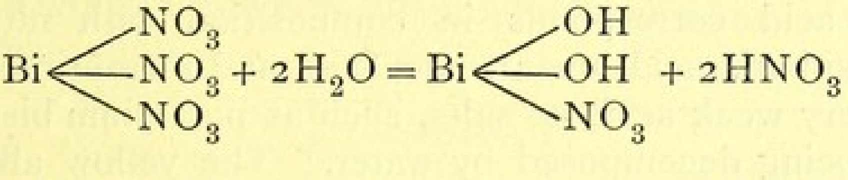
Experiment 60.—Dissolve 2 grams. of bismuth oxide in 10 cc. of hydrochloric acid and evaporate on the water bath. Dissolve the residue in a little hydrochloric acid, and—

1. To a small portion add excess of ammonia,—a white

flocculent precipitate of the hydroxide is formed, which is insoluble in excess of ammonia.

2. Pour the remainder into 250 cc. of water in a beaker,—a white precipitate of the oxychloride is formed, which is soluble in hydrochloric acid and insoluble in tartaric acid.

Bismuth Nitrate, $Bi(NO_3)_3 + 5H_2O$, is prepared by dissolving the metal, or its oxide, or carbonate, in concentrated nitric acid and evaporating. Prismatic crystals are formed which deliquesce on exposure to the air. This salt, like the chloride, is decomposed by a large quantity of water, **basic bismuth nitrate** being precipitated as a white crystalline powder. This basic nitrate is formed by the removal of two of the three acid groups of the nitrate and their replacement by hydroxyl groups,—



$$Bi\begin{cases} NO_3 \\ NO_3 \\ NO_3 \end{cases} + 2H_2O = Bi\begin{cases} OH \\ OH \\ NO_3 \end{cases} + 2HNO_3$$

The basic nitrate may, therefore, be regarded as bismuth hydroxide, in which only one hydroxyl group has reacted with nitric acid.

It is largely used in medicine and as a cosmetic for softening the skin.

Normal Bismuth Carbonate, $Bi_2(CO_3)_3$, is not known, the white powder formed when sodium carbonate is added to a solution of the nitrate and the precipitate dried being the **basic carbonate, $Bi_2O_2CO_3$.** This, as is seen from the formula, corresponds in composition with the oxychloride, allowance being made for the fact that the acid group, CO_3, combines with 2 atoms of hydrogen, and is therefore equivalent to 2 atoms of chlorine or 1 atom of oxygen,—

$BiCl_3$	$BiOCl$
$Bi_2(CO_3)_3$	$Bi_2O_2(CO_3)$.

Bismuth Sulphide, Bi_2S_3, occurs as the mineral bismuthite, and is precipitated as a black powder when an acid solution of the chloride is treated with sulphuretted hydrogen. It is insoluble in alkalis and alkali sulphides, and thus differs from the sulphides of antimony and arsenic in the same way as the oxide differs from the corresponding oxides of these elements. It readly dissolves in hot dilute nitric acid, forming the nitrate.

EXPERIMENT 61.—Pass sulphuretted hydrogen through an acid solution of bismuth chloride. A black precipitate of the sulphide is produced which is soluble in hot dilute nitric acid, but insoluble in caustic soda and ammonium sulphide.

Bismuth Pentoxide, Bi_2O_5, and Bismuthic Acid, $HBiO_3$.—When bismuth hydroxide is suspended in a solution of potash and a current of chlorine passed into the liquid, a red powder is formed which contains impure bismuthic acid $HBiO_3$,—

$$Bi(OH)_3 + Cl_2 = HBiO_3 + 2HCl.$$

This acid corresponds in composition with nitric acid, metaphosphoric acid, metarsenic acid, and metantimonic acid. It is a very weak acid, its salts, such as potassium bismuthate, $KBiO_3$, being decomposed by water. The yellow alkali salts can be prepared nearly pure by dissolving the crude acid in hydrofluoric acid and adding the solution to caustic soda or potash. When these salts are treated with nitric acid, the free bismuthic acid is obtained as a red powder.

When this is heated it decomposes forming bismuth trioxide, free oxygen and water,—

$$2HBiO_3 = Bi_2O_3 + O_2 + H_2O$$

General Properties of the Elements of the Nitrogen Group

It will be seen from the foregoing that the elements nitrogen, phosphorus, arsenic, antimony and bismuth form a true chemical group or family just as do the halogen elements.

These elements all form oxides of the empirical formulæ R_2O_3 and R_2O_5. As the atomic weight of the elements increases these oxides become gradually less acid and more basic in their character. Thus arsenic acid is a much weaker acid than nitric acid, and in the same way bismuthic acid is still weaker than arsenic acid. The lower oxide shows this change in a still more marked degree. The trioxides of nitrogen and phosphorus are purely acid-forming oxides; arsenious oxide occupies an intermediate position, since it yields unstable salts by the action of powerful acids, such as hydrochloric acid and sulphuric acid; the corresponding oxide of antimony readily yields salts with most acids, although it still acts as an acid-forming oxide and yields salts with alkalis; finally, bismuth trioxide is a purely basic oxide, and yields a well defined series of salts with acids, but none at all with alkalis.

The sulphides of arsenic, antimony and bismuth show a similar progressive change of properties; those of arsenic and antimony are soluble in alkalis and alkali sulphides, whilst that of bismuth does not dissolve in either of these reagents.

Very characteristic are the volatile compounds with hydrogen, the gradual change in the properties of which is shown in the following table:—

Element.	Formula.	Temperature of Decomposition.	Properties.
Nitrogen .	NH_3	Red heat.	Combines readily with acids.
Phosphorus	PH_3	...	Combines only with hydriodic and hydrobromic acids.
Arsenic .	AsH_3	230°	Does not combine with acids.
Antimony .	SbH_3	below 150°	Do.
Bismuth .	Does not exist.		

The appearance and physical properties of the elements themselves also vary gradually as the atomic weight increases. Nitrogen is a gas, or at a very low temperature a transparent ice-like mass. Phosphorus is a yellow transparent solid or red mass. Arsenic has a metallic lustre, and volatilises without melting when heated. Finally, antimony and bismuth have the true metallic appearance, and melt readily when heated.

Arsenic and antimony thus stand out very clearly as being intermediate in character between the non-metal phosphorus on the one hand and the metal bismuth on the other.

Exercises on Lesson XIV

1. How is metallic bismuth prepared?

2. Contrast the physical and chemical properties of bismuth with those of arsenic.

3. What is an alloy? In what respects does an alloy usually differ from the metals of which it is composed?

4. Describe the composition and properties of fusible metal.

5. What occurs when bismuth trioxide is (*a*) heated; (*b*) treated with nitric acid and the product poured into water; (*c*) suspended in caustic potash solution and treated with chlorine?

6. How does bismuth sulphide differ from the sulphides of antimony and arsenic?

7. Why are the elements nitrogen, phosphorus, antimony, arsenic, and bismuth placed together in one group or family of elements?

8. In what respects are arsenic and antimony intermediate between phosphorus and bismuth?

LESSON XV

DETERMINATION OF THE ATOMIC WEIGHT FROM THE SPECIFIC HEAT OF THE SOLID ELEMENT

MANY of the elements, and more especially of the metals, either form no volatile compounds, or very few, so that the method of determining the atomic weight based on Avogadro's theory (p. 4) cannot be applied. In such cases, therefore, it is necessary to have recourse to some other property of the elements, and it has been found that the problem may be solved by a method which depends on the study of the specific heat of the elements in the solid state.

When any hot solid substance, such as a piece of metal, is brought into water of the ordinary temperature, the substance is cooled and the water heated, until finally both attain the same temperature, the water having gained the heat which the solid substance has lost.

The amount of heat requirea to raise the temperature of 1 *gram. of water from* 0° *to* 1° *C. is called a unit of heat or calorie*, and all quantities of heat are measured by this unit. Thus "10 units of heat" means the amount of heat which will raise the temperature of 10 grams. of water from 0° to 1° C. It is found by experience that the heat required to raise 1 gram. of water from 0° to 100° C. is practically equal to 100 units; and hence we may say that 10 units of heat will raise the temperature of 1 gram. of water from 0° to 10°, or from 10° to 20°, or of 2 grams. of water from 0° to 5°. Hence it follows that the number of units of heat gained or lost by a given weight of water is found by multiplying the weight of the water in grams. by the number of degrees C. by which its temperature has been changed.

All other substances are compared with water in this respect, and *the number of units of heat required to raise the temperature of* 1 *gram. of the substance through* 1° *C. is called the specific heat of the substance.*

It has already been pointed out (R. and L., p. 112) that very different quantities of heat are required when equal weights of different substances are heated through the same range of temperature. Hence, if equal weights of two substances are heated to the same temperature and then brought into equal weights of water standing at the temperature of the air, the inequality between the amounts of heat which the solid substances have taken up is shown by the differences between the temperatures to which the water in the two vessels is heated. Moreover, the results of such an experiment may be used to ascertain the actual specific heat of the substances. The amount of heat lost by a solid body in cooling from one temperature to another is equal to *the specific heat* × *the number of degrees by which it is cooled* × *the weight of the substance in grams.* Thus when 2 grams. of mercury, the specific heat of which is 0.032, are cooled from 100° to 15°, the amount of heat lost is $0.032 \times (100 - 15) \times 2 = 0.032 \times 85 \times 2 = 5.44$ units. The same amount would of course be gained if the mercury were heated from 15° to 100°.

The specific heat of a solid substance can therefore be determined by bringing a known weight of the substance at a known temperature into a weighed amount of water at a lower temperature, thoroughly stirring and then taking the resulting temperature of the water. This process, known as the "Method of Mixtures," may be roughly illustrated by the following experiment, which also exemplifies the way in which the value of the specific heat is derived from the numbers obtained.

EXPERIMENT 62.—Weigh out into one test-tube 50 grams. of mercury and into a second 50 grams. of granulated zinc. Fit each tube with a cork carrying a tube bent once at right angles, to prevent the entrance of steam, and support both the test-tubes in a beaker of boiling water, keeping the water boiling for about ten minutes. In the meantime, place 100 cc. of water in each of two small beakers, stir well with a thermometer, and finally read off and note the temperature of each. The thermometer used should be as sensitive as possible, since the difference of temperature to be observed is only small. One graduated in 1/10° C. gives quite satisfactory results.

Next as quickly as possible remove one tube from the boiling water and pour its contents into one of the beakers, stir well for about half a minute, and read the temperature. Repeat the same process with the second tube and the remaining beaker of water and note the two results.

In an actual experiment the following numbers were thus obtained :—

	Mercury.	Zinc.
Original temperature of water . .	23.2°	23.6°
Final temperature of water . .	24.2°	27.0°

Calculation.—50 grams. of mercury have been cooled from 100° to 24.2°, *i.e.* through $100 - 24.2 = 75.8°$.

The heat lost in this process is therefore $S \times 75.8 \times 50$, where S is the specific heat of mercury.

This amount of heat has been gained by the water, 100 grams. of which have been heated from 23.2° to 24.2°, *i.e.* through 1°. The water has therefore gained

$$100 \times 1 = 100 \text{ units of heat.}$$

Hence, since the heat lost by the metal has been gained by the water,—

$$S \times 75.8 \times 50 = 100.$$

$$S = \frac{100}{50 \times 75.8} = .026.$$

Calculating the specific heat of the zinc in the same way it is found that—

$$S \times (100 - 27) \times 50 = 100\ (27 - 23.6).$$

$$S \times 73 \times 50 = 100 \times 3.4.$$

$$S = \frac{100 \times 3.4}{73 \times 50} = .093.$$

These numbers are both rather lower than the correct values (p. 128). The reason for this is that several corrections have been omitted which are necessary for accurate determinations. The three most important of these are :—

1. *The water value of the calorimeter.*—The beaker and thermometer are both heated as well as the water, so that in effect more than 100 grams. of water are really present.

2. *Loss of heat of the water* to the surrounding atmosphere, so that the temperature attained by the water is lower than it would otherwise be.

3. *Errors of thermometer.*—The graduation of the thermometer should be very carefully examined, and any errors taken into account.

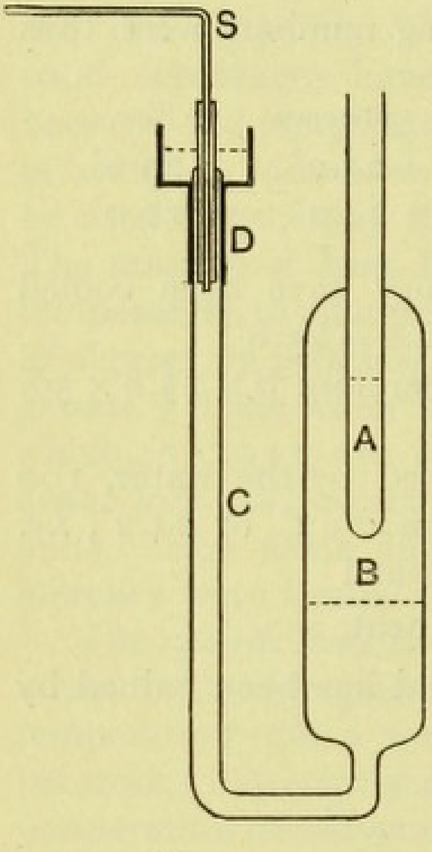


Fig. 15.

The foregoing process can only be used for substances which are not affected by water, and moreover requires a considerable quantity of material.

When **Bunsen's ice calorimeter** (Fig. 15) is employed, the determination can be carried out with a much smaller amount of material, and the substance is not brought into contact with water. This apparatus consists of a test-tube (A), sealed into a wider glass vessel (B), the latter being provided with a long, horizontal, glass index-tube (S) attached to the vessel (B) by the joint (D). The outer vessel is partially filled with pure water, the remainder of the vessel from the dotted line downwards and the index-tube containing mercury. The inside tube is then strongly cooled internally by passing a rapid current of air through some ether placed in the tube, so that a cake of ice is formed round it, and the whole apparatus is then carefully packed in snow and thus kept at the constant temperature of 0° C. When the hot body is introduced into the test-tube its heat is given up to the surrounding ice, part of which is thus melted, producing water of 0°, whilst the body itself is also cooled to 0°. Since ice is more bulky than water at the same temperature, a contraction is produced and the mercury in the index-tube alters its position. 80 units of heat are required to melt 1 gram. of ice, and this causes a contraction of 0.0907 cc. Hence by measuring the change of position of the mercury in the index-tube, the number of units of heat lost, and hence the specific heat of the body, can be calculated.

Relation between the Atomic Weight and the Specific Heat

Many of the metals form a number of volatile compounds, so that their atomic weights can be determined by the ordinary method, which has been previously described (p. 4). When the specific heats of these metals are considered, it is found that in every case a very remarkable relation exists,—*the specific heat multiplied by the atomic weight always gives nearly the same product*, and this is about 6.4. This is well shown in the following table :—

Element.	A. Atomic Weight.	S. Specific Heat.	A. × S. Atomic Heat.
Aluminium . .	27.1	0.219	5.9
Zinc	65.4	0.094	6.1
Arsenic . . .	75.0	0.083	6.2
Tin	119.0	0.055	6.5
Antimony . . .	120.2	0.050	6.0
Mercury . . .	200.0	0.032	6.4
Lead	207.1	0.031	6.4
Bismuth . . .	208.0	0.030	6.2

The product of the specific heat and the atomic weight is called the *atomic heat*, because it represents the heat required to raise a number of grams. of the metal numerically equal to its atomic weight through 1° C. We may therefore say that all the metals in the foregoing list have about the same atomic heat. Since this relation holds in the cases in which the atomic weight can be independently determined, we are justified in assuming that it also holds for the other solid elements, the more so as the results obtained on this assumption are in perfect agreement with all the other properties of these elements.

This relation was first discovered by the two French chemists, Dulong and Petit, in 1819, and hence the theory is known by their name and is usually stated in the form,—*The atoms of different elements possess the same capacity for heat.*

The atomic weight of an element can therefore be approximately determined by dividing the atomic heat by the specific heat, and this method is now employed for all such elements as can be obtained pure in the solid state, and is of the utmost importance for those which form no volatile compounds.

Thus the specific heat of mercury is 0.0319, and hence its atomic weight must be about $6.4/0.0319 = 200$.

The following table contains a list of some of the commoner elements, together with the atomic weight, specific heat and atomic heat of each, arranged in the order of their atomic weights.

Element.	S. Specific Heat.	A. Atomic Weight.	A. × S. Atomic Heat.
Sodium	0.2930	23.00	6.7
Magnesium	0.2500	24.32	6.1
Aluminium	0.2190	27.1	5.9
Potassium	0.1662	39.10	6.5
Calcium	0.1700	40.09	6.8
Chromium	0.1208	52.0	6.3
Manganese	0.1217	54.93	6.7
Iron	0.1162	55.85	6.5
Nickel	0.1084	58.68	6.3
Cobalt	0.1030	58.97	6.1
Copper	0.0936	63.57	6.0
Zinc	0.0935	65.37	6.1
Arsenic	0.0830	74.96	6.2
Bromine	0.0843	79.92	6.7
Silver	0.0562	107.88	6.1
Cadmium	0.0548	112.40	6.2
Tin	0.0551	119.0	6.6
Antimony	0.0495	120.2	5.9
Iodine	0.0541	126.92	6.9
Barium	0.0500	137.37	6.9
Platinum	0.0323	195.2	6.3
Gold	0.0316	197.2	6.2
Mercury	0.0319	200.0	6.4
Lead	0.0310	207.1	6.4
Bismuth	0.0304	208.0	6.3

It will be noticed at once that the atomic heats of the different elements are not exactly equal to each other, but vary from about 5.9 to 6.9. It follows from this that the atomic weight calculated by this method from the atomic heat can only be approximate. It must, therefore, be corrected by an exact determination of the equivalent of the element, that multiple of the equivalent being selected as the atomic weight which comes nearest to the number obtained from the atomic heat.

Examples.—1. Silver has the specific heat 0.056. Hence its atomic weight must be approximately

$$\frac{6.4}{0.056} = 114.$$

Exact experiments (p. 64) show that 107.88 is the equivalent of silver, and hence this number is taken as the exact atomic weight of silver.

2. Magnesium is a metal which has the equivalent 12.16. Its specific heat is 0.25, and hence its atomic weight must be about

$$\frac{6.4}{0.25} = 25.8.$$

Now the multiple of 12.16 which is nearest to 25.8 is obviously $12.16 \times 2 = 24.32$, and hence this number is taken as the exact atomic weight of magnesium. The atomic weight in this case, therefore, is double the equivalent.

3. Platinum has the low specific heat 0.0323, and hence its atomic weight must be about

$$\frac{0.0323}{6.4} = 198.$$

Accurate experiments have shown that in platinic chloride 48.8 parts of platinum combine with 35.46 of chlorine. The multiple of this which is nearest to 198 is obviously $48.8 \times 4 = 195.2$, and this is accordingly taken as the correct atomic weight of platinum.

This process is in many respects similar to that with which we have already become familiar for obtaining the atomic weight by ascertaining the smallest amount of the substance ever present in a molecule. This, it will be remembered, also gives only an approximate number, which must be corrected by means of the equivalent as determined by accurate experiments.

It follows from the foregoing examples that the products of the *equivalents* of the metals and their specific heats all stand in some simple ratio to each other. Thus taking the three cases just mentioned, the product in the case of silver is $107.88 \times 0.056 = 6.0$; in the case of magnesium it is $12.16 \times 0.25 = 3.04$, and in the case of platinum it is $48.8 \times 0.0323 = 1.54$. These three numbers, 6.0, 3.04 and 1.54, stand in the simple ratio of 4 : 2 : 1. This was the *fact* which was first discovered by Dulong and Petit, and led them to their *theory* that the *atoms* of all the elements have the *same* capacity for heat.

Exceptions to Dulong and Petit's Theory

It will be noticed that several of the commoner solid elements are not included in the list on p. 128. The most important of these are carbon, boron and silicon. When the specific heats of these elements are determined at the ordinary temperature, it is found that the atomic heats are considerably below the average for the other elements (column 4).

	1	2	3	4	5	6	7
	At. Wt.	Temp.	Sp. Heat.	At. Heat.	Temp.	Sp. Heat.	At. Heat.
Boron . . .	11	50°	0.307	3.4	Red heat	0.50	5.5
Diamond . .	12	50°	0.146	1.8	985°	0.459	5.5
Graphite . .	12	50°	0.190	2.3	985°	0.467	5.6
Silicon . . .	28.3	55°	0.173	4.9	232°	0.203	5.7

Investigation has shown that in all these cases the specific heat varies considerably with the temperature at which it is determined. At a high temperature more heat is required to raise the temperature by 1° C. than at a low temperature, as is seen by comparing the figures in columns 2 and 3, 5 and 6. At higher temperatures, consequently, the atomic heat (column

7) becomes much more nearly equal to that of the other elements, and also becomes almost constant, so that a further rise of temperature does not greatly influence its value.

It has in fact been found that the specific heat of almost every element varies to a greater or less extent with the temperature at which it is determined, but in most cases the variation is so slight that its influence on the atomic heat can be neglected.

Molecular Heat of Compounds.—When two elements combine, the specific heat of the resulting compound is found to depend on the number of atoms which have united to form the new molecule. The specific heat × the molecular weight of the compound is called *the molecular heat* of the compound, and it is found that this *is equal to the sum of the atomic heats of the atoms contained in the molecule.* Thus, potassium bromide has the formula KBr, so that the molecular weight, according to this formula, is $39.1 + 79.92 = 119.02$. The specific heat of potassium bromide is 0.107, and hence the molecular heat is $119.02 \times 0.107 = 12.7$, and this is almost equal to the sum of the atomic heats of potassium and bromine, $6.5 + 6.7 = 13.2$. Again lead iodide has the formula PbI_2, and hence its molecular weight is 460.9; its specific heat is 0.0427, so that its molecular heat is $460.9 \times 0.0427 = 19.7$, and this is almost identical with the numbers calculated from the atomic heats of lead and iodine, $6.4 + 2 \times 6.9 = 20.2$. This relation may be used to calculate roughly the atomic heat (and hence the specific heat) of elements which cannot readily be obtained in the solid state when free, such as hydrogen, oxygen, or chlorine. Thus the specific heat of silver chloride is 0.084, and its molecular heat, therefore, $0.084 \times 143.3 = 12$. The atomic heat of chlorine may then be found by subtracting from this the atomic heat of silver, and is therefore equal to $12 - 6.1 = 5.9$, a value which it has in nearly all the solid compounds of chlorine with the metals.

In a similar way the following atomic heats have also been ascertained, and it will be noticed that in all cases they are lower than the average for the metals,—

Nitrogen,	5.3,
Oxygen	4.0,
Hydrogen,	2.3.

The fact that the molecular heat of a compound depends chiefly on the number of atoms present in the molecule, and not on their particular nature, can also be made use of to determine the number of atoms present in the molecule of a salt, even when the atomic weight and specific heat of one of the elements present are unknown. The metal strontium, for example, is very difficult to prepare pure, so that the determination of its specific heat cannot easily be carried out, and as this metal forms no volatile compounds, the atomic weight of the metal must be determined indirectly. Analysis proves that 35.46 of chlorine combine with 43.8 of strontium, and from this the atomic weight can of course be calculated, provided that the *formula* of the chloride is known. In order to ascertain which of the possible formulæ—such as $SrCl$, $SrCl_2$, $SrCl_3$, etc.—is the correct one, the molecular heat may be calculated from the number of atoms present in the molecule, assuming strontium to have about the same atomic heat as the other metals, and this can be compared with the value obtained by multiplying the specific heat of the salt by the molecular weight corresponding with the formula in question. This is done in the following table, the atomic heat of chlorine being taken as 5.9, and it is seen that only in the case of the formula $SrCl_2$ do the two values for the molecular heat agree. This is, therefore, taken as the true formula for the salt; whence it follows that one atom of strontium combines with two atoms of chlorine, and that the atomic weight is twice the equivalent $= 43.8 \times 2 = 87.6$.

Formula	Molecular Wt. A.	Specific Heat of Strontium Chloride.	Molecular Heat. A.×S.	Molecular Heat calculated from the Formula.
$SrCl$.	79.3	0.12	9.5	$6.4 + 5.9 = 12.3$
$SrCl_2$.	159.3	0.12	19.1	$6.4 + 5.9 \times 2 = 18.2$
$SrCl_3$.	237.8	0.12	28.5	$6.4 + 5.9 \times 3 = 24.1$

SUMMARY

According to Dulong and Petit's theory, the atoms of all the solid elements have the same capacity for heat. Hence the product of the specific heat and the atomic weight, known as the atomic heat, is a constant quantity ; the value of this quantity varies somewhat for the different elements, but on the average is about 6.4. An approximate value for the atomic weight of any solid element can therefore be obtained by dividing 6.4 by the specific heat of the element. The atoms of the various elements have the same capacity for heat in compounds as in the pure element.

EXERCISES ON LESSON XV

1. What is meant by the terms unit of heat, specific heat, atomic heat, molecular heat?

2. How can the specific heat of a metal be determined?

3. What relation exists between the atomic weight of an element and its specific heat?

4. A certain element has the equivalent 9 and the specific heat 0.22. What is its atomic weight?

5. 1.028 grams. of the chloride of a metal are just sufficient to precipitate 2 grams. of silver as silver chloride. The specific heat of the metal is 0.17. Find (*a*) the equivalent of the metal ; (*b*) the atomic weight of the metal ; (*c*) the formula of the chloride.

6. The specific heat of mercuric oxide (HgO) is 0.048, and that of ice is 0.478. Calculate from these numbers the atomic heats of oxygen and hydrogen in these compounds.

7. 2.772 grams. of a certain metal yield 3.614 grams. of the pure nitrate. The specific heat of the metal is 0.0335. Calculate the atomic weight of the metal.

8. 1 gram. of a metal unites with 0.541 gram. of chlorine to form the chloride, which has the specific heat 0.136. What is the atomic weight of the metal?

9. What solid elements do not conform to Dulong and Petit's theory? How does the specific heat of these elements vary with the temperature at which it is determined?

LESSON XVI

CRYSTALS—ISOMORPHISM

When a solid substance is dissolved in water and the liquid slowly evaporated, it is usually found that the solid is deposited in separate *crystals*, which are characterised (1), by their definite geometrical shape, and (2), by the fact that their properties are not the same in all directions within the crystal, but differ considerably in different directions. Crystals are also frequently formed when a fused solid is allowed to cool, and when the vapour of a volatile substance, such as iodine or arsenious oxide, is allowed to condense slowly.

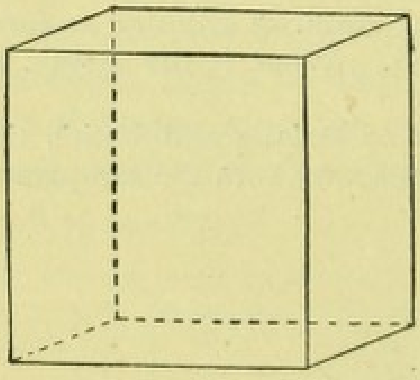


Fig. 16.

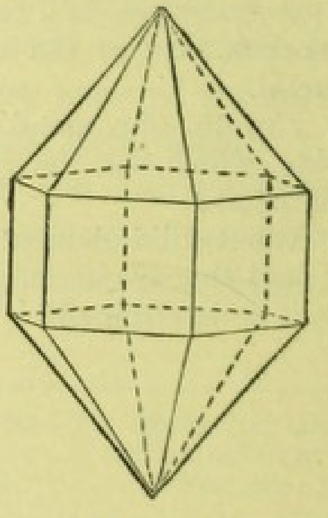


Fig. 17.

Crystals are bounded by smooth shining plane *faces*, which cut one another in sharp straight *edges*, whilst three or more faces meet together forming *angles*. Thus a crystal of rock-salt has the shape of a cube, bounded by six square faces (Fig. 16); a crystal of quartz consists of a six-sided prism, capped at either end by a six-sided pyramid (Fig. 17), and a crystal of calc-spar (calcium carbonate) is a rhombohedron or six-faced solid, which resembles a cube, with the difference that the six faces are not squares, but rhombs (Fig. 18).

These crystals all differ in a remarkable manner from solids of similar shape made of such substances as glass or resin. When a cube of glass is struck a smart blow with a hammer it breaks up into irregular fragments. When, however, a piece of rock-salt is treated in the same way it breaks up into smaller cubes, or fragments with all their intersecting faces at right angles. A piece of calc-spar, on the other hand, always breaks up into smaller rhombohedra, in which the faces all meet at the same angles as in the rhombohedron shown in the figure.

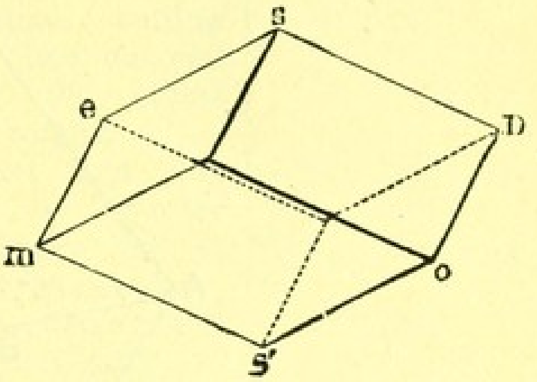


Fig. 18.

In every crystal there are some directions in which fracture takes place more easily than in others, and the planes in which these lie are called *planes of cleavage*. The existence of these planes shows that the cohesion between the molecules of which the crystal is made up is less in some directions than in others, so that we may say that crystals possess a definite internal structure, usually known as *crystalline structure*.

Solid substances which do not possess this kind of structure but have identical properties in every direction, and break up into irregular fragments when struck, are said to be *amorphous* (Greek, without form), examples being glass, resin, flint, etc. Crystals also differ from amorphous solids in their behaviour towards light and heat (p. 142).

The external form of a crystal can easily be ascertained by simply measuring the angles between the various faces. It is thus found that crystals differ widely among themselves in symmetry of form. In order to represent this more clearly we may imagine that the faces of each crystal are arranged about straight lines called *axes*, which intersect at the centre of the crystal. Thus Fig. 19 represents a double pyramid on a square base, the faces of which are arranged about three axes, all at right angles, two of which, AC and BD, are equal, whilst the third, EF, is longer than these. Any plane which divides a crystal into two parts which are exactly similar in shape and position is called a *plane of symmetry*. Thus in Fig. 19 three planes of symmetry are shown, viz., ABCD, BEDF, and AECF, each of which divides the crystal into two precisely similar halves. If the whole form (Fig. 19) be rotated about the axis EF through an angle of 90°, the axis AC will take the position BD and the figure then presents precisely the same appearance as before. EF is therefore termed an *axis of symmetry*, and this name is given to any axis which possesses a similar property, although the angle through which the crystal must be rotated may be different. When each face of a crystal is accompanied by a parallel face, the crystal is said to possess a *centre of symmetry*. Thus in Fig. 19 the faces occur in parallel pairs, *e.g.* ABE and DCF, about the point of intersection of the dotted axes, which point is therefore the centre of symmetry of the crystal.

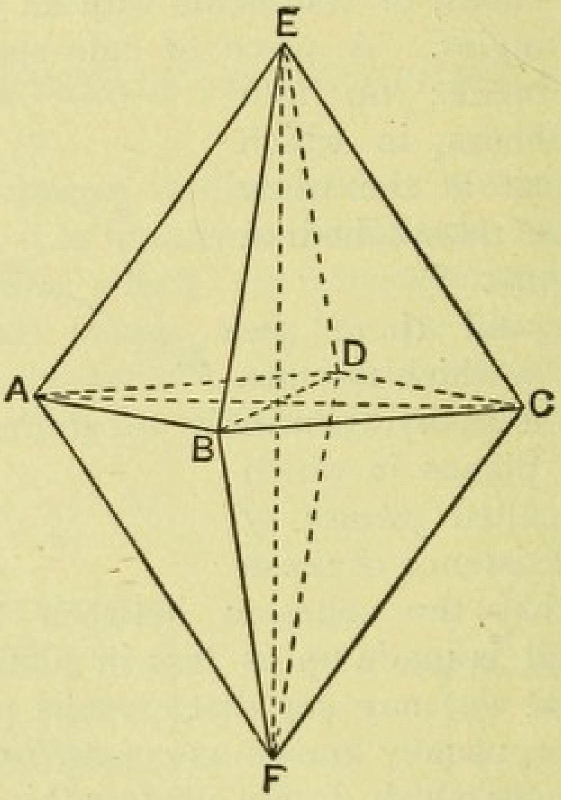


Fig. 19.

Crystals are classified according to their symmetry, and all the thousands of forms of both natural and artificially prepared crystals which are known can be arranged in 32 classes. All these classes belong to the following six crystallographic systems, each system being characterised by the nature of the crystallographic axes. All the crystals of a system have the same crystallographic axes, but do not have the same degree of symmetry, this being different in the different classes.

Name of System.	Axes.	Number of Classes in the System.
1. Regular . . .	Three equal and all at right angles.	5
2. Hexagonal . .	Three equal, cutting at 60° ; one unequal meeting the others at right angles.	12
3. Tetragonal . . (Quadratic)	Two equal and one longer or shorter than these ; all at right angles.	7
4. Rhombic . .	Three all unequal and at right angles.	3
5. Monosymmetric . (Monoclinic)	Three unequal ; two at right angles, the third inclined to the other two.	3
6. Asymmetric . . (Triclinic)	Three unequal and inclined at different angles.	2

1. The Regular System.—This system is characterised by three equal axes, all at right angles. The simplest forms are the *octahedron* (Fig. 20), each face of which cuts all three axes at equal distances ; the *cube* (Fig. 16), in which each face only cuts one axis and is parallel to the plane containing the other two, and the *rhombic dodecahedron* (Fig. 21), a figure with twelve faces, each of which cuts two axes. Another form is the *tetrahedron* (Fig. 22), which has only half the number of faces of the octahedron, and is hence known as a *hemihedral* form. Its relation to the octahedron is shown in Fig. 23.

Faces belonging to several of these simple forms are often found on a single crystal. Thus Fig. 24 represents a crystal of alum on which faces of the cube (marked ∞ o ∞) and

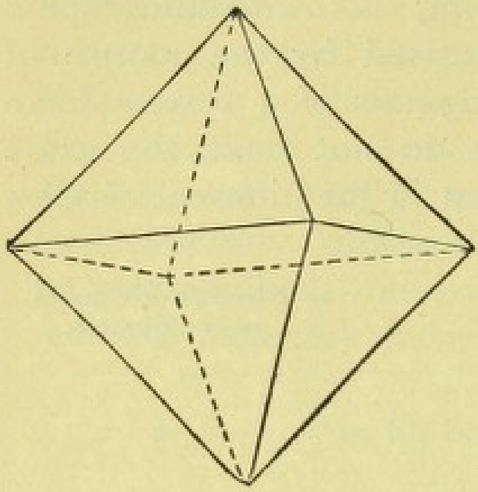


Fig. 20.

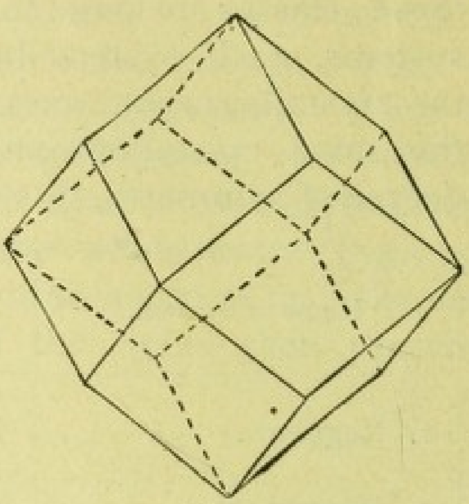


Fig. 21

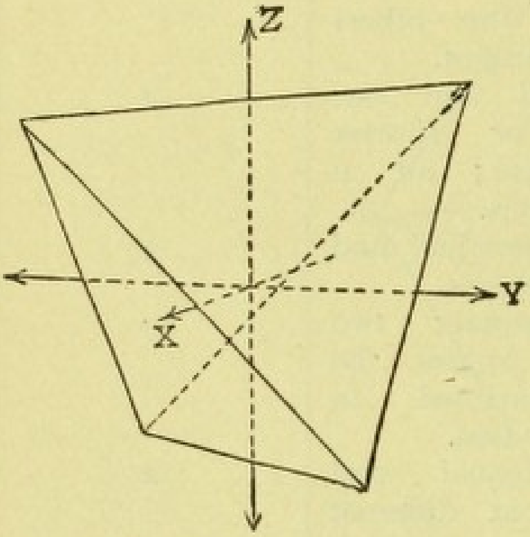


Fig. 22

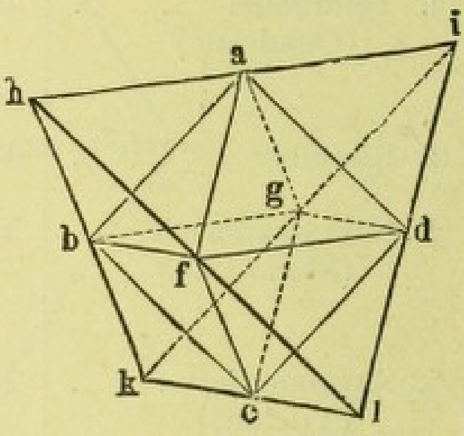


Fig. 23.

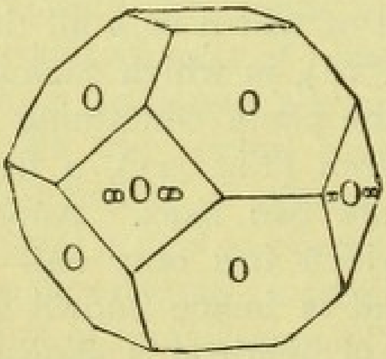


Fig. 24.

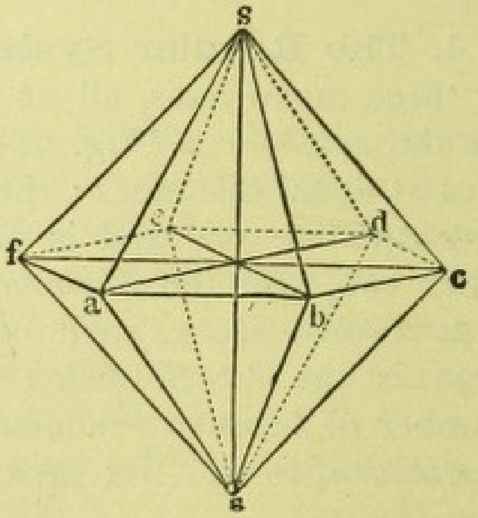


Fig. 25.

of the octahedron (marked o) are both seen. The most important substances which crystallise in this system are the diamond, fluorspar, common salt, alum, garnet and iron pyrites.

2. The Hexagonal System.—This system is characterised by three secondary equal axes cutting one another at 60° and a fourth principal axis at right angles to these (Fig. 25). The simplest forms are the *hexagonal pyramid* and *prism*, which often occur on the same crystals (Fig. 17), and the *rhombohedron* (Fig. 18), which is a hemihedral form, the relation of which to the pyramid is shown in Fig. 26. Some important substances belonging to this system are quartz, ice, calc-spar, sodium nitrate and emerald,

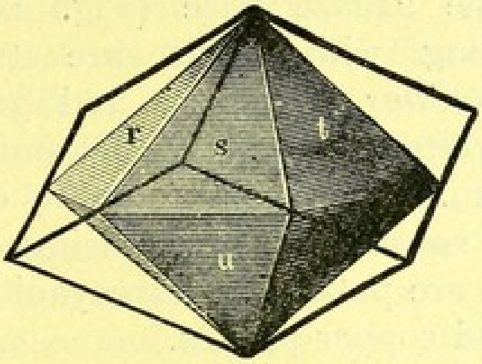


Fig. 26.

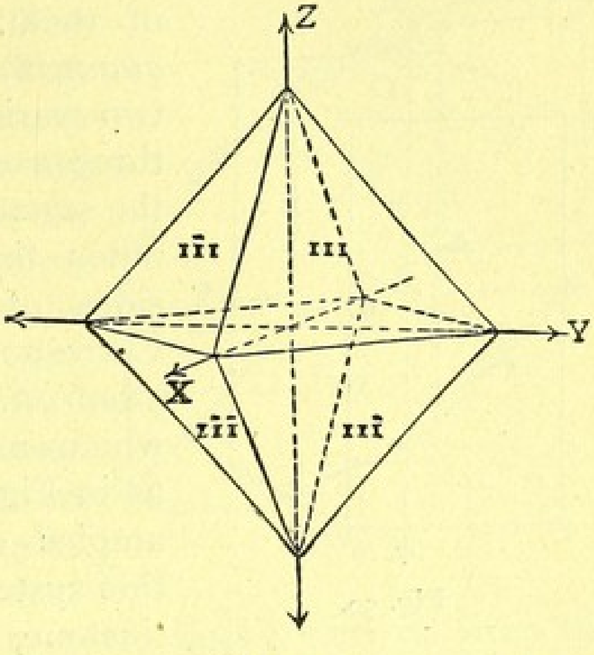


Fig. 27.

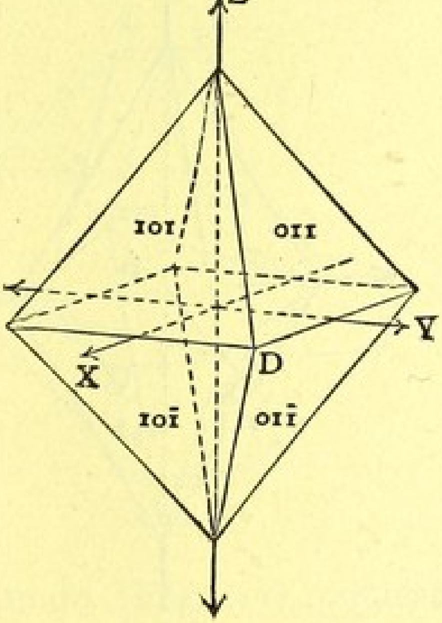


Fig. 28.

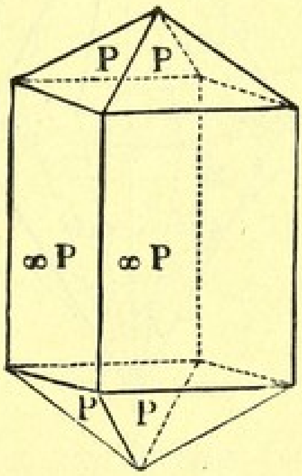


Fig. 29.

3. The Tetragonal System.—This system is characterised by two equal axes at right angles, and a third longer or shorter than these at right angles to both of them. The simplest form is the *quadratic pyramid*, of which there are two varieties. In one of these the three axes pass through the corners of the square base (Fig. 27), whilst in the other the secondary axes bisect the sides of the square base (Fig. 28). Corresponding with these are two *quadratic prisms* (Figs. 29 and 30), which are often capped by pyramids as in Fig. 29. The most common examples of substances crystallising in this system are potassium ferrocyanide, tinstone, and copper pyrites.

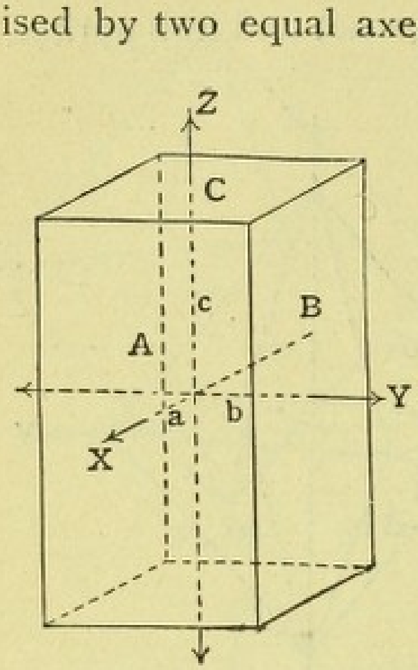


Fig. 30.

4. The Rhombic System.—This system is characterised by three unequal axes all at right angles. The chief forms are the rhombic *pyramid* (Fig. 31) and rhombic prism. Sulphur, potassium nitrate, arragonite, zinc sulphate and heavy-spar (barium sulphate) crystallise in this system.

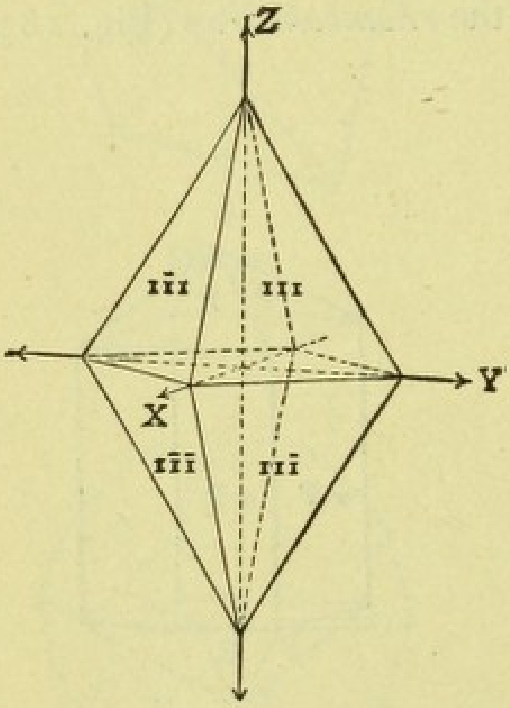


Fig. 31.

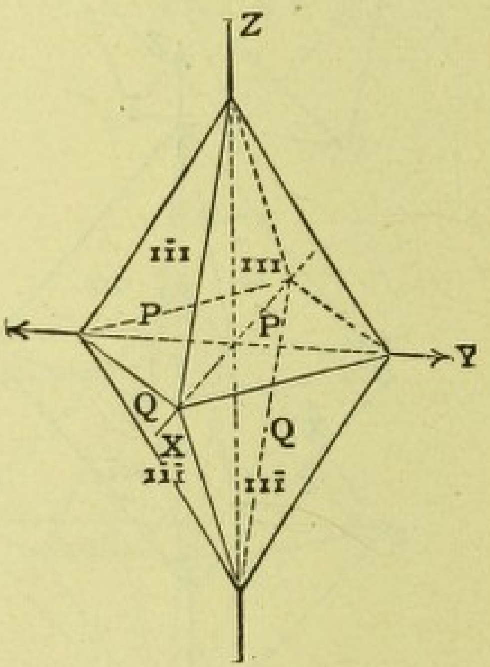


Fig. 32.

5. The Monosymmetric System.—This system is characterised by three unequal axes, two of which are at right angles, whilst the third is inclined to both of them. The simplest form is the pyramid (Fig. 32). A large number of substances crystallise in this system, among them being washing soda, borax, potassium chlorate, sodium phosphate and arsenate, gypsum, Glauber's salt and ferrous sulphate.

6. The Asymmetric System.—In this system all the axes are unequal and at various angles. There is no plane or axis of symmetry and the crystals are very complicated, derived from the asymmetric pyramid and prism. Amongst the most important substances belonging to the system may be mentioned copper sulphate (Fig. 33), potassium dichromate, and albite (sodium felspar).

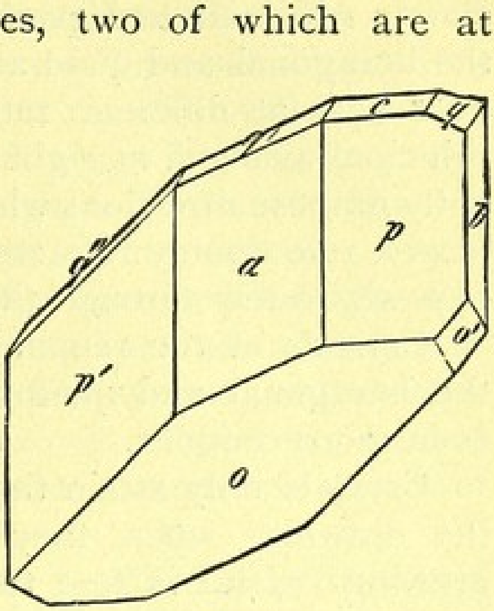


Fig. 33.

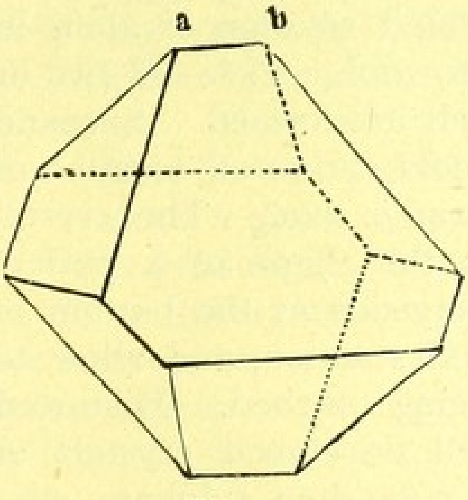


Fig. 34.

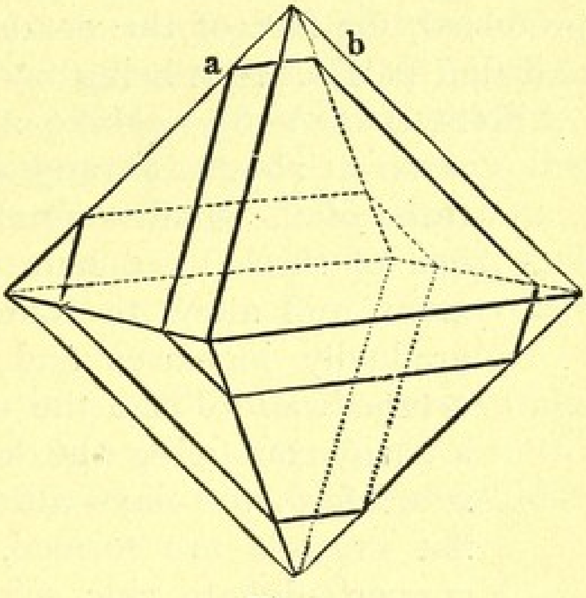


Fig. 35.

Crystals of the regular system are much simpler in their physical properties than those belonging to the other systems. They conduct heat and electricity equally in every direction, and when heated expand equally in all directions. Moreover, when a ray of light falls upon the face of such a crystal it is simply refracted and passes on as a single ray. Crystals of the hexagonal and quadratic systems, on the other hand, conduct heat at different rates in the directions parallel to the principal axis and at right angles to it, and also expand differently in these directions when heated. A ray of light, moreover, is as a rule doubly refracted or broken up into two rays, which pass separately through the crystal.

Crystals of the remaining three systems resemble those of the hexagonal and quadratic systems, but their behaviour is even more complex.

Crystals only attain the perfection of shape represented in the drawings when they are slowly formed and when the growing crystal is free to increase on every side. In other cases distortion occurs, owing to the undue development of particular faces, but however distorted the form appears, the *angles* between the faces remain constant. This is well shown in the case of alum, which crystallises in regular octahedra (Fig. 20). When crystals of alum are allowed to develop at the bottom of a basin, the flattened form shown in Fig. 34 is produced, the face of the octahedron on which the crystal lies and that parallel to it being unduly developed (Fig. 35).

EXPERIMENT 63.—Make a saturated solution of alum in water at about 25°, and allow to cool. Pick out two or three of the small crystals which are formed. Suspend one of these by a hair in a cold saturated solution of alum, and allow to stand for some time. The crystal gradually increases and takes the shape of a perfect octahedron. Place the other crystals at the bottom of a basin containing the saturated solution, and allow to stand for some days without being touched. Distorted flat crystals are formed. Well developed crystals of copper sulphate, zinc sulphate, potassium sulphate, etc., can be prepared in a similar manner to that employed for alum.

Dimorphism.—Each solid chemical substance has its own definite form, and this distinguishes it, as a rule, from all other substances, although an important class of exceptions to this statement exists (p. 143).

Many substances, however, crystallise in two different forms, and are known as *dimorphous substances.* Several striking instances of this are known among the allotropic forms of the elements. Thus carbon, in the form of diamond, crystallises in transparent octahedral forms of the regular system, whilst as graphite it forms opaque six-sided plates belonging to the monosymmetric system. Sulphur, again, forms rhombic or monosymmetric crystals according to circumstances. Many examples are also met with among the compounds of the elements. Thus calcium carbonate crystallises as calc-spar in rhombohedra, belonging to the hexagonal system, and as arragonite in rhombic prisms ; silica, moreover, forms the six-sided prisms and pyramids of quartz and the asymmetric plates of tridymite (p. 342).

A striking instance of dimorphism is afforded by mercuric iodide, which is precipitated as a red powder when potassium iodide is added to mercuric chloride. This red modification consists of minute crystals belonging to the quadratic system. When it is heated the mass becomes yellow, and then consists of crystals belonging to the rhombic system. When allowed to cool and then rubbed, the yellow mass again becomes red, owing to a change back into the original crystalline form.

EXPERIMENT 64.—Prepare a little mercuric iodide by adding potassium iodide solution to one of mercuric chloride. Filter through a small paper, and dry the paper in the air. Heat the paper gently over a flame, and notice that the red mass becomes yellow. Allow to cool, and draw a glass rod over the yellow deposit. A red streak is produced.

Some substances crystallise in three different forms, and are known as *trimorphous* substances. The general term *polymorphous* is also applied to all substances which crystallise in more than one form.

Isomorphism

Many compounds form exceptions to the general rule that each chemical substance has its own distinct crystalline form. Thus, for example, crystals of the phosphates of sodium and potassium can scarcely be distinguished by measurement from those of the corresponding arsenates; potassium sulphate and potassium chromate crystallise in precisely similar forms, and very many other cases of the same kind are known. Striking instances are also afforded by the alums (p. 318), and by the double salts which the sulphates of zinc, iron, nickel, cobalt, manganese and magnesium form with the sulphates of the alkali metals. Thus the salts $ZnSO_4 + K_2SO_4 + 6H_2O$ and $NiSO_4 + K_2SO_4 + 6H_2O$ crystallise in the same forms, as do also the corresponding compounds formed by the remaining metals mentioned above.

Such substances are said to be *isomorphous* (Greek, having the same form), and not only crystallise in the same geometrical forms, but also crystallise together when they are both present in the same solution, in quantities varying with the amount of each present in solution, forming *mixed crystals*. They cannot, therefore, be separated by crystallisation, since the crystals which are deposited contain both the substances which are present in the solution. Further, a crystal of a pure substance will continue to grow and develop in a solution of an isomorphous substance. When, for example, a crystal of the dark violet-coloured chrome alum, $Cr_2(SO_4)_3 + K_2SO_4 + 24H_2O$, is suspended in a saturated solution of ordinary colourless potassium alum, $Al_2(SO_4)_3 + K_2SO_4 + 24H_2O$, it continues to grow, so that a transparent layer of the colourless alum is formed around the dark violet nucleus of chrome-alum. Extremely accurate measurements, however, show that the crystals of isomorphous substances differ very slightly from each other, so that the replacement of one element by another in such crystals—for example, zinc by nickel in the double sulphate—produces a small but definite change in the crystallographic constants.

It has been found that *isomorphous substances always have a similar chemical composition*, and contain the same number of atoms combined in a similar way. Thus, between the formulæ of potassium phosphate, KH_2PO_4, and potassium arsenate, KH_2AsO_4, the only difference is that the former contains one atom of phosphorus and the latter one atom of arsenic. Similarly potassium sulphate, K_2SO_4, and potassium chromate, K_2CrO_4, only differ by the presence of an atom of sulphur in the one compound and an atom of chromium in the other, and all other isomorphous substances stand in a similar relation. This relation between the chemical composition of isomorphous substances was first established by Mitscherlich in 1819.

This phenomenon of isomorphism is very frequently observed in minerals. Many of these contain small quantities of various metals or acid radicals (p. 198), and have such a complicated composition that it would be very difficult to express it by means of a formula. Such minerals are in reality isomorphous mixtures, a portion of the metal or acid radical having been isomorphously replaced by an equivalent amount of some other. Thus common limestone, $CaCO_3$, often contains small amounts of the isomorphous magnesium carbonate, $MgCO_3$, whilst the mineral known as spathic iron ore consists of ferrous carbonate, $FeCO_3$, varying amounts of which have been replaced by the isomorphous carbonates of manganese, calcium, and magnesium. The form of the crystals of ferrous carbonate is only very slightly altered by this replacement, so that crystals containing calcium carbonate can scarcely be distinguished by angular measurement from those of pure ferrous carbonate.

The formula of such a mineral is determined in the usual way, allowance being made for the fact that a portion of the compound has been replaced by another substance. A sample of limestone, for example, gave the following results on analysis :—

	%		Combining Weight.			Ratio.
CaO,	51.2	÷	56	=	.914	9
MgO,	4.1	÷	40	=	.102	1
CO_2,	44.7	÷	44	=	1.016	10

If we proceed as usual to obtain the formula of the compound by dividing the percentage of each constituent by its combining weight, we find that the amount of carbon dioxide is just equivalent to the amounts of lime and magnesia, since their sum of their equivalents present in the compound,

$$9 + 1 = 10,$$

exactly equals the equivalent of the carbonic acid present.

The substance may therefore be regarded as calcium carbonate, in which a portion of the calcium has been replaced by magnesium, and the formula is therefore written (**Ca**, Mg)CO_3 to indicate this.

The amount of magnesia present is capable of combining with 1/10 of the total carbon dioxide, and hence the mixture may be regarded as calcium carbonate in which 1/10 of the metal has been replaced by magnesium.

In a similar manner the formula of spathic iron ore might be written (**Fe**, Ca, Mg, Mn)Co_3, the symbol of the chief constituent being printed in darker type.

Determination of the Atomic Weight of an Element from the Isomorphous Relations of its Compounds.

Since all isomorphous substances have a similar chemical composition, it follows that if it can be shown that two compounds are isomorphous, and if the atomic composition of one of them be already known, the atomic composition of the second must be similar to it. Thus let us suppose that the sulphate of a certain metal, X, is found to be isomorphous with barium sulphate, and to crystallise along with it and in the same forms of the rhombic system. Since the formula of barium sulphate is $BaSO_4$, it follows that the formula of the new sulphate must be XSO_4, and that the atomic weight of X must be such an amount of this metal as replaces 137 parts (the atomic weight) of barium. This can readily be ascertained by simply analysing the sulphate, and is found to be 87. It hence follows that the atomic weight of the unknown metal is 87.

This method of determining the atomic weight gives the same result as that depending on the atomic heat of the metals, and is of great value in confirming the results obtained in that way.

SUMMARY

Crystals are distinguished from amorphous substances (*a*) by their definite geometrical form; (*b*) by their physical properties (cleavage, expansion, behaviour towards light, etc.). As a general rule each chemical substance has a definite and characteristic crystalline form which distinguishes it from other substances. Many substances, however, crystallise in the same forms, and are capable of forming mixed crystals. Such substances are said to be isomorphous, and invariably have a similar chemical constitution.

Some compounds crystallise in several distinct forms, and are known as dimorphous (two-formed), trimorphous (three-formed), or polymorphous (several-formed) substances.

When one element replaces a second in a compound isomorphously (without change of crystalline form), each atom takes the place of an atom of the second element. Hence the atomic weight of the first element can be calculated if (1) the atomic weight of the second element and (2) the equivalents of the two elements are known.

EXERCISES ON LESSON XVI

1. What is meant by the term *crystal*? How can crystals be obtained?

2. What are the six systems in which crystals are classified? Give examples of substances crystallising in each system.

3. What is meant by the terms *isomorphism* and *dimorphism*?

4. How are isomorphous substances related in chemical composition?

5. A certain metal has the equivalent 29.3, and forms a sulphate which is isomorphous with zinc sulphate. What is the atomic weight of the metal? (Zn = 65.)

6. A sample of native silver bromide was found to have the following percentage composition,—

Silver,	67
Bromine,	20
Chlorine,	13
	100

What proportion of the silver is present as chloride in this isomorphous mixture of the chloride and bromide?

7. A mineral has the following percentage composition,—

Manganous oxide,	MnO,	48.2,
Ferrous oxide,	FeO,	2.0,
Calcium oxide,	CaO,	10.5,
Carbonic acid,	CO_2,	39.3.

Calculate the formula of the mineral. What proportion of the total carbonic acid is combined with each of the three oxides?

LESSON XVII

THE ALKALI METALS

THE name alkali was originally given by chemists to all soluble substances which had the properties of restoring the colour of certain vegetable colouring matters, after they had been previously altered by the addition of acids, of producing a soapy feeling when dissolved and placed on the skin, and of having a characteristic unpleasant taste. Several different substances were known which had all these properties, and these were distinguished as :—

1. The *fixed vegetable alkali*, obtained by burning wood.

2. The *fixed mineral alkali*, deposited in the hot countries of the East by the evaporation of the waters of many lakes.

3. The *volatile alkali*, obtained by the distillation of camel's dung, hartshorn, and other similar substances.

This last named alkali disappeared entirely when heated, unlike the others, which were not altered by heat, or, as it was then termed, were *fixed*.

4. The *alkaline earths*, of which lime was the most important.

It has since been found that the fixed mineral and vegetable alkalis are in reality compounds of two metals, sodium and potassium, and hence these are termed the *metals of the alkalis*, or more shortly the *alkali metals*. The volatile alkali, on the other hand, does not contain a metal but the compound gas ammonia (R. and L., p. 162).

Sodium and potassium combine very readily with other elements and form compounds which cannot easily be decomposed. Hence, although the compounds of these elements are very widely distributed, the metals sodium and potassium were not isolated until the year 1807. Humphry Davy, the discoverer of both of these alkali metals, had observed that many substances are decomposed when a current of electricity is passed through them. He therefore tried the effect of a powerful current on caustic potash and caustic soda, and found that these substances, which had never previously been decomposed, were at once broken up by the current, the new metals being formed and oxygen evolved. As we shall see, the very process (called electrolysis) by which these metals were first discovered is now used for the manufacture of sodium (p. 305). The alkali metals resemble one another very closely and must be considered as members of a chemical group or family, just as are fluorine, chlorine, bromine and iodine.

Three other metals (Lithium, Rubidium and Caesium) belong to the same family, all of which occur in extremely small quantities and are similar in general properties to sodium and potassium; for a detailed description of their properties and compounds the larger manuals must be consulted.

Sodium, Na, 23

Native sodium carbonate was known by the names soda and natrum, as well as being termed the fixed mineral alkali. From the first of these terms has been derived the name *sodium*, which is commonly used for the metal in England and France, whilst the second has yielded the name *natrium*, which is used in Germany, and has given us the symbol for the element Na. The compounds of sodium are widely distributed and occur in enormous quantities. The most plentiful of all of these is the chloride, common salt, which occurs in all sea-water, and is also found in vast deposits, which often extend to a thickness of several hundred feet. Sodium also occurs in large quantities as sodium nitrate, or Chili saltpetre in South America, and as cryolite or sodium aluminium fluoride in Greenland. It is also a constituent of many silicates, and is present in all soil as well as in all animal organisms, and, to a much smaller extent, in plants.

Various compounds of sodium are very largely employed in the arts and manufactures, and almost the entire quantity thus required is derived from common salt. Sodium nitrate is chiefly used as a source of nitric acid, and as a manure, whilst cryolite is mainly valued for the aluminium which it contains.

Metallic Sodium.—As already mentioned, metallic sodium is now manufactured by the electrolysis of caustic soda, the process by means of which it was discovered (see Lesson XXVIII.). A few years ago metallic sodium was comparatively rare, now it is manufactured on the large scale, the annual output being measured by thousands of tons. It is used in the preparation of cyanides.

The metal possesses such remarkable properties that when it was first discovered many chemists refused to recognise it as a true metal (p. 70). At the ordinary temperature it can easily be cut with a knife and has a bright silvery metallic lustre, best seen on a freshly-cut surface. The specific gravity of the metal is 0.973, so that it is distinctly lighter than water. It melts at 95.6°, forming a liquid which looks like mercury, and boils at 877°, producing a purple vapour, which can readily be observed by heating a fragment of the metal in a hard glass bulb through which a stream of hydrogen is passed to remove the air.

Sodium combines so readily with oxygen that it is rapidly converted into the oxide or hydroxide when it is exposed to the air. The metal is therefore either kept under petroleum, or in thick sticks in stoppered bottles, a layer of oxide being formed on the surface of the sticks which protects the remainder. The metal readily burns when heated in the air, forming the peroxide. It rapidly decomposes water, liberating hydrogen and forming sodium hydroxide or caustic soda, $NaHO$,—

$$2H_2O + 2Na = 2NaHO + H_2.$$

Being lighter than water, the metal floats on the surface when thrown into water as a molten globule, which is surrounded by the hydrogen evolved, and this can easily be ignited by means of a lighted taper. If the metal be thrown on to wet filter paper, or thick starch paste, so that it cannot move about and thus become cooled, or if it be thrown on to warm water, the hydrogen takes fire spontaneously and burns with a yellow flame, due to the presence of the vapour of the metal.

Sodium also readily burns when it is melted and plunged into chlorine, common salt being thus produced,—

$$2Na + Cl_2 = 2NaCl.$$

EXPERIMENT 65.—Throw a *small* piece of sodium on to water coloured red by litmus. Apply a light to the globule and notice that the hydrogen with which it is surrounded takes fire and burns with a yellow flame. The litmus becomes blue, owing to the production of the strongly alkaline caustic soda.

Sodium Amalgam.—When a small piece of metallic sodium is placed on some mercury in a mortar and pressed with a pestle, vigorous combination takes place, a flash of yellow light and a small explosion being produced. As soon as 1 part of sodium has been added to 80 parts of mercury, the mass solidifies on cooling. The product of this action is known as sodium *amalgam*, the term amalgam being used for all the substances formed by the union of metals with mercury. Sodium amalgam decomposes water much more slowly than metallic sodium, and is therefore often used as a more convenient reducing agent than the metal.

The Equivalent and Atomic Weight of Sodium.—Our knowledge of the equivalent of sodium is derived from the careful analysis of common salt. The method adopted by Stas and later by Richards for this purpose consisted in dissolving a known weight of pure silver in nitric acid, and finding out exactly how much sodium chloride was requisite to convert it into silver chloride. It has thus been found that 107·88 parts of silver require 58.46 parts of sodium chloride.

Since this weight of silver combines with 35.46 of chlorine (p. 66), it follows that 58.46 of sodium chloride contain 35.46 of chlorine and $58.46 - 35.46 = 23.00$ parts of sodium. Since 35.46 is the equivalent weight of chlorine, 23 is the equivalent of the metal.

Sodium does not form any easily volatile compounds and hence its atomic weight must be settled from the value of its specific heat. This has been found to be 0.293, and hence the atomic weight must be that multiple of the equivalent which is approximately equal to $\frac{6.4}{.293} = 21.8$. Since this is not far removed from the value of the equivalent itself, the latter is taken as the exact atomic weight of sodium.

We further learn from this that 1 atom of sodium is capable of replacing only 1 atom of hydrogen in acids, and this is found to be the case in all the known salts of sodium.

The sodium salts must, therefore, be looked upon as derived from the corresponding acids by the replacement of each atom of hydrogen by 1 atom of sodium, as shown in the following examples—

Formula of Acid.	Formula of Salt.
HCl	$NaCl$
HNO_3	$NaNO_3$
H_2SO_4	$NaHSO_4$ Na_2SO_4
H_3PO_4	NaH_2PO_4 Na_2HPO_4 Na_3PO_4

The Oxides of Sodium.—When sodium is heated in the air it unites with oxygen, but the nature of the oxide produced depends on the temperature which is employed and the amount of air which is admitted. When the metal is freely heated in a good supply of air, the peroxide, Na_2O_2, is formed, whilst when it is heated at a low temperature and in a limited supply of air the monoxide, Na_2O, is produced.

Sodium Peroxide, Na_2O_2, is manufactured by heating sodium in a stream of dry air freed from carbonic acid gas, and is a white or yellowish-white powder. It cannot easily be decomposed by heat, although at a high temperature it does decompose with evolution of oxygen. It is decomposed by water with formation of a solution containing caustic soda and hydrogen peroxide,—

$$Na_2O_2 + 2H_2O = 2NaHO + H_2O_2,$$

and it is also decomposed by acids, hydrogen peroxide and a salt of sodium being formed,—

$$Na_2O_2 + H_2SO_4 = Na_2SO_4 + H_2O_2.$$

These solutions contain hydrogen peroxide, and therefore decompose when they are heated, oxygen being evolved.

Many peroxides, such for example as barium peroxide, BaO_2, resemble sodium peroxide in this respect, and yield hydrogen peroxide when they are acted on by acids (see p. 228), whilst others, such as lead peroxide, PbO_2, and manganese peroxide, MnO_2, do not yield this substance.

A peroxide of the former class may be regarded as derived from hydrogen peroxide by the replacement of the hydrogen atoms by a metal, just as a basic oxide is derived from water:

Water	H.O.H	Hydrogen Peroxide	H.O.O.H
Sodium Monoxide	Na.O.Na	Sodium Peroxide	Na.O.O.Na.

When Na_2O_2 is brought into contact with paper or wood, etc., oxidation occurs so rapidly that the inflammable material is set fire to.

Sodium peroxide is used on the large scale for the production of hydrogen peroxide, which is employed for bleaching purposes.

It absorbs carbon dioxide with formation of sodium carbonate and liberation of oxygen and is therefore sometimes used for the regeneration of air in closed spaces, such as submarines and the safety helmets worn in atmospheres containing poisonous gases,—

$$2Na_2O_2 + 2CO_2 = 2Na_2CO_3 + O_2$$

EXPERIMENT 66.—Dissolve 1 gram. sodium peroxide in water, add dilute sulphuric acid and test for hydrogen peroxide by adding a solution of potassium permanganate. Oxygen is at once evolved (see R. and L., p. 99).

Sodium Monoxide, Na_2O, and Sodium Hydroxide, or Caustic Soda, NaOH.

Sodium Monoxide is formed, as mentioned above, when the metal is oxidised at a low temperature in a limited supply of oxygen. It is a gray mass which is violently acted on by water, with formation of sodium hydroxide, NaOH,—

$$Na_2O + H_2O = 2NaOH.$$

This new substance is a strong base (R. and L., p. 81), which has the characteristic alkaline taste and action on the skin and on vegetable colouring matters. Hence sodium monoxide is called a basic oxide. All the salts of sodium may be obtained by the action of acids on sodium hydroxide or its solution in water,—

$$NaHO + HNO_3 = NaNO_3 + H_2O$$

Sodium hydroxide or caustic soda is a substance which is very largely used for various manufacturing purposes, and is usually made by boiling sodium carbonate solution with slaked lime, insoluble calcium carbonate being precipitated,

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3.$$

EXPERIMENT 67.—Dissolve 70 grams. of crystallised sodium carbonate $Na_2CO_3 + 10H_2O$, in about half a litre of water in a flask. Weigh out 20 grams. of quicklime, slake it in a basin with a little water, which should be added very gradually, add more water, stir, and add the resulting milk of lime to the sodium carbonate solution. Boil on a sand-bath and test the liquid periodically by allowing it to settle, drawing off a little of the clear liquid with a pipette, and adding an excess of hydrochloric acid to it. If effervescence occurs, undecomposed sodium carbonate is still present and the boiling must be continued until no gas is evolved when the liquid is treated in this manner. As soon as the reaction is complete, allow to settle, pour off the clear liquid and evaporate it to dryness in a clean iron sand-tray. The solution cannot be filtered through paper or evaporated in a porcelain basin because caustic soda attacks both of these substances very vigorously.

A similar process to the above is adopted for making caustic soda on the large scale (p. 174), but the product thus obtained is never pure, invariably containing sodium chloride and sulphate, as well as smaller quantities of alumina and other substances. A less impure material is now prepared from sodium chloride by direct electrolysis. On the small scale the crude caustic may be purified by treating it with strong alcohol, which dissolves the caustic soda but not the impurities, and then pouring off the clear liquid and evaporating. Perfectly pure caustic soda can only be obtained by dissolving pure sodium in distilled water and evaporating the liquid to dryness in a silver basin, silver being less attacked than any other convenient metal.

Caustic soda dissolves in less than half its weight of water, forming a heavy, strongly alkaline solution, which rapidly attacks the skin and destroys vegetable fibre. Both the solid substance and its solution readily absorb carbonic acid from the air, sodium carbonate being produced,—

$$2NaHO + CO_2 = Na_2CO_3 + H_2O,$$

and they are therefore largely employed in the laboratory for absorbing this gas.

Sodium hydroxide decomposes the salts of those metals which form insoluble hydroxides, a soluble sodium salt being formed and the hydroxide of the metal precipitated. Thus, when it is added to copper sulphate solution, sodium sulphate is formed and copper hydroxide is precipitated,—

$$CuSO_4 + 2NaOH = Cu(OH)_2 + Na_2SO_4.$$

In other cases the oxide of the metal is precipitated,—

$$2AgNO_3 + 2NaOH = Ag_2O + H_2O + 2NaNO_3.$$

In many cases the precipitate thus produced is characteristic of the metal, and caustic soda is therefore largely employed as a reagent in analytical work.

The hydroxides of many metals decompose when they are heated, water being given off and the oxide of the metal formed. Thus when calcium hydroxide (slaked lime) is heated, water and calcium oxide (quicklime) are produced,—

$$Ca(OH)_2 = CaO + H_2O.$$

This is not the case with sodium hydroxide or potassium hydroxide, so that these compounds differ in this respect from other hydroxides.

Volumetric Analysis—Estimation of Acids and Alkalis

When an acid is gradually added to a base, the point at which neutrality is reached can readily be ascertained by the use of litmus or some substance of similar properties, the colour of which is altered by acids or alkalis. Substances of this kind are known as *indicators* and differ greatly from one another in sensitiveness. Among the most important of these indicators are the following three :—

1. Litmus, prepared from a variety of lichen, is blue in alkaline solution, red in acid solution.

2. Phenol-phthalein, a product obtained indirectly from coal-tar, is a deep pink in alkaline solution and colourless in acid solution.

3. Methyl-orange, also obtained indirectly from coal-tar, is yellow in alkaline solution and pink in acid solution.

Litmus and phenol-phthalein are both affected even by such a weak acid as carbonic acid, whereas methyl-orange is not acted on in any way by this substance.

EXPERIMENT 68.—Measure out three quantities of 5 cc. of dilute hydrochloric acid into three beakers, dilute with water to about 50 cc. and add to one a drop of litmus, to the second phenol-phthalein and to the third methyl-orange. Add caustic soda solution slowly from a burette to each of the three and notice in each case the change of colour which occurs as soon as a small excess of alkali is present. Into each of the three alkaline solutions pass carbonic acid gas. The litmus becomes red and the phenol-phthalein colourless, whilst the methyl-orange is not affected but remains yellow.

Indicators, which are affected by acids and alkalis, are usually themselves very weak acids, the salts of which differ in colour from the original acids. Thus the blue salts formed by the red acid of "litmus" are decomposed even by carbonic acid, whilst the yellow salts of "methyl-orange" are more stable and are not decomposed by this substance.

By the use of one of these indicators it becomes easy to neutralise a solution of caustic soda exactly with an acid. It is obvious that this method can be used for estimating the amount of caustic soda present, provided that an acid of known strength be employed and the volume required carefully measured,—

$$\underset{40}{NaOH} + \underset{36.5}{HCl} = NaCl + H_2O.$$

We see from the above equation that 40 parts of caustic soda require 36.5 parts of hydrochloric acid for exact neutralisation. If now we prepare a solution of hydrochloric acid containing 36.5 grams. of the acid in 1 litre (1000 cc.) we know that this litre of solution will exactly neutralise 40 grams. of caustic soda.

Hence, since 1000 cc. neutralise 40 grams. caustic soda, 1 cc. neutralises 0.04 gram.

If then a given solution of caustic soda requires 15 cc. of this solution of hydrochloric acid, we know that the amount of caustic soda present in it is $15 \times 0.04 = 0.6$ gram. This method of analysis is called *volumetric analysis* because it depends on the measurement of the volume of a *standard solution*, containing a known amount of the particular reagent which is required to react with the substance undergoing analysis. In *gravimetric analysis*, on the other hand, as we have seen, the constituent which is being estimated is brought into the form of some substance of known composition, and the weight of this ascertained (see p. 66).

A solution of an acid containing in each litre 1 gram. (or more accurately 1·008 gram.) of hydrogen which can be replaced by a metal is called a *normal solution.* Thus a normal solution of hydrochloric acid, HCl, contains 36.5 grams. of the acid, whilst a normal solution of nitric acid, HNO_3, contains 63 grams. of the acid. A normal solution of sulphuric acid, H_2SO_4, in the same way contains 49.05 grams. of the acid, since we see from the formula of this dibasic acid that 98.1 parts of it contain 2 grams. of replaceable hydrogen.

All these normal solutions will neutralise exactly the same amount of caustic soda, viz. 40 grams. per litre, and hence a solution of caustic soda of this strength is called normal caustic soda solution. Solutions are often used which are exactly one-tenth of the normal strength, and these are known as *decinormal solutions.*

In volumetric analysis the accuracy of the whole process depends on an exact knowledge of the strength of the standard solution employed. Thus the exact strength of a solution of hydrochloric acid can be found by adding an excess of silver nitrate, weighing the silver chloride produced, and from this calculating the amount of hydrochloric acid present. Or again it may be ascertained by weighing out a known quantity of pure sodium carbonate and finding how much of the acid solution is required to neutralise it exactly,—

$$Na_2CO_3 + 2HCl = 2NaCl + CO_2 + H_2O.$$

The strength of the acid can then be found by calculation from the foregoing equation.

Thus if it were found that 18 cc. of the acid exactly neutralised 1 gram. of pure sodium carbonate, the volume of this acid which should be diluted to 1 litre in order to make a normal solution would be calculated as follows.

It follows from the equation that—

106 grams. sodium carbonate require 73 grams. of HCl.

Hence 1 gram. sodium carbonate requires $\frac{73}{106} = 0.689$ gram. HCl.

Now since 0.689 gram. of HCl is present in 18 cc. of the acid,

1 ,, ,, ,, $\frac{18}{0.689}$,, ,,

and 36.5 ,, ,, ,, $\frac{18 \times 365}{0.689} = 954$ cc.

of the acid.

Hence, 954 cc. of this acid must be measured out and diluted to 1 litre, so that this volume of the diluted acid contains exactly 36.5 parts of hydrochloric acid, and is therefore a normal solution. The diluted solution would then be again tested with pure sodium carbonate, in order to check the accuracy of the various operations. The pure sodium carbonate used in such experiments is obtained by heating pure sodium bicarbonate or sodium carbonate, until no further loss of weight occurs.

The strength of solutions of the alkalis may then be ascertained by direct comparison with the standard solution of hydrochloric acid.

The process of volumetrically estimating the amount of a substance present by means of a standard solution is usually termed *titration*.

Many other reactions, in addition to those which occur between acids and alkalis, are employed for the purposes of volumetric analysis, and numerous instances of these will be mentioned in the following lessons. In all cases, however, it is essential (1) that the strength of the standard solution is accurately known; (2) that there is some means of indicating to the eye the point at which the reaction is complete.

EXPERIMENT 69.—1. Prepare a normal solution of sulphuric acid, standardising it by means of pure sodium carbonate.

2. Determine the percentage of sodium carbonate in a sample of soda crystals, by weighing out 5 grams. of the crystals, dissolving them in 250 cc. of water and titrating 50 cc. of this solution with normal sulphuric acid in presence of a suitable indicator (p. 156).

Sodium Hydride, NaH.—When sodium is heated in hydrogen at about 370°, it unites with it to form the hydride NaH, which sublimes in colourless crystals, and decomposes when it is strongly heated in a vacuum. It is decomposed by water,—

$$NaH + H_2O = NaOH + H_2$$

Similar compounds are formed by the other alkali metals.

The Salts of Sodium

Sodium Chloride, or Common Salt, NaCl, is the most plentiful of all the compounds of sodium and occurs in all river water to a small extent and to a larger extent in sea-water, accompanied by smaller quantities of the chlorides, bromides, sulphates and carbonates of magnesium, calcium and potassium. The water of the Atlantic Ocean contains about 37 parts of solid matter in 1000 parts by weight, and about 78 per cent of this or 28.9 parts consists of sodium chloride. It is also found in vast deposits, which appear to have been formed by the drying up of ancient seas. The salt is sometimes obtained from these deposits by mining, the solid material, which is usually reddish coloured, being known as *rock-salt*, whilst in other cases it is procured by boring into the deposit, and introducing water, which soon becomes saturated with salt and is then pumped out and evaporated. Salt is also obtained in many places by the evaporation of sea-water, and is then known as Bay salt. All crude salt contains magnesium chloride, which is deliquescent and renders the salt damp when exposed to moist air. This can be removed and pure salt obtained for laboratory purposes by dissolving the whole in water and passing in a current of hydrochloric acid gas. The pure salt is precipitated whilst the magnesium salts remain in solution. The salt is then filtered off at the pump, washed with hydrochloric acid and heated in a platinum basin. Crude salt can also be freed from most of its impurities on the large scale by washing with saturated brine, in which the magnesium chloride dissolves.

Common salt crystallises in cubes having the specific gravity 2.16; it melts at 815° and volatilises perceptibly at a bright red-heat.

100 parts of water dissolve 35.9 parts of salt at the ordinary temperature, and only very little more, viz. 39 parts, at 100°. When salt is mixed with powdered ice and snow, the whole mass liquefies and the temperature falls to about $-22°$, so that this mixture is largely used for freezing or cooling small quantities of material, and for making ice-creams, etc.

Sodium Bromide and Sodium Iodide closely resemble the potassium compounds (p. 185), but crystallise with two molecules of water.

Sodium Carbonate, Na_2CO_3.—The manufacture of this salt, which is carried out on an enormous scale, is described in the lesson on the Alkali Manufacture (p. 172). The dry salt can be fused without undergoing any decomposition. It dissolves readily in water and the solution yields on evaporation crystals of the formula $Na_2CO_3 + 10H_2O$, which are usually known as *soda crystals*. These crystals effloresce in the air and form a solution in water which somewhat resembles that of sodium sulphate in its behaviour when heated (p. 21). The solution in water is alkaline both to litmus and to methyl-orange, and this is frequently found to be the case with normal salts which are formed from strong bases and weak acids. On the other hand salts which are formed from weak bases and strong acids often form solutions which have an acid reaction. Finally, salts produced from strong acids and strong bases usually yield neutral solutions. Thus the normal salts produced by the action of the strong bases soda and potash on hydrochloric, nitric, sulphuric, hydrobromic and hydriodic acids, all of which are strong acids, are all neutral to litmus. Those formed from carbonic acid, sulphurous acid, acetic acid or phosphoric acid, all of which are weak acids, are alkaline in reaction, whilst those formed from weak bases, such as the hydroxides of copper and zinc, with sulphuric or nitric acid are generally acid.

EXPERIMENT 70.—Test the reactions to litmus of solutions of copper sulphate, zinc nitrate, sodium chloride, sodium carbonate, sodium sulphide, potassium iodide, ammonium sulphate and sodium acetate.

Sodium carbonate was formerly used for the preparation of metallic sodium, which is now made by the electrolysis of caustic soda. In this old and expensive process it was mixed with charcoal and the mixture strongly heated, sodium being liberated as a vapour and carbonic oxide evolved,—

$$Na_2CO_3 + 2C = 2Na + 3CO.$$

Sodium Hydrogen Carbonate or Sodium Bicarbonate $NaHCO_3$ is formed in solution when carbonic acid gas is passed into a cold solution of sodium carbonate, whilst the dry salt is prepared by the action of gaseous carbonic acid on soda crystals (p. 173). It is neutral to phenolphthalein and decomposes when heated, as does also its solution in water, carbonic acid being evolved and the normal carbonate formed,—

$$2NaHCO_3 = Na_2CO_3 + CO_2 + H_2O.$$

A solution of sodium bicarbonate gives no precipitate with a dilute solution of calcium chloride, whereas a solution of normal sodium carbonate produces a white precipitate. This is because the normal carbonate of calcium is insoluble in water whilst the bicarbonate is soluble.

EXPERIMENT 71.—1. Dissolve 5 grams. of soda crystals in 5 cc. of water and pass in carbonic acid gas for some time. Sodium bicarbonate, which is less soluble than the normal carbonate, separates out.

2. Dissolve about 1 gram. of pure sodium bicarbonate in water and add a drop of blue litmus solution. The litmus becomes purple. Add a few drops of this solution to a dilute solution of calcium chloride: no precipitate is produced. Boil the solution for some time, carbonic

acid gas is evolved (test by passing the gas into lime-water) and the litmus becomes blue. Again test the solution with calcium chloride solution—a white precipitate is at once produced.

Sodium Cyanide, NaCN.—When sodium is heated in a current of ammonia in an iron retort at 400°, it replaces one atom of the hydrogen of the ammonia forming free hydrogen and *sodamide*, NH_2Na,—

$$2NH_3 + 2Na = 2NH_2Na + H_2.$$

This is a white, waxy solid, and when it is heated with carbon forms sodium cyanide and hydrogen,—

$$NH_2Na + C = NaCN + H_2.$$

Sodium cyanide is manufactured in this way and is largely used for the extraction of gold (p. 284). In its general properties it resembles the potassium salt (p. 338).

Sodium Nitrate (Chili Saltpetre), $NaNO_3$.—This salt occurs in large quantities in the rainless regions of South Peru and Bolivia. The crude material is known as Caliche and contains, in addition to the nitrate, sodium chloride, calcium sulphate and a very small amount of sodium iodate. The nitrate is simply purified by recrystallisation from water and is then brought into the market. The iodate of sodium accumulates in the mother-liquors and is used, as already described (p. 25), for the manufacture of iodine.

Sodium nitrate is very soluble in water and deliquesces when exposed to moist air, and on this account cannot be used for making gunpowder (p. 189). Its crystals have exactly the same shape as those of calc-spar. When heated it first melts and then at a high temperature loses oxygen and yields sodium nitrite,—

$$2NaNO_3 = 2NaNO_2 + O_2.$$

It is largely employed for the manufacture of nitric acid, and as the source of oxides of nitrogen in the manufacture of sulphuric acid (R and L., p. 207). Its chief use, however, is as a fertiliser, since plants growing in soil with which it has been "dressed" are able to take up from it the nitrogen which is essential to their proper development (see p. 186).

Sodium Nitrite, $NaNO_2$, is formed when sodium nitrate is strongly heated and may be obtained at a lower temperature by heating the nitrate with finely-divided iron, which combines with the oxygen.

EXPERIMENT 72.—Fuse 5 grams. of sodium nitrate in a crucible and add an equal weight of iron filings. Extract the cool mass with warm water, filter, evaporate to small bulk and add sulphuric acid; brown fumes are evolved showing the presence of a nitrite, and a green solution of nitrous acid is formed.

Sodium nitrite is also formed when nitrous fumes are passed into caustic soda solution. It is readily decomposed even by weak acids, such as acetic acid, nitrous acid being formed which can be detected, if the solution be strong, by the evolution of brown fumes; if the solution be dilute, by its oxidising action on an acid solution of potassium iodide,—

$$2HNO_2 + 2HI = I_2 + 2NO + 2H_2O.$$

EXPERIMENT 73.—1. To a strong solution of sodium nitrite add acetic acid; brown fumes are evolved.

2. To a dilute solution of sodium nitrite add potassium iodide solution, starch solution and acetic acid; the characteristic blue colour of starch iodide is produced.

Sodium nitrite is chiefly used for the preparation of artificial organic colouring matters.

Sodium Sulphate, Na_2SO_4, occurs, as has already been mentioned, in small amount in sea-water, and is also found in many mineral springs. It is obtained on the large scale by the action of sulphuric acid on common salt, and is known as salt cake (Alkali Manufacture, p. 171). It crystallises from water at the ordinary temperature with 10 molecules of water, this hydrate being known as *Glauber's salt*, because it was described by a German chemist named Glauber in 1658. These crystals lose water and effloresce in the air; the solubility of sodium sulphate has already been discussed (p. 20).

Sodium Sulphite, Na_2SO_3.—This salt is prepared by dividing a solution of sodium carbonate into two equal parts, saturating one with sulphur dioxide and then adding the second,—

(1) $Na_2CO_3 + 2SO_2 + H_2O = 2NaHSO_3 + CO_2$.

(2) $2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + CO_2 + H_2O$.

The first half of the carbonate is converted into sodium bisulphite, $NaHSO_3$, and this then reacts with the second half to form the normal salt.

EXPERIMENT 74.—Dissolve 5 grams. of soda crystals in 10 cc. of water. Take half of this and pass in sulphur dioxide until the liquid smells strongly of the gas. Then add the second half, ascertain the reaction of the solution to litmus, and keep the solution for the tests described below.

Sodium sulphite crystallises with seven molecules of water and forms a solution which is alkaline to litmus. It is difficult to prepare pure because the solution of the salt readily absorbs oxygen from the air forming the sulphate. Sulphites are, moreover, very readily converted into sulphates by oxidising agents, such as chlorine, iodine, nitric acid, etc.,—

$$Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI,$$

and this reaction can be used for their detection and estimation.

EXPERIMENT 75.—To a few drops of a solution of sodium sulphite add barium chloride. A white precipitate of barium sulphite is formed which is soluble in hydrochloric acid. Add hydrochloric acid and filter from any barium sulphate which may be present. To the clear filtrate add a solution of iodine in potassium iodide. An immediate white precipitate of barium sulphate is produced.

Sodium Thiosulphate, $Na_2S_2O_3$, is often known as hyposulphite of sodium, which was the old name for the salt, but is now given to another compound. Sodium thiosulphate is slowly formed when sodium sulphite is boiled with flowers of sulphur,—

$$Na_2SO_3 + S = Na_2S_2O_3.$$

The reaction is somewhat similar to the conversion of the sulphite into sulphate by oxygen,—

$$Na_2SO_3 + O = Na_2SOO_3 = Na_2SO_4.$$

It crystallises with five molecules of water and forms a neutral solution in water, which slowly decomposes and deposits sulphur when exposed to the air. This salt is largely employed in photography because it dissolves the unaltered chloride, bromide, or iodide of silver from the film after development, but does not affect the image.

Solutions of sodium thiosulphate are decomposed by acids with liberation of thiosulphuric acid,—

$$Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + H_2S_2O_3.$$

This acid is, however, very unstable, and rapidly decomposes into sulphurous acid and free sulphur,—

$$H_2S_2O_3 = H_2SO_3 + S.$$

The sulphur forms a very finely-divided precipitate, and the solution acquires a smell of sulphur dioxide.

EXPERIMENT 76.—Dissolve 10 grams. of sodium sulphite in about 25 cc. of water, add 1 gram. of flowers of sulphur and boil gently for some time, adding water as the solution evaporates.

Filter, and to 5 cc. of the solution add dilute sulphuric acid. A yellowish precipitate of sulphur is produced, whilst the solution acquires a smell of sulphur dioxide.

Sodium thiosulphate undergoes a very interesting reaction with free iodine. When solutions of these substances are mixed the iodine is converted into sodium iodide, NaI, at the expense of half of the sodium of the thiosulphate and a complicated salt known as sodium tetrathionate is formed,—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6.$$

This reaction is used for the volumetric estimation of iodine. The solution of sodium thiosulphate is standardised by weighing out a known amount of pure iodine, dissolving this in potassium iodide solution, and titrating with sodium thiosulphate solution until the iodine is exactly used up. The final point is ascertained by adding a few cc. of starch solution to the liquid while it is still yellow with iodine ; a deep blue colour is produced and the exact point at which this disappears can be seen with great sharpness.

It is usual to make the sodium thiosulphate solution of such a strength that each cc. exactly suffices for 1 cc. of a decinormal solution of iodine, containing 12.69 grams. of iodine per litre. The amount of pure crystallised sodium thiosulphate required is therefore 24.82 grams. per litre.

Supersaturated Solutions.—It often happens that when a saturated solution of a salt in hot water is allowed to cool without being exposed to dust, or in any way disturbed, no solid salt separates out, although there is far more salt present than would be taken up by the water in the cold. This behaviour is shown in a very marked manner by both sodium sulphate and sodium thiosulphate. Thus, when a solution of sodium sulphate is saturated with the salt at about 30°, and the clear liquid allowed to cool in a flask or test-tube plugged with cotton wool, or covered with tinfoil, no solid matter separates out on cooling. The same thing happens when crystals of sodium thiosulphate are carefully melted in a tube closed by cotton wool and then allowed to cool. These solutions are said to be *supersaturated* and are in a condition of unstable equilibrium. It was at one time thought that any particle of dust was able to bring about the crystallisation of such a solution, but it is now known that this can only be brought about under ordinary conditions by a crystal of the salt itself. When the plug is removed and a small crystal of the salt dropped in, the whole at once solidifies, and since a considerable evolution of heat accompanies the change from the liquid to the solid state, the temperature suddenly rises.

EXPERIMENT 77.—Melt 10 grams. of crystallised sodium thiosulphate in a test-tube, taking care that no solid crystals remain on the side of the tube. Close the tube by a plug of cotton wool and allow to cool. No crystallisation takes place. Remove the plug and add a fragment of a crystal of the solid salt. Crystallisation at once begins and rapidly spreads through the whole mass. Insert a thermometer and notice that the temperature rises considerably during the crystallisation.

General Reactions of the Sodium Compounds

Sodium is distinguished among the metals by the fact that with very few exceptions (p. 109) its salts are soluble in water, and hence they do not yield precipitates with the ordinary reagents. Under these circumstances, recourse is had for the detection of the compounds of the metal to the property which all sodium salts possess of imparting a yellow colour to the colourless flame of a Bunsen burner, when they are brought into it on a clean platinum wire. The reaction is extremely delicate, and a faint and transitory yellow coloration is produced by almost any object which has been exposed to the air for some time, because atmospheric dust contains sodium and will itself produce the yellow flame (see Spectrum Analysis).

EXPERIMENT 78.—Clean a platinum wire by repeatedly dipping it in strong hydrochloric acid and heating it in the flame until it no longer causes any coloration.

Moisten the wire and dip it into some sodium carbonate, and again bring it into the flame—a brilliant yellow coloration is produced.

SUMMARY

Metallic sodium is lighter than water, oxidises readily in the air and decomposes water with evolution of hydrogen.

Sodium burns in the air, forming the peroxide, Na_2O_2, and the monoxide, Na_2O. The latter is a strong basic oxide and unites with water to form caustic soda, $NaOH$.

Sodium only forms one series of salts; these are produced by the replacement of 1 atom of hydrogen in the various acids by 1 atom of sodium. These salts are all soluble in water and impart a yellow coloration to the flame.

EXERCISES ON LESSON XVII

1. Describe the chief chemical and physical properties of metallic sodium and compare them with those of arsenic.

2. 5.42 grams. of sodium chloride exactly precipitate 10 grams. of silver from a solution of the nitrate in the form of silver chloride. Calculate the equivalent of sodium. (The equivalent of silver is 107.88 and that of chlorine 35.46.)

What considerations would guide you in deciding the atomic weight of sodium?

3. Describe the preparation of caustic soda. What happens when this substance is added to solutions of (*a*) copper sulphate, (*b*) hydrochloric acid, (*c*) sodium bicarbonate?

4. Whence is common salt obtained on the large scale and how can it be purified?

5. What occurs when carbonic acid gas is passed into a strong solution

of caustic soda? How can sodium bicarbonate be converted into sodium carbonate; and sodium carbonate into sodium bicarbonate?

6. What is meant by a normal solution of an acid? How can a decinormal solution of nitric acid be prepared?

7. What is meant by an indicator? Describe the effect of caustic soda, hydrochloric acid and carbonic acid on litmus, phenol-phthalein, and methyl-orange.

8. 15 cc. of a solution of sodium carbonate require 45 cc. of normal acid for neutralisation. What is the strength of the sodium carbonate solution in grams. per litre?

9. What is the action of hydrochloric acid on solutions of (*a*) sodium nitrite, (*b*) sodium sulphite, (*c*) sodium thiosulphate?

LESSON XVIII

THE ALKALI MANUFACTURE

Sulphuric Acid. Salt Cake. Soda Ash. Caustic Soda.
Chlorine. Bleaching Powder. Potassium Chlorate

THE sodium salts which are manufactured on the large scale for use in the various industries are almost entirely made from common salt, NaCl. The most important of these products are the following :—

		Uses.
Sodium sulphate or Salt cake	Na_2SO_4	Glass making. Ultramarine.
Sodium carbonate or Soda ash	Na_2CO_3	Source of most of the sodium salts of commerce. Metallurgical purposes.
Caustic soda	NaHO	Soap. Paper and Bleaching.
Hydrated sodium carbonate or Soda crystals	$Na_2CO_3 + 10H_2O$	Washing.
Sodium bicarbonate	$NaHCO_3$	Baking powder. Medicinal purposes and effervescing drinks.

The chlorine of the salt is also utilised for the production of the valuable products—Hydrochloric acid, HCl ; Bleaching powder, $CaOCl_2$; and Potassium chlorate, $KClO_3$.

Several different processes are in use for the conversion of common salt into these various products, but only the most important of them can be here touched upon.

It must be remembered that in all commercial processes of manufacture success depends essentially on the cost at which they can be carried out, and hence the various operations involved must each of them be executed with due regard to economy, so that as little waste of material as possible takes place. In many cases it has been found possible to recover costly elements or compounds from the secondary products of the manufacture and use them over again, whereas these were formerly entirely lost. Instances of this will be met with in the recovery of sulphur from alkali waste, and of manganese dioxide in the manufacture of chlorine.

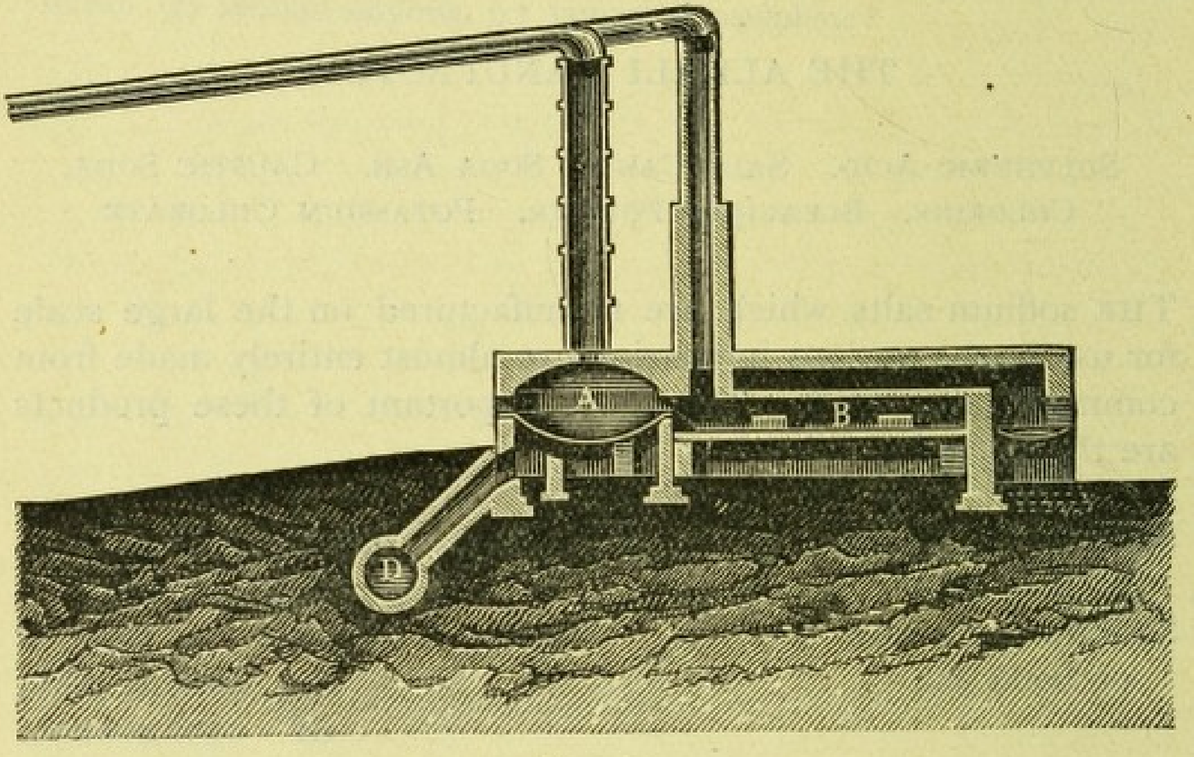


Fig. 36.

I. Manufacture of Soda Ash (Sodium Carbonate) from Common Salt by the Le Blanc Process.

The Le Blanc process is carried out in two stages.

(1) The salt is treated with sulphuric acid which produces sodium sulphate and hydrochloric acid,—

$$2NaCl + H_2SO_4 = Na_2SO_4 + 2HCl.$$

(2) The sodium sulphate is converted into sodium carbonate by being fused with coal and calcium carbonate,—

$$Na_2SO_4 + CaCO_3 + 2C = Na_2CO_3 + CaS + 2CO_2.$$

Sulphuric Acid.—The principles involved in the manufacture of sulphuric acid, a necessary part of the alkali manufacture by the Le Blanc process, have already been described (R. and L., pp. 207-211).

1. The Salt-Cake Process.—The salt (about 15 cwt.) is placed in a large shallow iron pan (A, Fig. 36), and the necessary amount of sulphuric acid run in and well mixed with the salt by stirring, the pan being gently heated by a fire placed beneath it. The salt is thus decomposed, sodium hydrogen sulphate, $NaHSO_4$, being formed and hydrochloric acid gas evolved, which escapes by a special flue and passes to the condensing towers, which have already been described (R. and L., p. 177),—

$$(a)\quad NaCl + H_2SO_4 = NaHSO_4 + HCl.$$

The contents of the pan are then pushed by a rake on to the bed of a furnace or roaster (B) placed at the side of the pan, which is heated from the top, the gases from the furnace passing into the flue (D), whilst the hydrochloric acid gas evolved leaves the roaster by a special flue leading to the condensing towers. The temperature during this stage of the operation is much higher than in the first part of the process, and the conversion of the salt into normal sulphate is here completed, hydrochloric acid being evolved,—

$$(b)\quad NaHSO_4 + NaCl = Na_2SO_4 + HCl.$$

The product consists of anhydrous sodium sulphate known as *salt cake*, and forms a hard yellowish white mass.

Salt cake is also manufactured to some extent by a modification of the foregoing method known as the *Hargreaves process*, by which the use and hence also the manufacture of sulphuric acid are avoided. Sulphurous acid gas, prepared by burning iron pyrites or sulphur, is mixed with air and water vapour, and is then passed over carefully moulded lumps of the dried and heated salt, which becomes completely converted into sodium sulphate,—

$$4NaCl + 2SO_2 + 2H_2O + O_2 = 2Na_2SO_4 + 4HCl.$$

2. The Black Ash Process.—The sodium sulphate obtained by the salt-cake process is broken into lumps, mixed with coal and limestone, and the whole mass strongly heated. This is done in large hollow horizontal cylinders of iron plate lined with fire-brick (B, Fig. 37), the cylinder being about 18 feet long and 12 feet in diameter. This cylinder is made to revolve about its axis and is heated by a furnace (A) placed at one end, the flames from which pass right through the interior. As soon as the mass in the cylinder becomes pasty and is seen to be covered with small yellow flames, the revolution of the cylinder is stopped, the man-hole is opened and the fused material is run out into iron trucks, in which it solidifies. The oxygen of the sulphate is removed by the carbon, sodium carbonate and calcium sulphide being then formed by double decomposition,—

$$(a)\ Na_2SO_4 + 2C = Na_2S + 2CO_2.$$

$$(b)\ Na_2S + CaCO_3 = CaS + Na_2CO_3.$$

The porous grey mass which results is known as *black-ash*, and consists mainly of sodium carbonate and calcium sulphide, together with smaller amounts of lime, coal, calcium carbonate, chloride and sulphate of sodium, and smaller quantities of various other substances, such as silica, etc.

Since calcium sulphide is insoluble in water, the sodium carbonate can be removed by means of washing with water, this process being known as *lixiviation*. The black-ash is broken into lumps and placed in wooden tanks and repeatedly treated with water, the process being carried out in such a way that the same black-ash is first treated by nearly saturated liquor, and finally by fresh water, which removes the last traces of soluble sodium salts.

The *tank-liquor* thus obtained invariably contains a large proportion of caustic soda, which is formed by the action of the lime produced at the high temperature of the black-ash furnace from the excess of limestone employed. The liquor is therefore treated with sufficient carbonic acid gas to convert this caustic soda into carbonate, and is then evaporated in pans heated from the top by the waste heat from the revolving furnace (D, D, Fig. 37). The crude carbonate is deposited as the liquor evaporates and is scraped out into the drainers (E, E, Fig. 37), and is then removed and strongly heated on the bed of a reverberatory furnace, the product being *finished soda ash.*

The commercial article usually contains about 84 per cent of sodium carbonate, 8 per cent of sodium sulphate, 3 per cent of sodium chloride, and smaller quantities of caustic soda, silica, alumina and insoluble matter.

Soda Crystals or Washing Soda, $Na_2CO_3 + 10H_2O$, are made by dissolving soda ash in warm water, allowing the liquid to settle, running off the clear liquor and allowing it to crystallise in large vats. The crystals contain about 36.5 per cent of sodium carbonate, and 62 per cent of water, together with small amounts of sodium sulphate and chloride, and are considerably freer from impurity than the original soda ash.

Sodium Bicarbonate is prepared by exposing soda crystals to carbonic acid gas, until no more of the latter is absorbed,—

$$(Na_2CO_3 + 10H_2O) + CO_2 = 2NaHCO_3 + 9H_2O.$$

The clear transparent crystals become opaque and soft but do not change in

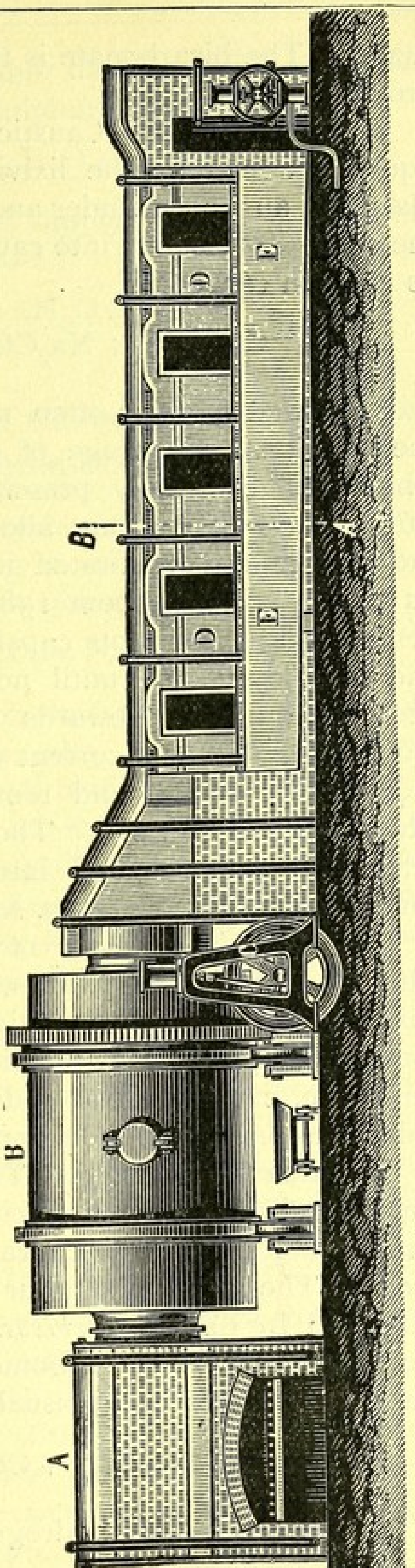


Fig. 37.

shape. The bicarbonate is then dried at about 40°, and finely ground.

Caustic Soda.—Caustic soda is prepared from the tank-liquor obtained by the lixiviation of the black-ash. This is placed in an iron cylinder and heated with lime, which converts the sodium carbonate into caustic soda and is itself precipitated as calcium carbonate,—

$$Ca(OH)_2 + Na_2CO_3 = CaCO_3 + 2NaOH.$$

A current of air is often used to agitate the liquid, and has the additional advantage of oxidising the sulphur compounds which are invariably present. The finely-divided calcium carbonate is then either allowed to settle or filtered off, and the clear liquid evaporated in shallow boat-shaped pans until its boiling-point is about 138°. It is then run off into large hemispherical iron pots capable of holding 10 tons of caustic and strongly heated until nearly the whole of the water has been driven off. Towards the end of the process sodium nitrate is added or a current of air is blown through the mass in order to oxidise and remove the sulphides and cyanides which are still present. The liquid soda is then allowed to settle and finally ladled into sheet iron drums, in which it comes into the market as a solid white mass.

Caustic soda is made of very varying strengths, differing amounts of water being allowed to remain in it. The highest quality of the commercial article made by the Le Blanc process contains 95 per cent of caustic soda, 2 to 3 per cent of sodium carbonate, 2 per cent of sodium sulphate, a small amount of sodium chloride, and frequently a little alumina.

Sulphur Recovery.—The residue left in the lixiviating tanks consists chiefly of calcium sulphide, the whole of which was at one time thrown away, and known as *alkali maker's waste.* The valuable sulphur contained in this material is now recovered by *Chance's process*, which consists in decomposing the moist waste with carbonic acid gas, produced by heating limestone in kilns in the usual way,—

$$CaS + H_2O + CO_2 = CaCO_3 + H_2S.$$

The sulphuretted hydrogen which is evolved is either completely burned, and the sulphur dioxide which is produced utilised for the manufacture of sulphuric acid,—

$$2H_2S + 3O_2 = 2H_2O + 2SO_2,$$

or the gas is burned in a limited supply of air, and the sulphur thus obtained in the free state,—

$$2H_2S + O_2 = 2H_2O + 2S.$$

II. Manufacture of Sodium Carbonate from Common Salt by the Ammonia-Soda Process.

In this process sodium bicarbonate is produced directly from common salt by saturating a solution of the latter with ammonia and then passing in carbonic acid gas,—

$$NaCl + NH_3 + H_2O + CO_2 = NaHCO_3 + NH_4Cl.$$

The salt is dissolved in water, and the brine, carefully freed from magnesium and calcium salts, is first of all saturated with ammonia, the clear liquid being then allowed to flow down a tower where it meets an upward current of carbonic acid gas. The reaction described above takes place in this tower, so much heat being evolved that it is necessary to cool the lower portion of the tower with a current of cold water. The sodium bicarbonate is only very slightly soluble in dilute ammonium chloride solution, and separates out in the crystalline state. The resulting pasty mass of bicarbonate is then filtered from the ammonium chloride solution and freed from all adhering ammonia by being washed with a little water and then dried in pans. The resulting mass is finally calcined in a reverberatory furnace, and thus converted into soda ash,—

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2.$$

The ammonium chloride solution is returned to the ammonia stills, where it is heated with lime or magnesia, and the resulting ammonia again used for the saturation of the brine.

The whole of the chlorine of the salt is thus finally obtained in the form of calcium chloride or magnesium chloride, substances from which it is extremely difficult to obtain free chlorine by any economical process. This constitutes a disadvantage of the ammonia soda process as compared with the Le Blanc process, since in the latter the chlorine of the salt is obtained in the form of hydrochloric acid, from which chlorine and the valuable products bleaching powder and potassium chlorate can readily be prepared. On the other hand, the soda ash obtained by the ammonia-soda process is of a superior quality, and the process is simpler and more economical.

The crude sodium bicarbonate obtained as described above can be converted into finished bicarbonate, suitable for use in baking powder and for medicinal purposes, by carefully drying it in a current of warm carbonic acid gas, the presence of which prevents the decomposition of the bicarbonate, whilst the objectionable ammonia is driven off by the heat.

III. The Manufacture of Bleaching Powder and Potassium Chlorate

Bleaching Powder.—The first step in the manufacture of bleaching powder is the production of gaseous chlorine, which is then absorbed by slaked lime,—

$$Ca(OH)_2 + Cl_2 = CaOCl_2 + H_2O.$$

Several important methods exist by which this can be effected.

1. **The Weldon Chlorine Process.**—In this process the chlorine is produced by the action of hydrochloric acid on manganese dioxide,—

$$MnO_2 + 4HCl = MnCl_2 + H_2O + Cl_2.$$

The dioxide, in the form of manganese mud (p. 177), is placed in stills made of Yorkshire flag-stone (Fig. 38), and is there treated with the concentrated hydrochloric acid obtained by the absorption of the gas evolved in the manufacture of salt cake, the contents of the still being heated by steam admitted at D (Fig. 38). The manganese dioxide is recovered by running off the solution of manganese chloride, neutralising the excess of acid with calcium carbonate, and then adding an excess of milk of lime. The manganese is thus precipitated as manganous hydroxide,—

$$MnCl_2 + Ca(OH)_2 = CaCl_2 + Mn(OH)_2,$$

and this is then placed in a cylindrical vessel, known as the *oxidiser*, in which it is gently heated by steam and treated with a current of air which is pumped through the mass. The oxygen thus admitted converts the manganous hydroxide in the presence of lime into the dioxide which unites with the excess of lime,—

$$Mn(OH)_2 + O = MnO_2 + H_2O.$$

The mass is then allowed to settle, the calcium chloride solution run off, and the black mud containing the dioxide, which is known as *manganese-mud*, run back into the chlorine stills. Nearly one half of the original chlorine of the salt is thus obtained in the form of gaseous chlorine, the remainder being converted into calcium chloride, which is only of small commercial value.

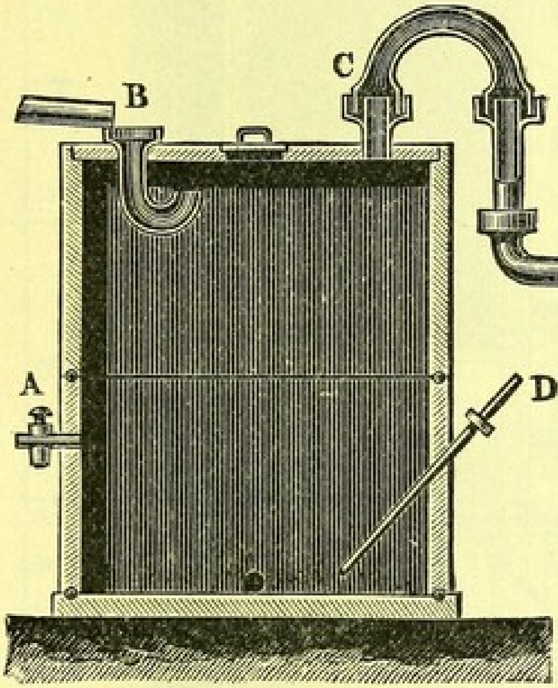


Fig. 38.

The chlorine is then passed into large chambers made of sheet lead (Fig. 39), on the floor of which slaked lime is exposed, in a layer 3 or 4 inches deep raked into furrows. As soon as all the air of the chamber has been replaced by chlorine, the chamber is closed and allowed to stand for twenty-four hours, and if necessary more chlorine is then passed in until the lime is saturated. Air is then admitted, the chlorine aspirated into a chamber containing fresh lime, and the bleaching powder removed.

The bleaching powder thus produced, when treated with acids, yields 36-38 per cent of chlorine, known as the *available chlorine*. It usually contains about 16 per cent of water and small amounts of calcium carbonate and chlorate, as well as traces of silica, alumina, etc.

2. **The Deacon Chlorine Process.**—In this process the hydrochloric acid gas, evolved by the action of sulphuric acid

on salt, is not absorbed by water but is mixed with air, dried, and then heated and passed through heated cast-iron cylinders containing broken bricks impregnated with cupric chloride, $CuCl_2$. Under these circumstances the hydrochloric acid of the gas is oxidised by the oxygen of the air present, free chlorine being produced,—

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

This oxidation only takes place at a high temperature when the two gases are simply heated together, but occurs at a much lower temperature in the presence of cupric chloride, which plays a somewhat similar part to that of the manganese dioxide in the preparation of oxygen from potassium chlorate and manganese dioxide (R. and L., p. 76).

The resulting gases are washed with water to remove the excess of unaltered hydrochloric acid, dried and then passed over slaked lime, exposed in very thin layers on a series of slate shelves. It is impossible

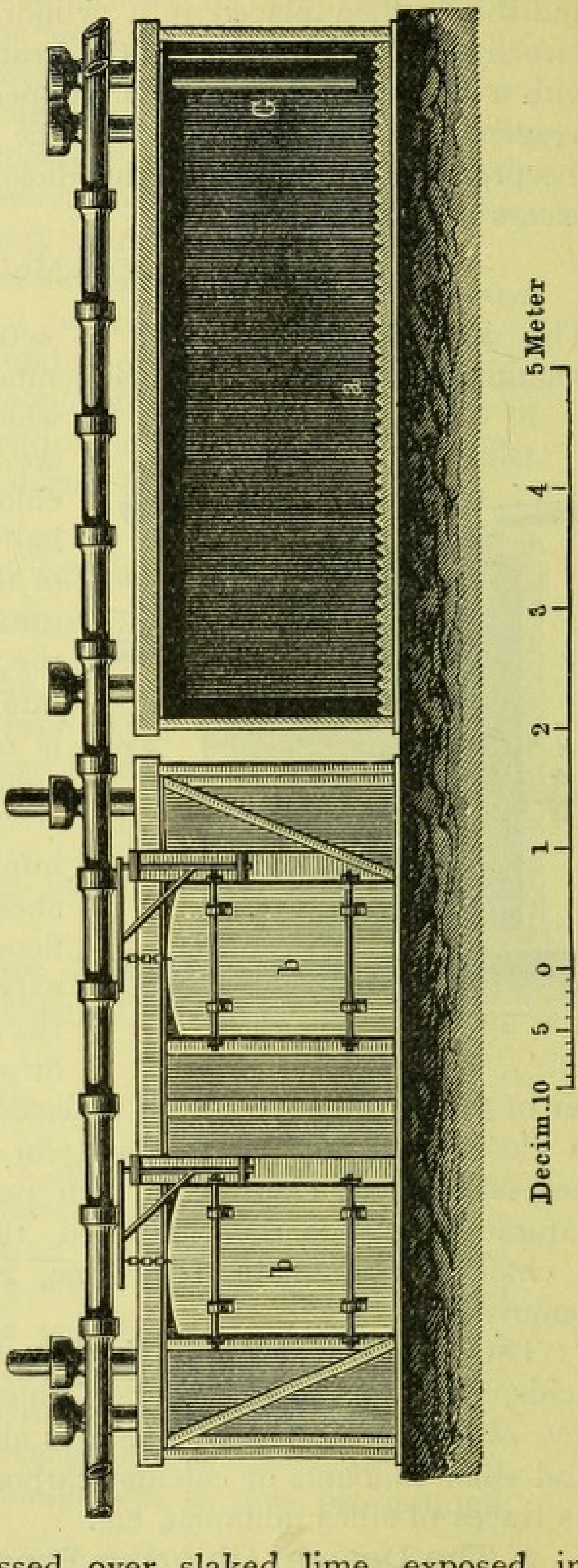


Fig. 39.

to use the chambers employed in the ordinary method of making bleaching powder, because the chlorine is diluted with a very large volume of nitrogen and air, only about 5 to 7 per cent of chlorine being present in the gas.

Potassium Chlorate.—The manufacture of potassium chlorate is not carried out by passing chlorine into caustic potash solution (p. 46), because in this reaction 5/6 of the valuable potash is converted into potassium chloride, and only 1/6 into the chlorate. For this reason the method is adopted of first preparing calcium chlorate by the action of an excess of chlorine on hot milk of lime, a cheap substance,—

$$6Ca(OH)_2 + 6Cl_2 = 5CaCl_2 + Ca(ClO_3)_2 + 6H_2O.$$

Potassium chloride is then added to the liquid, the sparingly soluble potassium chlorate being precipitated,—

$$Ca(ClO_3)_2 + 2KCl = CaCl_2 + 2KClO_3.$$

The milk of lime is contained in cylindrical vessels, into which the chlorine is passed. During the operation the temperature rises considerably, and the treatment with chlorine is continued until an excess is present. The solution is then allowed to settle and the clear liquid run off into the evaporating pans. Here the necessary amount of potassium chloride is added, and the whole boiled down until it is sufficiently concentrated. On cooling crude potassium chlorate separates out, which is recrystallised from boiling water, washed with cold water and dried.

Potassium chlorate is now also made by an electrolytic process, in which caustic potash and chlorine are simultaneously formed by the electrolysis of a solution of potassium chloride (p. 305) and immediately react upon each other in the ordinary way. By repeating the operation upon the mother-liquors, the whole of the original potassium chloride is ultimately converted into potassium chlorate, this final result being represented by the equation,—

$$KCl + 3H_2O = KClO_3 + 3H_2.$$

IV. Electrolytic Decomposition of Common Salt

Caustic soda and chlorine are now also made directly from salt by an electrolytic process, which is described in Lesson XXVIII.

Exercises on Lesson XVIII.

1. Describe the various steps in the manufacture of soda ash from salt by the Le Blanc process.
2. Describe the chief points in the manufacture of sulphuric acid.
3. How can sodium bicarbonate be prepared directly from common salt, and how can it be purified?
4. Describe the most important methods for the preparation of chlorine on the large scale.
5. How are bleaching powder and potassium chlorate manufactured?
6. How much soda ash is it possible to obtain from a ton of salt containing 95 per cent of sodium chloride? What weight of aqueous hydrochloric acid containing 30 per cent of acid would also be formed?
7. How much salt is required for the production of a ton of (*a*) bleaching powder containing 37 per cent of available chlorine, (*b*) potassium chlorate?

LESSON XIX

THE ALKALI METALS (*Cont.*)

Potassium, K, 39.1

As in the case of sodium (p. 149), the symbol for this element is the initial letter of the Latinised name of the metal, *kalium*. This term itself is derived from the Arabic *kali*, which with the prefix *al* has come into use as the general term *alkali*. The compounds of potassium are almost as widely distributed as those of sodium, although they are not as a rule found in such large quantities. Potassium forms an essential constituent of many of the igneous rocks of which the crust of the earth originally consisted. Thus felspar, which occurs in granite, gneiss and basalt, and also mica, which is likewise a constituent of granite and gneiss, both contain potassium. By exposure to the continued action of air, rain, wind, frost and running water, aided by plants and bacteria, these rocks are gradually broken up, first at the surface and then more completely, and at the same time undergo a very important chemical alteration. The various minerals present, such as quartz, felspar, mica, etc., first become separated from one another, and then, in many cases, undergo a further change. Felspar, for example, is converted into a soft mass of clay (aluminium silicate, usually containing iron), whilst the potassium and calcium in it are converted into carbonates or nitrates. In this way the salts of these metals are slowly converted into the soluble form and disseminated throughout the soil. They are then gradually washed out by drainage water, and thus pass into the rivers and thence into the sea. A portion of the potassium salts contained in fertile soil is taken up by plants, which cannot grow unless this element be supplied to them. Hence when plants are burned the ash is always found to contain salts of potassium, and this ash formerly constituted the chief source of the compounds of the element, so that the name of *vegetable alkali* was given to the carbonate on this account.

Potassium chloride occurs in sea-water, but to a very much smaller extent than sodium chloride, only about 0.75 gram. being contained in 1000 grams. of the water. In spite of this it can be prepared from sea-water, because it accumulates in the mother liquors from which the sodium chloride has separated. When the water is evaporated the sodium chloride separates out first, and only after most of this has been removed are the salts of potassium and magnesium deposited. The phenomenon has occurred in this way during the drying up of many former seas, and in some localities the overlying beds of potassium and magnesium salts have been preserved, although in most places they have been subsequently washed away by the action of water, in which they are much more soluble than the sodium chloride. Thus in Cheshire no such overlying potassium salts are found, but at Stassfurt in Germany they have been preserved and still exist in a bed, 70 to 100 feet in thickness. This deposit has become the chief source of the potassium salts.

Preparation of Metallic Potassium.—Metallic potassium is not manufactured on any very large scale, because the cheaper sodium can be used for most purposes for which it would be useful. It is either prepared by the electrolysis of caustic potash, or by heating cream of tartar (potassium hydrogen tartrate) in a closed crucible and submitting the finely divided mixture of potassium carbonate and carbon to a high temperature in a wrought-iron bottle,—

$$K_2CO_3 + 2C = 2K + 3CO.$$

Potassium vapour is produced and is condensed between two flat iron plates, the outside surfaces of which are exposed to the air (Fig. 40). If the vapour is not very rapidly cooled an explosive compound is formed between the potassium and the carbonic oxide, and many serious accidents have at various times occurred from this cause.

Properties of Potassium.—In its chemical and physical properties potassium resembles sodium very closely, but is characterised by being chemically more energetic. Thus when potassium is thrown on to cold water, the hydrogen which is evolved takes fire spontaneously, a beautiful violet flame being produced. Potassium, moreover, explodes when brought into contact with bromine, whilst sodium does not react at all with bromine at ordinary temperatures. Potassium is even lighter than sodium, having the specific gravity 0.875 at 13°. It melts at 62.5° and boils at 757.5°, yielding a beautiful green vapour.

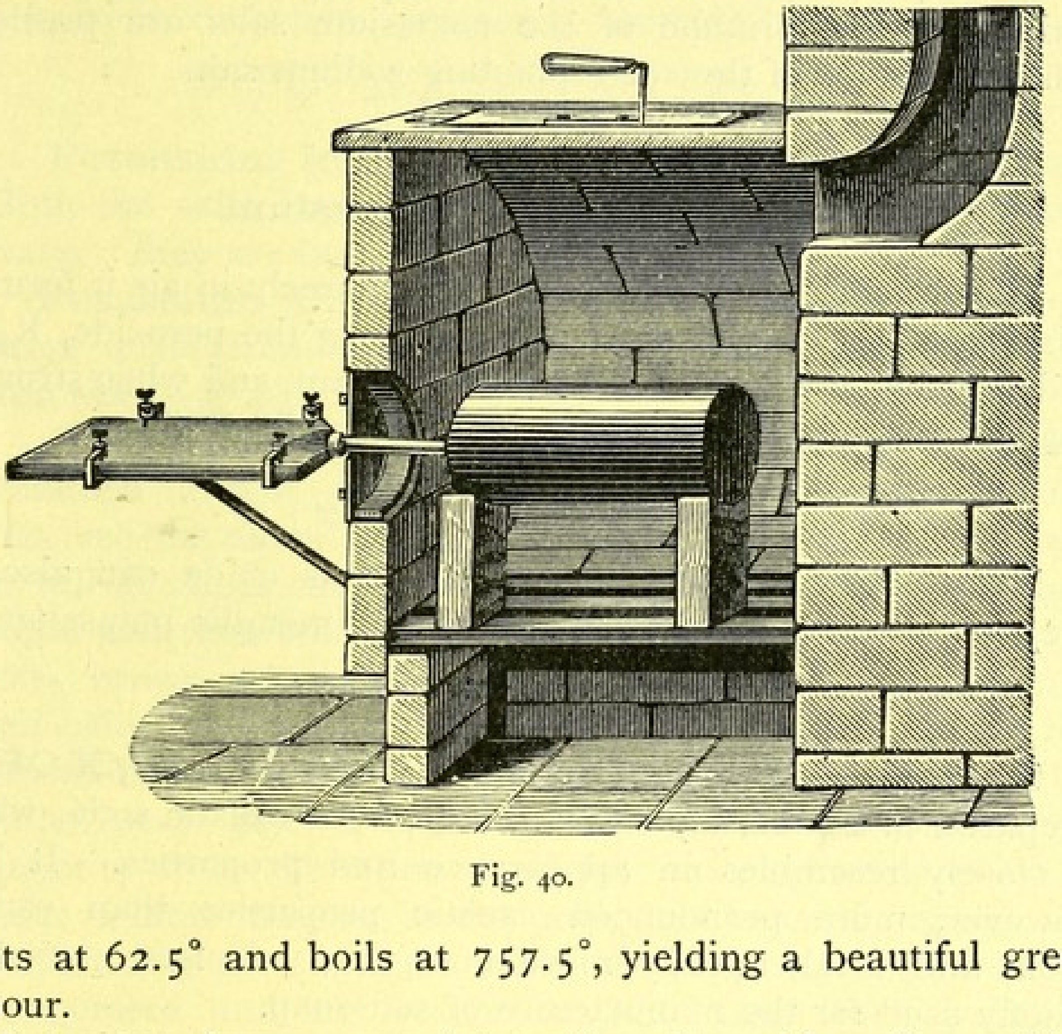


Fig. 40.

Potassium forms a very interesting alloy with sodium, which is an excellent example of the general rule that alloys melt at a lower temperature than their constituents (p. 116). When the two metals are melted together in the proportion of their atomic weights, the mixture remains liquid at the ordinary temperature, resembling mercury in appearance, and only solidifies at about 8°, although sodium melts at 95.6° and potassium at 62.5°.

The Equivalent and Atomic Weight of Potassium

and the Composition of the Potassium Salts have been ascertained in precisely the same way as the corresponding data for sodium. The equivalent of potassium is, as already mentioned (p. 67), 39.1. The specific heat of the metal is 0.166, and hence the atomic weight must be about $\frac{6.4}{0.166} = 38.6$. The accurate atomic weight is, therefore, identical with the equivalent and equals 39.1. The atom of potassium, like that of sodium, replaces one atom of hydrogen, and hence the formulæ of the potassium salts are precisely similar to those of the corresponding sodium salts.

The Oxides of Potassium

When potassium is allowed to burn freely in air it forms a mixture of oxides, the chief product being the peroxide, K_2O_4. This substance is a powerful oxidising agent, and when strongly heated loses oxygen and yields the monoxide, K_2O,—

$$2K_2O_4 = 2K_2O + 3O_2.$$

Potassium Monoxide, K_2O.—This oxide can also be prepared by heating caustic potash with metallic potassium,—

$$2KHO + 2K = 2K_2O + H_2.$$

Potassium Hydroxide or Caustic Potash, KOH, is prepared in a precisely similar manner to caustic soda, which it closely resembles in appearance and properties. It has, however, more pronounced caustic properties than caustic soda, and is chemically more energetic. Caustic potash is chiefly used for the manufacture of soft soap.

Potassium Chloride, KCl, occurs, as already described, in the Stassfurt deposits. It is found there either as a crystalline mass, known as *sylvine*, or combined with magnesium chloride to form *carnallite*, $KCl + MgCl_2 + 6H_2O$.

The potassium chloride is extracted from these materials by fractional crystallisation. The carnallite is dissolved in hot water and the solution allowed to cool. Under these circumstances the less soluble potassium chloride crystallises out, leaving the magnesium chloride in solution.

Potassium chloride is much more soluble in hot water than sodium chloride, 100 parts of water at 100° dissolving 56.5 parts. It is now used as the source of all the potassium salts, but these are not manufactured on nearly such a large scale as the sodium salts, although the same methods are used. The chloride is largely employed as an artificial manure.

Potassium Bromide, KBr, is prepared on the large scale by acting with bromine on iron filings and water; a bromide of iron is thus produced, which is then treated with potassium carbonate, potassium bromide being formed,—

$$2FeBr_3 + 3K_2CO_3 = 6KBr + Fe_2O_3 + 3CO_2.$$

Potassium Iodide, KI, is prepared in a similar manner. Both the salts crystallise in cubes and are freely soluble in water; they are both used in medicine.

Potassium Chlorate, $KClO_3$, is manufactured on the large scale from the calcium salt, and has already been described (p. 46).

Potassium Carbonate, K_2CO_3.—This salt was formerly obtained almost exclusively by burning wood, and hence received the name of the *vegetable alkali*. The process, which is still in use in countries rich in forests, consists in burning the wood and then boiling the ash with water and evaporating the dark brown solution to dryness, the crude reddish material left behind being known as *pot-ashes*. This is purified by re-crystallisation from water, the white salt thus obtained being called *pearl ash*. Potassium carbonate is also made in small quantity from the water used for washing wool, which contains a large amount of the potassium salts of organic acids, constituting the sweat or suint of the sheep. The liquid is evaporated and the residue calcined and then purified as described above. The potassium salts in the suint are of course derived from the vegetable matter which forms the diet of the sheep. By far the largest amount of potassium carbonate is now made from potassium chloride by processes similar to those used for the manufacture of sodium carbonate (p. 170).

Potassium carbonate is deliquescent and very soluble in water, 100 parts of the latter dissolving 120 parts of the salt at 20°. As it takes up water so readily, it is often used for removing small amounts of water mixed with other liquids, such as alcohol.

EXPERIMENT 79.—Mix 5 cc. of alcohol (methylated spirits) with 15 cc. of water, and ascertain that this mixture cannot be made to burn. To 10 cc. of this liquid in a test-tube add solid potassium carbonate until no more dissolves. A layer of strong alcohol separates at the top of the fluid. Remove this and show that it burns readily with a colourless flame, like the original methylated spirit, the greater part of the water having been removed by the potassium carbonate.

Potassium Bicarbonate, $KHCO_3$, closely resembles the sodium salt.

Potassium Nitrate, KNO_3, was formerly known by the name of saltpetre (Latin, *sal-petrae*, rock-salt) or nitre.

It is formed in all soil containing decaying organic matter, and the manner in which it is produced is one of great interest.

All decay or putrefaction of organic matter is brought about by the aid of minute living organisms known as *bacteria*, whilst in the absence of these, vegetable and animal matter can be preserved indefinitely without undergoing any decomposition. The nitrogen of such organic matter is chiefly present in the form of substances known as *albuminoids*, which resemble the white of egg in composition and in many of their properties, and are of very complex and still unknown chemical constitution. The effect of putrefaction on these compounds is to break them up into simpler substances, and finally to liberate the nitrogen as ammonia, generally in the form of one of its salts. This ammonia, however, does not remain unchanged, but is seized upon by other bacteria, which are present in all fertile soil, and have the power in presence of atmospheric oxygen of oxidising the ammonia to nitrous acid,—

$$2NH_3 + 3O_2 = 2HNO_2 + 2H_2O.$$

Even this, however, is not the end of the change, for soil contains a third variety of bacterium, which has no effect on albuminoid substances or ammonia, but can convert nitrites into nitrates, again by the aid of atmospheric oxygen,—

$$2HNO_2 + O_2 = 2HNO_3.$$

Free nitric acid is not produced, because soil contains the carbonates of potassium and calcium, and hence the nitrates of these metals are formed.

Three different sets of bacteria are therefore concerned in the production of nitrates from animal and vegetable matter: the ordinary *putrefactive* organisms, which liberate the nitrogen as ammonia; and the *nitrifying* organisms, one set of which converts the ammonia into nitrous acid, whilst the other completes the oxidation to nitric acid. A similar process goes on in water to which animal matter, such as sewage, has been added. Such contaminated water is now frequently purified by filtration through sand or coke, during which process it is exposed to the action of the bacteria, and at the same time thoroughly aerated.

Nitre or saltpetre was formerly entirely obtained by the putrefaction and nitrification of animal and vegetable refuse, especially in the hot countries of the East, and is still prepared in this way in some districts. The soil containing such substances is removed at intervals of several years and extracted with water. If calcium nitrate be present, potassium carbonate is added to convert it into potassium nitrate,—

$$Ca(NO_3)_2 + K_2CO_3 = CaCO_3 + 2KNO_3.$$

The liquid is then evaporated and the crude nitre purified by recrystallisation.

Potassium nitrate is now generally manufactured by adding potassium chloride to sodium nitrate in hot concentrated solution. Sodium chloride separates out from the boiling liquid, and is filtered off, whilst potassium nitrate remains dissolved in the liquid, and is deposited on cooling. The crude nitre contains some sodium chloride, and is purified by recrystallisation. The sodium chloride which separates out from the hot liquid is washed with water to remove the adhering potassium nitrate, and the washings utilised in the succeeding process,—

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

Double Decomposition.—It is a general rule that when two salts are brought together in solution, if any one of the possible salts which can be formed from the acid and basic radicals present is insoluble, it is precipitated. Thus when solutions of silver nitrate and potassium chloride are mixed, silver chloride, being insoluble, is precipitated,—

$$KCl + AgNO_3 = KNO_3 + AgCl.$$

When solutions of equivalent amounts of silver sulphate and barium chloride are mixed, both barium sulphate and silver chloride are precipitated, since they are both insoluble,—

$$BaCl_2 + Ag_2SO_4 = BaSO_4 + 2AgCl.$$

A reaction of this kind is usually termed a double decomposition.

In the case of sodium nitrate and potassium chloride, all the four possible salts, comprising the two original salts, together with sodium chloride and potassium nitrate, are readily soluble in water, but potassium chloride, potassium nitrate, and sodium nitrate are all more soluble in boiling water than sodium chloride. Hence by choosing such an amount of water as is insufficient to retain in solution, at the boiling-point, the whole of the sodium chloride formed, it is possible to carry out the process described above on the manufacturing scale.

The fact that in such a case the course of the reaction depends on the amount of water present, is illustrated by the following experiments :—

EXPERIMENT 80.—1. Dissolve 10 grams. of potassium chloride and 11.5 grams. of sodium nitrate in 60 cc. of hot water and allow to cool,—no solid salt is deposited.

2. Dissolve the same amounts of the two salts in 25 cc. of boiling water and allow to cool. Potassium nitrate crystallises out in long needles. Filter these off, if possible, by means of a filter pump ; recrystallise from boiling water (5 cc.), and show that the crystals after draining are free from chloride of sodium.

3. Add the same weights of the two salts to 10 cc. of boiling water. A white granular substance remains undissolved. Filter this off whilst still hot through a funnel previously warmed by boiling water. The filtrate on cooling deposits potassium nitrate, which may be purified by recrystallisation. The deposit consists of

common salt, which, after washing with a few cc. of water, may be dissolved in hot water and the liquid allowed to cool. No crystallisation occurs, or only a few granules of salt are deposited, which can easily be distinguished by their appearance from the characteristic needles of potassium nitrate.

The reaction is therefore similar in principle to the familiar instances of double decomposition in which an insoluble salt is precipitated. It may be taken as a general rule that when a solution containing equivalent quantities of two salts is evaporated, the least soluble of the four possible salts will be first deposited, although in some cases two of the salts crystallise out together as a double salt.

EXPERIMENT 81.—Dissolve 14 grams. of sodium sulphate (anhydrous) and 10 grams. of potassium nitrate in hot water. Allow the solution to cool and show that the solid salt which is deposited is potassium sulphate.

Potassium nitrate is readily soluble in water, 100 parts of which dissolve 26 parts of the salt at 15° and 246 parts at 100°. It crystallises in very characteristic prismatic needles belonging to the rhombic system. It is a very powerful oxidising agent, and readily gives up its oxygen to other substances, especially when heated.

EXPERIMENT 82.—Fuse some potassium nitrate on a clean sand tray and throw on to the surface of the fused salt a few small pieces of charcoal—a vivid combustion ensues.

On this account potassium nitrate is very largely employed in the manufacture of gunpowder.

Gunpowder. — Ordinary black gunpowder consists of an intimate mixture of potassium nitrate with charcoal and sulphur. The proportions of the constituents vary slightly in different qualities of powder, but the average percentage composition is approximately the following,—

Saltpetre	75
Charcoal	14
Sulphur	10
Water	1
	100

The three solid constituents are separately ground as finely as possible, and are then carefully mixed together with enough water to make a thick paste. This is afterwards formed into grains of the required size, and very gradually dried at a low temperature. When the grains are large they usually receive a final coating of graphite. Gunpowder contains sufficient oxygen in its saltpetre to produce the oxidation of the charcoal and sulphur present, and can therefore be fired in a closed space without the presence of atmospheric oxygen. Under these circumstances the carbon yields carbon dioxide, part of which goes to form potassium carbonate, whilst the remainder is liberated in the gaseous state, accompanied by a smaller volume of carbon monoxide. The nitrogen of the potassium nitrate is liberated as gas, whilst the sulphur unites with the potassium and some of the oxygen, forming potassium sulphide, sulphate, and thiosulphate, a small amount of sulphuretted hydrogen being also produced. Free hydrogen is also liberated, together with traces of marsh gas and other gases. The relative proportions in which the various gases are present are, on the average,—

Carbon dioxide	50
Nitrogen	35
Carbon monoxide	10
Sulphuretted hydrogen	2.5
Hydrogen	2.5
	100.0

The exact proportions of the gases produced depend, however, on the pressure under which the powder is fired.

The gases evolved occupy 280 times the volume of the powder, and it is the sudden increase of pressure thus produced which renders the powder so valuable as an explosive.

The various constituents of gunpowder can readily be separated by treatment with appropriate solvents. Thus the saltpetre can be completely removed by washing with water, whilst carbon disulphide dissolves the whole of the sulphur.

Potassium Nitrite, KNO_2, closely resembles the sodium salt, and is prepared in a similar manner.

Potassium Sulphide, K_2S.—When potassium carbonate is heated with sulphur, a liver-coloured mass is obtained, which is known as *liver of sulphur*. It contains a number of different sulphur compounds of potassium, and yields a precipitate of sulphur when an acid is added to its solution. Pure potassium sulphide is best prepared by saturating caustic potash with sulphuretted hydrogen, and then adding an equal amount of caustic potash (compare p. 163). It readily absorbs oxygen and carbon dioxide from the air.

Potassium Hydrosulphide, KHS.—This salt is formed when potassium is heated in sulphuretted hydrogen, just as potassium hydroxide, KOH, is produced by the action of potassium on water,—

$$2H_2S + 2K = 2KHS + H_2.$$

It may be obtained in solution by saturating caustic potash with sulphuretted hydrogen,—

$$KHO + H_2S = KHS + H_2O.$$

Potassium Sulphate, K_2SO_4.—This salt is manufactured either by the action of potassium chloride or magnesium sulphate or from the mineral *kainite*, $KCl + MgSO_4 + 3H_2O$, which occurs in the Stassfurt beds. It crystallises in six-sided prisms, terminated by pyramids, is only sparingly soluble in water, and does not unite with water of crystallisation. It is largely used as a manure.

Potassium Hydrogen Sulphate or Potassium Bisulphate, $KHSO_4$.—This acid salt is formed when potassium chloride or nitrate is acted on by sulphuric acid at a low temperature. When strongly heated it loses sulphuric acid and forms the normal sulphate, K_2SO_4 (compare the behaviour of sodium bicarbonate, p. 161),—

$$2KHSO_4 = K_2SO_4 + H_2SO_4.$$

General Reactions of the Potassium Salts

Although the potassium salts are in some cases less soluble in water than those of sodium, very few of them are so sparingly soluble as to serve as a means of detecting the presence of potassium compounds. The reagent usually employed for this purpose is chloroplatinic acid (platinic chloride), H_2PtCl_6, which produces with potassium salts a yellow crystalline precipitate of potassium chloroplatinate, K_2PtCl_6, almost insoluble in water or dilute acids, still less soluble in alcohol,—

$$2KNO_3 + H_2PtCl_6 = K_2PtCl_6 + 2HNO_3,$$

Sodium yields a salt of similar composition, but it is freely soluble in water and alcohol. The salts of many other metals and of ammonium give similar precipitates with chloroplatinic acid, and hence potassium must be tested for with this reagent after the other metals have been removed. The solution, which then only contains salts of potassium, ammonium, and sodium, is evaporated to dryness and strongly heated, the ammonium salts being thus completely decomposed. The residue is dissolved in a small quantity of water, the chloroplatinic acid added, together with an equal bulk of alcohol, and the whole well stirred. On standing a yellow crystalline precipitate is produced. The same method is used for the quantitative separation of potassium and sodium, an excess of chloroplatinic acid being added and the precipitate well washed with alcohol which removes the soluble sodium chloroplatinate. Potassium salts yield a precipitate of potassium perchlorate when perchloric acid is added to their solutions, and potassium is frequently estimated quantitatively in this form.

The salts of potassium impart a characteristic colour to the flame, the coloration produced being of a violet tint, not so intense or so easily recognised as the yellow coloration produced by the sodium salts. In mixtures of the two salts the violet due to potassium is entirely masked to the eye by the yellow sodium flame.

General Properties of the Alkali Metals

The group of alkali metals differs in several important respects from the nitrogen group of elements. Even the element of lowest atomic weight in this group (lithium, 6.94, p. 193) is as well marked a metal as sodium or potassium. The elements, however, show a certain gradation in properties with increase of atomic weight, since the melting- and boiling-points become lower as the atomic weight increases, whilst the oxides and hydroxides of the elements of higher atomic weight are the more strongly basic. All the elements of the group, as already mentioned (p. 149), closely resemble sodium and potassium, both in physical and chemical properties.

Some of the properties of these elements are summarised in the following table :—

Element.	Symbol.	Atomic Weight.	Melting Point.	Boiling Point.	Specific Gravity.
			°	°	
Lithium . .	Li	6.94	186	...	0.59
Sodium . .	Na	23·00	95·6	877·5	0·97
Potassium . .	K	39·10	62.5	757·5	0·875
Rubidium . .	Rb	85·45	38·5	696	1·52
Caesium . .	Cs	132.81	26.5	670	1.88

SUMMARY

Potassium closely resembles sodium in its chemical and physical properties, but combines more energetically with oxygen, chlorine, etc.

It yields a basic oxide, K_2O, which combines with water to form the strongly basic potassium hydroxide, caustic potash, KOH.

Potassium, like sodium, only forms one series of salts, and in these 1 atom of the metal replaces 1 atom of hydrogen.

Nearly all the salts of potassium are soluble in water, the least soluble being the perchlorate and the chloroplatinate.

EXERCISES ON LESSON XIX

1. What is the source of the potassium compounds which are present in the soil?

2. Contrast the properties of metallic potassium with those of sodium.

3. Describe the occurrence and mode of extraction of potassium chloride.

4. How can potassium carbonate, caustic potash, and potassium nitrate be economically prepared from potassium chloride?

5. What is meant by nitrification? What processes are involved in the production of potassium nitrate in the soil?

6. What is the composition of gunpowder, and what are the chief products formed when gunpowder is fired?

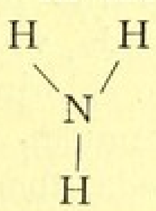
7. 5·517 grams. of potassium bromide yield on precipitation with

silver nitrate 8.704 grams. of silver bromide. Calculate the equivalent of potassium, the equivalents of silver and bromine being 107.88 and 79.92 respectively.

8. How would you attempt to prepare pure potassium sulphate from a mixture of potassium chloride and sodium chloride? How can the purity of the salt obtained be ascertained?

LESSON XX

CONSTITUTIONAL FORMULÆ—VALENCY—CONSTITUTION OF HYDROXIDES AND OXYACIDS

When the composition and molecular weight of a substance are known, it is possible to write for it a molecular formula which represents the number of atoms of each element present in the molecule. The chemical behaviour of a substance, however, often indicates that some of the atoms in the molecule stand in a special relation to each other, and this can be represented in the formula. Such a formula then indicates graphically the way in which the various atoms within the molecule are related to each other, and is therefore called a *constitutional*, *structural*, or *graphic* formula. For the simplest kind of compound substance, containing only 1 atom of one element combined with 1 or more of a second, these structural formulæ are usually very simple. Such a compound as water, for example, is represented by the formula $H \cdot O \cdot H$ or $H - O - H$, in which both the atoms of hydrogen are represented as being combined with the single atom of oxygen, because all the chemical properties of water go to show that this is the case. In the same way ammonia is represented by the formula , the three hydrogen atoms being arranged uniformly round the nitrogen atom, to indicate that we have no evidence that any one of them is related to it in a different way from the other two. For similar reasons the following compounds receive the structural or graphic formulæ given on the next page.

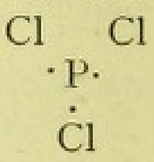
Hydrochloric Acid.

$H \cdot Cl$

Sulphuretted Hydrogen.

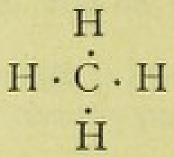
$H \cdot S \cdot H$

Phosphorus Trichloride.



$$\begin{array}{ccc} \text{Cl} & & \text{Cl} \\ & \cdot\text{P}\cdot & \\ & \dot{\text{Cl}} & \end{array}$$

Marsh Gas.



$$\begin{array}{c} \text{H} \\ \text{H}\cdot\dot{\text{C}}\cdot\text{H} \\ \dot{\text{H}} \end{array}$$

The fact that one atom is directly combined with another is indicated by a dot or short line placed between the two symbols.

In more complicated compounds, containing more than two elements, the matter is no longer so simple, and in any case it is necessary to consider carefully all the properties of a compound before assigning a structural formula to it. Caustic soda, for example, has the formula NaHO. What is its structural formula ?

Two reactions throw a considerable amount of light on this question.

1. Caustic soda is produced by the action of metallic sodium on water, 1 gram. of hydrogen being evolved for every 23 grams. of sodium which are used. This would lead us to suppose that in this reaction each *atom* of sodium replaces an *atom* of hydrogen, and hence that the formulæ of caustic soda and water should be written,—

$$H - O - H. \qquad Na - O - H.$$

2. When caustic soda is treated with hydrochloric acid, common salt, NaCl, and water are produced. This reaction can very readily be understood by the use of the following formulæ,—

$$Na - O - H \ + \ H - Cl \ = \ Na - Cl \ + \ H - O - H.$$

The hydrogen atom of the hydrochloric acid replaces the sodium of the caustic soda, water being formed, whilst the sodium combines with the chlorine to produce sodium chloride.

The constitutional formulæ, $H - O - H$ and $Na - O - H$ for water and caustic soda, therefore, enable us to obtain a clearer mental idea of the chemical behaviour of these substances than the ordinary formulæ, H_2O and NaHO, and in this lies the great value of constitutional formulæ to the chemist.

Two points are to be specially noticed with regard to the reactions referred to above.

1. **Valency of the Elements.**—One atom of sodium only replaces one atom of hydrogen, both in water and in hydrochloric acid, and the same relation holds for all the various compounds formed by sodium. Most of the non-metallic elements unite with hydrogen, and a comparison of the molecular formulæ of the compounds produced shows that the different elements unite with different numbers of hydrogen atoms. Thus chlorine, bromine, iodine, and fluorine each combine with one atom of hydrogen ; oxygen and sulphur with two ; nitrogen, phosphorus, arsenic, and antimony with three ; carbon and silicon (p. 322) with four. This combining power of the elements is known as their *valency*, and the elements themselves are termed *univalent*, *bivalent*, *tervalent*, *quadrivalent* (or sometimes *monovalent*, *divalent*, *trivalent*, *tetravalent*), according to the number of hydrogen atoms with which they can unite. The metals, on the other hand, do not as a rule combine directly with hydrogen, and their valency is therefore determined by the number of hydrogen atoms which they can *replace*. Thus sodium, one atom of which replaces one atom of hydrogen, is univalent ; calcium, one atom of which can replace two atoms of hydrogen, is bivalent ; bismuth is tervalent, etc.

The valency of an element is not, however, a fixed and definite property, for many elements have two or more different combining or replacing powers in the various compounds which they form. Thus the atom of phosphorus unites with three atoms of hydrogen to form phosphine, PH_3, and with three atoms of chlorine to form phosphorus trichloride, PCl_3, but also unites with five atoms of chlorine to form phosphorus pentachloride, PCl_5, and with five atoms of fluorine to form phosphorus pentafluoride, PF_5. Phosphorus is therefore tervalent in some compounds and quinquevalent in others. Numerous instances of this occur among the metals, many of which resemble phosphorus in being able to replace two or more different amounts of hydrogen, forming different series of compounds (see Copper, Mercury, Iron, Manganese, etc.).

2. **Compound Radicals.**—In the two reactions described above, the action of sodium on water, and the action of hydrochloric acid on caustic soda, the molecule of water is not completely broken up into separate atoms of hydrogen and

oxygen. The first reaction consists simply in the replacement of one atom of hydrogen by one of sodium, whilst the second reaction is simply the inverse of this, the replacement of an atom of sodium by one of hydrogen. Throughout these two reactions the remainder of the water molecule, the group $-O-H$, behaves just as though it were a single atom of a univalent element. This is well seen by comparing the equations expressing the action of sodium on water and on hydrochloric acid, both equations being written in the simplest possible manner,—

$$Na + H(OH) = Na(OH) + H.$$
$$Na + HCl = NaCl + H.$$

Such a group of atoms, which plays the part of a single atom in a number of reactions, is called a *compound radical.* This particular radical, (OH), occurs in a large number of compounds, and is known by the name *hydroxyl.* When the valencies of the two elements in it are considered, it is easily understood that it acts as a univalent radical, only one atom of univalent hydrogen being united with an atom of bivalent oxygen, forming a group still capable of combining with another univalent element or compound radical.

Numerous compound radicals are met with among the salts of the metals. Every salt may be regarded as containing a basic and an acid radical, and these may be either simple or compound. The potassium chloride, KCl, contains an atom of potassium acting as a basic radical, united with an atom of chlorine acting as an acid radical. Potassium nitrate, KNO_3, is similarly made up of an atom of potassium acting as a basic radical, united with the compound acid radical, NO_3. Ammonium nitrate, NH_4NO_3, again, is made up of two compound radicals, the basic radical, NH_4 (ammonium, see p. 203), and the acid radical, NO_3.

Constitution of the Hydroxides of the Metals and of the Oxyacids

All the hydroxides of the metals have a constitution similar to that of sodium hydroxide, and may be regarded as derived from one or more molecules of water by the replacement of hydrogen by the metal. Thus calcium hydroxide or slaked lime, which is formed when calcium acts on water (p. 215), and is also produced by the action of water on quicklime (calcium oxide, p. 217), has the formula $Ca(OH)_2$, and is formed by the replacement of two atoms of hydrogen in two different molecules of water by the bivalent element calcium.

In a similar manner aluminium hydroxide, $Al(OH)_3$, is derived from three molecules of water, and stannic hydroxide, $Sn(OH)_4$, from four. All these hydroxides, which are similarly constituted to caustic soda, have also similar chemical properties, and react with acids to produce water and a salt of the metal,—

$$2Al(OH)_3 + 6HCl = 2AlCl_3 + 6H_2O.$$

Since some of the hydroxides are formed by the action of water on the oxides,—

$$CaO + H_2O = Ca(OH)_2,$$

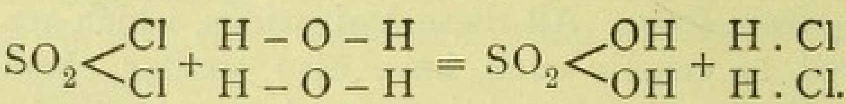
and since they generally decompose into water and the oxide when heated, they are sometimes called *hydrated oxides*,—

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

The Oxyacids.—In the days of Lavoisier, who discovered the true nature of the process of combustion, it was thought that the characteristic properties of the acids were conferred upon them by the oxygen which they contained.

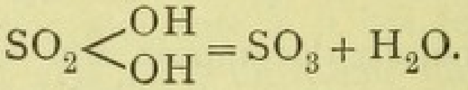
It was, however, afterwards discovered by Davy and others that some acids exist which contain no oxygen, hydrochloric acid being one of the earliest known examples of this kind of acid. Since that time it has been recognised that the characteristic properties of all acids are due to the presence in them of one or more atoms of hydrogen, which can be replaced by metals. Sulphuric acid, for example, contains two atoms of hydrogen in each molecule, either or both of which can be replaced by its equivalent of metal. These two atoms of hydrogen behave in precisely the same way, so that they are probably both combined in the same manner. The next question is, How are these atoms of hydrogen related to the other atoms in the molecule? It can easily be shown that they are present, combined with oxygen, in the form of hydroxyl groups, (OH), united with the radical SO_2.

Just as we have seen that an atom of chlorine may replace the hydroxyl group, as in the case of the action of hydrochloric acid on caustic soda, so of course may the inverse reaction take place, an atom of chlorine being replaced by hydroxyl. This occurs in the formation of sulphuric acid by the action of water on the compound known as *sulphonic chloride*, $\mathrm{Cl - SO_2 - Cl}$, which is produced by the direct combination of sulphur dioxide and chlorine under certain conditions,—



$$\mathrm{SO_2}\!<\!\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix} + \begin{matrix}\mathrm{H - O - H}\\ \mathrm{H - O - H}\end{matrix} = \mathrm{SO_2}\!<\!\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix} + \begin{matrix}\mathrm{H\,.\,Cl}\\ \mathrm{H\,.\,Cl.}\end{matrix}$$

This reaction renders it probable that the constitutional formula of sulphuric acid is $\mathrm{HO - SO_2 - OH}$, and this is confirmed by all the reactions of this acid. Thus when it is treated with powerful dehydrating agents, such as phosphorus pentoxide, a molecule of water is removed and sulphur trioxide produced,—

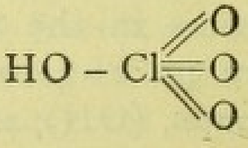


$$\mathrm{SO_2}\!<\!\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix} = \mathrm{SO_3 + H_2O.}$$

All the oxyacids have a similar constitution, and may be regarded as derived from water by the replacement of hydrogen atoms by some element or group of elements. Thus nitric acid, $\mathrm{HNO_3}$, is $\mathrm{(NO_2)OH}$, in which the group $\mathrm{(NO_2)}$ is univalent; the tribasic phosphorous acid, $\mathrm{H_3PO_3}$, has the formula $\mathrm{P(OH)_3}$, in which the atom of phosphorus is tervalent; the tribasic phosphoric acid, $\mathrm{H_3PO_4}$, has the formula $\mathrm{OP(OH)_3}$, in which the group OP is tervalent, and the corresponding acids of arsenic, antimony, and bismuth have similar constitutions.

It is obvious that the valency of an element in any particular compound, such as one of these acids, cannot be ascertained until the constitution of the compound is known. Chlorine, for example, is monovalent in hydrochloric acid, HCl, and sodium chloride, NaCl; what is its valency in an acid like perchloric acid, $\mathrm{HClO_4}$? Several different constitutional formulæ may be proposed for such an acid, two of which are given below,—

$\mathrm{H\,.\,O\,.\,O\,.\,O\,.\,O\,.\,Cl.}$



$$\mathrm{HO - Cl}\begin{matrix}/\!\!/\mathrm{O}\\ =\mathrm{O}\\ \backslash\!\!\backslash\mathrm{O}\end{matrix}$$

In the first of these, which was at one time adopted by chemists, the chlorine is represented as univalent, whilst in the second, which is the one now usually accepted, the chlorine acts as a septivalent element, being united with three bivalent oxygen atoms and a hydroxyl group. It is therefore impossible to say whether chlorine is univalent or septivalent in this compound, until one or other of these formulæ has been experimentally proved to be the correct one.

A similar state of doubt exists as to the valency of the metals in many of their compounds. This is partly due to the fact that the true molecular weights of many of the compounds of the metals are still unknown.

SUMMARY

Constitutional, structural, or graphic formulæ are intended to express the relations of the atoms within the molecule, as far as they can be learnt from the experimental study of the reactions of the compound.

The valency of an element is represented by the number of atoms of hydrogen with which it can unite, or which it can replace. The valency is not a fixed and invariable property of the element, since it often varies in the different compounds formed by the same element.

The valency of an element in any particular compound cannot be ascertained unless the constitution of the compound is known.

Many groups of atoms play the part of a single atom in many reactions; such groups are known as *compound radicals.*

The hydroxides of the metals are compounds derived from one or more molecules of water by the replacement of half the hydrogen by the metal. They contain the compound radical *hydroxyl,* and react with acids to form water and a metallic salt. The oxyacids also contain the hydroxyl group, united with a single element or a compound radical; the hydrogen atoms of the hydroxyl groups in the oxyacids can be replaced by metals. In the hydracids, which contain no oxygen, the replaceable hydrogen atoms are directly united with some other element or compound radical.

EXERCISES ON LESSON XX

1. What experimental facts lead us to suppose that the constitutional formula of slaked lime is $Ca(OH)_2$?

2. What are the basic and acid radicals of which the following salts are made up?—arsenic trichloride, sodium arsenate, potassium sulphate, sodium bicarbonate.

3. Name three compounds in which phosphorus is tervalent, and an equal number in which it is quinquevalent.

4. What is the constitution of phosphorous acid and of phosphoric acid? From what experimental facts are these formulæ deduced?

5. What evidence is there that the formula of arsenious acid is $As(OH)_3$?

6. Discuss the valency of iodine in its compounds with hydrogen and oxygen.

LESSON XXI

THE AMMONIUM COMPOUNDS—DISSOCIATION

AMMONIA very readily unites with acids to form neutral substances which closely resemble the salts of the alkali metals in their properties.[1] These cannot be considered as salts of ammonia itself, because they are not formed by the *replacement* of the hydrogen of the acid by the gas, but are produced by the direct *combination* of the acid with the gas,—

$$NH_3 + HCl = NH_4Cl.$$

An inspection of the formulæ of these compounds shows, however, that they may be regarded as salts formed by replacing the hydrogen of the acid by the group of atoms or compound radical NH_4. To this radical the name ammonium is given, the salts being termed the ammonium salts. When they are dissolved in water they react with other salts in precisely the same way as the salts of potassium or sodium, the radical NH_4 playing the same part in these reactions as the single atom of sodium or potassium,—

$$NaCl + AgNO_3 = NaNO_3 + AgCl,$$
$$NH_4Cl + AgNO_3 = NH_4NO_3 + AgCl.$$

The ammonium salts differ from those of potassium or sodium in one very important respect. When they are heated they decompose into their original constituents, ammonia and the acid from which they were originally produced. If the acid be a volatile one the whole salt volatilises, whilst if the acid be not volatile it is left behind, and the ammonia escapes. Thus ammonium sulphate, ammonium chloride, and am-

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[1] For the properties of ammonia, see R. and L., pp. 163-69.

monium carbonate, which are all formed from volatile acids, volatilise completely when heated, whereas ammonium phosphate, $(NH_4)_2HPO_4$, leaves a residue of phosphoric acid,—

$$(NH_4)_2SO_4 = 2NH_3 + H_2SO_4,$$
$$(NH_4)_2HPO_4 = 2NH_3 + H_3PO_4.$$

Ammonium nitrate and a few other ammonium salts undergo a different decomposition, the hydrogen being oxidised by the oxygen of the acid radical present, and an oxide of nitrogen or free nitrogen produced (p. 207).

All attempts to prepare a substance having the composition of ammonium, NH_4, have so far failed. Processes which yield the metals when they are carried out with salts of potassium and sodium only yield a mixture of ammonia and hydrogen when they are applied to ammonium salts. These salts, however, show one very interesting reaction, which was for a long time thought to be due to the isolation of the group NH_4. When a small piece of sodium amalgam is placed in a basin in a saturated solution of ammonium chloride the mercury swells up in a remarkable manner, forming a soft, buttery, metallic mass, which smells strongly of ammonia, and gradually evolves a mixture of this gas with half its volume of hydrogen. Some chemists consider that this is an amalgam of mercury and ammonium, the sodium of the sodium amalgam having been simply replaced by ammonium, NH_4, whilst others regard it as simply a frothy mass of mercury.

No oxide of ammonium is known, and no hydroxide, NH_4OH, corresponding with sodium hydroxide, NaOH, has ever been obtained in the pure state. A solution of ammonia in water, however, acts in many respects like one of sodium hydroxide, and produces precipitates of the metallic hydroxides of many metals, just as does this substance. Thus solutions of caustic soda and of ammonia in water have the same effect on a solution of ferric chloride, a reddish-brown precipitate of ferric hydroxide being produced in both cases,—

$$3NaOH + FeCl_3 = 3NaCl + Fe(OH)_3,$$
$$3NH_4OH + FeCl_3 = 3NH_4Cl + Fe(OH)_3.$$

A solution of ammonia in water is therefore generally regarded as containing ammonium hydroxide, NH_4OH. Such a solution, however, gives off all its ammonia when it is boiled for some time, the hydroxide being very unstable.

EXPERIMENT 84.—To separate portions of a dilute solution of ferric chloride add (1) caustic soda solution; (2) ammonia solution. In both cases a reddish-brown precipitate of ferric hydroxide is produced.

All the ammonium salts are decomposed when they are heated with caustic soda, both in the dry state and in solution, ammonia being evolved, and this constitutes the best test for the presence of the ammonium group,—

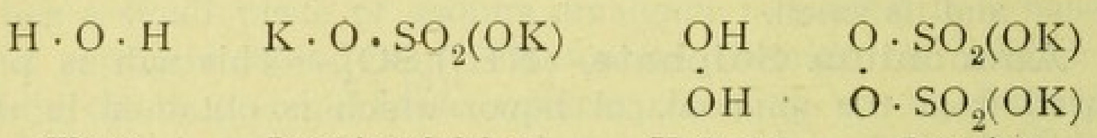
$$NaOH + NH_4Cl = NaCl + NH_3 + H_2O.$$

EXPERIMENT 85.—Heat a solution of ammonium chloride with caustic soda solution,—ammonia is evolved, and may be recognised by its action on red litmus paper, and its smell.

Ammonium Sulphate, $(NH_4)_2SO_4$.—This salt is prepared from the ammoniacal liquor which is obtained in the distillation of coal, and contains a portion of the nitrogen of the coal in the form of salts of ammonium. The liquor is distilled with lime and the resulting ammonia passed into sulphuric acid, the sulphate which separates out being afterwards recrystallised. It forms large transparent crystals of the same form as those of potassium sulphate, and is easily soluble in water. The salt is used as the source of the other ammonium salts, but chiefly as a manure. Plants do not as a rule make direct use of nitrogen which is supplied to them as ammonia or ammonium salts, but take up the nitrogen after it has been converted into the form of nitrates. The whole of the ammonia of the ammonium sulphate which is added, rapidly undergoes nitrification in the soil before it is utilised by the plant (p. 186). Chili saltpetre, $NaNO_3$, which contains the nitrate ready formed, is now much used instead of ammonium sulphate.

Ammonium Persulphate, $(NH_4)_2S_2O_8$.—When a solution of ammonium sulphate is electrolysed (p. 298) in presence of dilute sulphuric acid, the ammonium sulphate undergoes oxidation at the positive pole with formation of ammonium persulphate. If this be allowed to mix freely with the liquid it is again reduced, but if the positive pole be surrounded by a porous pot this is prevented and the new salt can be obtained in the crystalline form. It is very soluble in water, and is largely used as an oxidising agent. Many other salts of persulphuric acid are known, although the free acid cannot be obtained pure. Both the barium and lead salts are soluble in water.

Persalts.—It has been found that the salts of many acids undergo oxidation when submitted to electrolysis in the same way as ammonium sulphate. Thus potassium carbonate K_2CO_3 yields potassium percarbonate, $K_2C_2O_6$, and sodium borate $NaBO_2$ yields sodium perborate $NaBO_3$ (or $Na_2B_2O_6$). All these substances are strong oxidising agents and are used for bleaching purposes. They are to be regarded as derivatives of hydrogen peroxide, in the same way as the unoxidised salts are derivatives of water, as shown by the following formulæ,—



$$\begin{array}{cccc} H\cdot O\cdot H & K\cdot O\cdot SO_2(OK) & \begin{array}{c} OH \\ \cdot \\ OH \end{array} & \begin{array}{l} O\cdot SO_2(OK) \\ \cdot \\ O\cdot SO_2(OK) \end{array} \end{array}$$

Water.	Potassium Sulphate.	Hydrogen Peroxide.	Potassium Persulphate.

Some of the persalts can in fact be prepared from hydrogen dioxide or yield it when decomposed with dilute acids.

A strongly oxidising liquid, known as Caro's acid, is obtained when a persulphate is dissolved in concentrated sulphuric acid. It contains an acid of the formula $H_2S_2O_9$.

Ammonium Sulphide.—Ammonia gas unites with an equal volume of sulphuretted hydrogen to form the *hydrosulphide*, NH_4HS, which is a white amorphous solid,—

$$NH_3 + H_2S = NH_4HS.$$

The *normal sulphide*, $(NH_4)_2S$, can be prepared by the action of an excess of ammonia on sulphuretted hydrogen at a low temperature, and forms colourless volatile crystals. When sulphuretted hydrogen is passed into a strong solution of ammonia, a mixture of the sulphide and hydrosulphide is formed, which usually also contains a little ammonium hydroxide. This is the solution which is used in the laboratory as ammonium sulphide. When this is allowed to stand exposed to light, sulphur is liberated, a portion of the sulphuretted hydrogen being oxidised by the oxygen of the air,—

$$2H_2S + O_2 = 2H_2O + 2S.$$

This, then, unites with the ammonium sulphide to form a yellow solution containing compounds rich in sulphur, such as $(NH_4)_2S_4$. Yellow ammonium sulphide solution can also be prepared by warming the colourless sulphide with flowers of sulphur. Acids at once decompose the sulphide, sulphuretted hydrogen being evolved, whilst if an excess of sulphur be present this is precipitated.

EXPERIMENT 86.—Warm some colourless ammonium sulphide solution with flowers of sulphur,—a deep brownish-yellow coloured solution is produced. Add an excess of acid,—sulphuretted hydrogen is evolved and sulphur precipitated.

Ammonium sulphide is much used in the laboratory as a reagent. Thus it is employed to separate the sulphides of arsenic, antimony, and tin, which readily dissolve in it, from those of copper, mercury, bismuth, and cadmium, which are insoluble in it. It is also used to precipitate the sulphides of iron, nickel, cobalt, zinc, and manganese, which are not precipitated by sulphuretted hydrogen in presence of hydrochloric acid.

Ammonium Nitrate, $(NH_4)NO_3$.—This salt is formed by passing ammonia into nitric acid and carefully evaporating the solution. It forms colourless crystals, and is very soluble in water, a large amount of heat being absorbed during the process of solution. It melts when heated, and then decomposes, the hydrogen of the ammonium radical being oxidised by part of the oxygen of the acid radical and nitrous oxide formed,—

$$NH_4NO_3 = N_2O + 2H_2O.$$

Ammonium nitrate is a very vigorous oxidising agent, and since it is entirely converted into gaseous or liquid products on decomposition, is used as a constituent of some explosives.

EXPERIMENT 87.—Neutralise 25 cc. of dilute ammonia solution (1 vol. strong ammonia to 1 vol. water) with nitric acid (1 vol. strong acid to 1 vol. water), and evaporate over a flame until three-fourths of the liquid have been removed, and then over a water-bath until the residue solidifies on cooling. Heat some of the residue in a porcelain basin until it melts, and then cautiously add a small fragment of charcoal; a vivid combustion ensues, the charcoal burning at the expense of the oxygen of the nitrate.

Ammonium Nitrite, NH_4NO_2.—This salt is prepared by the action of nitrous fumes on ammonium carbonate, and is extremely unstable, and explodes when it is heated. Its solution in water decomposes when it is boiled, nitrogen being evolved,—

$$NH_4NO_2 = N_2 + 2H_2O.$$

This decomposition is quite analogous to that which ammonium nitrate undergoes when heated. Pure nitrogen can be prepared by means of this reaction, but it is not necessary for this purpose to prepare pure ammonium nitrite, since nitrogen is evolved when a mixture of ammonium chloride and potassium nitrite is dissolved in water and the solution heated.

Ammonium Carbonate.—The commercial substance known by this name is also termed *sal volatile* and *sesquicarbonate of ammonia.* It is prepared by heating a mixture of two parts of chalk and one of ammonium sulphate. The product sublimes as a white mass, which is in reality a mixture of ammonium bicarbonate, $(NH_4)HCO_3$, and a salt known as ammonium carbamate, $N_2H_6CO_2$. It is, however, converted by treatment with strong ammonia into the normal carbonate, $(NH_4)_2CO_3$. Both the carbonate and the bicarbonate decompose when their solutions are heated, ammonia and carbonic acid gas being evolved. Hence the ammonium salts are decomposed when they are boiled with sodium carbonate solution, ammonium carbonate being first formed and then decomposed.

EXPERIMENT 88.—Add sodium carbonate to a strong solution of ammonium chloride, warm and test the gas which is evolved for ammonia (by litmus) and for carbonic acid gas by decanting the gas into a test-tube containing lime-water.

Ammonium Chloride or Sal Ammoniac, NH_4Cl.—This salt is manufactured by passing the ammonia evolved when ammoniacal liquor is distilled with lime into hydrochloric acid, and is purified by sublimation. The crude salt is heated for this purpose in an iron vessel and sublimes on to the cover, which can be removed when the operation is finished. The salt can also be obtained by heating a mixture of ammonium sulphate and sodium chloride, when ammonium chloride sublimes.

EXPERIMENT 89.—Mix 10 grams. of ammonium sulphate and an equal weight of common salt in a mortar; place the mixture in a small beaker, and heat the latter on a sand-bath, placing a small basin containing water on the top of the beaker to prevent the escape of fumes. A white sublimate of ammonium chloride is formed on the upper portion of the beaker, which can easily be removed; test the product obtained to show that it is free from sulphuric acid, and that it volatilises completely when heated.

The chloride obtained by sublimation is in the form of fibrous masses which are very difficult to powder. In order to reduce these to a fine state of division it is best to dissolve the salt in boiling water, and evaporate nearly to dryness, stirring the mass throughout the operation.

Reactions of the Ammonium Compounds

In their behaviour towards reagents the ammonium salts closely resemble those of potassium. Thus they give a yellow precipitate of ammonium chloroplatinate, $(NH_4)_2PtCl_6$, with chloroplatinic acid, which cannot be distinguished in appearance from the potassium salt. The ammonium compounds, however, can easily be distinguished from those of all the other metals by the fact, which has been already mentioned, that when they are heated with excess of caustic soda, either in the dry state or in solution, ammonia gas is evolved, which can be detected by its smell, by its action on moist litmus paper, and by the white fumes of ammonium chloride which it produces with fuming hydrochloric acid.

Dissociation

When ammonium chloride, NH_4Cl, is heated in a test-tube it vaporises, forming a colourless gas, which condenses to a white sublimate on the cooler portion of the tube. This colourless gas does not, however, consist of the vapour of ammonium chloride, but is a mixture of equal volumes of the two gases, ammonia, NH_3, and hydrochloric acid, HCl, which recombine on cooling to form the original salt. This has been ascertained by determining the density of the vapour. If the vapour consisted of molecules of ammonium chloride, NH_4Cl, its density would be 26.7 (compared with hydrogen), whilst if it were a mixture of equal volumes of ammonia and hydrochloric acid it would only be half as great. Experiment has shown that it is actually 13.3. The fact that the vapour is in reality a mixture of ammonia and hydrochloric acid has also been confirmed by experiments on the diffusion of the vapour. Ammonia has the density 8.5, and is therefore much lighter than hydrochloric acid, the density of which is 18.2. Ammonia therefore diffuses more rapidly than hydrochloric acid in the inverse proportion of the square roots of the densities, or as $\sqrt{18.2} : \sqrt{8.5}$, or nearly 3 : 2. The simplest way of showing that this is actually the case is to heat some powdered ammonium chloride strongly in a platinum crucible, loosely closed by a lid. The ammonia diffuses out of the crucible more rapidly than the hydrochloric acid, and consequently a piece of moist blue litmus paper is at once reddened when plunged into the crucible. A more complete method of demonstrating the same fact is the following :—By means of two bored corks pass a piece of the stem of a long clay tobacco pipe through a wider glass tube containing some solid ammonium chloride at one end, and a piece of blue litmus paper at the other. Heat the glass tube until the ammonium chloride volatilises, and pass a slow current of air through the pipe stem. The ammonia diffuses through the walls of the pipe stem more rapidly than the hydrochloric acid, and hence the current of air emerges from the clay pipe laden with ammonia, which can easily be detected by means of red litmus paper. On the other hand, hydrochloric acid accumulates in the glass tube and turns the blue litmus paper red.

If a compound decomposes when heated, and the simpler substances thus produced recombine on cooling, the compound is said to *dissociate* when heated. Many other substances than sal-ammoniac undergo dissociation in this way, among the most common being phosphorus pentachloride, PCl_5, into phosphorus trichloride and chlorine, PCl_3 and Cl_2; nitrogen peroxide, N_2O_4, into the simpler molecules NO_2; the molecule of iodine, I_2, into the free atoms, I, etc. On the other hand many substances decompose at high temperatures, but are not reproduced when the products of decomposition cool down; such are ammonia, ozone, ammonium nitrate, hydrogen peroxide, etc.

The various stages of dissociation can be best studied in the case of gaseous substances, which also yield gaseous products of decomposition. When a gas which is capable of undergoing dissociation is heated and its density determined at regular intervals of temperature, it is found that the density of the gas, compared with air or hydrogen at the same temperature, remains constant up to a certain point, after which it becomes less, at first slowly, and then more quickly. Finally, it gradually becomes constant again, but is much lower than at first. This is due to the gradual decomposition of the molecules of the gas. At first only a few molecules are decomposed, but the number gradually increases until the dissociation is complete.

We have seen that in the case of ammonium chloride, which dissociates into two different substances, ammonia and hydrochloric acid, the two gases can be separated by their unequal rates of diffusion. Many substances, however, do not yield two different substances on dissociation, but decompose, so that each molecule of the original substance yields two simpler molecules precisely similar to each other, but having only half the weight of the original molecule. Thus the vapour of iodine has the density 126.9, corresponding with the molecular formula I_2, up to the temperature 700°. Above this temperature, however, the density gradually becomes less, but again becomes constant at about 1500°, at which temperature it has the value 63.45, corresponding with the molecular weight 126.9 and the molecular formula I. Each molecule of iodine has been decomposed into two less complex molecules, each consisting of a single atom of iodine. This change is represented by the equation,—

$$\underset{\text{2 vols.}}{I_2} = \underset{\text{2 vols.}}{I} + \underset{\text{2 vols.}}{I}.$$

In such cases the fact that dissociation has occurred is often rendered evident in some other way in addition to the decrease in density. Thus nitrogen peroxide, at temperatures above 140°, has the density 23, corresponding with the molecular weight 46 and the formula NO_2. As the gas cools, however, its relative density increases, until at a temperature a little above that at which it condenses into a liquid it becomes 41.4, almost double its original value. At this temperature, therefore, the gas is a mixture of a large number of molecules having the molecular formula N_2O_4, with a few having the simpler formula NO_2. The following table shows the density of the gas at various temperatures, together with the percentage of molecules of N_2O_4 and NO_2 present in it :—

Temp.	Density.	Percentage. NO_2	 N_2O_4
27°	41.4	20	80
60°	34.5	50	50
100°	27.8	79	21
135°	23.2	99	1
140°	23·0	100	0
250°	23.0	100	0

In this case the change in density is accompanied by a very marked change in colour. At low temperatures, at which the relative density is comparatively high, the gas has the well-known light brown colour. As the temperature rises and the relative density decreases, the colour becomes very much darker, until at about 100° the gas is almost opaque. On cooling again it goes through the inverse change, and becomes lighter in colour. This can be readily demonstrated by sealing up about 25 cc. of the gas in each of two similar tubes, heating one of them while the other is allowed to remain at the ordinary temperature, and comparing the colours of the hot and cold specimens.

SUMMARY

The substances formed by the combination of ammonia with acids are salts of the compound radical ammonium, NH_4, which has never itself been isolated, but plays the same part in these salts as an atom of sodium or potassium in the salts of these metals.

All the ammonium salts are decomposed by alkalis with evolution of ammonia, and they all decompose when they are heated. In their other properties they resemble the salts of potassium.

When a substance decomposes on being heated into simpler substances, which reunite on cooling, it is said to dissociate when heated. The fact that dissociation occurs can be ascertained, when the products are gaseous, by determining the relative density of the gas formed. It is, moreover, often rendered evident by changes of colour, or by the unequal rates of diffusion of the new substances which are produced.

EXERCISES ON LESSON XXI

1. From what sources can ammonia be obtained? Describe the manufacture of ammonium sulphate.
2. Why are the substances formed by the combination of acids with ammonia called the ammonium salts?
3. What happens when the following salts are heated: ammonium chloride, sodium chloride, ammonium phosphate, ammonium nitrate, potassium nitrate, ammonium nitrite?
4. How is ammonium sulphide prepared, and for what purposes is it used in the laboratory? Why does it become yellow when kept for some time?
5. How would you detect the presence of potassium chloride in a mixture of the chlorides of sodium, ammonium, and potassium?
6. How would you prepare (1) ammonium chloride, (2) ammonium nitrate from ammonium sulphate?
7. What is meant by dissociation? How can it be proved that the vapour produced when phosphorus pentachloride is heated is a mixture of the vapour of phosphorus trichloride with chlorine?
8. Describe the variations in density which occur when iodine vapour is heated. How are these to be interpreted?

LESSON XXII

THE METALS OF THE ALKALINE EARTHS

CALCIUM, Ca, 40.09. STRONTIUM, Sr, 87.63. BARIUM, Ba, 137.37

SEVERAL substances were classed together by the older chemists as earths, because they were all soft, earthy substances, insoluble in water, infusible and incapable of yielding a metal when treated by any process then known. These substances originally comprised limestone and lime, between which no distinction was at first made, magnesia, alumina, and silica, to which were added at a later date strontia and baryta. It was also observed that some of these substances had an alkaline reaction, and in other respects resembled the well-known fixed alkalis, and hence lime, strontia, and baryta, together with magnesia, were known as the *alkaline earths.* These alkaline substances had never been decomposed, and passed as elements until Davy applied to them the methods he had used in isolating potassium and sodium, and succeeded in proving that they were all the oxides of metals, which were hence called the metals of the alkaline earths. Magnesium is no longer classed with calcium, strontium, and barium, because it more closely resembles zinc, although, as we shall see later on, it presents many points of similarity to the metals of the calcium group.

Calcium, strontium, and barium form a very well marked family or group of elements. They all possess similar general properties, but there is a decided gradation in properties as the atomic weight increases, strontium and its compounds being intermediate in many respects between calcium and barium. An important point, to which special attention should be paid, is the difference between the solubilities of the corresponding salts of the three metals, which is of great practical importance, especially for their analytical detection and separation.

The metals themselves are by no means easy to prepare, and, since they are not manufactured on the large scale, are less frequently met with than many others of which the compounds are much less widely distributed.

Metallic Calcium, Strontium, and Barium

Metallic Calcium is obtained by the electrolysis of fused calcium chloride,—

$$CaCl_2 = Ca + Cl_2.$$

Sometimes calcium fluoride is added to the chloride because the mixture melts at a lower temperature than the pure chloride, but this is not essential. An iron rod is used for the negative pole (see p. 298) on which the metal is deposited and this is gradually raised as the electrolysis proceeds, drawing with it the adhering calcium, which is protected from the action of the air by the layer of fused chloride with which it is covered. It is made in this way on a fairly large scale and is sold at about a shilling per ounce, but has never found any important technical application. It is a silver-white metal of specific gravity 1.55, melts at about 800° and is malleable and somewhat harder than lead.

When thrown into water it decomposes it slowly with evolution of hydrogen and formation of calcium hydroxide,—

$$2H_2O + Ca = Ca(OH)_2 + H_2.$$

It is converted into the oxide by moist air, and when heated in the air takes fire and burns brilliantly, forming calcium oxide (quicklime), CaO,—

$$2Ca + O_2 = 2CaO.$$

Like magnesium (p. 239) it readily unites with nitrogen at a dull red heat to form the nitride, Ca_3N_2, which is decomposed by steam, forming ammonia and the hydroxide,—

$$Ca_3N_2 + 6H_2O = 3Ca(OH)_2 + 2NH_3.$$

As calcium combines with both oxygen and nitrogen it has been used to remove these gases from air for the isolation of argon and the allied gases (p. 432). It also combines with hydrogen at a dull red heat forming a crystalline hydride, CaH_2, which resembles sodium hydride in properties (p. 159).

Metallic Strontium and Barium are prepared in a similar manner to calcium, and behave like it towards water and oxygen. The specific gravity of strontium is 2.5, and that of barium 3.8.

Equivalents and Atomic Weights. — These three metals yield no volatile compounds, and their atomic weights have therefore been decided by a study of their specific heats and of the isomorphism of their compounds.

The equivalents of the three metals have all been determined in a precisely similar manner to those of sodium and potassium (p. 151) by the analysis of the chlorides and bromides, whilst that of calcium has also been determined by the conversion of the carbonate into oxide at a high temperature. It has thus been found that the equivalents of the metals are,—

Calcium	20.045
Strontium	43.815
Barium	68.685

The atomic weights of calcium and barium have been settled by the determination of the specific heats of these metals. Calcium has the specific heat 0.17, and therefore must have the atomic weight $\frac{6.4}{0.17} = 37.6$. Since $20.045 \times 2 = 40.09$, this last number is taken as the correct atomic weight of the metal. The atomic weight of calcium is, therefore, twice its equivalent, so that the atom of calcium is bivalent and replaces two atoms of hydrogen.

All the salts of calcium are formed in this way from the corresponding acids, as is seen from the following list of a few of the most important of them,—

Calcium chloride,	$CaCl_2$	Calcium sulphate,	$CaSO_4$
Calcium chlorate,	$Ca(ClO_3)_2$	Calcium phosphate,	$Ca_3(PO_4)_2$.

Exactly the same considerations hold for barium, the specific heat of which is 0.05.

The atomic weight of strontium has not been decided in quite the same way as those of calcium and barium, because the metal has not been obtained in a sufficiently pure state for the accurate determination of its specific heat. In the absence of this it has been necessary to make use of other methods depending on the specific heat of strontium chloride (p. 132), and on the isomorphism of the strontium salts with those of calcium and barium (p. 146), both of which have already been discussed. From these it follows that the atomic weight of strontium is 87.63, and that, like calcium and barium, this element is bivalent.

The Compounds of Calcium

The name of this metal is derived from the Latin *calx*, lime. The compounds of calcium are even more plentiful than those of sodium and are almost as widely diffused. Calcium is a constituent of a large number of the silicates which occur in igneous rocks, by the decomposition of which the soil is produced, and it is therefore present in soil, whence it passes into the systems of plants and animals, for both of which it is one of the necessities of life. In the animal organism it occurs chiefly as phosphate in the mineral matter of the bones and teeth. Calcium also occurs to a very large extent as carbonate, $CaCO_3$ (p. 220), and sulphate, $CaSO_4$ (p. 222), as well as in the minerals fluorspar, CaF_2, and apatite $3Ca_3(PO_4)_2 + CaF_2$.

Calcium Oxide, Quicklime, CaO, and Calcium Hydroxide, Slaked Lime, $Ca(OH)_2$. — Quicklime or calcium oxide is made on the large scale from calcium carbonate, which decomposes when it is strongly heated into carbon dioxide and quicklime,—

$$CaCO_3 = CaO + CO_2.$$

This decomposition is usually carried out in lime-kilns, in which the lumps of limestone are piled up with coal in such a way as to leave passages for the supply of air to the fuel. The coal is then set fire to and the heat evolved in its combustion is sufficient to bring about the decomposition of the limestone, the carbon dioxide passing off along with the products of combustion. This process is sometimes called burning limestone, the word *burning* being used in the sense of *strongly heating*.

The decomposition of calcium carbonate into lime and carbon dioxide is another example of a reversible reaction (p. 30), which differs from those already considered by the fact that the original substance and one of the products are solids. When calcium carbonate is heated at a fixed temperature in a closed space, it is not completely decomposed. Decomposition only goes on until a certain definite pressure of carbon dioxide is produced and the value of this depends on the temperature. Thus at 740°, the pressure thus produced is 255 mm. of mercury. Under these conditions the decomposition of the carbonate into lime and carbon dioxide is going on at exactly the same rate as the recombination of carbon dioxide and lime to form calcium carbonate, and a state of equilibrium exists,—

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

If the temperature be raised, further decomposition occurs; if it be lowered, more of the carbonate is produced. When the carbon dioxide is allowed to escape the decomposition becomes complete, because the pressure of carbon dioxide is thus kept below the equilibrium value and the decomposition therefore continues.

Pure lime is prepared by strongly heating a pure variety of calcium carbonate, such as Iceland spar (p. 221), in a crucible in which it is protected from the direct action of the flame.

Quicklime is a white amorphous mass, which can only be melted in the electrical furnace. It very readily combines with water to form calcium hydroxide, $Ca(OH)_2$, usually known as slaked lime, a very considerable amount of heat being evolved,—

$$CaO + H_2O = Ca(OH)_2.$$

The quicklime breaks up and falls to a white powder of the hydroxide, which can be dried at 100° without losing any of the combined water, although the latter is driven off at a red heat, quicklime being again formed. If the lime contain a large proportion of magnesia, it does not slake well. When slaked lime is stirred up with water a white opaque liquid is obtained which is known as *milk of lime*. A thick paste of slaked lime and water mixed with sand and hair is used as mortar and plaster for building purposes. The mortar first loses moisture and sets to a firm mass, which afterwards becomes gradually harder, owing chiefly to the absorption of carbonic acid gas from the air, calcium carbonate being produced.

100 grams. of water at 10° dissolve 0.14 gram. of slaked lime, whilst at 100° they only dissolve 0.07 gram., slaked lime being less soluble in hot than in cold water. The solution is known as lime-water, and has very similar properties to a solution of caustic soda of corresponding strength. It absorbs carbonic acid gas from the air and precipitates metallic hydroxides from their salts in precisely the same way as caustic soda. Since calcium carbonate is insoluble in water it is precipitated when carbonic acid gas is passed into lime-water, and hence the latter forms an excellent reagent for the detection of this gas; this precipitate, however, dissolves in excess of carbonic acid, giving rise to temporarily hard water.

Calcium hydroxide is precipitated as a white amorphous mass when a solution of caustic soda is added to a strong solution of calcium chloride, or nitrate, more of the hydroxide being produced than can be held in solution by the water present,—

$$CaCl_2 + 2NaOH = Ca(OH)_2 + 2NaCl.$$

EXPERIMENT 90.—1. Examine the behaviour of lime-water towards solutions of copper sulphate, ferric chloride, and sodium carbonate, and compare the effects with those produced by a solution of caustic soda prepared by adding 1 cc. of a 10 per cent solution to 100 cc. of water.

2. Add an excess of caustic soda solution to a strong solution of calcium chloride—a white precipitate of the hydroxide is produced, which readily dissolves in a large amount of water and in dilute acids.

Slaked lime is not only used for mortar, but also for the manufacture of bleaching powder and caustic soda, and in agriculture as a top dressing.

Calcium Chloride, $CaCl_2$.—This salt is prepared in the anhydrous state by dissolving the carbonate in hydrochloric acid, evaporating to dryness, and fusing the residue. It very readily takes up moisture and deliquesces when exposed to moist air. On this account it is used for drying gases, but cannot be employed for ammonia, since it unites with this substance. It dissolves in water with great evolution of heat, and forms a solution which deposits needle-shaped crystals of $CaCl_2 + 6H_2O$ on evaporation. Calcium chloride is readily soluble in alcohol.

EXPERIMENT 91.—Treat 25 grams. of marble with 50 cc. of concentrated hydrochloric acid, filter, and evaporate until a film of solid salt is formed on the boiling liquid. Allow to cool, filter, and drain the resulting crystals of $CaCl_2 + 6H_2O$.

Calcium bromide and iodide are very soluble salts which closely resemble the chloride.

Bleaching Powder, $CaOCl_2$, is manufactured on the large scale, as already described (p. 176). When it is dissolved in water it yields a mixture of calcium chloride and calcium hypochlorite,—

$$2CaOCl_2 = CaCl_2 + Ca(OCl)_2.$$

The solid powder, however, has not the properties of a simple mixture of these two salts, and it is more probable that it has the constitutional formula $Cl.Ca.OCl$.

For bleaching purposes a weak solution is employed, into which the fibre to be bleached is placed, usually after a preliminary treatment with alkali. The hypochlorite of the bleaching powder solution acts as an oxidising agent on the colouring matter and is thereby reduced to chloride. A much more energetic action is obtained by adding acid, or, as is usually done, transferring the fibre into an acid bath. The whole of the chlorine of the bleaching powder is thus liberated, the hydrochloric and hypochlorous acids first formed reacting with formation of water and chlorine,—

$$1.\ CaCl_2 + Ca(OCl)_2 + 2H_2SO_4 = 2CaSO_4 + 2HCl + 2HOCl.$$

$$2.\ HCl + HOCl = H_2O + Cl_2.$$

Calcium Carbonate, $CaCO_3$.—This salt occurs to a very large extent in nature and in a great variety of different forms. Whole mountain ranges are composed of this substance in the forms of limestone, chalk, and marble, and it also occurs as the minerals calc-spar and arragonite. These two minerals have the same composition, but differ completely in crystalline form, specific gravity, and other properties, and calcium carbonate is hence said to be dimorphous (p. 143).

The purest form of calc-spar is known as *Iceland spar*, and is found in transparent crystals of the hexagonal system, having the shapes shown in Figs. 18 and 41. These crystals show the phenomenon of double refraction very clearly, and are used for making optical apparatus. *Arragonite*, on the other hand, crystallises in the forms of the rhombic system shown in Fig. 42, and is identical in form with the crystals of the carbonates of strontium and barium.

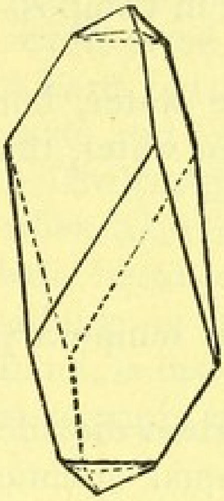


Fig. 41.

Chalk consists of the skeletons of minute sea animals known as foraminifera, which have the power of taking up calcium carbonate from solution in water, and thus making for themselves bony skeletons which remain after the death of the organism and the decay of the organic part, and gradually accumulate at the bottom of the sea. In this way the enormous deposits of chalk in the south of England and elsewhere have been formed, and the characteristic shape of the foraminiferal remains can easily be recognised under the microscope. Chalk is soft and porous, and contains a large amount of water, whereas *limestone*, which was probably originally formed in a somewhat similar manner, is much more compact and contains very little water. *Marble* has probably been formed by the action of great heat and pressure on limestone, and is much more distinctly crystalline than the latter.

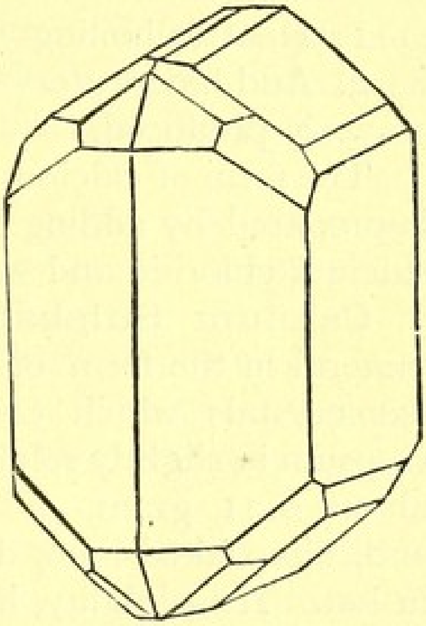


Fig. 42.

When calcium carbonate is strongly heated it decomposes into quicklime and carbon dioxide, as already described. The nature of this change was first explained by the celebrated Scottish chemist, Joseph Black. It was known that calcium carbonate acquired caustic properties when it was heated in the fire, but it was thought that this was due to the absorption of fiery particles, which gave to it its burning taste and violent effect on the skin. Black, however, proved that what actually happens is that carbon dioxide is evolved, and that the caustic lime which is left only differs from the carbonate in composition by the absence of this gas.

Calcium carbonate is almost insoluble in pure water, but easily dissolves in a solution of carbonic acid gas in water, the bicarbonate, $Ca(HCO_3)_2$, being probably formed,—

$$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2.$$

As already explained, this is the cause of the temporary hardness of water (R. and L., p. 123).

EXPERIMENT 92.—Pass a rapid current of carbon dioxide into 10 cc. of lime-water diluted with an equal volume of water; a precipitate of calcium carbonate is formed which finally redissolves. Divide the clear solution into two parts.

1. Heat to boiling—calcium carbonate is precipitated.
2. Add lime-water—a white precipitate of calcium carbonate is produced.

The form of calcium carbonate, known as precipitated chalk, is prepared by adding ammonium carbonate to a solution of calcium chloride and washing and drying the precipitate.

Calcium Sulphate, $CaSO_4$, occurs very widely as a mineral in the form of gypsum or selenite, $CaSO_4 + 2H_2O$, in flat crystals which can easily be split up into thin plates. Gypsum is slightly soluble in water, 100 parts of which dissolve about 0.21 gram. of gypsum at the ordinary temperature, and, like slaked lime, dissolves more readily in cold water than in hot. Its solubility, however, is so slight that it is precipitated whenever a sulphate is added to a strong solution of a calcium salt. It dissolves much more readily in dilute acids, even in acetic acid, than in water.

EXPERIMENT 93.—To 10 cc. of a 20 per cent solution of calcium chloride add dilute sulphuric acid — a thick crystalline precipitate of calcium sulphate is formed. Add a few drops of the turbid liquid to 10 cc. of water and shake—the precipitate dissolves.

This salt, as well as magnesium sulphate, is one of the chief causes of the permanent hardness of water. When gypsum is heated it loses about three-quarters of its water, and is converted into plaster of Paris (so called from the fact that gypsum occurs in large quantities in the Paris basin). When this is mixed with water and allowed to stand, it rapidly sets solid, becoming reconverted into gypsum, the interlacing crystals of which form a hard mass. It is on this account largely used for making casts and as a cement.

Sulphides of Calcium.—Calcium is not precipitated when ammonium sulphide is added to a solution of a calcium salt, because the hydrosulphide, $Ca(SH)_2$, which is formed is soluble in water. The *normal sulphide*, CaS, on the other hand, is insoluble in water and is formed when calcium sulphate is strongly heated with carbon,—

$$CaSO_4 + 4C = CaS + 4CO.$$

It is a white mass, which, after exposure to sunlight, gives out a bluish-white light when placed in the dark, and has therefore been used as a luminous paint. Calcium sulphide forms the greater part of the "alkali-maker's waste," produced in the manufacture of soda-ash by the Le Blanc process (p. 172).

When milk of lime is boiled with sulphur a deep red solution is formed, which contains a number of complex sulphides and oxy-sulphur compounds of calcium.

Calcium Nitrate, $Ca(NO_3)_2$, is a deliquescent salt produced by dissolving the carbonate in nitric acid and evaporating. It is insoluble in absolute alcohol. When heated it decomposes into lime, oxygen, and nitrogen peroxide.

It is now largely used as a nitrogenous fertiliser, and is manufactured from calcium carbonate and nitric acid produced from atmospheric nitrogen by an electrical process (p. 306).

Phosphates of Calcium.—The normal and monacid phosphates of calcium, strontium, and barium are insoluble in water, whereas the diacid salts are soluble. Hence ordinary sodium phosphate gives a precipitate with calcium chloride, which dissolves in acids, whilst sodium dihydrogen phosphate gives no precipitate.

Normal Calcium Phosphate, $Ca_3(PO_4)_2$, occurs, as already mentioned, in many mineral deposits and in bones (p. 76). It is insoluble in water, but dissolves in water containing common salt or ammonium chloride. It is in this way that the calcium phosphate of the soil is brought into solution before its absorption by plants, which derive their phosphorus from it.

The soluble acid phosphate, $CaH_4(PO_4)_2$, is made by treating burnt bones with sulphuric acid,—

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4.$$

The resulting mixture of phosphate and sulphate is known as *superphosphate*, and is largely used as an artificial fertiliser to supply phosphorus in a soluble form to the plants.

Calcium Carbide, CaC_2, is now largely employed for the production of acetylene and is manufactured on the large scale by heating lime or limestone with coke or anthracite coal in the electrical furnace (p. 307),—

$$CaO + 3C = CaC_2 + CO.$$

The pure carbide is a white mass, which is rapidly decomposed by water with evolution of pure acetylene,—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

EXPERIMENT 94.—Drop a piece of calcium carbide about the size of a bean into a basin of water, and bring over it a jar filled with water—acetylene is evolved. The gas burns with a brightly luminous smoky flame.

Calcium Cyanamide, $CaCN_2$. When calcium carbide is heated in nitrogen, a reaction takes place with evolution of heat which results in the absorption of the nitrogen and the formation of calcium cyanamide and carbon,—

$$CaC_2 + N_2 = CaCN_2 + C.$$

Pure nitrogen is obtained either by passing air over heated copper or by the fractionation of liquid air, and is introduced under pressure into furnaces in which powdered calcium carbide is electrically heated to about 800°. A hard mass resembling coke in appearance is produced, and this is ground and forms the commercial calcium cyanamide or, as it is called, *nitrolim*.

This material is of very great value as a nitrogenous fertiliser.

When it is brought into the soil, it gradually decomposes, forming calcium carbonate and ammonia,—

$$CaCN_2 + 3H_2O = CaCO_3 + 2NH_3.$$

The nitrogen of the air is thus made available as a plant food in the form of ammonia, and this process forms one solution of the great agricultural problem, how to obtain a cheap and inexhaustible supply of nitrogen in a form assimilable by plants (see also p. 306).

Calcium Oxalate, CaC_2O_4, is one of the least soluble salts of calcium, and is precipitated when a soluble oxalate is added to a solution of a calcium salt. It dissolves in strong acids, such as hydrochloric and nitric acids, but is insoluble in acetic acid. When gently heated it loses carbon monoxide and is converted into the carbonate, which decomposes at a higher temperature, forming quicklime,—

$$CaC_2O_4 = CO + CaCO_3.$$

Detection of Calcium.—Calcium is usually detected by the formation of the insoluble carbonate and oxalate. When its salts are strongly heated on charcoal, lime is left as an infusible white mass, which glows brightly when heated. The compounds of calcium when moistened with hydrochloric acid and heated in the Bunsen flame, colour it brick red. The sulphate should for this purpose be first heated in the reducing flame, which converts it into the sulphide, and this should then be moistened with hydrochloric acid, which converts it into the chloride, and heated in the flame (see Spectrum Analysis).

The Compounds of Strontium

The name strontium is derived from Strontian, a village in Argyllshire, where a mineral containing strontium was first discovered in 1790. This mineral is called *strontianite*, and consists of strontium carbonate, whilst the sulphate is also found and is known as *cœlestine* from its blue colour. Strontium compounds also occur in small quantities in various minerals containing calcium and barium, such as arragonite and heavy spar, many of the compounds of these three elements being isomorphous. The compounds of strontium, however, do not play any important part in the animal or vegetable organism, and are much less widely diffused than those of calcium and barium.

Strontium Oxide, Strontia, SrO, is best obtained by heating the nitrate. Like lime it readily combines with water to form the *hydroxide*, $Sr(OH)_2$, which is rather more soluble than slaked lime, but less soluble than baryta, and acts as a strong alkali.

Strontium Carbonate, Strontianite $SrCO_3$, crystallises in the same form as arragonite, with which it often forms isomorphous mixtures.

Strontium Sulphate, $SrSO_4$, is known as cœlestine, and occurs in peculiar fibrous masses. It is less soluble in water than calcium sulphate, 100 cc. of water only dissolving 0.1 gram. of the salt, and is therefore almost completely precipitated when a soluble sulphate is added to a solution of a strontium salt. It is converted into carbonate when it is fused with sodium carbonate (p. 228), and even when it is simply boiled with a solution of the same salt.

Strontium Chloride, $SrCl_2 + 6H_2O$, is prepared by dissolving the carbonate in hydrochloric acid and evaporating the solution. It differs remarkably from calcium chloride in being efflorescent instead of deliquescent, and in being much less readily soluble in water; it also dissolves in absolute alcohol.

Strontium Nitrate, $Sr(NO_3)_2 + 4H_2O$, is also an efflorescent salt, and is prepared by dissolving the carbonate in dilute nitric acid. The salt is insoluble in alcohol, and is much used for the manufacture of fireworks on account of the brilliant red colour which it imparts to the flame.

EXPERIMENT 95.—Add 20 grams. of strontium carbonate to 40 cc. of dilute nitric acid (1 of acid to 3 of water), taking care that some of the carbonate remains undissolved; filter, evaporate, and allow to crystallise.

Detection of Strontium.—Strontium can readily be detected by the formation of the insoluble carbonate and sulphate. The oxalate is soluble in acetic acid (distinction from calcium), and the sulphate in hydrochloric acid (distinction from barium). The most characteristic test for strontium is, however, the magnificent crimson coloration which is imparted to the flame by the chloride and nitrate of the metal. The test should be carried out in the manner described under calcium (see also Spectrum Analysis).

The Compounds of Barium

The first known compound of barium was the sulphate, which was called *heavy spar* on account of its great density. When the corresponding earth or oxide was subsequently obtained from heavy spar it was called baryta (from the Greek word meaning heavy), whilst the metal received the name of barium.

This element occurs chiefly in the form of sulphate, as heavy spar, $BaSO_4$, from which nearly all the other barium compounds are prepared, and is also found as witherite, which consists of barium carbonate, $BaCO_3$.

Barium Oxide, Caustic Baryta, BaO, is obtained in a similar manner to strontia by heating the nitrate,—

$$2Ba(NO_3)_2 = 2BaO + 4NO_2 + O_2.$$

It is a white mass, which resembles quicklime in its properties. When it is heated in the air or in oxygen, barium dioxide is formed,—

$$2BaO + O_2 = 2BaO_2.$$

This substance, again, decomposes at a higher temperature, oxygen being evolved and baryta reproduced,—

$$2BaO_2 = 2BaO + O_2.$$

These reactions are made use of for the isolation of oxygen from the air in Brin's process, as already described (R. and L., p. 77).

Barium Hydroxide, $Ba(OH)_2 + 8H_2O$, is formed with great evolution of heat by the action of water on baryta. It is prepared on the large scale by heating barium carbonate in a current of steam,—

$$BaCO_3 + H_2O = CO_2 + Ba(OH)_2.$$

It forms yellowish crystals, 6.8 parts of which dissolve at

20° in 100 of water, so that it is much more readily soluble in water than slaked lime or strontium hydroxide, which it resembles in its general properties.

Barium Dioxide or Barium Peroxide, BaO_2.—This substance is a grayish-white powder and, as described above, decomposes into baryta and oxygen when it is strongly heated.

When treated with dilute sulphuric acid it yields hydrogen peroxide (R. and L., p. 99),—

$$BaO_2 + H_2SO_4 = BaSO_4 + H_2O_2.$$

Barium Sulphate, $BaSO_4$, occurs very widely as the mineral heavy spar, and forms the source of most of the other barium compounds. It is insoluble in water and in hydrochloric and nitric acids, and hence it is necessary to adopt special means in order to convert it into a soluble compound of the metal. The method used is of great importance, because it is universally employed for bringing into solution substances which are insoluble in water and acids, whether for the purpose of analysis or for the preparation of derivatives. This method depends on the fact that when barium sulphate is fused with an *excess* of sodium carbonate the following reaction occurs,—

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4.$$

In order that this change may be effected completely the barium sulphate must be present in a very finely-divided state, and must be fused with a large excess of the carbonate. A mixture of equivalent quantities of sodium and potassium carbonates is generally used on the small scale for analytical purposes, because it melts at a lower temperature than either of the carbonates alone. The fused mass is extracted with boiling water, which removes the unaltered alkali carbonate and the sodium sulphate, leaving behind pure barium carbonate, which can then be used for the preparation of other salts.

Barium sulphate and some other insoluble sulphates can also be brought into solution by being heated with carbon or some other reducing agent, whereby they are converted into the corresponding sulphides, which are very readily attacked by acids.

Heavy spar forms crystals of the form shown in Fig. 43, and is often found together with metallic ores. It has a specific gravity of 4.5 and is almost insoluble in water, 100 parts of which dissolve only 0.0002 part of it at 15°. Both the precipitated sulphate and ground and purified heavy spar are employed as a white paint, but the artificial sulphate precipitated from a cold solution of barium chloride by sodium sulphate is much superior as a paint to the powdered mineral.

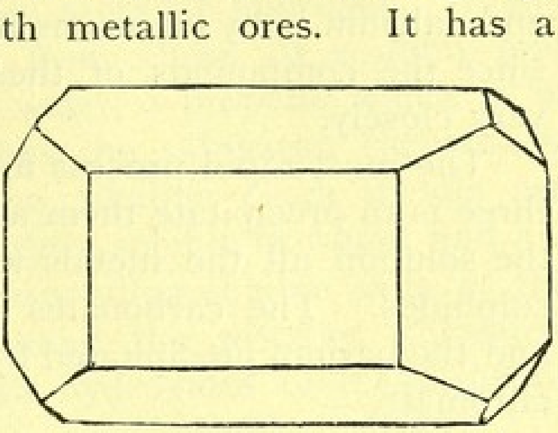


Fig. 43.

Barium Chloride, $BaCl_2 + 2H_2O$, is prepared by dissolving the carbonate in hydrochloric acid, and forms flat crystals which neither deliquesce nor effloresce in the air, and are insoluble in alcohol.

Barium Nitrate, $Ba(NO_3)_2$, may be prepared by dissolving the carbonate in nitric acid or by mixing hot saturated solutions of barium chloride and sodium nitrate (compare the preparation of potassium nitrate, p. 188),—

$$BaCl_2 + 2NaNO_3 = Ba(NO_3)_2 + 2NaCl.$$

It is insoluble in alcohol and is used for the preparation of green fire.

EXPERIMENT 96.—Dissolve 8 grams. of sodium nitrate and 12 grams. of barium chloride separately in the smallest possible amounts of boiling water. Mix the hot solutions, cool, filter, and drain the crystals. Recrystallise from boiling water and show that the product is pure barium nitrate, free from chlorides and sodium salts.

Barium Carbonate, $BaCO_3$, occurs as the mineral witherite, and, like the carbonates of calcium and strontium, is insoluble in water.

Detection of Barium.—Barium is detected by the formation of the insoluble carbonate and sulphate. The salts produce an apple-green coloration when brought into the Bunsen flame.

Detection of Calcium, Strontium, and Barium in

Mixtures.—The analytical separation of barium, strontium, and calcium is by no means an easy one to effect with accuracy, since the compounds of these metals resemble one another very closely.

The most rapid process for the qualitative detection of the three is to precipitate them as carbonates, after removing from the solution all the metals which form insoluble chlorides or sulphides. The carbonates are then dissolved in acetic acid and the barium precipitated by means of an excess of potassium chromate,—

$$BaCl_2 + K_2CrO_4 = BaCrO_4 + 2KCl.$$

The chromates of calcium and strontium are soluble in acetic acid and pass into the filtrate. The strontium may then be precipitated with sulphuric acid, and the calcium in the filtrate from this by ammonium oxalate. All the precipitates should be tested by the flame reaction.

A more accurate method depends on the facts that barium chloride is insoluble in absolute alcohol, whereas the chlorides of calcium and strontium are soluble, and that calcium nitrate is soluble in alcohol, whereas strontium nitrate is not.

Barium is almost always estimated quantitatively in the form of barium sulphate, whilst calcium is usually precipitated as calcium oxalate, and is then strongly heated and thus converted into the oxide.

General Properties of the Alkaline Earth Metals

The elements calcium, strontium, and barium resemble sodium and potassium in certain of their properties, whilst in other respects they differ from these very widely. The most important points of resemblance are to be found in the properties of the metals themselves and of their oxides.

All three metals decompose water readily at the ordinary temperature, whilst no other known metals except those of the alkalis have this property in the pure state. These metals, moreover, readily burn when heated in the air or in oxygen, forming oxides which unite with water to form soluble alkaline hydroxides, very similar in their chemical properties to the hydroxides of the alkali metals. Calcium, strontium, and barium, however, differ from sodium and potassium in the very important respect that each of their atoms is capable of replacing *two* atoms of hydrogen, whereas the atom of sodium or potassium can only replace *one* atom of hydrogen. Many of their salts, moreover, differ from those of sodium and potassium in their solubility in water, a property which is of great practical importance. Thus the sulphates, carbonates, phosphates, and oxalates of the alkaline earth metals are either insoluble or only very slightly soluble in water, and are thus distinguished from the corresponding soluble salts of the alkali metals. On the other hand the nitrates, chlorates, chlorides, bromides, iodides, and hydroxides of these metals are all soluble in water.

As regards the properties of the three elements themselves it is found that strontium occupies an intermediate position between the other two, both in atomic weight and physical and chemical properties. This is shown in the first place by a comparison of the atomic weights and specific gravities of the three metals, which also brings out the fact that the numbers for strontium are nearly the average of those for calcium and barium,—

	Calcium.	Strontium.	Barium.
Atomic weight .	40.09	87.63	137.37
Specific gravity .	1.55	2.5	3.8

A similar relation is noticed between the solubilities of many of the salts of these metals, especially the sulphate and hydroxide, as shown in the following table, which gives the number of grams. of each dissolved by 100 grams. of water at 15°,—

	Calcium.	Strontium.	Barium.
Sulphate . .	0.21	0.011	0.0002
Hydroxide . .	0.127	0.57	2.89

In both cases the solubility of the strontium compound falls between the values for calcium and barium.

SUMMARY

The metals calcium, strontium, and barium all decompose water in the cold and burn when heated in the air, forming the corresponding oxides, which unite with water vigorously, producing the soluble strongly basic hydroxides.

Each of these elements is bivalent and only forms one series of salts.

The chlorides and nitrates are soluble, the carbonates and phosphates insoluble, whilst the sulphates of calcium and strontium are sparingly soluble, and that of barium almost insoluble in water.

The compounds of these metals all impart characteristic colorations to the Bunsen flame.

EXERCISES ON LESSON XXII

1. How can metallic calcium be prepared, and what are its properties?

2. Describe the various forms of calcium carbonate which occur in nature. What is known about the origin of these?

3. How can the following substances be prepared, starting with calcium carbonate: (*a*) bleaching powder; (*b*) calcium carbide; (*c*) calcium chloride.

4. From what sources is calcium phosphate obtained? What is the action of sulphuric acid on normal calcium phosphate?

5. What volume of carbon dioxide can be produced from 1000 kilos. of limestone containing 90 per cent of calcium carbonate?

6. How would you prepare (*a*) barium chloride, (*b*) barium nitrate, and (*c*) baryta, from heavy spar?

7. Describe the preparation and properties of barium peroxide. What is the action of dilute sulphuric acid on this substance?

8. How have the atomic weights of calcium, strontium, and barium been decided?

9. Compare the compounds of strontium with those of calcium.

10. Compare the properties of calcium and its compounds with those of sodium and its compounds.

LESSON XXIII

THE METALS OF THE ZINC GROUP

MAGNESIUM. ZINC. CADMIUM. MERCURY.

THESE four metals form another well-marked group or family of elements, zinc being in many of its properties intermediate between magnesium and cadmium, just as strontium is between calcium and barium. In their general chemical properties these elements are allied to the members of the group of the alkaline earth metals, and like these differ in many important respects from the alkali metals.

Magnesium, zinc, cadmium, and mercury are all well-known metals, being manufactured on the large scale and employed for various useful purposes in the arts.

Magnesium, Mg, 24·32

The first compound of magnesium to be recognised as different from all other known salts was the sulphate, which was discovered in a spring at Epsom in 1695, and was therefore known as Epsom salts. Compounds of magnesium also occur in many other springs, and hence also in sea-water and the mineral deposits formed by the drying up of sea-water, such as the deposits at Stassfurt (p. 182), and nearly all beds of rock-salt.

Magnesium carbonate, $MgCO_3$, also occurs in enormous quantities as *magnesite*, and, along with calcium carbonate, as *dolomite* or *magnesian limestone*. Other well-known minerals containing magnesium are asbestos and meerschaum, both of which are silicates of the metal. Small quantities of magnesium salts occur in both animal and vegetable organisms.

Metallic Magnesium was first prepared by Davy by a method similar to that which he used for potassium, etc. It is not easy to prepare the metal, because it combines with oxygen and other elements very vigorously and forms very stable compounds with them. Thus when magnesium chloride or magnesium oxide is heated in a current of hydrogen, no reduction takes place, and the same is the case when the oxide is heated with carbon. When, however, the chloride, or a mixture of this with sodium chloride, is fused with metallic sodium, decomposition occurs and metallic magnesium is formed,—

$$MgCl_2 + 2Na = 2NaCl + Mg.$$

The metal is now manufactured according to the above reaction and purified by distillation, which is carried out by strongly heating the mixture in an iron cylinder, through the bottom of which a vertical exit tube passes, the vapour of the metal being condensed in an iron box placed underneath the cylinder. All the metals of this group can be distilled, and, as we shall see, this property is made use of in the preparation of all of them. The temperature of distillation is highest in the case of magnesium, which requires a white heat (about 1100° C.), and lowest for mercury. Magnesium is now also made by the electrolysis of a fused mixture of the chloride with potassium chloride made by heating carnallite, $MgCl_2 + KCl + 6H_2O$. Magnesium is usually sold in the form of ribbon, which is made by pressing the hot metal into wire and then flattening this between rollers.

Properties of Magnesium.—Magnesium is one of the lightest of the common metals, having the specific gravity 1.75, and melts at 633°. It is not acted on by dry air at the ordinary temperature, only tarnishes very slowly in moist air, and does not decompose water at the ordinary temperature, so that all these properties distinguish it from the metals of the preceding group. When heated in the air it burns with a dazzling white light, forming the oxide, MgO.

The light evolved is very rich in rays which can produce photographic effects on silver salts, and hence the metal is frequently used for producing artificial light for photography.

Magnesium combines so vigorously with oxygen that it decomposes many oxides when it is heated with them, forming magnesium oxide and liberating the element which was previously combined with the oxygen. Thus when the metal is heated in steam it burns almost as brightly as in air, hydrogen being liberated,—

$$Mg + H_2O = MgO + H_2.$$

In order to demonstrate this, place 3 or 4 short pieces of magnesium ribbon in a bulb blown on a piece of hard glass tubing, one end of which is connected with a flask containing boiling water, and the other with a delivery-tube dipping under the water of a pneumatic trough. Pass steam through the bulb-tube until all the air is expelled, warming the tube gently at the same time in order to prevent the condensation of water in it. As soon as all the air has been driven out, place a large test-tube filled with water over the end of the delivery-tube and heat the bulb strongly. The magnesium burns with a bright white light and hydrogen is evolved, which passes into the test-tube.

The metal also burns in carbon dioxide, liberating carbon and forming magnesium oxide,—

$$2Mg + CO_2 = 2MgO + C.$$

EXPERIMENT 97.—Heat a piece of stout magnesium wire in the air, and when it is burning brightly plunge it into a jar containing carbon dioxide—the metal continues to burn. (The ordinary magnesium ribbon does not readily burn in carbon dioxide unless a little air be present.) When the flame dies out pour a few ccs. of hydrochloric acid into the jar in order to dissolve the magnesium oxide and any magnesium which remains unburnt. An abundant black residue of carbon is left, which may be filtered off, dried and heated in a current of air or oxygen, in order to show the production of carbon dioxide by its combustion, and thus prove that it is carbon.

Magnesium also decomposes many other oxides, both of the metals and non-metals at a high temperature, and is employed for the preparation of boron and silicon from their compounds with oxygen. Magnesium readily dissolves in dilute hydrochloric and sulphuric acids, hydrogen being evolved,—

$$Mg + H_2SO_4 = MgSO_4 + H_2.$$

The metal also combines with nitrogen when it is heated in this gas, a nitride being formed.

Equivalent and Atomic Weight of Magnesium.— The equivalent of magnesium has been accurately determined by converting a known weight of the metal into oxide. This was done by purifying the magnesium by distillation, and then dissolving a weighed amount of the pure metal in nitric acid, evaporating to dryness, and decomposing the nitrate by heat, the resulting oxide being finally weighed. It has thus been found that 8 parts of oxygen unite with 12·16 parts of magnesium, so that this number represents the equivalent of the metal.

The atomic weight has been settled from a consideration of the atomic heat of the metal. The specific heat of magnesium being 0.25, the atomic weight must be about $\frac{6.4}{0.25} = 25.6$. Hence $12.16 \times 2 = 24.32$ is taken as the atomic weight of magnesium. One atom of magnesium, therefore, replaces two atoms of hydrogen, so that in this respect magnesium agrees with the metals of the calcium group.

The Compounds of Magnesium

Magnesium Oxide, Magnesia, MgO, is formed when the metal is heated in air or oxygen. Magnesium nitrate and carbonate readily decompose when heated, in a similar manner to the corresponding calcium salts, a residue of magnesia being left,—

$$MgCO_3 = MgO + CO_2.$$

The oxide is usually prepared from the carbonate in this way, and is then known as *calcined magnesia* or *magnesia usta.* It is only very slightly soluble in water (1 part in 55,000 of water), but when moist turns red litmus blue.

Magnesia is largely used in medicine, and since it is unaltered by very intense heat is employed for lining furnaces and crucibles, as well as for the production of the electric light.

Magnesium Hydroxide, $Mg(OH)_2$, is formed when caustic soda is added to a solution of a magnesium salt, and is a white flocculent precipitate which is almost insoluble in water and caustic soda solution,—

$$MgSO_4 + 2NaOH = Mg(OH)_2 + Na_2SO_4.$$

It is not precipitated, however, in the presence of ammonium salts, and this property is made use of in the analytical detection and separation of magnesium.

EXPERIMENT 98.—1. To a solution of magnesium sulphate add an excess of caustic soda solution—a white precipitate of the hydroxide is produced.

2. To another portion of magnesium sulphate solution add ammonium chloride solution and then caustic soda—no precipitate is produced.

A solution of magnesium sulphate or chloride, to which ammonium chloride and then excess of ammonia have been added, is known as *magnesia mixture*, and is used in the laboratory for the detection and estimation of phosphates.

Magnesium Carbonate, $MgCO_3$, occurs as magnesite, and, along with calcium carbonate, as dolomite, minerals of which whole mountain ranges are composed in the Pennines in England and in the Tyrol. Both of these substances serve as important sources of the magnesium compounds. The preparation of pure magnesium compounds from dolomite can easily be carried out by treating the powdered mineral with dilute sulphuric acid. Magnesium sulphate is formed, which can readily be freed by recrystallisation from the sparingly soluble calcium sulphate, which is also produced.

EXPERIMENT 99.—Add 10 cc. of concentrated sulphuric acid to 90 cc. of water, heat to boiling, and *gradually* add powdered dolomite until the liquid is neutral, and a small amount of the dolomite remains undissolved. Filter, on the pump if possible, from the insoluble calcium sulphate, and evaporate the filtrate until a crystalline crust is formed. On cooling magnesium sulphate separates out, which can be purified by recrystallisation from the smallest possible quantity of boiling water.

The precipitate formed when a solution of sodium carbonate is added to one of Epsom salts is not pure magnesium carbonate, $MgCO_3$, but a basic carbonate of variable composition, which is known as *magnesia alba.* Although magnesium carbonate is almost insoluble in pure water it dissolves even more readily than calcium carbonate in water containing carbonic acid. This solution behaves precisely like one of calcium carbonate in aqueous carbonic acid, and both of these carbonates are often present together in spring and well waters, in which they produce temporary hardness (R. and L. p. 123).

EXPERIMENT 100.—To 10 cc. of a dilute solution of magnesium chloride add sodium carbonate solution—a thick, white precipitate of basic magnesium carbonate is produced. Pass a current of carbonic acid gas through the liquid—the precipitate gradually dissolves, forming a perfectly clear solution. Divide this into three parts.

1. Add soap solution—a thick, white precipitate of an insoluble magnesium soap is produced.
2. Boil the clear solution—the basic carbonate is reprecipitated.
3. Add lime-water—a mixture of the carbonates of calcium and magnesium is precipitated.

Magnesium carbonate, like the hydroxide, is readily soluble in ammonium salts, and the separation of magnesium salts from those of calcium in the ordinary course of qualitative analysis depends upon this property.

EXPERIMENT 101.—To a solution of magnesium sulphate add ammonium chloride, and then sodium carbonate or ammonium carbonate—no precipitate is produced.

Magnesium Sulphate, $MgSO_4$, is found combined with 7 molecules of water, as *Epsom salts*, which are readily soluble in water, and also combined with 1 molecule of water, as *kieserite*, which is almost insoluble in water. Kieserite occurs in the deposits at Stassfurt, and is purified by being simply washed with water to remove the soluble salts of potassium and sodium. It is also produced when Epsom salts are heated at 150°.

EXPERIMENT 102.—Heat 1 gram. of powdered Epsom salts on a watch-glass in a hot-air oven at 150° for an hour. Shake the remaining salt with 5 cc. of water, and compare its behaviour with that of 1 gram. of the original Epsom salts when treated with the same amount of water.

When equivalent amounts of potassium sulphate and magnesium sulphate are dissolved in water and the solution evaporated, it is found that the least soluble salt, potassium sulphate, does not crystallise out first, but that crystals of a double salt, $MgSO_4 + K_2SO_4 + 6H_2O$ are deposited.

EXPERIMENT 103.—Dissolve 5 grams. of potassium sulphate and 6.5 grams. of Epsom salts in about 50 cc. of boiling water, evaporate until crystals begin to separate and allow to cool. The double sulphate crystallises out and cannot be separated into its constituent salts by recrystallisation.

Magnesium Chloride, $MgCl_2$, occurs along with potassium chloride at Stassfurt, and is prepared in the manner already described (p. 184). It forms crystals having the composition $MgCl_2 + 6H_2O$, and forms a very soluble deliquescent mass. When this crystalline salt is heated it decomposes, forming hydrochloric acid, water, and magnesia,—

$$MgCl_2 + 6H_2O = MgO + 2HCl + 5H_2O.$$

The anhydrous salt can be obtained pure by evaporating the aqueous solution in a current of hydrochloric acid.

Magnesium Nitride. — When metallic magnesium is heated in nitrogen, the gas is absorbed and a compound of the formula Mg_3N_2 is produced, which is known as magnesium nitride. This substance is decomposed by boiling water, ammonia being evolved and magnesium hydroxide formed,—

$$Mg_3N_2 + 6H_2O = 3Mg(OH)_2 + 2NH_3.$$

The formation of this substance has been utilised in the separation of atmospheric nitrogen from the gases of the argon group (p. 432).

Magnesium Ammonium Phosphate, $Mg(NH_4)PO_4 + 6H_2O$, is a crystalline salt which is precipitated when a solution of magnesium chloride containing ammonium chloride and ammonia is added to a solution of ordinary sodium phosphate,—

$$MgCl_2 + NH_4(OH) + Na_2HPO_4 = \\ MgNH_4PO_4 + 2NaCl + H_2O.$$

It is very sparingly soluble in water (1 part in 15,000), and even less readily in dilute ammonia. On this account it is used for the qualitative detection and quantitative estimation of both phosphoric acid and magnesium.

Magnesium Sulphide, MgS, like calcium sulphide, is not formed when sulphuretted hydrogen is passed into a solution of a magnesium salt, but may be obtained by heating magnesium and sulphur together, and is almost insoluble in water. The hydrosulphide, $Mg(SH)_2$, again like the corresponding calcium compound, is readily soluble. The solution decomposes when heated, and evolves sulphuretted hydrogen.

Detection of Magnesium.—Magnesium is not precipitated by any of the group reagents employed in the ordinary course of analysis, and is therefore present in the filtrate from the calcium group. The most characteristic test for its presence is the formation of the magnesium ammonium phosphate described above.

Zinc, Zn, 65·37

The metal zinc was discovered by the alchemists, and was at first regarded as only a semi-metal, because it was brittle, took fire, and burned when strongly heated, and in other ways differed from the seven metals previously known to them (p. 69). The chief compounds of this metal which occur in nature are the carbonate (*calamine*), $ZnCO_3$, the sulphide (*zinc blende*), ZnS, and the silicate, $ZnSiO_3 + H_2O$, which is termed *siliceous calamine* or *hemimorphite.* Zinc is not a usual constituent of the igneous rocks of which the crust of the earth is composed, and hence it does not as a rule occur in soil which is the product of the decomposition of these rocks. Moreover, it does not form an essential part of animal or vegetable organisms, zinc compounds usually acting rather as poisons.

Preparation of Metallic Zinc.—Zinc does not combine with oxygen nearly so vigorously as does magnesium, and the oxide is much more readily decomposed than is magnesia. Thus metallic zinc can be manufactured by heating the oxide with carbon, whilst, as we have seen, magnesia cannot be decomposed in this way. The extraction of zinc from its ores is carried out in two stages, the ores being first converted into the oxide, and the latter then reduced by means of carbon. When zinc blende is employed, it is first freed from sulphur and converted into the oxide by being heated in a current of air,—

$$2ZnS + 3O_2 = 2ZnO + 2SO_2.$$

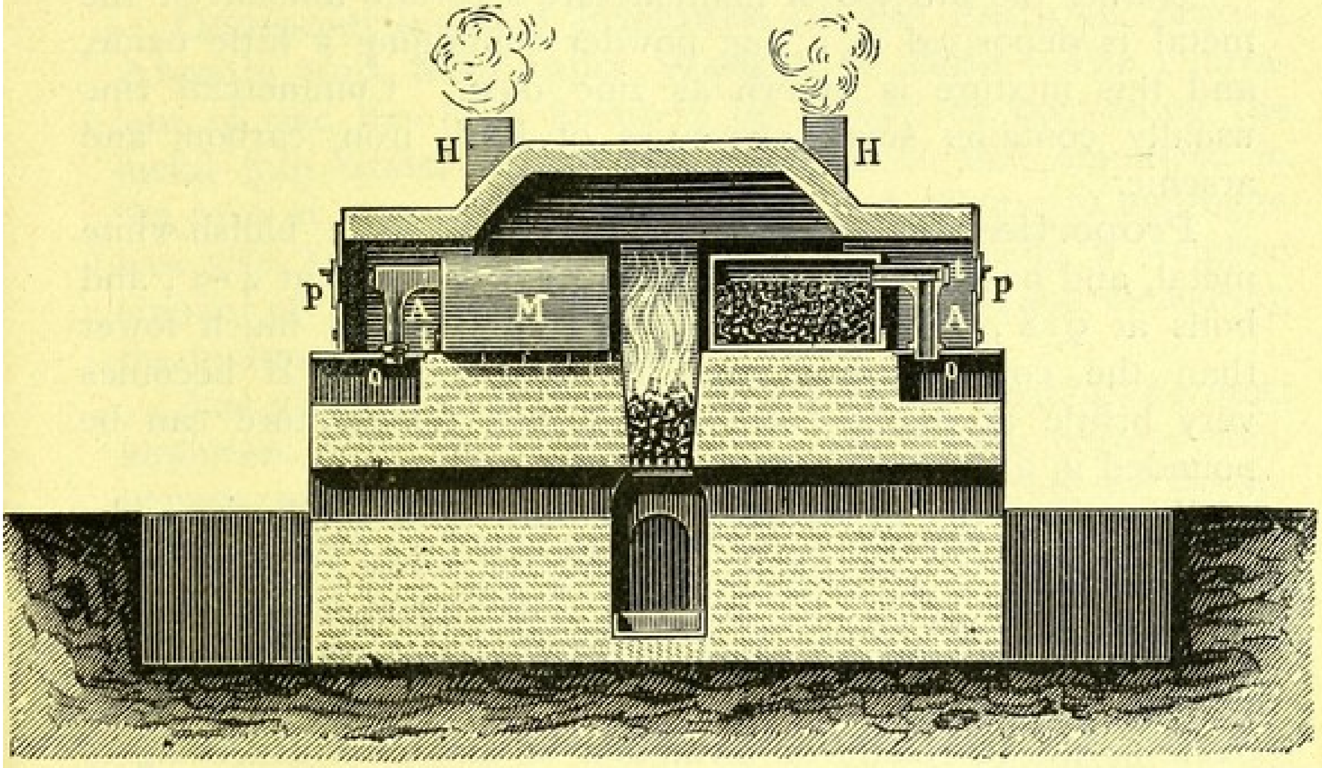


Fig. 44.

The carbonate and silicate, on the other hand, are simply strongly heated, usually in kilns resembling lime-kilns, in order that the carbonic acid of the former and the water of the latter ore may be removed.

The crude oxide is then mixed with coal or coke and strongly heated, and the metallic zinc passes off in the form of vapour, which is then condensed,—

$$ZnO + C = Zn + CO.$$

This second stage of the process is carried out by various methods, the most important of which are the Silesian and

Belgian processes and a combination of these, the chief difference between them being in the kind of furnace employed. In the Silesian process the mixture of roasted zinc ore and coal is placed in clay muffles or retorts, about 40 of which are heated side by side in a single furnace (Fig. 44). The muffle (M) is provided with a side tube (A), through which the vapour of the zinc passes into the iron box (O), in which it is condensed.

In the Belgian process the mixture is heated in a horizontal fire-clay tube, connected by a conical clay tube with a sheet-iron condenser.

During the process of manufacture a certain amount of the metal is deposited as a fine powder containing a little oxide, and this mixture is known as zinc dust. Commercial zinc usually contains small quantities of lead, iron, carbon, and arsenic.

Properties of Metallic Zinc.—Zinc is a bluish-white metal, and has the specific gravity 6.9. It melts at 419°, and boils at 918°, both of these temperatures being much lower than the corresponding ones for magnesium. It becomes very brittle at about 200°, and at this temperature can be pounded in a mortar.

Zinc dissolves in dilute hydrochloric and sulphuric acids, with evolution of hydrogen. When the metal is quite pure, however, these acids only act very slowly upon it, whilst they act rapidly on a metal which contains small amounts of impurities. Nitric acid dissolves zinc with evolution of nitric oxide or nitrous oxide or formation of ammonia according to the concentration of the acid (see p. 265). A very important fact is that zinc dissolves in hot solutions of the alkalis, hydrogen being evolved, and a soluble compound known as sodium zincate formed,—

$$Zn + 2NaOH = Na_2ZnO_2 + H_2.$$

This property of the metal distinguishes it sharply from magnesium, which is not affected by alkalis.

Zinc dust and caustic soda solution are often used for bringing about the reduction of other compounds. Potassium nitrate, for example, when treated with this mixture, yields the whole of its nitrogen in the form of ammonia,—

$$KNO_3 + 8H = KHO + NH_3 + 2H_2O.$$

EXPERIMENT 104.—Warm some zinc dust with caustic soda solution in a test-tube—hydrogen is evolved with effervescence. To the mixture add a few drops of potassium nitrate solution and again warm—ammonia is at once evolved.

Zinc burns when strongly heated in the air, or better in oxygen, with a beautiful greenish light. This may be shown by strongly heating some thin zinc-foil in the air and directing a jet of oxygen on to the hot metal. It does not, however, burn in carbon dioxide, and does not decompose steam even at a red heat (compare the behaviour of magnesium, p. 235).

Composition and Formulæ of the Salts of Zinc—Atomic and Molecular Weight of Zinc.—The equivalent of zinc has been found to be 32·685 by converting the metal into oxide, by a method similar to that employed in the case of magnesium. The equivalent of zinc to hydrogen has also been directly determined by dissolving a weighed amount of pure metal in dilute sulphuric acid, and measuring the hydrogen which is evolved.

Zinc yields several compounds which are volatile, the most important being the chloride, $ZnCl_2$, and certain organic compounds such as zinc ethide, $Zn(C_2H_5)_2$, and from the vapour densities and composition of these it follows that the atomic weight must be about 65 or some fraction of this. Thus the vapour density of the chloride is 68.15, and its molecular weight therefore 136.3. Of this 70.9 are due to chlorine, so that the remaining 65.4 parts are zinc. The conclusion that the atomic weight of zinc is about 65 is confirmed by the specific heat of the metal. This is 0.0935, and hence the atomic weight must be about $\frac{6.4}{0.0935} = 68$. The nearest multiple of the equivalent to this is $32.685 \times 2 = 65{\cdot}37$, which is therefore taken as the atomic weight of zinc. Zinc is thus seen to be a bivalent metal, one atom of which replaces two atoms of hydrogen in acids, the zinc salts being similar in formula to those of magnesium.

Metallic zinc boils at 918°, yielding a vapour which has a density of 32.7, so that the molecular weight of gaseous zinc is $32.7 \times 2 = 65.4$. This is the same as the atomic weight of the metal, and we thus learn that the molecules of zinc consist of only one atom, so that this metal differs very strikingly from such substances as iodine, oxygen, hydrogen, etc., the molecules of which consist of two atoms.

Compounds of Zinc

Zinc Oxide, ZnO, occurs in nature as zincite, and is prepared by distilling metallic zinc, burning the vapour, and allowing the flocculent white oxide which is produced to settle in chambers or flues. It is also formed when the carbonate is heated and is prepared for medicinal use in this way. When cold it is white, but at high temperatures it becomes yellow, regaining its original colour on cooling.

EXPERIMENT 105.—Heat about 0.5 gram. of zinc carbonate in a test-tube. Show that carbon dioxide is evolved by pouring the gas from the test-tube into a tube containing lime-water, and observe that the mass left in the tube is yellow when hot, white when cold.

Zinc hydroxide, $Zn(OH)_2$, is formed when a caustic alkali is added to a solution of a zinc salt. It is a white powder and readily dissolves either in acids or in an excess of the alkali,—

$$Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$$

$$Zn(OH)_2 + 2HCl = ZnCl_2 + 2H_2O.$$

The hydroxide therefore acts as a base towards acids, whilst it also acts as an acid towards strong bases. The salts formed with the alkalis are called zincates, and are very unstable, being decomposed by such weak acids as carbonic acid.

EXPERIMENT 106.—1. To a solution of zinc sulphate add a small amount of caustic soda solution—a thick, white precipitate is formed which readily dissolves in hydrochloric acid.

2. To another portion of the solution of zinc sulphate add caustic soda drop by drop—the precipitate redissolves, forming a strongly alkaline solution.

3. Into the alkaline solution obtained above pass carbon dioxide—a white precipitate of zinc carbonate is at once formed.

Zinc hydroxide, therefore, differs in this respect from magnesium hydroxide, which is insoluble in caustic soda.

Zinc Carbonate, $ZnCO_3$, is one of the chief ores of zinc, and is precipitated when sodium carbonate is added to a solution of the sulphate.

Zinc Sulphate, $ZnSO_4$, is one of the best known salts of zinc, and was formerly known as white vitriol. It is made on the large scale by roasting zinc blende in excess of air, extracting the mass with water, and evaporating,—

$$ZnS + 2O_2 = ZnSO_4.$$

In the laboratory it is prepared by treating an excess of zinc with dilute sulphuric acid, filtering and evaporating.

EXPERIMENT 107.—Carefully add 10 cc. of concentrated sulphuric acid to about 40 cc. of water in a basin. Stir and add about 15 grams. of granulated zinc. As soon as all effervescence has ceased and some zinc is still left undissolved, heat to boiling, filter, and evaporate if necessary, and allow to cool. Zinc sulphate separates out in characteristic prismatic crystals.

It crystallises in the same forms as Epsom salts, the crystals having the formula, $ZnSO_4 + 7H_2O$.

Zinc Nitrate, $Zn(NO_3)_2 + 6H_2O$, is a deliquescent mass, and decomposes when it is heated, leaving a residue of zinc oxide.

Zinc Chloride, $ZnCl_2$, is best prepared by passing chlorine over heated zinc, or heating zinc dust in hydrochloric acid. The chloride volatilises and solidifies to a white mass. It is deliquescent and absorbs water very vigorously, so that it is often used as a dehydrating agent. It is decomposed by boiling water, a basic salt which is insoluble in water being formed.

Zinc Sulphide, ZnS, occurs as zinc blende in masses which are yellowish when pure, but are more generally dark coloured. The amorphous sulphide is white, and is formed when sulphuretted hydrogen is passed into a solution of a zinc salt, made alkaline with ammonia, or acidified with acetic acid. It is not formed in the presence of strong acids, such as hydrochloric acid, by which it is at once decomposed.

EXPERIMENT 108.—To separate portions of a solution of zinc sulphate, add—

1. Ammonium sulphide solution—a white precipitate of the sulphide is formed. (This precipitate is often gray

in colour, owing to the presence of small traces of iron.)

2. Hydrochloric acid and then sulphuretted hydrogen—no precipitate is formed.
3. Acetic acid and then sulphuretted hydrogen — the sulphide is precipitated, but dissolves at once when hydrochloric acid is added.

Detection of Zinc.—The reactions by which zinc is detected are the formation of the hydroxide soluble in excess of ammonia or caustic soda, and the formation of the white sulphide, insoluble in acetic acid, ammonia, or caustic soda, but readily soluble in hydrochloric acid.

The oxide also unites with oxide of cobalt to form a bright green mass, the production of which is often used as a blowpipe test for the presence of compounds of zinc.

Cadmium, Cd, 112.40

Cadmium resembles zinc very closely in its chemical properties, most of its salts and other compounds being very similar to those of zinc. It is not a very common metal, but occurs in small quantities in zinc ores, such as calamine and zinc blende, in many localities, and is therefore obtained when such ores are smelted. It is more easily volatile than zinc, and like it burns in the air, so that the first portion of crude zinc dust obtained from the zinc ores contains all the cadmium. This crude material, consisting of zinc and cadmium mixed with their oxides, is then again heated with coal or charcoal, and the more volatile cadmium collected, the process being again repeated if necessary. Cadmium may also be purified by dissolving the crude product in hydrochloric acid and precipitating the cadmium with metallic zinc,—

$$CdCl_2 + Zn = ZnCl_2 + Cd.$$

The metal is white and harder and denser than zinc, its specific gravity being 8.6. It melts at 322°, and boils at 778°, and its vapour, like that of zinc, has a density which shows that the molecules of cadmium consist of a single atom, the molecular formula of the element being therefore Cd.

The equivalent of the metal has been found by converting the pure metal into the oxide, whilst the atomic weight, like those of zinc and magnesium, has been decided from the specific heat, which is 0.0548 ; like the other members of the group the metal is bivalent.

Cadmium is used for making alloys, which melt at a low temperature, and are known as fusible metals (p. 116).

Cadmium Oxide, CdO, is a brown powder, and is obtained by igniting the white carbonate or nitrate, whilst it is also formed when the metal burns in air or oxygen.

Cadmium Hydroxide, $Cd(OH)_2$, like zinc hydroxide, is a white mass, readily soluble in alkalis.

Cadmium Chloride, $CdCl_2 + 2H_2O$, differs from zinc chloride by not being deliquescent but efflorescent.

Cadmium Sulphide, CdS, is a bright yellow coloured amorphous mass, and is insoluble in dilute hydrochloric or nitric acid. It is, however, soluble in the strong acids and in boiling dilute sulphuric acid, whilst it is insoluble in ammonium sulphide. By means of this compound cadmium can readily be separated and distinguished from zinc, the sulphide of which is white, and dissolves readily even in dilute hydrochloric acid.

EXPERIMENT 109.—To separate portions of a solution of cadmium chloride or nitrate—

1. Add caustic soda solution drop by drop—a white precipitate is formed which dissolves in excess of caustic soda solution.
2. Pass sulphuretted hydrogen — a yellow precipitate is formed, which is insoluble in ammonium sulphide and dilute hydrochloric acid ; soluble in boiling dilute nitric acid.

SUMMARY

Magnesium, zinc, and cadmium all form a single series of salts, in which the metal is bivalent. These three metals all dissolve readily in dilute sulphuric acid, whilst zinc and cadmium are also soluble in caustic soda solution. They can all be distilled.

Magnesium melts at a high temperature and readily burns in the air, forming the stable white oxide. The hydroxide is insoluble in water and in caustic soda solution. The carbonate is insoluble in water, whilst the chloride, nitrate, and sulphate are readily soluble. The hydroxide and carbonate are readily soluble in ammonium salts.

Zinc melts below a red heat, and does not readily burn in the air. The hydroxide is insoluble in water, but is readily soluble in solutions of caustic soda and ammonia. The white sulphide is insoluble in water and acetic acid, but readily dissolves in dilute hydrochloric acid. The carbonate, chloride, sulphate, and nitrate behave in a similar manner to those of magnesium. The hydroxide and carbonate are not affected by ammonium salts.

Cadmium melts at a still lower temperature than zinc, which it closely resembles in properties. The sulphide is yellow and is insoluble in hydrochloric acid; the oxide is a brown mass, and the hydroxide is soluble in alkalis.

EXERCISES ON LESSON XXIII

1. What are the chief compounds of magnesium occurring in nature? Describe the preparation of pure magnesium sulphate from any one of them.

2. How is metallic magnesium prepared, and what are its properties?

3. What happens when metallic magnesium is heated in (*a*) hydrogen; (*b*) oxygen; (*c*) nitrogen; (*d*) chlorine; (*e*) carbon dioxide; (*f*) steam?

4. Describe the preparation of metallic zinc from its ores.

5. How are the following substances obtained: (*a*) zinc dust; (*b*) magnesia; (*c*) zinc sulphate; (*d*) cadmium sulphide?

6. What is the action of (*a*) hydrochloric acid; (*b*) caustic soda solution, on metallic zinc? How could you detect the presence of zinc oxide in zinc dust?

7. 10 grams of pure zinc, when it is dissolved in nitric acid and the resulting nitrate decomposed by heat, yield 12.458 grams. of zinc oxide. Calculate the equivalent of zinc.

8. 1.298 gram. of zinc when dissolved in dilute acid yields 444 cc. of pure hydrogen at N.T.P. Calculate the equivalent of zinc.

9. How would you attempt to prepare pure zinc from an alloy of the metal with cadmium?

LESSON XXIV

THE METALS OF THE ZINC GROUP (*Cont.*)

Mercury, Hg, 200.0

MERCURY or quicksilver is one of the metals which was known to the Greek alchemists. The striking appearance of this liquid metal led to the Greek name *hydrargyrum* (liquid silver), from which the symbol of the element Hg is derived, whilst the English term quicksilver (live silver) is simply a translation of the Greek expression. The metal was associated by the alchemists with Hermes or Mercury, the messenger of the gods, and this name is the only one of the old alchemical names for the metals which has remained in general use.

Mercury occurs in small quantity in the free state, but its most important ore is the sulphide known as *cinnabar*, HgS, which is found in Austria, Bavaria, California, China, and Japan.

The manufacture of the metal is carried out by simply heating the ore in a current of air, the sulphur being converted into sulphur dioxide, whilst the mercury, which does not readily combine with oxygen under these conditions, is set free and volatilises,—

$$HgS + O_2 = Hg + SO_2.$$

The process is conducted by heating the ore on perforated arches, placed in a furnace so that the heated air passes through the mass. The mercury volatilises and passes along with the sulphur dioxide through a long series of chambers, where it is cooled and condensed, the last traces being removed from the gases by means of a spray of water.

The crude mercury is either distilled, a process which is best carried out in vacuo at a low temperature, or it is allowed to run in a thin stream through a column of dilute nitric acid which dissolves out the impurities. Metallic mercury is liquid at the ordinary temperature, but freezes at – 38.8°, forming a soft crystalline mass of metallic appearance, which has the specific gravity 14.19, and is therefore denser than liquid mercury, the specific gravity of which at 0° is 13.595. The metal boils at 357°, forming a colourless vapour.

Mercury very readily unites with other metals to form alloys, termed *amalgams.* In many cases the amalgam is formed at once when the metal in question is simply brought in contact with mercury, but it is necessary that the surface be clean, as otherwise combination does not take place. When, for example, mercury is simply rubbed on to a clean coin of copper, silver, or gold, amalgamation occurs immediately. Many metals also become amalgamated when they are dipped into a solution of a salt of mercury. Thus copper is at once coated with mercury when it is dipped into a solution of mercuric chloride, metallic mercury being precipitated on to the surface of the metal, with which it then unites whilst an equivalent quantity of the copper is dissolved,—

$$Cu + HgCl_2 = CuCl_2 + Hg.$$

All amalgams are decomposed by heat, which causes the mercury to volatilise.

EXPERIMENT 110.—Clean a piece of copper foil or a copper coin by dipping it in nitric acid and washing it with water.

1. Rub on to a portion of the foil a few globules of mercury—a bright silvery surface is at once produced. Heat the foil gently—the mercury volatilises and leaves the unaltered copper of the original colour.
2. Place a portion of the foil in a solution of mercuric chloride and allow to stand for some time. A dull deposit of mercury is formed which becomes bright when rubbed. To show the presence of copper in the solution, add excess of ammonia and filter—a deep blue solution is obtained.

Amalgamated metals are often not so vigorously acted on by reagents as the metal alone; thus sodium amalgam reacts much less violently with water and acids than sodium itself, and amalgamated zinc is used in batteries for the production of an electric current because it is only dissolved by dilute sulphuric acid during the passage of the current.

On the other hand, the amalgams of magnesium and aluminium decompose water at the ordinary temperature, at which the unamalgamated metals have no action on water.

Mercury does not tarnish in the air at the ordinary temperature, but slowly combines with oxygen when it is heated in the air for a long time just below its boiling-point, forming the red oxide, HgO, which again decomposes at a higher temperature. The metal is not acted upon by hydrochloric acid or dilute sulphuric acid, but when heated with strong sulphuric acid is converted into the sulphate, sulphur dioxide being evolved,—

$$Hg + 2H_2SO_4 = HgSO_4 + SO_2 + 2H_2O.$$

Priestley, who was the first to collect and examine sulphur dioxide, prepared it by this method, although the cheaper copper is now generally used for the preparation of this gas on the small scale. Mercury dissolves in nitric acid to form the nitrate, oxides of nitrogen being evolved, just as in the more familiar case of copper (p. 265),—

$$3Hg + 8HNO_3 = 3Hg(NO_3)_2 + 4H_2O + 2NO.$$

On account of its liquid form, high boiling-point, and permanence in the air, mercury is largely used in the construction of physical apparatus, such as barometers and thermometers, and for silvering mirrors; it is also employed in the electrolytical process for the manufacture of caustic soda (p. 306), and in the mercury vapour electric lamp.

Atomic Weight of Mercury—Composition of the Salts of Mercury.—Mercury differs chemically from the metals of the alkalis and alkaline earths and the other members of the zinc group in a very important respect. Each of these elements only forms one well-defined series of salts, all of which are derived from the corresponding acids by the replacement of the same number of hydrogen atoms by one atom of the element. Thus one atom of sodium or potassium always replaces one atom of hydrogen, whilst the atoms of calcium, strontium, barium, magnesium, zinc, and cadmium each replace two atoms of hydrogen. Mercury, on the other hand, forms two distinct series of compounds, two oxides, two chlorides, etc., and in one series each atom of the metal replaces two atoms of hydrogen and in the other only one atom.

Mercury is therefore a metal which has two different equivalents, that is to say, it can combine with two different amounts of the same element, forming two distinct compounds. Taking, for example, the chlorides, it is found by analysis that in one of these, which is soluble in water, 35.5 parts of chlorine are combined with 100 of mercury, whereas in the other, which is insoluble in water, the same amount of chlorine is united with 200 of mercury. Mercury, therefore, has the two equivalents 100 and 200.

Many of the compounds of mercury are volatile, and a study of the molecular weights and composition of these shows that the atomic weight of mercury must be about 200. The same result is obtained from a consideration of the specific heat of the metal, which is 0.0319, so that the atomic weight must be about $\frac{6.4}{0.0319} = 200$. The accurate atomic weight is therefore taken as 200.

It follows from this that in the soluble chloride one atom of the element replaces two atoms of hydrogen and unites with two atoms of chlorine, whilst in the insoluble chloride it replaces only one atom of hydrogen. The same relation is found to exist between the other salts formed by the metal, and the two series are known as the *mercuric* compounds, in which mercury replaces two atoms of hydrogen, and the *mercurous* compounds, in which it replaces one atom of hydrogen.

When a metal forms two series of salts, the termination *-ic* is always used for the name of that series which contains less of the metal; the termination *-ous* for that which contains more of the metal.

The formulæ of some of the chief compounds of mercury are given in the following list—

	Mercuric.	Mercurous.
Oxide . . .	HgO	Hg_2O
Chloride . . .	$HgCl_2$	$HgCl$
Nitrate . . .	$Hg(NO_3)_2$	$HgNO_3$
Sulphate . . .	$HgSO_4$	Hg_2SO_4

The formulæ of the mercurous compounds in the above list are empirical formulæ, since these compounds decompose when they are heated, and hence their vapour densities and true molecular formulæ are unknown.

It has already been pointed out that the valency of an element in a compound cannot be ascertained until the constitution of the compound is known (p. 200). In the case of the mercurous compounds, the constitution is not certainly known. If these compounds have the simple formulæ given above, mercury acts in them as a univalent element. Many facts, however, point to the probability that these compounds have twice the molecular weight corresponding with this simple formula. Mercurous chloride would thus receive the formula Hg_2Cl_2. In this case the constitution would be represented by the formula $Cl \cdot Hg \cdot Hg \cdot Cl$, in which each atom of mercury is combined both with an atom of chlorine and with a second atom of mercury and is therefore bivalent. As the question is not yet definitely settled, the simple empirical formulæ of the mercurous compounds are here used.

Molecular Weight of Mercury. — The density of mercury vapour is 100 compared with hydrogen, and since the atomic weight is 200, it follows that the molecule of mercury consists of a single atom, so that in this respect the metal resembles zinc and cadmium (pp. 244, 246).

The Mercuric Compounds

Mercuric Oxide (Red Oxide of Mercury), HgO, is left behind as a heavy red powder when mercuric nitrate is gently heated, and is also formed in small amount when mercury is heated to the boiling-point in the air for a considerable time. It can also be obtained as a yellow powder, known as yellow or precipitated mercuric oxide, by adding caustic soda to a solution of a mercuric salt, and heating the hydroxide to 175°,—

$$Hg(NO_3)_2 + 2NaOH = Hg(OH)_2 + 2NaNO_3.$$

$$Hg(OH)_2 = HgO + H_2O.$$

It decomposes when heated into mercury and oxygen, and it was by this process that Priestley first obtained oxygen gas.

It was, moreover, by the formation of this compound and its subsequent decomposition that Lavoisier first clearly proved the presence of oxygen in the air.

EXPERIMENT 111.—Heat 2 or 3 crystals of mercuric nitrate in a dry test-tube—brown fumes are evolved and a residue of mercuric oxide left, which is almost black when hot, red when cold. Shake out the oxide into a second dry test-tube and heat strongly—oxygen is evolved (test by glowing splint), and a mirror of mercury is formed on the tube, which runs into globules when it is rubbed with a glass rod.

Mercuric Chloride, Corrosive Sublimate, $HgCl_2$, cannot be obtained by the action of hydrochloric acid on mercury, but is prepared by heating the sulphate with common salt,—

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4.$$

The mercuric chloride volatilises and condenses in the upper part of the vessel. It is only sparingly soluble in water, 100 parts of which dissolve 7 parts of the salt at 15°, and is also soluble in alcohol and ether. It crystallises in needles, and volatilises without melting when heated in an open tube, but when heated under pressure melts at 288° and boils at 303°. The vapour density has been found to be 135.5, corresponding with the molecular weight 271 and the formula $HgCl_2$.

Mercuric chloride is a violent poison, but in small quantities is a valuable medicine. A dilute solution is largely used as an antiseptic, as it is found to be fatal to all forms of bacteria.

When ammonia is added to a solution of the chloride, a white precipitate is produced which consists of the compound $Hg(NH_2)Cl$, known as *infusible white precipitate.*

EXPERIMENT 112.—To separate portions of a solution of mercuric chloride add—

1. Caustic soda solution—a yellow precipitate of mercuric hydroxide is formed.
2. Ammonia—infusible white precipitate is produced.

Mercuric Iodide, HgI_2, is a beautiful scarlet powder, which is formed when mercury and iodine are rubbed together in a mortar, and is also precipitated when potassium iodide is added to mercuric chloride solution,—

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

The precipitate readily dissolves in an excess of potassium iodide, a double salt being formed. This solution made strongly alkaline with caustic potash or soda is known as *Nessler's reagent*, and is used for the detection of small quantities of ammonia or ammonium salts, with which it produces a brown coloration, whilst a brown precipitate is formed when a larger amount of ammonia is present.

EXPERIMENT 113.—To a solution of mercuric chloride add potassium iodide solution gradually until the scarlet precipitate of mercuric iodide which is first produced has redissolved, and then make strongly alkaline with caustic soda. No precipitate of mercuric hydroxide is produced, but the solution remains clear. Add a few drops of this solution to a solution of ammonium chloride — a thick, brown precipitate is produced. Dilute a fresh portion of ammonium chloride solution and add a few drops of the Nessler's reagent — a yellowish-brown coloration is produced.

Like the chloride the iodide readily volatilises when heated, and forms a colourless vapour, which has the normal density 227, corresponding with the formula HgI_2. As already mentioned mercuric iodide is dimorphous (p. 143).

Mercuric Nitrate $Hg(NO_3)_2$, is prepared by boiling mercury with an excess of nitric acid. When it is treated with water partial decomposition occurs, basic salts being formed.

Mercuric Sulphate, $HgSO_4$, is prepared by boiling mercury with concentrated sulphuric acid, and, like the nitrate, readily forms a basic salt when treated with water.

Mercuric Sulphide, Cinnabar, HgS, is the most important ore of mercury, and occurs as a red crystalline mass. The artificial crystalline sulphide is known as vermilion, and is prepared by heating mercury and sulphur together, or by grinding the two together in the presence of water and a small amount of potash. The sulphide is precipitated as a black amorphous mass when sulphuretted hydrogen is passed into an acid solution of a mercuric salt.

When a small amount of sulphuretted hydrogen is added to an excess of mercuric chloride solution, a white precipitate is first formed, which on the addition of more sulphuretted hydrogen becomes yellow and then black. These differently coloured substances are compounds of mercuric chloride with mercuric sulphide.

The sulphide is insoluble in nitric acid and in hydrochloric acid, but dissolves in aqua regia, and this serves to distinguish it from the sulphides of copper, bismuth, and cadmium, which are soluble in nitric acid; the sulphide is also insoluble in ammonium sulphide.

> EXPERIMENT 114.—To a solution of mercuric chloride gradually add sulphuretted hydrogen water, shaking well after each addition. A white precipitate is first formed, which becomes yellow, orange, and finally black, when an excess of sulphuretted hydrogen is present. Allow the black precipitate to settle, pour off the clear liquid, and show that the precipitate is insoluble in boiling dilute nitric acid, but soluble in aqua regia.

The Mercurous Compounds

The mercuric compounds are converted by metallic mercury and by reducing agents into mercurous compounds, which are reconverted into mercuric salts by oxidising agents.

As the molecular formulæ of these salts are not known, the empirical formulæ are here used.

Mercurous Oxide, Hg_2O, is formed as a dark brown powder when caustic soda is added to a mercurous salt,—

$$2HgNO_3 + 2NaOH = Hg_2O + H_2O + 2NaNO_3.$$

Mercurous Chloride, Calomel, $HgCl$, is precipitated when hydrochloric acid or any chloride is added to a solution of mercurous nitrate. It is usually prepared by grinding together mercury and mercuric chloride and then heating the mixture.

Both the constituents volatilise and combine during condensation to form a white sublimate of mercurous chloride. Calomel readily volatilises when heated, but the vapour is always found to be a mixture of the vapours of mercury and mercuric chloride, so that the true molecular formula of the salt is not known. Calomel is insoluble in water and dilute acids, and can for this reason be readily freed from corrosive sublimate, which is often present in the crude material. All that is necessary is to boil the mass with water, filter and dry.

When it is boiled with aqua regia it is converted into soluble mercuric chloride.

On the other hand, it is formed from mercuric chloride by the action of many reducing agents, especially phosphorous acid (p. 87), and stannous chloride, $SnCl_2$ (p. 357). The latter is a substance which readily combines with chlorine to form stannic chloride, $SnCl_4$. When stannous chloride is brought into contact with mercuric chloride it first produces mercurous chloride,—

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$

If, however, an excess of the stannous salt be present, the mercurous chloride loses the whole of its chlorine, metallic mercury being produced,—

$$SnCl_2 + 2HgCl = SnCl_4 + 2Hg.$$

EXPERIMENT 115.—To 5 cc. of a solution of mercuric chloride add two drops of stannous chloride solution—a white precipitate of calomel is produced.

Now add an excess of stannous chloride and warm—a gray precipitate of finely divided mercury is formed.

Calomel is largely used in medicine, and is much less poisonous than corrosive sublimate.

Ammonia converts calomel into a black mass, which is a mixture of metallic mercury and a complicated compound containing nitrogen.

Mercurous Iodide, HgI, is a dark green insoluble powder.

Mercurous Nitrate, $HgNO_3$, is obtained by dissolving mercury in cold dilute nitric acid, or by digesting mercuric nitrate with metallic mercury,—

$$Hg(NO_3)_2 + Hg = 2HgNO_3,$$

When it is boiled with nitric acid it is converted into mercuric nitrate,—

$$4HgNO_3 + 6HNO_3 = 4Hg(NO_3)_2 + NO + NO_2 + 3H_2O.$$

It is soluble in water, a large amount of which, however, decomposes the salt, basic compounds being precipitated,

EXPERIMENT 116.—Boil a globule of mercury with 5 cc. of dilute nitric acid until all action ceases, taking care that some of the mercury remains. Pour off the solution of mercurous nitrate, and use separate portions of it for the following experiments :—

1. Add hydrochloric acid—a white precipitate of mercurous chloride is produced, which becomes black when excess of ammonia is added.
2. Add potassium iodide—a dark green precipitate of mercurous iodide is formed.
3. Add caustic soda—a dark brown, almost black, precipitate of mercurous oxide is formed.
4. Add about one-third the volume of strong nitric acid and boil. Brown fumes are evolved, and mercuric nitrate formed. Add excess of caustic soda—a yellow precipitate of mercuric hydroxide is produced.

Detection of Mercury.—The dry tests for the detection of mercury depend on the fact that all the compounds of mercury yield the metal when they are heated with sodium carbonate and a reducing agent, and that the metal thus produced volatilises. The reaction is therefore carried out in a bulb-tube (as in the case of arsenic, p. 94), in the stem of which the mercury condenses in minute globules.

Each of the two series of mercury salts has its own characteristic reactions, those of the mercuric compounds being quite different from those of the mercurous salts. This is in accordance with the general rule that the reactions of different series of salts of the same metal are quite as distinct as those of different metals. Thus the mercurous salts give a white insoluble precipitate of mercurous chloride with hydrochloric acid, and are, therefore, precipitated in the ordinary course of analysis along with the salts of silver and lead. The mercuric salts, on the other hand, yield no precipitate with hydrochloric acid, but are precipitated by sulphuretted hydrogen in acid solution along with the salts of copper, bismuth, cadmium, arsenic, antimony, and tin. Mercuric sulphide differs from all the other sulphides which are insoluble in hydrochloric acid and in ammonium sulphide, by being insoluble in nitric acid. An excellent test for the mercuric salts is the production of mercurous chloride by the action of hydrochloric acid and a reducing agent, such as stannous chloride.

SUMMARY

Mercury is liquid at the ordinary temperature and boils at 357°. It forms two series of salts—the mercuric salts, HgR'_2, and the mercurous salts, HgR'. The mercuric salts are converted by metallic mercury or reducing agents into mercurous salts; whilst the latter are reconverted into mercuric salts by treatment with oxidising agents.

The mercuric salts are in many respects similar in properties to those of zinc, but are as a rule less soluble. The black amorphous sulphide is insoluble in hydrochloric or nitric acid, but dissolves in *aqua regia*.

The mercurous salts, on the other hand, more closely resemble the silver salts and the cuprous salts (p. 270). The chloride is insoluble in water and the sulphate only sparingly soluble.

General Properties of the Elements of the Zinc Group

The metals magnesium, zinc, cadmium, and mercury are closely allied in properties. They are all white metals and oxidise when heated in the air or oxygen, whilst they do not decompose water at the ordinary temperature. They all melt and boil at moderate temperatures, the melting and boiling-points becoming lower as the atomic weight increases, whilst the specific gravity increases. This is well shown in the following table of physical properties :—

	Magnesium.	Zinc.	Cadmium.	Mercury.
Atomic weight . . .	24.32	65.37	112.40	200.0
Melting-point . . .	633°	419°	322°	−38.8°
Boiling-point . . .	1100°	918°	778°	357°
Specific gravity . . .	1.75	6.9	8.6	13.59

These elements all form series of salts in which they are bivalent, and form oxides and hydroxides which are insoluble in water, as are also their carbonates, phosphates, and sulphides. On the other hand, the chlorides, nitrates, and sulphates are all soluble in water.

The hydroxides of zinc and cadmium act as weak acids towards strong-bases, whilst those of magnesium and mercury do not. All the hydroxides readily dissolve in acids forming salts. Magnesium, zinc, and cadmium dissolve readily in dilute acids, zinc and cadmium being also soluble in alkalis. Mercury, on the other hand, is insoluble in dilute hydrochloric or sulphuric acid. The stability of the oxides decreases as the atomic weight rises, mercuric oxide being easily decomposed by heat, whereas magnesium oxide cannot easily be decomposed even at high temperatures and in the presence of reducing agents, whilst the oxides of zinc and cadmium are intermediate between these. Mercury differs from the other three metals of the group in forming a series of salts of the empirical formula HgR'; these to some extent resemble the salts of silver and of lead in their properties, the chloride being insoluble in water.

Exercises on Lesson XXIV

1. What is the chief ore of mercury, and how is the metal obtained from it?

2. Describe what happens when the following substances are heated in the air: (*a*) mercury, (*b*) mercuric oxide, (*c*) mercurous chloride, (*d*) mercuric nitrate.

3. Describe the preparation of mercuric nitrate and mercurous nitrate from the metal. How can each of these salts be converted into the other?

4. What is meant by an amalgam? How can amalgams be (*a*) prepared, (*b*) decomposed?

5. 110 cc. of mercury vapour, measured at 760 mm. and 409°, weigh 0.393 gram. Calculate the molecular weight of mercury. The atomic weight of mercury being 200, what is the molecular formula?

6. 7.65 grams. of mercuric chloride were distilled with lime and the metallic mercury liberated was found to weigh 5.65 grams. Calculate the equivalent of mercury. The equivalent of chlorine $= 35.5$.

7. Contrast the physical and chemical properties of mercury with those of magnesium and zinc.

8. Compare the properties of the metals of the zinc group with those of the alkaline earth metals.

LESSON XXV

THE METALS OF THE COPPER GROUP

COPPER. SILVER. GOLD.

Copper, Cu, 63.57

THE name copper (Latin *cuprum*, from which the symbol for the element is taken) is derived from the name of the island of Cyprus, where the metal was produced, and since this island was sacred to Venus, the name of this goddess was always associated with copper by the alchemists, who were well acquainted with the metal. Ores of copper are found in many parts of the world, the most important being the sulphide, CuS, known as *copper glance*, *copper pyrites*, $CuFeS_2$, and the basic carbonate, known as *malachite*. The metal is also found in the free state, often in large masses, the region near Lake Superior being very rich in this native copper. Copper is extracted from its ores on a very large scale by processes which will be better understood after some of the properties of the metal have been studied (p. 265). Either in the pure state or alloyed with other metals copper is used for an immense variety of industrial purposes.

Properties of Metallic Copper.—Pure copper has a very decided red colour, which is best seen by bending a strip of the clean metal at an acute angle, and looking at the surface near the bend. The light is there reflected from the copper surfaces several times and the colour thus intensified. Copper has the specific gravity 8.9, and melts at the high temperature of 1080.5°. It is, moreover, very soft and tough, so that it can be rolled and hammered into very thin leaf (Dutch metal), and drawn out into very thin wire. It is an extremely good conductor of heat and electricity, and is largely used for mains, cables, and wires for conveying the electric current.

Alloys of Copper.—Copper forms a number of very valuable alloys, the most important of which are *bronze* and *gun-metal* (p. 352), containing copper and tin; *German silver* (p. 394), containing copper and nickel; and *brass.* The last of these usually contains about 2 parts of copper to 1 of zinc, and is prepared by adding zinc to melted copper. It has a yellow colour, and is malleable and easily worked, and at the same time much harder and stronger than pure copper. Copper is also frequently alloyed with silver, gold, and aluminium, the alloys being described under these metals.

Equivalent and Atomic weight of Copper.—Like mercury (p. 251) copper forms two well-defined series of salts, which are known as the cupric and the cuprous salts, in which it has two different equivalents. Thus, it has been found by careful analysis that in cupric oxide 31.785 parts of copper are united with 8 parts of oxygen, whilst in cuprous oxide twice this amount of copper, 63.57 parts, are combined with the same amount of oxygen.

The atomic weight of the metal has been decided from the specific heat, which is 0.94. Hence the atomic weight must be about $\frac{6.4}{0.94} = 68$. The correct atomic weight is, therefore, taken as 63.57 and we see that in the cupric compounds the atom of copper replaces two atoms of hydrogen, whilst in the cuprous compounds it only replaces one atom. These two series of compounds, therefore, correspond in composition with the mercuric and mercurous salts (p. 253), and their empirical formulæ, as may be seen in the following list, are precisely analogous to the formulæ of the corresponding mercury compounds—

	Cupric.	Cuprous.
Oxide	CuO	Cu_2O
Sulphide	CuS	Cu_2S
Chloride	$CuCl_2$	$CuCl$

As in the case of the corresponding mercury compounds some doubt exists as to the true molecular formula of the cuprous compounds. It is, however, most probable that the chloride has the formula Cu_2Cl_2, its constitutional formula being Cl·Cu·Cu·Cl.

Metallic copper does not decompose water either at the ordinary temperature or when heated to redness in steam. It however, readily combines with oxygen when it is heated in the air or oxygen, forming the two oxides.

EXPERIMENT 117.—Heat a few pieces of thick copper wire for some time in a small porcelain basin over a large flame. The metal oxidises and becomes black on the surface, and if this black layer be stripped off it is found to be red on the under surface.

The red lining of the layer of oxide is cuprous oxide, Cu_2O, whereas the outer black portion is cupric oxide, CuO.

Both the oxides readily lose their oxygen to reducing agents and are converted into metallic copper, and hence copper does not act as a strong reducing agent, as do the metals sodium and magnesium, which form very stable oxides. On the other hand, the oxides readily act as oxidising agents, as do the oxides of silver and mercury.

EXPERIMENT 118.—Mix a few grams. of charcoal with copper oxide, place the mixture in a hard glass-tube closed at one end, and provided with a cork and glass conducting-tube bent at a right angle, and dipping into some lime-water. When the mixture is heated the carbon burns at the expense of the oxygen of the copper oxide, carbon dioxide is evolved, and metallic copper formed,—

$$2CuO + C = 2Cu + CO_2$$

Copper is not acted on to an appreciable extent by dilute sulphuric or hydrochloric acid, and in this respect resembles both mercury and silver. Concentrated sulphuric acid acts upon it when heated, sulphur dioxide being evolved and copper sulphate formed (compare mercury and silver),—

$$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2.$$

Nitric acid, dilute or concentrated, acts on it readily, oxides of nitrogen being evolved and copper nitrate produced (R. and L., p. 156),—

$$3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 2NO + 4H_2O.$$

The action of nitric acid on metals is a very complex one and as a rule yields instead of hydrogen a mixture of products derived from nitric acid by reduction. The exact mixture produced in any particular case depends on the temperature, the concentration of the acid and the nature of the metal.

The equations generally stated as representing the change, such as that given above, are therefore only applicable to a part of the reaction which occurs. The nitric oxide formed from copper according to the above equation, for example, is usually accompanied by nitrogen peroxide, formed as follows,—

$$Cu + 4HNO_3 = 2NO_2 + Cu(NO_3)_2 + 2H_2O$$

When a more concentrated acid is used, this becomes the chief reaction. The oxides NO_2, NO, N_2O, free nitrogen, ammonia and hydroxylamine are all formed by the action of metals on nitric acid under the proper conditions. The action of the acid moreover seems to depend on the presence of nitrous acid, as pure nitric acid has no action on metals.

EXPERIMENT 119.—Treat some copper turnings in a test-tube with the following acids, both dilute and concentrated, and note the action in each case, first in the cold and then on warming :—

Hydrochloric acid, nitric acid, sulphuric acid.

The Metallurgy of Copper.—The ore which is most largely employed as a source of metallic copper is copper pyrites, which in the pure state has the composition $CuFeS_2$, but usually occurs mixed with iron pyrites, FeS_2, and often with the sulphides of zinc, lead, and other metals. In order to obtain metallic copper from this ore a somewhat lengthy series of operations is necessary. The process depends on the fact that when the ore is calcined or roasted, *i.e.* heated in a current of air, the iron and other metals are oxidised before the copper, so that when only a small amount of air is admitted, a portion of the iron and the other metals is oxidised, whilst most of the copper remains combined with sulphur.

In order to remove the metallic oxides thus formed, the roasted ore is next smelted, or melted up with sufficient silica, in the form of sand or quartz, to unite with the oxides and form an easily fusible silicate, such as $FeO \cdot SiO_2$ or $FeSiO_3$, which is known as *slag*. This floats on the denser mass of fused sulphides, and can readily be run off and thus separated from the latter.

1. These two processes are carried out with the ore, and the product is then known as *coarse metal*, and consists of

almost equal amounts of copper, iron and sulphur, whereas the original ore often contains only 10 to 20 per cent of copper.

2. The coarse metal is then again subjected to similar treatment. It is first calcined, by which process most of the remaining iron is converted into oxide, whilst the copper is left for the most part still combined with sulphur. Silica is then added, and the whole mass melted in a reverberatory furnace, the slag being separated as before. The product is known as *white metal*, and has almost the composition of cuprous sulphide, Cu_2S, but contains a small amount of iron and other impurities.

3. The white metal is then roasted in a reverberatory furnace in a slow current of air, and the sulphur is thus removed in the form of sulphur dioxide, metallic copper being left behind,—

$$Cu_2S + O_2 = 2Cu + SO_2.$$

The metal thus produced is full of cavities caused by the escaping sulphur dioxide, and is therefore known as *blister copper.*

4. The metal is then refined in order to free it from the foreign metals which it still contains. This is done by melting the blister copper and exposing it to air, which converts the foreign metals into their oxides; these float as a scum on the surface of the copper and are removed. A small amount of copper oxide is also produced, which would render the finished metal hard and brittle if it were allowed to remain. This is removed by the process of *poling*, which consists in stirring the molten metal with a pole of green wood, the gases from which reduce the oxide to metal and thus leave the copper soft and tough.

It will be observed that the whole of the sulphur of the ore is removed in the form of sulphur dioxide, whilst the iron passes into the slag as ferrous silicate.

The various stages of the process may be summarised as follows:—

1. *a.* Roasting for coarse metal.
   b. Smelting for coarse metal.
2. *a.* Roasting for white metal.
   b. Smelting for white metal.
3. Roasting for blister copper.
4. Refining.

The foregoing is the process chiefly employed in England, but numerous other dry processes exist, for the details of which a work on metallurgy must be consulted. The crude copper obtained by smelting is frequently refined by a process of electrolysis which is described on p. 306.

Extraction of Copper by the Wet Method.—The ore is heated with common salt and then washed with water, which extracts the copper chloride. The copper is precipitated from the solution by metallic iron, and is then fused and refined,—

$$CuCl_2 + Fe = FeCl_2 + Cu.$$

This process is largely used for the extraction of the small percentage of copper which is present in the pyrites used for the manufacture of sulphuric acid. The pyrites is burnt in the usual way for the production of sulphur dioxide, and the burnt residue treated as described above.

The Cupric Compounds

Cupric Oxide, Black Oxide of Copper, CuO, is formed, as already mentioned, when copper is heated for a considerable time in a good supply of air, and is often made by heating thin copper wire, the form of which it retains. It can also be prepared by heating the carbonate or nitrate,—

$$2Cu(NO_3)_2 = 2CuO + 4NO_2 + O_2.$$

It is readily reduced to metallic copper by hydrogen, coal-gas, or carbon, and is used in organic analysis for the combustion of organic compounds. The following equation, for example, represents its action on alcohol,—

$$6CuO + C_2H_6O = 2CO_2 + 3H_2O + 6Cu.$$

When fused with borax it gives rise to a blue mass, whilst it colours glass green.

Cupric Hydroxide, $Cu(OH)_2$, is not formed by the direct action of water on the oxide, but is precipitated as a light blue mass when caustic soda is added to a solution of copper sulphate. If the precipitation be carried out in the boiling solution, the hydroxide loses part of its water and becomes brown. Copper is frequently estimated gravimetrically by being precipitated in the form of this hydroxide, which, after careful washing, is dried, converted by heat into the oxide, and weighed,—

$$Cu(OH)_2 = CuO + H_2O.$$

The hydroxide dissolves readily in acids, forming the cupric salts, which form blue or green solutions in water.

EXPERIMENT 120.—1. Heat a crystal of copper nitrate in a dry test-tube. Water is given off, and then the nitrate decomposes—a brown gas is evolved and black copper oxide left behind.

2. To a cold solution of copper sulphate add caustic soda solution—a light blue amorphous precipitate is produced, insoluble in excess of caustic soda, readily soluble in acids.

3. To a boiling solution of copper sulphate add caustic soda solution—a brown precipitate is formed.

Cupric Sulphate, $CuSO_4 + 5H_2O$, has long been known as blue vitriol or blue stone. It is often formed in nature by the partial oxidation of the sulphide, and is artificially prepared on the large scale by roasting the sulphide,—

$$CuS + 2O_2 = CuSO_4,$$

and extracting the resulting sulphate by water. It may be prepared on the small scale by heating copper in the air and dissolving the resulting oxide in dilute sulphuric acid. It forms blue crystals (Fig. 34, p. 137), and is readily soluble in water, forming a solution which is acid to litmus paper (p. 160). As previously described (p. 20), the salt loses water and becomes white when heated to 200°.

EXPERIMENT 121.—Dissolve about 5 grams. of copper oxide in dilute sulphuric acid (1 of acid to 3 of water), taking care that some of the oxide is left undissolved; filter and evaporate until crystals begin to form on the surface. On cooling copper sulphate crystallises out.

When ammonia solution is added in excess to copper sulphate solution, the precipitate which is at first formed redissolves, and a deep blue liquid is formed, which contains *cuprammonium sulphate*, $CuSO_4 + 4NH_3 + H_2O$, and this salt is deposited in deep blue crystals when alcohol is added to the solution. It may be regarded as hydrated copper sulphate, $CuSO_4 + 5H_2O$, in which four of the molecules of water have been replaced by ammonia, and this ammonia is evolved when the salt is heated or exposed to the air, just as is the case with the water of the crystallised copper sulphate. Similar compounds are formed by other cupric salts.

EXPERIMENT 122.—To 5 cc. of a cold saturated solution of copper sulphate add strong ammonia until the precipitate redissolves—a deep blue solution results.

Cupric Sulphide, CuS, is produced as a black precipitate when sulphuretted hydrogen is passed into a solution of a cupric salt. It is insoluble in hydrochloric acid, but dissolves in nitric acid. The moist precipitated sulphide absorbs oxygen from the air, forming the soluble sulphate.

EXPERIMENT 123.—Pass sulphuretted hydrogen into 5 cc. of a solution of copper sulphate. Filter, wash with water, and treat a portion of the precipitate with hot dilute nitric acid. Allow the remainder of the precipitate to remain on the filter paper for half an hour, and again wash with water; the filtrate comes through blue, and contains copper sulphate, formed by the oxidation of the sulphide by the atmospheric oxygen.

Cupric Nitrate, $Cu(NO_3)_2$, is prepared by dissolving metallic copper in nitric acid and evaporating the solution. It forms blue crystals, containing 3 molecules of water, and decomposes when heated, leaving the black oxide.

EXPERIMENT 124.—Dissolve 5 grams. of copper turnings in hot dilute nitric acid (1 of acid to 3 of water), evaporate to small bulk, cool and filter off the crystals of the nitrate.

Cupric Chloride, $CuCl_2$, is obtained in a similar manner to the other salts by dissolving the oxide or carbonate in hydrochloric acid. It forms soluble green crystals, $CuCl_2 + 2H_2O$, which lose their water on heating and leave the anhydrous chloride as a dark brown mass. When more strongly heated the chloride decomposes, forming cuprous chloride and free chlorine,—

$$2CuCl_2 = Cu_2Cl_2 + Cl_2.$$

Cupric Carbonate is not known in the pure state. The precipitate produced by sodium carbonate in a solution of a cupric salt and the beautiful green mineral malachite are both basic carbonates.

The latter is a valuable ore of copper, and is also used for ornamental purposes. The green "rust" formed by the action of air and water on copper has the same composition as malachite, and is often known as *verdigris*, although this name is also applied to copper acetate.

The Cuprous Compounds

The cuprous compounds contain a larger proportion of copper than the cupric compounds, from which they are prepared by treatment with metallic copper, or by removing a portion of the element with which the copper is combined.

Cuprous Chloride, Cu_2Cl_2, can be prepared from cupric chloride by both of the methods just referred to. When an acid solution of cupric chloride is treated with sulphurous acid, the following reaction occurs,—

$$2CuCl_2 + H_2SO_3 + H_2O = Cu_2Cl_2 + 2HCl + H_2SO_4,$$

and cuprous chloride is precipitated as a white powder. It is usual to employ a mixture of the cheaper cupric sulphate with sodium chloride instead of cupric chloride.

Cuprous chloride can also be prepared by boiling cupric oxide with metallic copper, in the form of turnings, and concentrated hydrochloric acid. The oxide dissolves, forming cupric chloride, which is then acted on by the metallic copper,—

$$CuCl_2 + Cu = Cu_2Cl_2.$$

The cuprous chloride remains dissolved in the hydrochloric acid, but is precipitated by the addition of water. It is a white powder, which, like silver chloride, becomes coloured violet on exposure to light. It dissolves easily in ammonia, forming a colourless solution if all oxygen has been excluded. This solution very readily absorbs oxygen, and becomes blue from the formation of a cupric salt, and also absorbs both carbon monoxide and acetylene, and is much used in gas analysis for the estimation of these two gases and in water analysis for the estimation of dissolved oxygen. When strongly heated cuprous chloride volatilises, forming a vapour which has the density 99, corresponding with the formula Cu_2Cl_2

EXPERIMENT 125.—1. Place in a flask 5 grams. of copper turnings, 6 grams. of cupric oxide, and 50 cc. of concentrated hydrochloric acid and boil for 15 minutes. Pour the resulting solution into 500 cc. of water, allow to settle, wash by decantation, and finally filter off the white cuprous chloride which is formed.

2. Dissolve 25 grams. of crystallised copper sulphate and 12 grams. of common salt in about 70 cc. of water in a beaker, and pass in sulphur dioxide until the liquid smells strongly of the gas, even after standing for some time. Cuprous chloride slowly crystallises out. Filter off, wash, drain, and allow to dry. About 7 grams. of the chloride should be obtained.

The sulphur dioxide may be prepared by the action of hot sulphuric acid on copper turnings, or, more conveniently, by gradually adding concentrated sulphuric acid to a saturated solution of sodium bisulphite. The cuprous chloride becomes slightly yellow when washed with water, and when dried in the air becomes gradually green, owing to the formation of an oxychloride.

3. Dissolve 1 gram. of cuprous chloride in ammonia and pour the solution into a jar of acetylene. The gas is absorbed and a thick red precipitate of cuprous acetylide produced. The acetylene may be prepared by placing a small piece of calcium carbide in the water of a pneumatic trough, and inverting over it a jar filled with water.

Cuprous Oxide, Red Oxide of Copper, Cu_2O, is formed when cupric oxide is very strongly heated, one-half of the oxygen being evolved, and it is therefore also produced when metallic copper is strongly heated in the air. It is, however, best prepared by warming a cupric salt in presence of caustic soda with some reducing agent, such as grape sugar or invert sugar, when the oxide is precipitated as a bright red crystalline powder.

EXPERIMENT 126.—Add 1 cc. of a 10 per cent solution of grape sugar to 5 cc. of 3 per cent copper sulphate solution, and then add an excess of caustic soda solution. In presence of the sugar the copper hydroxide redissolves, forming a deep blue solution. Warm gently—a bright red precipitate of cuprous oxide is formed.

When cuprous chloride is decomposed by caustic soda a yellow mass of *cuprous hydroxide*, $Cu_2(OH)_2$, is produced.

Cuprous oxide imparts a red colour to the borax bead, and hence the blue copper bead becomes red when it is strongly heated in the reducing flame.

Cuprous Iodide, Cu_2I_2, is the only known iodide of copper. When potassium iodide is added to copper sulphate, this iodide is formed together with free iodine, instead of the cupric iodide which might have been expected,—

$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4.$$

Cupric salts can be estimated volumetrically by means of this reaction, the amount of iodine liberated being ascertained by titration with sodium thiosulphate (p. 165). In order to prepare the pure iodide and utilise the whole of the iodine, a reducing agent such as sulphurous acid or ferrous sulphate is added,—

$$2CuSO_4 + 2KI + H_2SO_3 + H_2O = Cu_2I_2 + 2KHSO_4 + H_2SO_4.$$

This reaction may be employed for the qualitative separation of iodides from chlorides and bromides, since the last two do not give any precipitate with copper sulphate and sulphurous acid, except in concentrated solutions.

Cuprous iodide, like the chloride, is a white powder which is insoluble in water.

EXPERIMENT 127.—1. To 5 cc. of a 10 per cent solution of potassium iodide add copper sulphate solution—a brown solution and a thick precipitate are formed. Filter and wash. The white precipitate is cuprous iodide, whilst the filtrate contains free iodine (test by starch solution).

2. To a second 5 cc. of potassium iodide solution add a crystal of sodium sulphite and acidify with dilute sulphuric acid, then add copper sulphate solution until the supernatant liquor is green. No iodine is liberated in

this case, and twice as much cuprous iodide is formed as in the preceding experiment.

Cuprous Sulphide, Cu_2S, is a black mass which is produced when copper burns in sulphur vapour, and when cupric sulphide is gently heated in absence of air,—

$$2CuS = Cu_2S + S.$$

Detection of Copper.—All copper compounds yield the metal when they are strongly heated with reducing agents in the reducing flame on charcoal. Moreover, they colour the borax bead blue in the oxidising flame and red in the reducing flame, a colourless bead being obtained when the reduction is incomplete. Compounds of copper when moistened with strong hydrochloric acid colour the Bunsen flame a brilliant green.

Copper is precipitated from acid solutions of the cupric salts by sulphuretted hydrogen in the form of cupric sulphide, which is insoluble in ammonium sulphide and dissolves in hot dilute nitric acid, forming a pale blue solution of the nitrate. Ammonia added to this produces a deep blue coloration.

SUMMARY

Copper is a red metal, which only melts at a high temperature. It becomes oxidised when it is heated in the air, but the oxide is easily decomposed by reducing agents. It dissolves readily in nitric acid and in hot sulphuric acid, but not in hydrochloric acid.

Copper forms two series of salts: the cupric salts, in which each atom of copper replaces two atoms of hydrogen, and the cuprous salts, in which each atom of copper replaces one atom of hydrogen.

The *cuprous salts* readily undergo oxidation and pass into the cupric salts. The best known are the chloride and iodide, which are white and very sparingly soluble in water. Cuprous oxide is red and has basic properties, whilst the sulphide is black. The *cupric salts* form blue or green crystalline hydrates, and aqueous solutions of the same colour, whilst the anhydrous salts are often of a different colour. The chloride, nitrate, and sulphate are all readily soluble in water; the carbonate and sulphide are insoluble. The oxide is black and forms salts with acids but not with bases.

EXERCISES ON LESSON XXV

1. What are the chief physical properties of copper?

2. What are the chief ores of copper? How can the metal be obtained from copper pyrites?

3. Describe the action of (*a*) hydrochloric acid; (*b*) nitric acid; (*c*) sulphuric acid on copper. How does this metal differ from zinc in its behaviour to these acids?

4. How would you attempt to prepare pure copper oxide from brass?

5. How are copper sulphate and copper nitrate prepared? How much metallic copper is contained in one ton of crystallised copper sulphate?

6. What occurs when the following substances are added to a solution of copper sulphate:—(*a*) metallic iron; (*b*) metallic mercury; (*c*) caustic soda solution; (*d*) potassium iodide solution; (*e*) ammonia?

7. Describe the preparation of cuprous chloride and cuprous oxide from copper sulphate. How can cuprous chloride be converted into cupric chloride?

8. 1.253 grams. of pure cupric oxide yield 1 gram. of copper when heated in hydrogen. Calculate the equivalent of copper.

LESSON XXVI

THE METALS OF THE COPPER GROUP (*Cont.*)

Silver, Ag, 107.88

SILVER was one of the seven metals known to the early alchemists, and was associated by them with the moon, the name Luna and the symbol of the crescent moon being given to it. This old association still exists in the common name given to silver nitrate when used as a caustic, it being termed *lunar* caustic. The Latin name for this metal is *argentum*, from which the modern symbol for the metal is derived.

The metal is sometimes found in the free state, but more usually combined with sulphur, antimony or chlorine, as silver sulphide or *silver glance*, Ag_2S, silver thiantimonite or *pyrargyrite*, Ag_3SbS_3, and silver chloride or *horn silver*, $AgCl$. It also occurs as the sulphide in *galena* or lead sulphide, and in the process of lead manufacture from this ore, the silver remains with the lead.

Properties of Metallic Silver.—Silver is a white metal which has the density of 10.5 and melts at 960°. It conducts both heat and electricity better than any other metal and can readily be drawn out into wire and hammered into thin leaf. A very thin film of the metal transmits blue light. At the high temperature of the oxyhydrogen flame or the electrical furnace silver can readily be distilled, forming a blue vapour. The fused metal absorbs oxygen from the air, but this is given out with effervescence as the metal cools, this phenomenon being known as the "spitting" of silver.

Silver is not altered by being heated in the air, and does not form an oxide under these circumstances. It behaves towards acids in a similar manner to copper, being dissolved by nitric acid with evolution of oxides of nitrogen, and by concentrated boiling sulphuric acid with evolution of sulphur dioxide, whilst it is insoluble in hydrochloric acid. It readily combines with sulphur to form the insoluble black sulphide, and with chlorine to form the insoluble chloride.

Atomic Weight of Silver—Formulæ of the Silver Salts. — The equivalent of silver has been very carefully determined in the manner which has already been described (p. 63), and has been found to be 107.88 The metal does not form any volatile compounds, and its atomic weight has therefore been settled by the atomic heat method, and has thus been found to be identical with the equivalent.

Silver forms only one series of salts, and in these replaces a single atom of hydrogen, so that the formulæ of these salts are analogous to those of the salts of potassium and sodium, as well as to the empirical formulæ of the cuprous and aurous salts.

Alloys of Silver.—Pure silver, like pure copper, is too soft to be used for coinage or jewellery, and it is therefore usually alloyed with a certain amount of copper. The standard British coinage contains 7.5 per cent of copper or 925 parts of silver per thousand, and has been made of this particular percentage since the year 1477.

Preparation of Pure Silver.—In order to prepare pure silver from the alloy with copper, the latter is dissolved in nitric acid, which converts both the metals into their nitrates. Hydrochloric acid is then added which precipitates the silver in the form of the insoluble chloride, whilst the copper remains in solution. The silver chloride is then filtered off, well washed, and converted by reduction into metallic silver. This may be done in several ways, the most convenient of which on the small scale is to boil the chloride with pure caustic soda and grape sugar, and then filter and wash the mass obtained, or to reduce the chloride by means of pure zinc and dilute sulphuric acid, or by heating it in a current of hydrogen.

EXPERIMENT 128.—Dissolve about 0.5 – 1 gram. of ordinary silver coin (half a threepenny piece) in hot dilute nitric acid (1 of concentrated acid to 1 of water), dilute with water, and add hydrochloric acid until no further precipitate is produced. Allow to settle, pour off the clear liquid, add hot distilled water, and repeat this washing by decantation until the clear liquid is free from hydrochloric acid and gives no precipitate with silver nitrate solution. Add two or three fragments of pure zinc and 25 cc. dilute sulphuric acid, and stir at intervals until all the zinc has been dissolved. Boil, allow to settle, and wash the reduced silver by decantation until it is free from acid.

The Metallurgy of Silver. — The process which is adopted for the extraction of silver from its ores depends largely upon the character of the latter and on the amount of fuel which is available. In England the ores are decomposed by being heated with metallic lead, the excess of which forms an alloy with the silver,—

$$2AgCl + Pb = 2Ag + PbCl_2.$$

In order to separate these two metals a process known as *cupellation* is adopted, which depends on the fact that silver does not unite with oxygen when it is heated in the air, whereas lead forms an easily fusible oxide, termed litharge. The alloy of the two metals is heated in a current of air on a hearth made of bone-ash or fire-clay, which is termed a *cupel*. The lead is thus gradually converted into litharge, which flows away in the molten state, whilst the silver is left behind. A large amount of silver is also extracted by this method from the metallic lead obtained by the smelting of galena. A concentrated alloy of silver is first obtained by a process which is described under lead (p. 363), and this is then cupelled.

In Mexico, where fuel is scarce, an entirely different process is employed, the silver being converted into an amalgam with mercury. The ore is finely ground with water and is then thoroughly mixed with common salt, and afterwards with impure copper sulphate, metallic mercury being subsequently added. Copper chloride is formed, and this converts the silver sulphide present into chloride,—

$$2CuCl_2 + 2Ag_2S = 4AgCl + Cu_2S + S.$$

The silver chloride thus produced, together with that originally present in the ore, is decomposed by the mercury, yielding metallic silver and mercurous chloride,—

$$AgCl + Hg = HgCl + Ag.$$

The silver forms an amalgam with the excess of mercury, and this is washed, strained through canvas, and distilled from an iron retort. The mercury volatilises, leaving the metallic silver behind.

Silver is also extracted from certain ores in the wet way. The roasted ore is first heated with salt which converts the silver into the chloride. This is then dissolved out by means of sodium thiosulphate solution and the silver precipitated by sodium sulphide solution. The sodium thiosulphate is thus regenerated and is used over again,—

$$2AgCl + 3Na_2S_2O_3 = Ag_2S_2O_3 \cdot 2Na_2S_2O_3 + 2NaCl.$$
$$Ag_2S_2O_3 \cdot 2Na_2S_2O_3 + Na_2S = Ag_2S + 3Na_2S_2O_3.$$

The resulting silver sulphide is then roasted in the air and the crude silver finally melted with lead and cupelled.

Compounds of Silver

Silver Nitrate, $AgNO_3$, is prepared by dissolving the metal in nitric acid and evaporating to dryness. It crystallises in plates and is very readily soluble in water. Since most of the silver salts are insoluble in water the nitrate is largely used for the preparation of the remaining salts for use in photography and for electroplating, etc., as well as in analytical chemistry for the detection of many acids, which form characteristic silver salts; when cast into thin sticks or pencils it is a valuable surgical material, *lunar caustic.* The nitrate decomposes when strongly heated, metallic silver being produced.

EXPERIMENT 129.—1. Heat a portion of the metallic silver obtained in Experiment 128 with dilute nitric acid, filter if necessary, and evaporate to complete dryness. The residue consists of silver nitrate, which must be gently heated on a sand-bath until it melts, in order to remove free nitric acid.

2. Heat a small portion of the nitrate strongly in a test-tube—brown fumes are evolved and metallic silver left.

Silver Oxide, Ag_2O, is a brown powder which is formed when pure caustic soda is added to a solution of silver nitrate,—

$$2AgNO_3 + 2NaHO = Ag_2O + H_2O + 2NaNO_3.$$

It dissolves in ammonia, but is insoluble in caustic soda. When it is heated it decomposes into silver and oxygen,—

$$2Ag_2O = 4Ag + O_2.$$

The solution obtained by adding ammonia to silver nitrate until the precipitated oxide is redissolved, deposits a bright film of silver when it is heated with grape sugar, milk sugar, or a tartrate, the oxide of silver being reduced and the organic compound oxidised,—

$$Ag_2O + \text{organic compound} = 2Ag + [O + \text{organic compound}].$$

This process is used for producing a film of bright silver on the mirrors of reflecting telescopes.

EXPERIMENT 130.—1. To 5 cc. of a 0.5 per cent solution of silver nitrate solution add a drop of a solution of pure caustic soda—a brown precipitate of silver oxide is formed, which is insoluble in excess.

2. To a second 5 cc. add dilute ammonia solution until the brown precipitate redissolves. Then add a few drops of a solution of grape sugar and warm gently—a bright mirror of silver is deposited on the walls of the test-tube.

Silver Chloride, AgCl, is formed as a white curdy precipitate when hydrochloric acid or a soluble chloride is added to a solution of silver nitrate. It is also found as a mineral, known from its semi-transparent appearance as *horn silver*. The chloride is readily soluble in dilute ammonia, forming a compound, $2AgCl + 3NH_3$. Silver is usually estimated gravimetrically in the form of silver chloride, which is practically insoluble in water and can be melted without undergoing any decomposition. The volumetric estimation of soluble chlorides also depends on the formation of this salt. For this purpose a standard solution of silver nitrate is used, and this is added to the solution containing the chloride (to which a few drops of potassium chromate solution have been added), until the whole of the chloride has been precipitated. As soon as this is the case the further addition of silver nitrate produces a permanent red precipitate of silver chromate, thus indicating the end of the reaction.

EXPERIMENT 131.—1. To 1 cc. of a 10 per cent solution of potassium chromate add a few drops of silver nitrate solution—a red precipitate of silver chromate is formed. To this add a few drops of a solution of sodium chloride and shake—the red precipitate is decomposed and white silver chloride formed.

This is due to the fact that silver chromate is decomposed by chlorides, and is therefore not formed until the whole of the latter have been precipitated.

2. *To this solution* now add silver nitrate gradually, shaking after each addition; as soon as all the chloride has been decomposed, a permanent red precipitate of silver chromate is formed.

Silver Bromide, AgBr, is a pale yellow powder which is formed when bromine acts on silver, and when potassium bromide is added to a solution of silver nitrate. This compound is insoluble in nitric acid, but is much less readily soluble in dilute ammonia than the chloride.

Silver Iodide, AgI, is an insoluble yellow powder which closely resembles the bromide, but is insoluble in dilute ammonia, and only very sparingly soluble in concentrated ammonia.

EXPERIMENT 132.—1. To 5 cc. of 0.5 per cent silver nitrate solution add excess of potassium bromide solution—a pale yellow precipitate is produced which is insoluble in nitric acid, but is soluble in a large amount of dilute ammonia.

2. To 5 cc. of silver nitrate solution add excess of potassium iodide solution, and test the solubility of the precipitate in nitric acid and ammonia.

Action of Light on the Silver Salts; Photography.—When silver chloride is exposed to light it becomes violet.

EXPERIMENT 133.—To a solution of silver nitrate add a slight excess of sodium chloride solution, and wash well by decantation until a portion of the clear liquid gives no precipitate with silver nitrate. Expose the precipitate in presence of a little water to sunlight for half an hour, filter and add silver nitrate—a white precipitate is at once produced.

This shows that chlorine is evolved when the chloride blackens under water. The amount of the chloride which undergoes the change is, however, very small, and no change occurs at all in the absence of air or moisture. The amount of chlorine evolved under the action of light becomes greater when some substance capable of absorbing the chlorine, such as excess of silver nitrate, is present.

This decomposition of silver chloride is made use of for the production of photographic pictures on paper. Paper is coated with an emulsion of silver chloride in gelatine containing dissolved silver nitrate, and this is exposed to light under the negative (see below). A brown coloured image is thus produced, which can be made permanent by simply washing out the excess of silver nitrate with water, and removing the unaltered silver chloride by means of a "fixing" solution of sodium thiosulphate. It is usual before fixing the image in this way to "tone" the print, that is to say, to place it in a solution containing a salt of gold. The silver of the image is thus replaced by gold, a print of more agreeable tone being produced,—

$$3Ag + AuCl_3 = Au + 3AgCl.$$

The salt of gold generally employed is the chloride, or a mixture of a solution of this salt with one of potassium thiocyanate.

An ordinary dry plate or piece of bromide paper, on the other hand, is coated with an emulsion of finely-divided silver bromide and iodide with gelatine, no silver nitrate being present. When this is exposed in the camera no visible change occurs, but the parts of the film which have been exposed to light are found to be more easily reduced to metallic silver than the original bromide. Hence when the plate is treated with certain mild reducing agents, such as ferrous oxalate, an alkaline solution of pyrogallic acid, etc., the unexposed part of the film is not affected, whereas the exposed part is reduced to metallic silver, the thickness of image produced at each spot depending on the brightness of the light which has fallen upon it, and a dark image of metallic silver is thus developed. The unaltered silver bromide is then dissolved out by sodium thiosulphate, so that an image is obtained which is called a *negative*, because it is dark and opaque wherever the original object was bright and white, whilst it is clear and transparent where the original was dark. A *positive* picture is finally obtained by allowing light to pass through this negative on to a second sensitive film, and developing and fixing as before, or by printing an image by means of the gelatino-chloride paper described above.

Silver Sulphide, Ag_2S, occurs as the mineral *silver glance*, and is precipitated as a black amorphous mass when sulphuretted hydrogen is passed into a solution of silver nitrate.

This substance is also formed by the action of sodium sulphide or of sulphuretted hydrogen on metallic silver, hydrogen being evolved,—

$$2Ag + H_2S = Ag_2S + H_2,$$

$$2Ag + Na_2S + 2H_2O = Ag_2S + H_2 + 2NaOH.$$

This reaction is made use of in testing by the dry method for sulphur compounds.

EXPERIMENT 134.—Heat a crystal of zinc sulphate along with sodium carbonate on charcoal in the reducing flame of the blowpipe, and place the fused mass on a moistened silver coin; a black stain of silver sulphide is at once produced.

Silver Sulphate, Ag_2SO_4, is best prepared by dissolving the carbonate in dilute sulphuric acid; it is a white salt which is only slightly soluble in water, and is precipitated when a soluble sulphate is added to a concentrated solution of silver nitrate.

Silver Cyanide, AgCN, is precipitated as an amorphous white mass when a solution of potassium cyanide is added to one of silver nitrate. It dissolves in excess of potassium cyanide, a double salt, KCN.AgCN, being formed. The solution is much used as a source of silver in electroplating.

Detection of Silver.—Silver can very readily be detected by means of the characteristic properties already described. The following are the tests usually employed:—

1. All the compounds of silver are reduced to the metal when they are heated with sodium carbonate on charcoal before the blowpipe—

$$2AgNO_3 + Na_2CO_3 = Ag_2CO_3 + 2NaNO_3,$$
$$2Ag_2CO_3 = 4Ag + 2CO_2 + O_2.$$

2. Hydrochloric acid added to a solution of a silver salt produces a white precipitate of the chloride, soluble in dilute ammonia, insoluble in nitric acid.

SUMMARY

Silver is a white metal, which melts at a somewhat lower temperature than copper. It dissolves in dilute nitric acid and in hot concentrated sulphuric acid, but not in hydrochloric acid. It does not form an oxide when heated in the air.

Silver only forms one series of salts, and in these each atom of the metal replaces one atom of hydrogen. The nitrate is easily soluble in water and the sulphate sparingly soluble, whereas most of the other salts are insoluble. The brown oxide has basic properties, and decomposes when it is heated.

Gold, Au, 197.2

Gold has always been prized on account of its beauty, its permanence in the air, and its rarity. The whole aim of the alchemists, the first students of chemistry, was to prepare this precious metal from the more common and baser metals which were known to them. In token of its superiority gold was associated by them with the sun.

Gold is nearly always found in the free state in nature, but alloyed with silver, and often with copper and other metals. It occurs disseminated through quartz veins, penetrating other rocks, and the metal is often present in a very finely divided state, often in no larger proportion than 1 to 70,000 of quartz, although it is sometimes found in comparatively large masses or nuggets. The sand and soil formed by the gradual breaking up of gold-bearing rocks also contain the gold, and these alluvial deposits are usually the first to be worked for the metal, as has been the case in California (1849), Australia (1851), and Klondike (1896). The gold-bearing rock itself is also attacked, shafts being sunk into the quartz reefs, and the rock mined and brought up to the surface for extraction.

Extraction of Gold.—The gold which occurs in the alluvial beds of soil, gravel, sand, etc., is extracted by the simple process of washing, which is carried out by stirring the whole up with water and pouring off the lighter materials, the heavy gold being left at the bottom. In some districts the soil is broken up by jets of water under great pressure, and is washed into carefully prepared channels, at the bottom of which the metallic gold collects (Fig. 45). In order to extract gold from quartz, the latter is pounded up as in a mortar by a steel "stamp," and the finely powdered ore, mixed with water, is then allowed to flow over copper plates amalgamated with mercury, with which the gold combines.

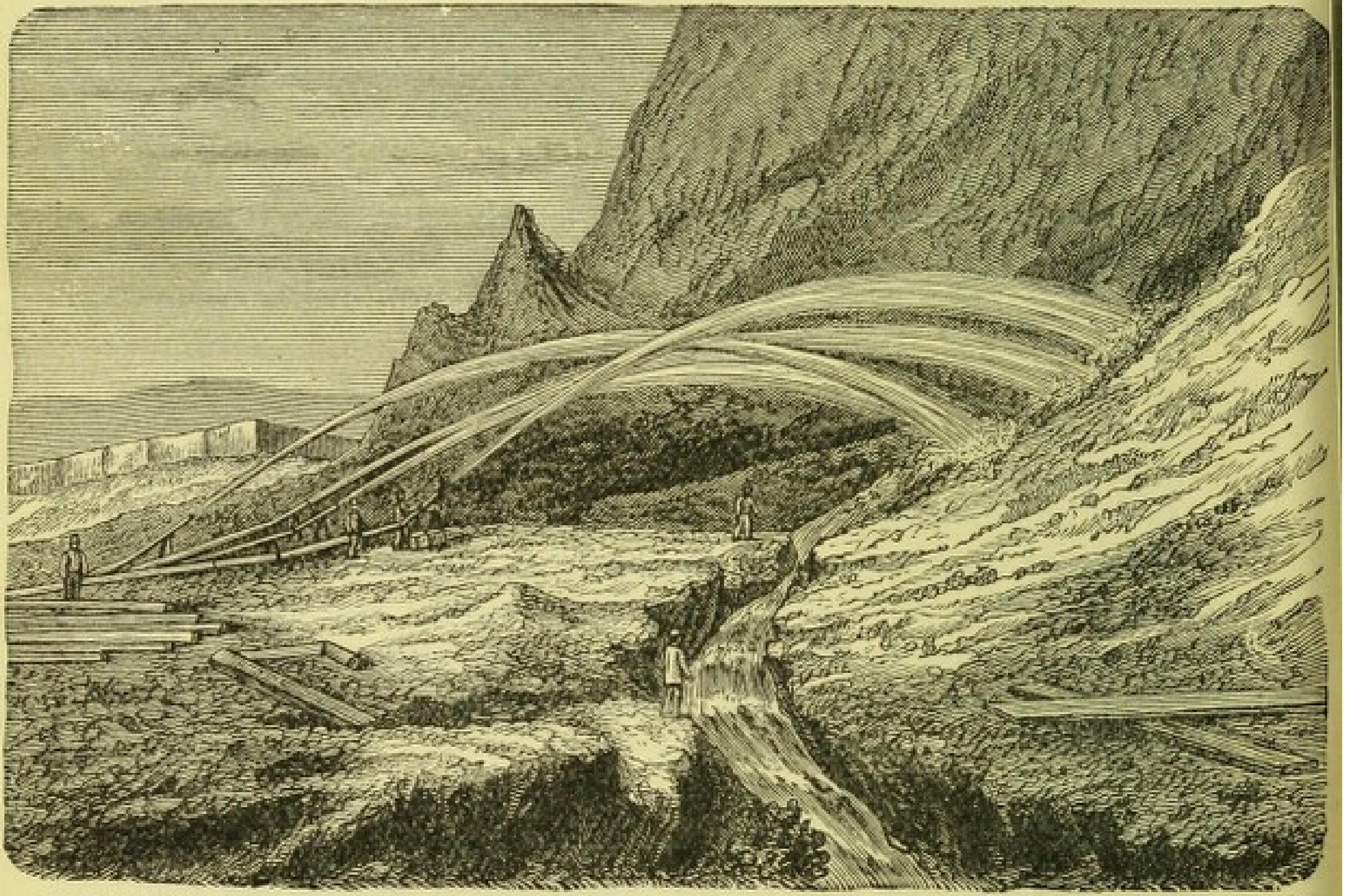


Fig. 45.

When the quartz only contains an extremely small proportion of gold, the latter can be extracted by the action of dilute potassium cyanide solution on the finely divided mass. In the presence of air the cyanide dissolves the gold according to the equation,—

$$2Au + 4KCN + O + H_2O = 2KAu(CN)_2 + 2KOH.$$

The solution containing the gold is then run on to metallic zinc, which precipitates the metal,—

$$2KAu(CN)_2 + Zn = 2KCN + Zn(CN)_2 + 2Au.$$

Gold can also be extracted by treating the ore with chlorine, and washing out the gold chloride which is produced by means of water.

Properties of Gold. — Gold is characterised by its brilliant yellow colour, which remains unaltered in the air. It is the most malleable and ductile of all the metals, and can be beaten out into leaves of which 280,000 make a pile 1 inch in height, and drawn into wire of which about 2 miles weigh 1 gram. Ordinary gold-leaf has a thickness of 0.0001 mm., and transmits green light. The metal has the specific gravity 19.3, and melts at the high temperature of 1061.7°. Pure gold is too soft for use either as coin or jewellery, and for these purposes it is alloyed with copper or sometimes with both copper and silver. English gold coin contains 961.67 parts of gold per 1000. The amount of gold is, however, usually expressed in *carats*, 24 carat gold being the pure metal. Gold coin, is, therefore, 22 carat gold, *i.e.* it contains 22 parts of gold in 24 of the coin. The alloy with copper is much harder and redder than pure gold, whilst that with silver is of a fainter yellow than gold itself. When more than 36 per cent of silver is present the alloy is known as *electrum.* Gold-leaf is much used for gilding, painting, and lettering in gold; gold is usually deposited on metallic objects by the electrolytic process (p. 306).

Gold does not combine directly with oxygen, whereas it is at once attacked by chlorine or bromine. It is insoluble in hydrochloric, nitric, and sulphuric acids, but dissolves at once in aqua-regia or in any liquid in which chlorine is being generated.

Most of the compounds and salts are very unstable, and easily yield metallic gold when they are heated, or treated with reducing agents. Thus the chloride is at once reduced to metallic gold by ferrous salts, such as the chloride or sulphate, or by oxalic acid,—

$$AuCl_3 + 3FeCl_2 = Au + 3FeCl_3,$$
$$2AuCl_3 + 3C_2H_2O_4 = 2Au + 6HCl + 6CO_2.$$

EXPERIMENT 135.—1. Place two small portions of gold-leaf in two test-tubes, and to one add hydrochloric and to the other nitric acid—no action occurs in either case. Mix the contents of the two tubes—the gold is at once dissolved.

2. To separate portions of a solution of gold chloride add (1) dilute sulphuric acid and ferrous sulphate; (2) oxalic acid—in both cases a dark-coloured precipitate of finely divided gold is produced.

The equivalent of gold has been determined by analysing the bromide and certain of its double salts, and has been found to be 65.73. The atomic weight is calculated from the specific heat, which is 0.0316, to be about $\frac{6.4}{0.0316} = 202$, and hence the exact atomic weight is $65.73 \times 3 = 197.2$. One atom of gold has therefore replaced 3 atoms of hydrogen in hydrobromic acid, and the formula of the bromide is $AuBr_3$. Gold, however, forms two series of compounds, the *auric* compounds, in which it is tervalent, and the *aurous* compounds, in which it is univalent. The compounds of this second series correspond in composition and in many of their properties with the salts of silver and the cuprous salts; thus aurous chloride is, like silver chloride and cuprous chloride, insoluble in water.

Compounds of Gold

The Chlorides of Gold.—Auric Chloride, $AuCl_3$, is formed when gold is gently heated in chlorine, and dissolves readily in water. When it is heated it first decomposes into chlorine and *aurous chloride*, AuCl, which is a yellowish powder, and is insoluble in water.—

$$AuCl_3 = AuCl + Cl_2.$$

This salt also decomposes when it is more strongly heated, metallic gold and free chlorine being produced.

When the trichloride is evaporated with hydrochloric acid, or when gold is dissolved in aqua regia and the solution is evaporated, long yellow needles separate out which have the composition $HAuCl_4 + 3H_2O$. This substance is formed by the union of auric chloride with hydrochloric acid, and acts as an acid which is known as *aurichloric acid.* Gold chloride also combines with the chlorides of potassium, and many other metals forming crystalline salts, such as *potassium aurichloride*,—

$$KAuCl_4 + 2H_2O.$$

The chloride is used in photography for toning silver prints, the metallic silver of the image being replaced by gold (p. 281). The *bromide* is prepared in a similar manner to the chloride and resembles it closely in chemical properties.

Oxides of Gold.—Gold, as has already been mentioned, does not combine directly with oxygen, and the oxides are therefore prepared indirectly, usually from the chlorides.

Auric Hydroxide, $Au(OH)_3$, is formed as a brown precipitate when caustic potash is added to a solution of the trichloride. When gently heated it yields *auric oxide* (gold trioxide), Au_2O_3, as a brown powder which readily decomposes on further heating into gold and oxygen. The oxide has slight acid forming properties, and the hydroxide dissolves in an excess of caustic potash, forming a salt known as *potassium aurate.*

Aurous Oxide (Gold Monoxide), Au_2O.—Aurous chloride is converted by caustic potash into a dark brown powder consisting of *aurous hydroxide*, AuOH, which yields the oxide on heating. The latter readily decomposes on further heating into gold and oxygen.

Aurous Sulphide, Au_2S, is formed as a brown powder, mixed with sulphur and metallic gold, when sulphuretted hydrogen is passed into a solution of the trichloride. It dissolves in ammonium sulphide and is insoluble in hydrochloric acid.

Aurous Cyanide, AuCN.—When ammonia is added to a solution of gold in aqua regia, and the precipitate dissolved in potassium cyanide, *potassium aurocyanide*, $KAu(CN)_2$, is produced, which is colourless and readily soluble in water, forming a solution which is largely used for electro-gilding.

When an acid is added to this solution, *aurous cyanide*, AuCN, is precipitated as a yellow powder, which is insoluble in water, but readily soluble in potassium cyanide solution. In this respect the compound resembles silver cyanide, which is insoluble in water and acids, but dissolves readily in potassium cyanide solution. Potassium aurocyanide is also formed, as already mentioned, by the action of potassium cyanide on metallic gold in the presence of air.

Purple of Cassius.—When a mixture of stannic and stannous chlorides is added to a solution of gold, a purple coloured precipitate is produced which is known as purple of Cassius, and is used for the production of ruby glass. It contains oxide of tin together with very finely divided gold and appears to be a mixture of these substances.

Assay of Gold.—Gold bullion, such as coin or plate, is tested, or as it is called assayed, by adding a certain amount of lead and silver to a weighed quantity of the metal, and exposing at a red-heat on a *cupel* made of bone-ash to a current of air until the whole of the lead has been removed by oxidation, taking with it all the oxidisable impurities. The resulting bead of gold and silver is then rolled out and boiled with nitric acid. This dissolves out the silver but leaves the gold, which is then dried and weighed.

SUMMARY

Gold is a yellow metal which melts at a high temperature, and does not unite with oxygen when it is heated in the air. It is not affected by nitric, hydrochloric, or sulphuric acid, but dissolves in aqua regia.

Gold forms two series of salts: the aurous salts, in which each atom of the metal replaces one atom of hydrogen; and the auric salts, in which each atom replaces three of hydrogen.

The aurous salts are very unstable and decompose when heated. The chloride is a yellowish powder, insoluble in water.

The auric salts are yellow and soluble in water, but are easily decomposed by reducing agents and by heat, metallic gold being formed.

The chloride unites with hydrochloric acid to form a compound, which acts as an acid and forms salts with bases.

The hydroxide acts as a base towards acids, but also has weak acid properties.

General Properties of the Metals of the Copper Group

The elements copper, silver, and gold do not resemble each other so closely, or show such a definite gradation in properties, as the members of many of the other families of elements, but certain of their properties point to the fact that they form a true chemical group.

The metals all melt at high temperatures and have high specific gravities, which increase with the atomic weight. The oxides of these metals are all very easily decomposed; those of silver and gold decompose readily when heated, whilst that of copper is easily decomposed by reducing agents.

Each of the metals, moreover, forms a series of salts of the empirical formula MR', where R' represents a univalent atom or radical, and these salts resemble each other in properties. Thus cuprous chloride, silver chloride, and aurous chloride are all insoluble in water. In addition to these salts copper forms the cupric salts, CuR'_2, and gold forms the auric salts, AuR'_3.

Exercises on Lesson XXVI

1. How is metallic silver extracted from its ores?

2. How does gold occur in nature, and how is it obtained from its ores?

3. Compare the physical properties of copper, silver, and gold.

4. How can pure silver and gold be obtained from silver and gold coins?

5. What happens when solutions of the following substances are added to a solution of silver nitrate: (*a*) caustic soda, (*b*) potassium iodide, (*c*) potassium cyanide, (*d*) ammonia, (*e*) sodium sulphate, (*f*) sulphuretted hydrogen?

6. Describe the preparation and properties of auric chloride. How can aurous chloride be prepared from this substance and what are its properties?

7. How much of the following metals can be precipitated by 1 gram. of copper: (*a*) silver, (*b*) gold, (*c*) mercury?

8. How can the amount of gold in an alloy of the metal be ascertained?

9. Mercury precipitates metallic gold from a solution of auric chloride, and it is found by experiment that 3 grams. of mercury precipitate 1.972 grams. of gold. Calculate the equivalent of gold.

10. Point out the chief points of resemblance and difference between the chemical properties of copper, silver, and gold.

LESSON XXVII

THERMOCHEMISTRY

It has already been remarked that chemical change is often accompanied by evolution of heat. Now heat is not a material substance and cannot be weighed, and we must therefore endeavour to understand whence it springs and how it is that it is produced in a chemical change. It is, in fact, now known that heat is simply a *form of energy*, the word energy being used to mean the power of doing work. Work is done whenever a mass is moved in opposition to a force, as, for example, when a weight is lifted from the ground. In this case the quantity of work done is measured by the product of the weight lifted into the height through which it is lifted. The unit of work usually adopted in England is that done when a weight of 1 pound is lifted through one foot, and is called the foot-pound. In the metrical system, on the other hand, the kilogram-metre or the gram-centimetre is taken as the unit.

Any system of bodies which has the power of doing work is said to possess energy, and the amount of energy is measured by the amount of work which it is capable of performing. Thus, an engine which is capable of lifting 33,000 pounds through one foot, *i.e.* doing 33,000 foot-pounds of work, every minute, is said to be of one-horse power.

A moving body such as a cannon ball or the piston of a working engine, for example, is said to have energy, because it is capable of performing work, and the energy of such a moving body is called *kinetic energy* or energy of motion.

A system of bodies may, however, possess energy, although its parts are not moving towards or away from each other. Thus, when a stone or other heavy body is held at some height above the ground, the system made up of the earth and the stone possesses a certain amount of energy, because it is capable of doing work. Thus, if the stone be connected with a smaller stone on the surface of the earth by means of a string passing over a pulley, and then be allowed to fall, it lifts the second stone and thereby performs work. The energy of such a system as the earth and a stone held above its surface is called *potential energy* (an expression which means possible energy), because although no work is actually being done by the system, it is possible to get work from it as soon as the proper means are tried, *i.e.* in the above case as soon as the stone is allowed to drop.

Conservation of Energy.—When work is done by a body or system of bodies, the energy which is apparently destroyed is not really lost, but is simply converted into other forms of energy. Thus, when a stone falls to the ground, the potential energy which the stone at first possesses is gradually converted into energy of motion as the velocity of the falling stone increases. When the stone reaches the surface of the earth its motion is suddenly stopped, but both the stone itself and the surrounding parts of the surface become heated, so that the energy of motion is converted into heat energy. The amount of heat which is produced when a heavy body is stopped after falling through a given height has been very carefully determined by experiment, and it has thus been found that when a weight of 1 gram. falls from rest through 42,500 centimetres, the energy it possesses is just sufficient when converted into heat to warm 1 gram. of water 1° C., in other words, 42,500 gram.-centimetres of work are exactly equivalent to 1 calorie.[1]

It is found to be universally true that *energy is never destroyed but only changed in form*, so that the total amount of energy in the universe remains a constant quantity, and this principle is known as the **Law of the conservation of energy.**

Energy of Chemical Systems. — The energy of a chemical system is a form of potential energy, and usually

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[1] In the units now in use in England the mechanical equivalent of heat is the energy developed by the fall of 772 lbs. avoirdupois through the space of 1 foot; and this is equivalent to the heat capable of raising 1 lb. of water from 32° to 33° Fahr.

appears in the form of heat when a chemical change occurs. Thus in a mixture of 2 grams. of hydrogen with 16 grams. of oxygen at the normal temperature and pressure no work is actually being done, but as soon as a spark is passed through the mixture combination ensues, and a very large amount of energy appears in the form of heat, the total quantity evolved being 68,000 calories. Hence 18 grams. of water at 0° contain less energy than a mixture of 16 grams. of oxygen with 2 grams. of hydrogen by the amount equal to 68,000 units of heat. Since each calorie corresponds, as we have seen, with 42,500 gram.-centimetres of work, this amount of heat corresponds with $42,500 \times 68,000$ gram.-centimetres $=$ 2,890,000,000 gram.-centimetres, or would be produced by a weight of 18 grams. falling through 1605 kilometres.

When two elements unite to form a compound with evolution of heat, as is the case with hydrogen and oxygen, it is found that exactly the same amount of energy as has been lost during combination must be restored to the compound in order to decompose it.

Thus when metallic mercury is gently heated in oxygen a portion of it combines to form mercuric oxide, HgO, and it is found that for every 16 grams. of oxygen which unite with mercury 20,700 units of heat are evolved. When the oxide is more strongly heated, however, it decomposes again into mercury and oxygen, and it is then found that for every 16 grams. of oxygen which are liberated exactly the same amount of heat is absorbed as was set free by its combination. The mercury and oxygen are then in the same state as before, and are capable of recombining with evolution of heat when brought together under the proper conditions.

This case is exactly analogous to that of the stone and the earth, which has already been discussed. When the stone is dropped from a height, it loses the potential energy due to its elevated position, this being finally converted into the energy of heat. In order to restore this lost potential energy to the stone an exactly equal amount of work must be spent upon it. It must be lifted to the height at which it was formerly supported, and it then of course possesses exactly the same amount of potential energy as before.

The energy possessed by substances which are capable of combining chemically plays a very important part in the ordinary course of life. Thus the heat energy of a furnace or flame, which can so readily be converted by suitable means into the energy of motion of an engine, is derived from the potential energy existing in the system made up of the fuel and the oxygen of the air, which is converted into heat in the process of combustion, and can then be partially converted into other forms of energy.

In a similar manner the power of doing work which we ourselves possess is to be ascribed to the potential energy existing in the system made up of the food we take and the oxygen of the air. In the body this food is gradually oxidised in such a way that some of the energy thus given out can be converted into work at our will, whilst a portion of it is utilised in maintaining the high temperature of the body, etc. The energy necessary for the work which we perform is therefore provided by the oxidation of the food we consume.

We may now say that chemical changes are accompanied by changes of energy, sometimes by gains, sometimes by losses. Many substances are formed with loss of energy, such as water, carbonic acid gas, etc., and these then require the addition of energy for their decomposition. Other substances, again, such as ozone, carbon disulphide, acetylene, etc., are formed with gain of energy, their formation being accompanied by absorption of heat. Such substances lose energy when they decompose, and this usually appears in the form of heat. In this way, if the decomposition be once started, the temperature rises as it proceeds, and the whole mass of the substance decomposes, often so rapidly that what is called an explosion occurs. This is the case, for example, with liquid ozone, which gives out heat on decomposition and explodes violently when it is slightly heated. Acetylene and carbon disulphide, moreover, can readily be made to explode by subjecting them to a violent shock.

The explosion produced by the combination of hydrogen with oxygen or hydrogen with chlorine, on the other hand, is due to the fact that the gases contained in these mixtures only begin to combine rapidly at a certain temperature, but when this is once reached the combination of a part of the mixture causes an evolution of heat which quickly raises the temperature of the surrounding parts and causes them to unite, so that the whole mass combines very rapidly and expands suddenly, owing to the high temperature produced, thus causing an explosion. In the case of gunpowder, dynamite, etc., a similar process goes on, and in addition the small amount of solid explosive used is converted into gaseous products which occupy a vastly greater volume, and thus when the reaction takes place in a confined space produce an enormous pressure.

In some cases the energy evolved in a chemical change makes its appearance to some extent in the form of light or of electrical energy, so that chemical energy may be used as a source of light or electricity. This latter case is specially treated in the following lesson.

Thermochemistry—Calorimetry.—The heat produced in a chemical change can readily be determined by carrying out the change in a calorimeter (p. 126), measuring the rise of temperature produced, and from this calculating the amount of heat evolved. These determinations are of great importance, since they give us the means of expressing numerically the amount of energy which is required to produce a given chemical change, or, conversely, the amount which will be developed by a given chemical change.

The amount of heat evolved by the combination or reaction of two substances can be readily expressed by writing after the equation, which represents the change, the number of calories evolved when the number of grams. represented by the formulæ employed react with one another. In such cases it is usual to employ the simplest possible formulæ, and not in every case the correct molecular formulæ of the substances. Thus the fact that when 2 grams. of hydrogen unite with 16 grams. of oxygen to form water 68,000 units of heat are evolved, may be expressed in the equation—

$$H_2 + O = H_2O + 68{,}000 \text{ cal.}$$

This quantity of heat is, moreover, termed the *heat of formation* of water from its elements.

Again, the fact that when a solution of hydriodic acid is decomposed by chlorine 26,000 calories are evolved is expressed in the equation—

$$HIaq + Cl = HClaq + I + 26{,}000 \text{ cal.}$$

The symbol *aq* signifies that the substance in question is present in dilute solution.

This information cannot always be obtained by a direct experiment owing to experimental difficulties. In such a case it is necessary to determine the change of energy indirectly. It has been found that the amount of heat evolved in any one definite chemical change is always the same, and depends only on the state of the system at the beginning and at the close of the change, but is independent of the intermediate steps and of the rate at which the change occurs. Thus, if we wish to find the amount of heat evolved in the production of a dilute solution of ammonium chloride from the two gases ammonia and hydrochloric acid, we may either (1) allow these two gases to combine directly, and then dissolve the product in water, or (2) dissolve the two gases separately in water and mix the solutions. In both cases we start with the same substances, gaseous ammonia and hydrochloric acid, and liquid water, and in both cases we end with the same substance, a dilute solution of ammonium chloride; the amount of heat evolved in both cases is accordingly found to be the same, although the intermediate steps are different.

This law, which is known as the *law of Hess*, from the name of its discoverer, can readily be applied to obtain information as to the heat evolved in a change which cannot be carried out directly in a calorimeter. Thus, if it be required to ascertain the amount of heat evolved when carbon unites with oxygen to carbon monoxide, this can be done by ascertaining experimentally (1) the heat evolved when carbon burns to form carbon dioxide; (2) the heat evolved when carbon monoxide burns to form carbon dioxide. Expressing these two changes by equations we have—

$$(1)\ C + O_2 = CO_2 + 97{,}000,$$

$$(2)\ CO + O = CO_2 + 68{,}000.$$

Now, since we may imagine that carbon dioxide is formed in two stages by first of all producing carbon monoxide from carbon and oxygen, and then burning the carbon monoxide to carbon dioxide, it is obvious that the amount of heat evolved in the first of these processes is to be found by subtracting the heat of combustion of carbon monoxide (68,000) from the heat of formation of carbon dioxide (97,000), the result being the heat of formation of carbon monoxide,—

$$97{,}000 - 68{,}000 = 29{,}000 \text{ cal.}$$

The following list gives the heats of formation from their elements of a number of substances, the quantities of heat being in every case those evolved in the formation of the number of grams. of each substance represented by the formula given :—

		Calories.
Hydrochloric acid	HCl	22,000
Hydrobromic acid	HBr	8,400
Hydriodic acid	HI	– 6,200
Ozone	O_3	– 36,000
Ammonia	NH_3	12,000
Nitric Oxide	NO	– 22,000
Water	H_2O	68,000
Sulphur dioxide	SO_2	71,000
Phosphorus pentoxide	P_2O_5	370,000
Carbon dioxide	CO_2	97,000
Sodium oxide	Na_2O	100,000
Calcium oxide	CaO	145,000
Magnesia	MgO	143,000
Zinc oxide	ZnO	85,000
Copper oxide	CuO	37,000
Silver oxide	Ag_2O	6,000
Boron trioxide	B_2O_3	273,000
Sodium chloride	$NaCl$	97,700
Calcium chloride	$CaCl_2$	169,800

Compounds which are formed from their elements with great evolution of heat are as a rule stable and difficult to decompose, since an equal expenditure of energy is required. On the other hand, when combination is accompanied by only a small evolution of heat the compound is less stable, whilst if heat be absorbed in the act of combination the compound is still less stable.

Thus magnesia, which is formed from its elements with an evolution of 143,000 units of heat, is a very stable substance, and cannot be decomposed by heat. Silver oxide, on the other hand, which is formed with an evolution of only 6000 units, readily decomposes when it is heated. Finally ozone, which is formed with an *absorption* of about 36,000 units, is readily decomposed by heat, and in the compressed or liquid state is liable to explode with great violence.

SUMMARY

Energy is the power of doing work and exists in many forms, such as the energy of a moving body, potential energy due to position, the energy of a chemical system, the energy of an electric current, etc. Energy is never destroyed but is simply changed from one form to another. The work done in lifting a weight of 1 gram. through 42,500 centimetres is equivalent to 1 unit of heat, and the number 42,500 is called the mechanical equivalent of heat. The energy of a chemical system is usually converted into heat when a chemical change occurs, and this heat can be measured by means of a calorimeter.

The amount of energy required to cause the decomposition of a substance is exactly equal to the amount of heat evolved in the formation of the compound.

Compounds formed with great evolution of heat are, as a rule, more stable than those formed with a small evolution of heat.

The quantity of heat evolved in a chemical change depends only on the initial and final states of the substances concerned, and is the same whatever the intermediate stages may be.

EXERCISES ON LESSON XXVII

1. What is meant by the terms work, energy, unit of heat, mechanical equivalent of heat, heat of formation?

2. State the law of the conservation of energy?

3. What transformations of energy occur when a weight is raised by a steam engine?

4. How can the change of energy which accompanies a chemical change be measured?

5. What is the law of Hess?

6. The heat of formation of carbon dioxide is 97,000 cal. When 24.3 grams. of magnesium are burnt in the gas, carbon and magnesia are formed, and 46,000 cal. are evolved. Calculate the heat of formation of magnesia.

7. The heat of formation of sodium chloride is 97,700 cal., and that of magnesium chloride is 151,000 cal. Calculate the amount of heat evolved when magnesium chloride is decomposed by metallic sodium.

8. The heat of formation of cupric oxide is 37,000, and that of water is 68,000 cal. Calculate the heat evolved when 2 grams. of hydrogen are converted into water by being passed over heated copper oxide.

LESSON XXVIII

ELECTRO-CHEMISTRY

WHEN a current of electricity is passed through a metallic wire the wire becomes hot, the energy of the electric current being converted into heat. No chemical change occurs in the wire, and after it has been allowed to cool it is in all respects the same as it was before the current was passed through it. If an attempt be made to pass a current through water, it is found that pure water is practically a non-conductor of electricity, and will not allow the current to pass. When, however, a metallic salt, such as copper sulphate, or an acid or a base, is dissolved in the water, it is found that the solution now conducts electricity well, but behaves in a very different manner from the metallic wire. The passage of the current is invariably accompanied by a chemical decomposition of the dissolved substance. In such a case the current is passed by means of two plates of metal or carbon, known as the poles or *electrodes*, whilst the dissolved substance is termed the *electrolyte;* the simpler substances carrying electric charges into which it breaks up are called the *ions*, and the whole process is known as *electrolysis.*

Thus, for example, when an electric current is passed through concentrated hydrochloric acid by means of carbon poles, hydrogen is given off at the negative pole and an equal volume of chlorine at the positive pole. Each molecule of hydrochloric acid, HCl, is broken up into its constituent atoms, H and Cl. The hydrogen atom receives a charge of positive electricity and becomes a hydrogen ion which passes to the negative pole conveying with it this charge, which is given up to the negative electrode, where the hydrogen atom, having lost its charge, is liberated, and at once combines with another atom forming a molecule of gaseous hydrogen of the formula H_2. Similarly chlorine is evolved at the positive pole.

It often happens that when the charged ion loses its charge at the electrode, the resulting uncharged atom or group enters into reaction with the water of the solution or with the material of which the pole is made, or simply decomposes, so that secondary products appear. Thus, when cupric chloride is electrolysed the two ions are $Cu(+)$ and $Cl(-)$, the copper being deposited on the negative pole, and the chlorine liberated at the positive. When, however, sodium chloride is employed, hydrogen is liberated at the negative pole just as when hydrochloric acid is used. This is due to the fact that the sodium atoms, as soon as the ions lose their charge of electricity, decompose the water, forming caustic soda and liberating hydrogen,—

$$2Na + H_2O = 2NaHO + H_2.$$

Again, when dilute sulphuric acid is electrolysed, hydrogen is liberated at the negative pole and oxygen at the positive pole. In this case the actual ions are $H(+)$ and the compound group $SO_4(--)$. The latter, however, when it has lost its charge immediately reacts with the water of the solution, forming sulphuric acid, and setting free an atom of oxygen which unites with a second to form a molecule of gaseous oxygen,—

$$SO_4 + H_2O = H_2SO_4 + O.$$

When sodium sulphate is electrolysed the products are exactly the same as in the case of sulphuric acid, namely, free hydrogen and oxygen. The original ions are $Na(+)$ and $SO_4(--)$, but the sodium reacts with the water to form caustic soda which remains in solution, and hydrogen which is liberated, whilst the group SO_4 is decomposed as just described, forming sulphuric acid and oxygen. The production of alkali at one pole and acid at the other can be shown by filling a voltameter or a simple U-tube with sodium sulphate solution tinged with neutral litmus, and then passing a current between platinum electrodes from three or four small bichromate cells.

Hydrogen is evolved at the negative pole and the litmus near it becomes blue, whilst oxygen is evolved at the positive pole and the litmus in its neighbourhood becomes red.

In many cases the electrodes themselves are attacked by the products of electrolysis. Thus when a solution of copper sulphate is electrolysed by means of electrodes of metallic copper, copper is deposited on the negative electrode, whilst the SO_4 ions attack the copper of the positive pole, forming copper sulphate, which dissolves, thus keeping the amount of copper in the solution constant, one electrode being gradually dissolved and the other gradually increased.

Laws of Electrolysis.—The quantitative laws of electrolysis were first discovered by Faraday in 1833, and are of great importance.

1. The amount of substance decomposed is directly proportional to the quantity of electricity which passes through the solution.

2. When equal quantities of electricity are passed through solutions of different substances, the amounts of the elements which separate out are proportional to their chemical equivalents.

Thus, if the same quantity of electricity be passed through solutions of sulphuric acid, silver sulphate, and copper sulphate, it is found that for every gram. of hydrogen liberated, 107.88 grams. of silver and 31.785 grams. of copper are deposited, and these numbers, it will be remembered, represent the chemical equivalents of these elements : the amount of oxygen liberated is the same in all three cases.

This result is of great importance, because it shows that one *atom* of a bivalent element such as copper conveys twice as much electricity as an atom of the univalent silver or hydrogen. In the same way a tervalent atom, such as aluminium, would convey three times as much electricity as an atom of hydrogen, and in general the amount of electricity carried by the ion of an electrolyte depends on its valency.

It is obvious that if the same current of electricity be passed through solutions of two salts, and the weights of the metals which are deposited are carefully determined, the ratio of these numbers represents the chemical equivalent of the two metals. Thus, for example, it has been found that 3.3 grams. of silver are electrolytically equivalent to 1 gram. of zinc, from which it follows that the equivalent of zinc to hydrogen is $\frac{107.88 \times 1}{3.3} = 32.68$, when that of silver is 107.88.

Electrolysis is often employed in quantitative analysis for the estimation of metals. The substance to be analysed is dissolved in water and the solution electrolysed in a platinum vessel. The metal is thus deposited on the platinum, and is then carefully dried and weighed.

The atoms of hydrogen and the metals, which convey positive electricity, are termed *electropositive*; whilst the atoms of chlorine and the acid radicals, which convey negative electricity, are termed *electronegative*.

Theory of Constitution of Electrolytes in Dilute Solutions

In the opinion of many chemists dilute solutions of electrolytes, such as salts, acids, and bases, do not contain the greater part of the molecules of these substances in their ordinary condition, but broken up into their electrically charged ions. Thus, a dilute solution of sodium chloride contains only a few unaltered *molecules* of sodium chloride, but a large number of *positive* (+) *ions* of sodium and *negative* (–) *ions* of chlorine. As long as these are charged with electricity they do not appear as free sodium or chlorine, or react with the water, but as soon as they give up their charges at the oppositely charged electrodes, free sodium and chlorine are produced, the former of which decomposes the water, liberating hydrogen and producing caustic soda, whilst the chlorine is evolved as gas or attacks the electrode. It is on account of this that the ions only appear at the poles and not throughout the whole mass of the liquid. In the same way solutions of hydrochloric acid and caustic soda contain the ions $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{Cl}}$, and $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{OH}}$ respectively.

The Galvanic Cell

We are now prepared to follow to some extent what goes on in an ordinary galvanic cell. We have already seen that chemical action is always accompanied by a change in the energy of the reacting substances, and that when these lose energy it usually appears in the form of heat. Under certain circumstances, however, a portion of this energy makes its appearance in the form of electrical energy. When zinc is dissolved in sulphuric acid in the ordinary way, hydrogen is evolved, zinc sulphate is formed in solution, and heat is produced, according to the equation,—

$$Zn + H_2SO_4 = ZnSO_4 + H_2 + 37,600 \text{ cal.}$$

If, however, a piece of copper or platinum be dipped into the liquid, and that part of it which projects be connected to the projecting part of the zinc by a piece of copper wire, a very remarkable change occurs. The zinc is still dissolved, but the amount of heat produced in the liquid is much less than before, and it is now found that an electric current is passing along the wire, which can easily be used in various ways for performing work. The amount of electrical energy thus produced is of course exactly equivalent to the difference between the heat which is usually evolved when zinc is dissolved in sulphuric acid, and that which is evolved under the circumstances of the experiment. In other words, the total change of energy which occurs when a given weight of zinc is dissolved in sulphuric acid is invariably the same, but under ordinary circumstances it *all* appears in the form of heat, whereas in the cell described above only *part* of it appears as heat, whilst the *remainder* appears as the energy of the electric current which passes along the wire.

The experiment is made clearer by using either a stick of pure zinc or a plate of zinc amalgamated with mercury, which is scarcely acted on by dilute sulphuric acid at the ordinary temperature, but dissolves when the zinc is connected with the copper dipping into the same acid. When the two metals are placed in the liquid, but not connected by a wire, it is found that the zinc becomes negatively electrified, whilst the copper becomes positively electrified. As soon as the connecting wire is placed between them, a current of positive electricity passes along the wire from the copper to the zinc, and through the liquid from the zinc to the copper. We have already seen that electricity is conveyed through solutions by the ions of the dissolved substance, and therefore we should expect to find that the current passing from the zinc to the copper through the liquid would be conveyed by the hydrogen ions of the acid, which would then, after giving up their charges, appear as free hydrogen at the surface of the copper plate. This is exactly what happens; as long as the zinc and copper are not connected by a wire no change is apparent; directly the connection is made hydrogen appears, not at the surface of the zinc, but at that of the copper.

EXPERIMENT 136.—Attach a piece of copper wire to a stick of zinc, and another to a piece of sheet-copper or of platinum foil. Dip the zinc and the copper into dilute sulphuric acid in a beaker—no action takes place; connect the two copper wires—bubbles of hydrogen are at once formed at the surface of the copper.

Let us now employ this current to bring about the electrolysis of dilute sulphuric acid, and for this purpose cut the wire; fasten each end to a small piece of platinum-foil, and place these in a dilute solution of sulphuric acid. The current of positive electricity passes along the wire from the copper to the platinum electrode, dipping into the sulphuric acid. It is thence conveyed through the liquid by the + ions of hydrogen, which give up their charges at the other electrode, and appear as free hydrogen. The current is then conveyed by the wire to the zinc plate of the galvanic cell, and thence again through the liquid of the cell by hydrogen ions, free hydrogen being liberated at the surface of the copper. This is shown in the following diagram (Fig. 46, p. 304), in which the arrows show the course of the positive current of electricity.

In every current of electricity we may imagine that there are two currents going in opposite directions, one of positive and the other of negative electricity. In the above arrangement the negative electricity passes from the zinc through the wire to the electrode of the electrolytic cell, is conveyed through the liquid by the SO_4 ions, and then passes through the wire to the copper, whence it is conveyed through the liquid of the cell, again by the SO_4 ions. These are discharged at the surface of the zinc and at once combine with the metal, forming zinc sulphate, and it is the energy thus developed which supplies the energy of the electric current. In the electrolytic cell, on the other hand, the SO_4 ions are discharged at the positive electrode and at once react with the water, forming sulphuric acid and free oxygen, as already described.

EXPERIMENT 137.—The small cell described in the foregoing experiment only produces a very slow decomposition of water, but if the copper wires be bent over and dipped in dilute sulphuric acid in a beaker, bubbles of hydrogen slowly gather on the wire connected with the zinc. A more vigorous action may be obtained by connecting the terminals from a battery of three small bichromate cells with the electrodes of a voltameter. Hydrogen is evolved at the electrode connected with the zinc plate.

Galvanic Cells.—The above is not at all a convenient form of cell, because the copper or platinum plate becomes covered with a non-conducting film of hydrogen, and the current very soon diminishes considerably, this phenomenon being termed polarisation. In order to prevent this, many devices are used, a few of the most important of which are here described.

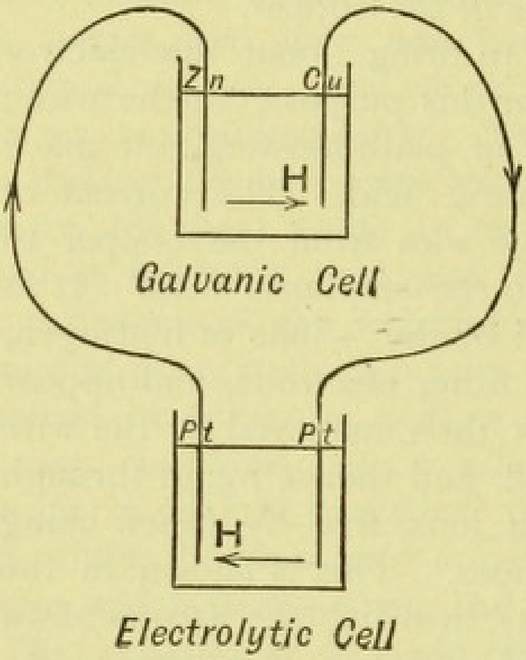


Fig. 46.

1. The Bichromate Cell.—The copper plate is replaced by one of gas carbon, and the liquid used is a solution of potassium bichromate in dilute sulphuric acid. The hydrogen is oxidised by the potassium bichromate and the polarisation is thus avoided. The other plate of the cell is made of amalgamated zinc.

2. Bunsen's cell contains a plate of amalgamated zinc dipping into dilute sulphuric acid, whilst the positive pole consists of a piece of gas carbon dipping in strong nitric acid, the latter being contained in a vessel of porous earthenware standing in the dilute sulphuric acid of the cell, so that the liquids are prevented from mixing rapidly, whilst the current can readily pass. The nitric acid oxidises the hydrogen as it is liberated, and is itself reduced with formation of nitrous acid. A cell in which a platinum plate is used instead of the carbon is known as **Grove's** cell.

3. The **Leclanché** cell consists of a negative pole of amalgamated zinc placed in a saturated solution of ammonium chloride, whilst the positive pole consists of gas carbon and manganese dioxide, the latter being reduced by the hydrogen, and thus preventing polarisation.

In all these cases the source of the energy of the current is the change of energy which is occasioned by the solution of the zinc in the liquid contained in the cell.

Such cells are only used for the production of currents on the small scale. On the large scale the current is produced by an electromagnetic machine known as a dynamo, by means of which the energy of motion of a rotating mass of metal is converted into the energy of an electric current.

Technical Applications of Electrolysis

As has been mentioned under sodium, this metal is now made on the large scale by the electrolysis of fused caustic soda. The caustic soda is contained in a large iron pot, and a current of electricity passed through it from a dynamo machine. Oxygen is evolved at the positive pole and hydrogen and metallic sodium at the negative pole,—

$$2NaHO = (2Na + H_2) + O_2.$$

The metal is removed in the molten state, and after cooling is remelted and cast into sticks.

The heat of formation of caustic soda from its elements is 101,900 cal., and this amount of energy is therefore required to liberate from it 23 grams. of sodium, according to the above equation, and must be supplied by the current. In practice more energy is needed owing to loss by conversion into heat and other causes. The value of the process as an economical one depends on the degree to which the theoretical numbers can be approached.

Another instance of the successful application of electrolysis to chemical industry is the simultaneous production of caustic soda and chlorine by the electrolysis of a solution of common salt. This is best done by liberating the sodium at a negative pole consisting of metallic mercury, with which it at once forms an amalgam. This amalgam is allowed to flow into a separate compartment of the electrolytic cell, where it is decomposed by water, a solution of practically pure caustic soda being thus produced, which is then evaporated down in the ordinary way for the production of solid caustic.

The chlorine is evolved at the positive pole, which is made of carbon, and is then led off into bleaching powder chambers. The advantage of this process over the purely chemical methods consists in the simplicity of the reaction, and in the comparatively small waste of energy involved.

Electrolysis is also largely employed for electroplating, especially with copper, silver, gold, and nickel. Thus, in order to plate articles made of Britannia metal with silver, the article is made the – pole in a solution of silver cyanide in potassium cyanide (p. 282), this salt being used because it yields a firm and adherent film of silver. The + pole is made of metallic silver, which is attacked by the CN ion, so that the solution is maintained of a constant strength. Other metals are deposited in a similar manner.

Electrolysis is also used for the refining of copper on the large scale. Slabs of crude copper form the + pole and a thin sheet of pure copper the – pole, whilst the bath contains an acid solution of copper sulphate. Copper is dissolved from the + pole and deposited on the – pole, whilst the impurities either dissolve in the bath or are precipitated as a slime.

Electrical Production of Nitric Acid from Atmospheric Nitrogen.—As already pointed out (p. 225), one of the great needs of agriculture is a cheap supply of nitrogen in a form assimilable by plants. The production of calcium cyanamide (p. 224) affords one solution of this problem, another is supplied by the direct conversion of atmospheric nitrogen into nitric acid. Nitrogen combines directly with oxygen in the electric arc to form nitric oxide, which then combines with free oxygen to form nitrogen dioxide. The combination only occurs at a very high temperature and the gases must be quickly cooled or decomposition occurs. This is accomplished in practice by making an electric arc in a current of air passing at a considerable speed. A volume of air of about 75,000 litres is treated in this way every hour and leaves the apparatus at a temperature of about 1000° containing only 1 to 2 per cent of nitric oxide. As the gases cool, nitrogen dioxide is formed and the mixture is then absorbed by water in a series of towers. The main reaction is,—

$$3NO_2 + H_2O = 2HNO_3 + NO.$$

and the nitric oxide thus regenerated combines with more oxygen and is thus almost completely converted into nitric acid, a little nitrous acid being also produced, which is finally absorbed by milk of lime or caustic soda.

The nitric acid is then neutralised with calcium carbonate and the solution evaporated by the waste heat of the gases from the arc. Calcium nitrate is thus produced which is sold as Norwegian saltpetre or air saltpetre, and this forms an extremely valuable and efficient fertiliser.

The Electrical Furnace.—Currents of electricity are also employed to produce higher temperatures than can be obtained in furnaces heated by the combustion of coal or coke. This is done by passing a very powerful current through the mass of materials to be heated, the resistance of which is so great that the material is raised to a very high temperature. Thus in the manufacture of calcium carbide (p. 224) a mixture of lime and coke is placed between carbon poles, and this reacts at the high temperature of the furnace, forming calcium carbide and carbon monoxide,—

$$CaO + 3C = CaC_2 + CO.$$

Other examples of the use of electrical methods on the large scale will be found under aluminium (p. 315) and carborundum (p. 350).

SUMMARY

When a current of electricity is passed through a solution of an electrolyte, such as hydrochloric acid or copper sulphate, the dissolved substance is decomposed into two electrically charged parts or ions, one of which appears at the positive electrode and the other at the negative electrode.

The ions on reaching the electrodes lose their charges and the uncharged atoms or groups which result are either liberated in the free state, combine to form molecules, react with the water of the solution, decompose or combine with the material of which the electrode is made.

The weight of an element liberated by a given quantity of electricity is proportional to its chemical equivalent (Faraday's law). The source of the energy of an electric current produced by a galvanic cell is to be found in the chemical action which goes on in the cell.

EXERCISES ON LESSON XXVIII

1. Describe what occurs when a current of electricity is passed through a solution of copper sulphate, (*a*) by means of platinum electrodes, (*b*) by means of copper electrodes.

2. What are Faraday's laws of electrolysis?

3. A current is passed through solutions of sulphuric acid, copper sulphate, and zinc sulphate until exactly 1 gram. of copper has been deposited. What volume of hydrogen and what weight of zinc would be liberated in the same time?

4. In an experiment it was found that a certain current liberated 50 cc. of hydrogen (N.T.P.) from dilute sulphuric acid. How much silver would it deposit from a solution of silver cyanide in potassium cyanide in the same time?

5. Describe some form of galvanic cell, pointing out, (*a*) the chemical changes which occur in the cell, (*b*) the source of the energy of the electric current.

6. Describe the manufacture of sodium by the electrolysis of caustic soda.

7. How much caustic soda and bleaching powder could be obtained from 100 kilos. of sodium chloride, if no loss occurred during the process of manufacture?

LESSON XXIX

THE ELEMENTS OF THE ALUMINIUM GROUP

BORON. ALUMINIUM

THE members of the aluminium group form oxides of the general formula R_2O_3, and halogen compounds RX_3, but do not form higher oxides or halogen derivatives than these. Only the first two members of the group, boron and aluminium, are described in this work, but the remaining members, gallium, indium, and thallium closely resemble aluminium, except that the last of these forms two series of salts, in one of which, like aluminium, it replaces three atoms of hydrogen, whilst in the other it only replaces one.

Boron, B, 11

The most commonly occurring compounds of boron are boric or boracic acid, H_3BO_3, and borax, $Na_2B_4O_7$, which are therefore first described.

Boric Acid, H_3BO_3, sometimes known as boracic acid, is found in certain lagoons in the volcanic districts of Tuscany, into which steam passes from jets, termed *suffioni*, which issue from volcanic vents. The steam contains traces of boric acid, and this material accumulates in the water of the lagoons, which is afterwards evaporated, and then yields crystals of the acid. The heat of the jets of steam themselves is utilised for the evaporation, and in this way the acid is obtained at an extremely low cost. A large amount of boric acid is now made by the decomposition of borax by means of dilute sulphuric acid (p. 311).

Boric acid crystallises in shining plates, which have a peculiar soft and smooth feeling to the touch; on this account the powdered acid is often used for producing a smooth surface on wood. It is also largely used as a preservative for articles of food, since it greatly hinders putrefaction. The crystallised acid dissolves in 25.7 parts of water at 19°, and in 3 parts at 100°, and can readily be recrystallised from hot water. When its solution is boiled it slowly volatilises along with the steam, whilst it volatilises rapidly when it is boiled with methylic alcohol. When brought into or even close to a Bunsen flame, it produces a green coloration, and the same coloration is produced when an alcoholic solution of the acid is allowed to burn.

EXPERIMENT 138.—To a concentrated solution of borax add half its volume of concentrated sulphuric acid and an equal volume of methylated spirit and apply a light—the flame of the alcohol is tinged green by the boric acid, which volatilises.

Boron Trioxide, B_2O_3.—When the acid is heated to redness it loses water and forms boron trioxide, which is the only known oxide of boron, and is also formed when free boron burns in the air. It is a white powder which only volatilises at a white heat. It unites with water to form boric acid.

The Salts of Boric Acid.—Boric acid, like phosphoric acid, is only a very weak acid, and colours litmus in the same way as carbonic acid, whilst it has no action on methyl orange. Like phosphoric acid it forms several series of salts, derived from the following—

Orthoboric Acid.	Metaboric Acid.	Biboric Acid.
H_3BO_3.	HBO_2.	$H_2B_4O_7 (= 2HBO_2 + B_2O_3)$.

The best known of these salts are the biborates, of which the sodium salt, borax, is by far the most important. Only the salts of sodium, potassium, and ammonium are readily soluble in water.

Borax, $Na_2B_4O_7$, occurs in Thibet as the crystallised mineral tincal, $Na_2B_4O_7 + 10H_2O$, and is also found in the water and dried up basins of the borax lakes in North

America; it can also be obtained by fusing boric acid with the requisite amount of sodium carbonate, and recrystallising the mass from water,—

$$4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + CO_2 + 6H_2O.$$

The solution in water has a strong alkaline reaction, like that of sodium carbonate, and may be used in alkalimetry like the latter salt, since boric acid does not affect methyl orange.

EXPERIMENT 139.—Make a solution of borax in water, and to separate portions add litmus and methyl orange. These indicators give an alkaline reaction. To each now add dilute hydrochloric acid, drop by drop,—the indicators remain alkaline until sufficient acid has been added to decompose the whole of the borax.

When the crystallised salt is heated it swells up and loses its water of crystallisation, and then melts to an anhydrous borax glass. Many metallic oxides dissolve in this and impart to it characteristic colours, so that it is much used in blowpipe analysis in the form of the borax bead.

When dilute sulphuric acid is added to a hot concentrated solution of borax, boric acid is produced and separates out in white crystals on cooling,—

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O = 4H_3BO_3 + Na_2SO_4.$$

EXPERIMENT 140.—Dissolve 20 grams. of crystallised borax in 25 cc. of boiling water, add 20 cc. of dilute sulphuric acid (1 of strong acid to 3 of water), and allow to cool. Filter off the boric acid, which separates out, wash with a small amount of cold water, and allow to dry in the air.

When borax is fused with one molecular proportion of sodium carbonate, sodium metaborate is produced,—

$$Na_2B_4O_7 + Na_2CO_3 = 4NaBO_2 + CO_2.$$

Borax is used for producing glazes on earthenware, and is also employed for metallurgical purposes and in the laundry for producing a gloss.

Free Boron is prepared by heating the anhydrous oxide with sodium, potassium, or magnesium. The mass is then carefully treated with dilute acid, which leaves the boron undissolved as an amorphous brown powder, containing a certain amount of impurity. This can, however, be removed by fusing the boron with borax and again treating with hydrochloric acid.

Boron has the specific gravity 2.45, and does not melt even at a white heat. It burns when heated in the air; forming the oxide, and also combines directly with chlorine, bromine, and fluorine, with nitrogen, and with many metals to form metallic borides.

When amorphous boron is heated with metallic aluminium, it dissolves in the molten metal, from which it separates on cooling in large transparent crystals, which are left behind when the mass is treated with acids. These crystals belong to the monosymmetric system and are extremely hard, but always contain small amounts of carbon and aluminium.

Boron, like carbon and silicon, has a much lower atomic heat than the metals, but, as already explained (p. 130), the specific heat increases very rapidly with the temperature at which it is determined.

Boron Fluoride, BF_3, is a colourless gas, whilst the *chloride*, BCl_3, and *bromide*, BBr_3, are colourless liquids which fume in the air and are decomposed by water,—

$$BCl_3 + 3H_2O = H_3BO_3 + 3HCl.$$

Boron Hydride, BH_3.—Boron forms several gaseous compounds with hydrogen, one of which corresponds in composition with the hydrides of the elements of the nitrogen group. The crude gas is formed, mixed with a very large proportion of hydrogen, when magnesium boride is treated with hydrochloric acid, and burns with a bright green flame.

Atomic Weight and Equivalent of Boron.—The equivalent of boron has been determined by the analysis of the bromide and of borax, and has been found to be 3.67. Its atomic weight is shown by a study of the molecular weights and composition of its numerous volatile compounds to be about 11.

Hence $3.67 \times 3 = 11.0$ is taken as the correct atomic weight.

Detection of Boric Acid.—Boric acid is usually detected by the green flame coloration which it produces or by its action on turmeric paper. When this paper is dipped into a solution of boric acid or a borate acidified with hydrochloric acid, and then dried, it becomes red. Dilute caustic soda, which turns ordinary turmeric paper brown, turns this reddened paper blue.

SUMMARY

Boron forms a very stable oxide, B_2O_3, and this unites with water to form boric acid, H_3BO_3, which is a very weak acid.

The most important salt of the acid is borax, $Na_2B_4O_7 + 10H_2O$, the solution of which has a strong alkaline reaction.

Free boron is a brown non-metallic powder, which burns when heated in the air. It forms a very unstable compound with hydrogen, BH_3, and a chloride, BCl_3, and bromide, BBr_3, which are decomposed by water.

Aluminium, Al, 27.1

The element aluminium is one of the most widely distributed of all the elements contained in the solid crust of the earth. Thus it forms an important constituent of felspar, a silicate of potassium and aluminium (p. 346), which is present in large quantities in many igneous rocks, such as granite, gneiss, etc. When these rocks are exposed to atmospheric conditions they gradually decompose, and, as already explained, certain of the constituents are rendered soluble and are washed away (p. 181), whilst the aluminium remains behind in the form of aluminium silicate or clay, which is sometimes almost pure, but more generally contains compounds of iron. Compounds of aluminium are, therefore, found in nearly all fertile soil, although they are not assimilated by plants or animals.

Aluminium also occurs in several minerals, the most important of which are an impure form of hydroxide containing oxide of iron, known as *bauxite*, and aluminium sodium fluoride or *cryolite*, Na_3AlF_6, which is a white substance resembling ice in appearance, and is found in large quantities in Greenland; both of these substances are now used for the extraction of the metal.

The name of the element is derived from the word alum

(Latin, *alumen*), which was applied to a salt well known even in very early times.

Properties of Metallic Aluminium.—Aluminium is a tin-white metal, and is very ductile and malleable, so that it can easily be drawn into wire and beaten out into thin foil. It is the lightest of the metals used in the arts, having the specific gravity of 2.6. It melts at 654° and becomes crystalline when it is allowed to cool slowly. The thin foil burns when heated in oxygen, but larger pieces merely become oxidised on the surface. The metal dissolves easily in hydrochloric acid, hydrogen being evolved, and the chloride formed in solution,—

$$2Al + 6HCl = 2AlCl_3 + 3H_2.$$

It also dissolves slowly in sulphuric acid and still more slowly in nitric acid, dilute or strong, but dissolves in alkalis even more readily than zinc, hydrogen being evolved,—

$$2Al + 6NaOH = 2Al(ONa)_3 + 3H_2.$$

EXPERIMENT 141.—Examine the action of hydrochloric, nitric, and sulphuric acids, and caustic soda on metallic aluminium.

Atomic Weight of Aluminium—Formulæ of the Salts.—The equivalent of aluminium to hydrogen has been directly determined by dissolving the pure metal in caustic soda solution, and measuring the hydrogen which is evolved. It has thus been found that exactly 1.008 gram. of hydrogen is evolved when 9.03 grams. of aluminium are dissolved, the weight of the hydrogen being calculated from its measured volume and its known density.

Aluminium forms a number of volatile compounds, especially among its organic derivatives, and its atomic weight has been found, both from the molecular weight and composition of these, and from the specific heat of the metal, to be about 27.

Hence $9.03 \times 3 = 27.1$ is taken as the exact atomic weight. It follows from this that the atom of aluminium replaces three atoms of hydrogen.

In all its compounds aluminium behaves in this way, only forming one series of salts, the formulæ of several of which are given below—

Aluminium chloride,	$AlCl_3$.
Aluminium sulphate,	$Al_2(SO_4)_3$.
Aluminium phosphate,	$AlPO_4$.
Aluminium oxide,	Al_2O_3.

Metallurgy of Aluminium

The oxide and chloride of aluminium are very stable compounds, so that the preparation of the metal is a matter of some difficulty. It was formerly made by heating the chloride with common salt and metallic sodium,—

$$AlCl_3 + 3Na = Ai + 3NaCl.$$

This process has, however, now been entirely given up, and the metal is made at present by decomposing the oxide by means of electricity,—

$$2Al_2O_3 = 4Al + 3O_2.$$

For this purpose alumina (aluminium hydroxide) is placed in an iron pot (Fig. 47), which forms the negative pole, and a current of electricity is passed through it. The temperature rises, owing to the resistance of the alumina, until the oxide melts and the fused mass then undergoes electrolysis, the aluminium falling to the bottom of the pot, whilst the oxygen unites with the carbon of the positive pole or anode and escapes as carbon monoxide.

In another form of the process cryolite is added in order to make the mass melt more readily.

Aluminium is now used to some extent instead of other metals because of its brightness and lightness, and because it does not readily oxidise in the air. Its alloys are also largely employed for similar purposes. One of the most important of these is that containing 90 per cent of copper, which is known as *aluminium bronze*, and resembles gold in appearance ; this alloy is malleable and almost as strong as cast steel.

Aluminium is largely used in the Thermite process for the production of carbon-free metals, especially manganese and chromium, and for the generation of intense heat to be used locally for the welding of steel rails, etc. For welding purposes, granulated aluminium is mixed with oxide of iron and the whole ignited by means of a small amount of a mixture of aluminium and barium peroxide, which takes fire when a lighted match is applied to it. The oxide of iron is reduced to metal and a temperature of 3000° C. attained,—

$$Fe_2O_3 + 2Al = Al_2O_3 + 2Fe.$$

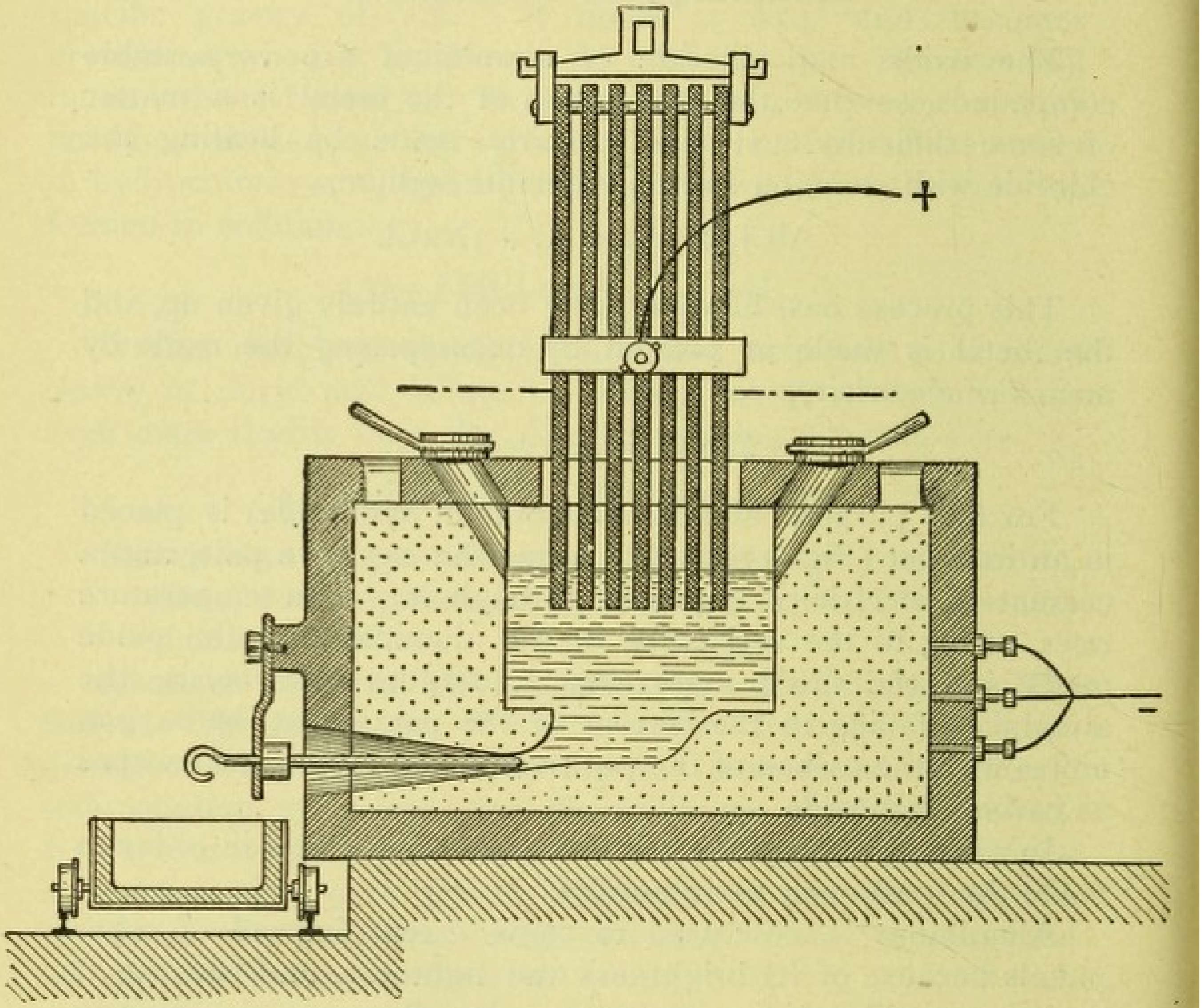


Fig. 47.

Compounds of Aluminium

Aluminium Oxide, or Alumina, Al_2O_3, occurs in the free state as *corundum*, which crystallises in six-sided prisms, and is the hardest natural mineral with the exception of the diamond. The ruby and sapphire simply consist of alumina coloured by very small quantities of the oxides of chromium and cobalt respectively. Both these precious stones can be obtained artificially by fusing alumina at a high temperature with a trace of these oxides and then allowing the mass to cool slowly.

A naturally occurring mixture of corundum with other softer minerals is known as *emery*, and is largely employed for polishing.

Aluminium Hydroxide $Al(OH)_3$ is precipitated when caustic soda is added to a solution of an aluminium salt, but readily dissolves in an excess of the alkali, and is also readily soluble in acids,—

$$Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O,$$
$$Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O.$$

This oxide, therefore, like zinc oxide, acts both as a basic oxide and a weak acid-forming oxide. Its solution in caustic soda solution is decomposed even by such weak acids as carbonic acid. The hydroxide is not soluble in ammonia except when a very large excess of the latter is present.

EXPERIMENT 142.—1. To a solution of aluminium nitrate or sulphate add caustic soda solution drop by drop—a gelatinous precipitate is formed which redissolves. Pass a current of carbon dioxide through the solution—the hydroxide is reprecipitated.

2. To another solution add ammonia in excess—the precipitate remains undissolved. To this add hydrochloric acid—the precipitate at once dissolves.

The hydroxide is prepared on the large scale from bauxite, which contains oxide of iron, by heating the mineral with caustic soda solution, drawing off the clear liquor and either decomposing it by a current of carbon dioxide, or allowing it to stand in contact with alumina, under which circumstances the pure hydroxide is deposited.

When aluminium hydroxide is gently heated it loses water and forms a white amorphous mass of alumina,—

$$2Al(OH)_3 = Al_2O_3 + 3H_2O.$$

In this form the alumina readily dissolves in concentrated hydrochloric acid; if, however, it be strongly heated the alumina becomes crystalline, and then is no longer affected by hydrochloric acid, in this respect resembling the naturally occurring corundum.

Aluminium hydroxide has the property of combining with colouring matters to form insoluble coloured compounds called lakes, and on this account is largely used as a *mordant* in dyeing. Many colouring matters do not dye ordinary cotton cloth, but if the fibre of the cloth be impregnated with alumina, an insoluble coloured lake is formed in the fibre and the dye thus retained.

EXPERIMENT 143.—To 5 cc. of a solution of alum or aluminium sulphate add 1 cc. of logwood extract, made by boiling logwood chips with water, and make alkaline with ammonia. The whole of the colouring matter is precipitated with the alumina, leaving a colourless solution.

Aluminium Sulphate, $Al_2(SO_4)_3 + 18H_2O$, is prepared by dissolving the hydroxide in dilute sulphuric acid or by boiling china clay (aluminium silicate) with sulphuric acid. It is a white crystalline salt which is easily soluble in water.

The Alums.—Aluminium sulphate forms a remarkable series of double salts with the sulphates of ammonium, potassium, sodium, and other monovalent metals, all of which crystallise in the same form and have a similar chemical composition. The compounds with potassium and ammonium sulphates are the best known of these, and are termed potash alum or potassium alum and ammonia alum.

Potassium Alum, $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O$, is prepared on a very large scale for use in dyeing from bauxite and from bituminous shale. The latter is first burnt in order to remove the organic matter and any sulphur, and is then boiled with sulphuric acid, which dissolves the alumina of the shale, forming aluminium sulphate. The solution thus obtained is mixed with potassium sulphate solution, and the whole stirred until cold. Finely divided alum is precipitated, which is then washed and recrystallised. Bauxite is treated in a somewhat similar manner; the potassium sulphate is made from potassium chloride by the action of sulphuric acid.

EXPERIMENT 144.—Dissolve 33 grams. of crystallised aluminium sulphate in 50 cc. of boiling water, and then add 8.5 grams. of powdered potassium sulphate. Boil until the whole of this has dissolved, and allow to cool. Filter and drain the crystals which are formed, and use them for preparing large crystals of alum as described on p. 142.

Potassium alum crystallises in transparent octahedra (Fig. 20, p. 138), and is only moderately soluble in water, 100 parts of which, at 10°, dissolve 9.5 of alum. Its solution has a very astringent taste and is acid to litmus (p. 160).

Ammonia Alum, $(NH_4)_2SO_4 + Al_2(SO_4)_3 + 24H_2O$, is prepared in a similar way to the potassium salt, ammonium sulphate being added to the crude aluminium sulphate. It resembles the potassium salt very closely in all its properties. The alums afford an excellent example of isomorphism, since they all crystallise in the same forms, and moreover, a crystal of one will grow in a concentrated solution of the others.

A number of other "alums" are known which have a similar composition to the above, but contain chromium or iron instead of aluminium, the formula of chrome alum being $K_2SO_4 + Cr_2(SO_4)_3 + 24H_2O$, and that of iron alum, $K_2SO_4 + Fe_2(SO_4)_3 + 24H_2O$. These salts are isomorphous with each other and also with the alums described above.

Alum is very largely used in dyeing and calico-printing, since it is very easily obtained pure and free from iron.

Aluminium Nitrate, $Al(NO_3)_3 + 8H_2O$, is a deliquescent crystalline salt, prepared by dissolving the hydroxide in nitric acid. It readily decomposes on heating, alumina being formed.

Aluminium Phosphate, $AlPO_4$, is an amorphous white precipitate, formed by adding sodium phosphate to a solution of an aluminium salt. It dissolves in mineral acids and caustic soda, but not in ammonia.

Aluminium Chloride, $AlCl_3$, is formed when aluminium is heated in a current of dry chlorine, and may also be prepared by heating a mixture of alumina and carbon in a current of chlorine,—

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

This method is frequently adopted for the preparation of chlorides from oxides, which cannot easily be reduced to the metal.

It is a white volatile solid, which fumes when exposed to moist air, and is decomposed by water,—

$$AlCl_3 + 3H_2O = Al(OH)_3 + 3HCl.$$

The solution obtained by treating aluminium hydroxide with hydrochloric acid decomposes when it is evaporated beyond a certain degree of concentration, and loses hydrochloric acid, a residue of aluminium hydroxide being finally left, so that the anhydrous chloride cannot be thus obtained.

The chloride is readily volatile and yields a vapour which at temperatures above 750° has the density corresponding with the formula $AlCl_3$.

Aluminium Sulphide, Al_2S_3.—The sulphide of aluminium is formed when the metal is heated with sulphur. It is decomposed by water, forming aluminium hydroxide and sulphuretted hydrogen,—

$$Al_2S_3 + 6H_2O = 2Al(OH)_3 + 3H_2S.$$

Hence aluminium sulphide cannot be obtained by precipitation, and is not formed by the action of sulphuretted hydrogen or ammonium sulphide on a solution of an aluminium salt. Ammonium sulphide under these circumstances acts as though it were simply ammonia, and produces a precipitate of the hydroxide.

Ultramarine is a beautiful blue substance which is produced when a pure form of clay is heated with sand, sodium sulphate, sulphur, and charcoal. A number of different varieties are known, all of which contain sulphur, part of which is given off as sulphuretted hydrogen when the ultramarine is treated with acids. Identical in composition is *lapis lazuli*, which occurs as a mineral in Central Asia. Ultramarine is largely used as a paint, and for paper staining and laundry purposes. The chemical constitution of ultramarine is unknown.

Detection of Aluminium. — Aluminium cannot be obtained in the metallic state by the reduction of its compounds on charcoal, nor does it yield a coloured borax bead, or produce a flame coloration. When strongly heated its compounds leave a white infusible residue of alumina, which is coloured blue when it is strongly heated with a salt of cobalt.

Aluminium is precipitated from solutions of its salts by ammonia or ammonium sulphide as the gelatinous white hydroxide, which is readily soluble in acids and in caustic soda.

SUMMARY

Aluminium is a white metal, which burns when strongly heated in the air, and dissolves readily in hydrochloric acid and in caustic soda, very slowly in sulphuric and nitric acids.

Aluminium only forms one series of salts, and in these it replaces three atoms of hydrogen. The oxide has basic, and at the same time weak acid-forming properties, so that the hydroxide dissolves both in acids and in alkalis.

The sulphate is readily soluble in water and forms characteristic double salts with the alkali sulphates, known as the alums.

EXERCISES ON LESSON XXIX

1. How are boric acid and borax obtained on the large scale?
2. How can boric acid be prepared from borax, and borax from boric acid?
3. Describe the preparation and properties of free boron. Give a short account of the most important compounds of this element.
4. 10.358 grams. of crystallised borax yield 5.478 grams. of anhydrous borax on careful drying. Assuming that the formula of the crystallised salt is $Na_2B_4O_7 + 10H_2O$, calculate from these numbers the atomic weight of boron.
5. What are the chief compounds of aluminium which occur in nature?
6. How is metallic aluminium prepared and what are its chief physical properties?
7. Give an account of the alums.
8. Describe the preparation of aluminium chloride, (*a*) from metallic aluminium, (*b*) from alumina. What are the properties of this compound?
9. Describe the chief chemical and physical properties of alumina and aluminium hydroxide.
10. Compare the chemical properties of boron and aluminium and their compounds with those of arsenic and its compounds.

LESSON XXX

THE ELEMENTS OF THE CARBON GROUP

CARBON. SILICON. TIN. LEAD.

THE relations which exist between the elements of this group are somewhat similar to those of the elements of the nitrogen group.

As in the case of the latter, the elements of lower atomic weight are non-metallic in character, whilst those of higher atomic weight are metals. Thus carbon and silicon are non-metals, whilst tin and lead are metals. All the elements of this group are quadrivalent and form characteristic oxides of the formula RO_2.

The Compounds of Carbon

Carbon is distinguished from all the other elements by the fact that it forms an enormous number of different compounds with hydrogen. Derivatives of these containing oxygen, nitrogen and other elements are also formed in very large numbers. Many of these occur in nature and form constituents of living animal and vegetable organisms, but the majority of them are not found in nature, but have been prepared in the laboratory. On account of this great number of compounds, it has become usual to study the carbon compounds as a special branch of chemistry, known as organic chemistry. It must, however, be clearly understood that there is no real distinction between the principles of organic and of inorganic chemistry, although it is true that many important chemical phenomena have been first observed among carbon compounds and are more characteristic of them than of other substances. In this book no attempt is made to do more than indicate by one or two simple examples the methods by which the study of the compounds of carbon with hydrogen, oxygen and nitrogen may be begun.

Carbon itself, the oxides and a few of its chief compounds have already been described (R. and L., pp. 216-239)

The Halogen Compounds of Carbon

Carbon unites so readily with fluorine that finely divided charcoal and lamp black take fire when brought into the gas, forming the gaseous fluoride, CF_4.

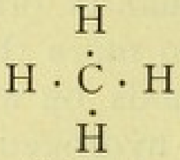
The remaining elements of the halogen group, however, do not combine directly with carbon, so that their compounds with this element must all be prepared by indirect methods from other carbon compounds. Many of these are of great interest and importance and several of them will be described.

Action of Chlorine on Marsh Gas. Substitution.— When equal volumes of chlorine and marsh gas are mixed and preserved in the dark, no change occurs, just as when hydrogen and chlorine are treated in the same manner. When the mixture is exposed to light, however, a reaction occurs, and hydrogen chloride is produced, together with a new gas which is found to have the formula CH_3Cl. The reaction which has occurred is represented by the equation—

$$CH_4 + Cl_2 = CH_3Cl + HCl.$$

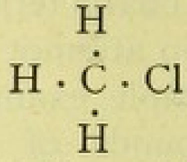
One hydrogen atom of the marsh gas, therefore, has been replaced by one atom of chlorine and this change is known as *substitution*. The characteristic of substitution is that the atoms which are replaced are chemically equivalent to the atoms or radicals which replace them. Thus in the case under consideration hydrogen and chlorine are both univalent and the carbon atom both in marsh gas and in the new gas,

CH_3Cl, remains combined with four univalent elements. This may be represented graphically by the following formulæ,—



$$\begin{array}{c} \mathrm{H} \\ \mathrm{H}\cdot\dot{\mathrm{C}}\cdot\mathrm{H} \\ \dot{\mathrm{H}} \end{array}$$

Methane.



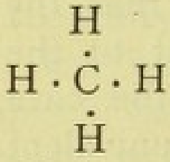
$$\begin{array}{c} \mathrm{H} \\ \mathrm{H}\cdot\dot{\mathrm{C}}\cdot\mathrm{Cl} \\ \dot{\mathrm{H}} \end{array}$$

Monochloromethane.

The same idea is expressed in the name of the new compound which is monochloro-methane, indicating that it is formed from methane by the substitution of one atom of hydrogen by one of chlorine.

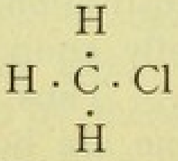
Monochloromethane or Methyl Chloride, CH_3Cl.— This gas can easily be liquefied and boils at − 23°. It is only slightly soluble in water, readily in alcohol. It burns with a green-bordered flame, which is characteristic of organic compounds containing a halogen element, forming carbon dioxide, water and hydrochloric acid. The solution in water is neutral and is not precipitated by silver nitrate solution. This is a fact of considerable interest, as it shows that monochloromethane differs from all the other chlorine compounds which we have so far considered in neither acting as a derivative of hydrochloric acid nor being decomposed by water with formation of hydrochloric acid. It is characteristic of the halogen substitution products of the hydrocarbons, that the halogen atom does not enter so readily into reactions as that present in the halogen compounds of many other elements, and that they do not as a rule act as salts, this being especially true of the chlorine compounds. In spite of this, however, monochloromethane is often termed methyl chloride, the name methyl being given to the group CH_3, which, as we shall see, often acts as a univalent compound radical (p. 327).

The process of substitution can be repeated in stages, resulting in the production of a series of compounds in which the hydrogen atoms of methane are successively substituted by chlorine, as shown by the following formulæ :—



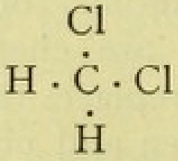
$$\begin{array}{c} \mathrm{H} \\ \mathrm{H}\cdot\dot{\mathrm{C}}\cdot\mathrm{H} \\ \dot{\mathrm{H}} \end{array}$$

Methane.



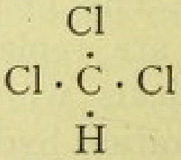
$$\begin{array}{c} \mathrm{H} \\ \mathrm{H}\cdot\dot{\mathrm{C}}\cdot\mathrm{Cl} \\ \dot{\mathrm{H}} \end{array}$$

Monochloromethane.



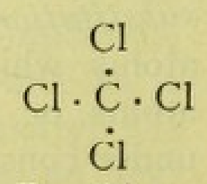
$$\begin{array}{c} \mathrm{Cl} \\ \mathrm{H}\cdot\dot{\mathrm{C}}\cdot\mathrm{Cl} \\ \dot{\mathrm{H}} \end{array}$$

Dichloromethane.



$$\begin{array}{c} \mathrm{Cl} \\ \mathrm{Cl}\cdot\dot{\mathrm{C}}\cdot\mathrm{Cl} \\ \dot{\mathrm{H}} \end{array}$$

Trichloromethane.



$$\begin{array}{c} \mathrm{Cl} \\ \mathrm{Cl}\cdot\dot{\mathrm{C}}\cdot\mathrm{Cl} \\ \dot{\mathrm{Cl}} \end{array}$$

Tetrachloromethane.

Tetrachloromethane CCl_4 or Carbon tetrachloride.—The final product is best prepared by acting on carbon bisulphide, CS_2 (p. 340), with chlorine in presence of antimony chloride. It is a colourless, mobile liquid, with a characteristic smell, boils at 77°, and does not burn in the air and is not decomposed by water or readily acted on by chemical reagents, in this resembling its parent hydrocarbon, methane. The physical properties of the three intermediate compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, are intermediate between those of CH_4 and CCl_4, as is shown in the following table in which the densities and boiling points are given. It will he seen that density and boiling point both increase with the number of chlorine atoms present.

	Density at 0°.	Boiling point.
CH_4 . . .	Gas	− 155°
CH_3Cl . .	Gas	− 23°
CH_2Cl_2 . .	1.36	+ 40°
$CHCl_3$ . .	1.52	+ 61°
CCl_4 . . .	1.61	+ 77°

This is an example of the general rule that *the physical properties of a series of substitution compounds themselves form a progressive series.*

The corresponding bromine and iodine compounds are all known, but only the monosubstitution derivatives CH_3Br and CH_3I can be considered here (p. 328).

Methyl Alcohol.—When monochloromethane is heated at 100° with caustic potash solution, in a sealed tube, it is decomposed and potassium chloride is formed along with a substance of the molecular formula, CH_4O. This compound is a colourless liquid which boils at 66° and mixes with water, from which it can again be separated by treatment with quicklime, which combines with the water but not with the new compound. It is found to be in all respects identical with a substance known as methyl alcohol or wood-spirit which is one of the products obtained when wood is subjected to dry distillation, i.e. heated in a retort in absence of air.

Chemical Properties and Constitution of Methyl

Alcohol.—Some idea of the chemical nature of this compound may be gained from the following properties :—

1. It readily burns with a colourless flame forming carbon dioxide and water.

2. Metallic sodium decomposes it with evolution of hydrogen. The sodium does not float as it does on water and does not melt, because the alcohol is lighter than sodium and its boiling point is below the melting point of sodium. A quantitative study of the reaction shows that only one of the four hydrogen atoms is replaced by the sodium, the reaction being,—

$$2CH_4O + 2Na = 2CH_3NaO + H_2.$$

One of the hydrogen atoms therefore differs from the other three in its chemical behaviour and we may indicate this by writing the formula $CH_3 \cdot HO$ or $CH_3(H)O$.

3. When saturated with hydrogen chloride, methyl chloride is formed together with water. Practically the yield is better if the reaction be carried out in the presence of zinc chloride, which acts as a dehydrating agent. Precisely similar reactions occur with hydrogen bromide and iodide and result in the production of CH_3Br and CH_3I.

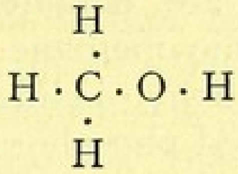
In these three reactions, therefore, a hydrogen and an oxygen atom are removed and replaced by a halogen atom. The simplest explanation seems to be that they are united together to form a group of atoms or radical which is capable of acting as, and being replaced by, a univalent element. Oxygen being bivalent and hydrogen univalent, it is evident that the group $\cdot O \cdot H$ would be univalent, and hence it is assumed that the oxygen and hydrogen are present in this form of combination in the molecule of methyl alcohol, which may therefore be written $CH_3 \cdot O \cdot H$. Methyl alcohol is therefore marsh gas in which one atom of hydrogen has been substituted by hydroxyl. The equation representing the action of the halogen acid on this substance is therefore,—

$$CH_3 \cdot OH + HCl = CH_3 \cdot Cl + H_2O.$$

The hydrogen of the compound CH_3Cl is not replaced by metallic sodium, and hence it is probable that the H atom of methyl alcohol which is replaced by sodium is the one combined with the oxygen atom, so that the equation for this reaction may now be written,—

$$2CH_3\cdot O\cdot H + 2Na = 2CH_3\cdot O\cdot Na + H_2.$$

The formula $CH_3{\cdot}OH$ may be written more fully



$$\begin{array}{ccccccc} & & \mathrm{H} & & & & \\ & & \cdot & & & & \\ \mathrm{H} & \cdot & \mathrm{C} & \cdot & \mathrm{O} & \cdot & \mathrm{H} \\ & & \cdot & & & & \\ & & \mathrm{H} & & & & \end{array}$$

and indicates that three of the H atoms are directly combined with C, whilst the fourth H atom is combined with O and this O with the C, so that the relations of the fourth hydrogen atom to carbon are different from those of the other three.

The group ·OH is known as hydroxyl and has already been discussed (p. 198) as being invariably present in oxy-acids and bases. The group $\cdot CH_3$ is known as the methyl group and also occurs in a very large number of compounds.

The group ·OH can also be replaced by chlorine by acting on methyl alcohol with phosphorus pentachloride,—

$$CH_3{\cdot}OH + PCl_5 = POCl_3 + HCl + CH_3Cl.$$

This is a reaction which can be carried out with so many compounds containing the group ·OH that it has become recognised as a test for the presence of this group.

It will be noticed that there is a very close analogy in formula and reactions between methyl alcohol and the metallic hydroxides. The action of concentrated hydriodic acid on caustic potash and on methyl alcohol is represented by similar equations,—

1. $K{\cdot}OH + HI = KI + H_2O.$
2. $CH_3{\cdot}OH + HI = CH_3I + H_2O.$

On this account a compound such as CH_3I is sometimes regarded as a salt derived from the alcohol and the corresponding acid, and this is expressed in the name methyl iodide. It must be remembered, however, that the solution of methyl alcohol in water is not alkaline, like that of caustic potash, and that it does not neutralise dilute acids, and also that moniodomethane or methyl iodide does not react with silver nitrate like potassium iodide. These facts find an explanation in the circumstance that methyl alcohol and methyl iodide are non-electrolytes and are not electrolytically dissociated in solution (p. 451). All such "salts" derived from an alcohol and an acid are termed *esters*.

Methyl alcohol serves as the source from which many of the derivations of methane are obtained, and is used for the preparation of monobromo-methane or methyl bromide and mono-iodomethane or methyl iodide. For this purpose the alcohol is treated with red phosphorus and bromine or iodine and the resulting compound removed by distillation,—

$$6CH_3OH + 2P + 3Br_2 = 6CH_3Br + 2H_3PO_3.$$

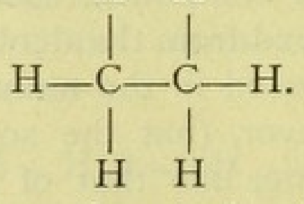
The boiling point and specific gravity both increase as chlorine is replaced by bromine and the latter by iodine, and this is usually the case in similar series of compounds.

	Boiling Point.	Specific Gravity at 0°.
Methyl chloride . .	−23	...
,, bromide . .	+4.5	1.73
,, iodide . .	45	2.19

Ethane, C_2H_6.—When methyl iodide is treated with sodium, the iodine is removed and a new gas of the molecular formula C_2H_6 is produced,—

$$2CH_3I + 2Na = 2NaI + C_2H_6.$$

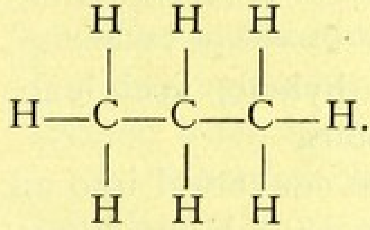
This gas resembles methane very closely in its chemical properties, being inert and not easily acted on by reagents. It boils at a higher temperature than methane, −93°.

The mode of formation of this gas leads to the formula $CH_3 \cdot CH_3$ or more fully  $\begin{matrix} & H & & H & \\ & | & & | & \\ H— & C & — & C & —H \\ & | & & | & \\ & H & & H & \end{matrix}$. This indicates that the two carbon atoms are each united with the other and with three hydrogen atoms. The full proof that this is the case can only be obtained by a further study of the derivatives of this substance. This formula fulfils the condition which has been established by experience that in the vast majority of its compounds carbon acts as a quadrivalent element. In this case it is seen that each carbon atom is united with 3 univalent hydrogen atoms and that the fourth valency is satisfied by the union of the atom with another carbon atom. The power which the carbon atom possesses of combining with one or more other atoms of carbon distinguishes it from all the other elements and affords the explanation of the enormous number and complexity of the carbon compounds.

Homologous Series.—The various reactions by which ethane C_2H_6 was obtained from methane CH_4 can be repeated with ethane. The iodine compound C_2H_5I, corresponding to CH_3I, can be prepared, and when this is mixed with methyl iodide and treated with sodium a similar reaction occurs,—

$$C_2H_5I + CH_3I + 2Na = C_2H_5 \cdot CH_3 + 2NaI.$$

The new compound is derived from ethane by replacing a hydrogen atom by the group CH_3, just as was ethane from methane, and its formula is accordingly $CH_3 \cdot CH_2 \cdot CH_3$ or



$$\begin{array}{ccccccc} & & H & & H & & H \\ & & | & & | & & | \\ H & — & C & — & C & — & C & — H. \\ & & | & & | & & | \\ & & H & & H & & H \end{array}$$

It is known as propane and chemically closely resembles ethane and methane, whilst its boiling point is -45°, considerably higher than that of ethane.

Further repetition of the process leads to a whole series of hydrocarbons, each of which is derived from the next lower one by the replacement of hydrogen by the group CH_3. Series of compounds like this are of very frequent occurrence among the carbon compounds and are known as *homologous series*, because the members of them bear a general resemblance to each other in chemical character, whilst their physical properties undergo a gradual and progressive change as the molecular weight increases.

The series of which methane is the starting-point is known as the *normal paraffin series*, because the hydrocarbons of which paraffin consists form the higher members of it. The formulæ of the succeeding members differ by CH_2 and may be expressed by the general formula C_nH_{2n+2}. In constitution and chemical properties they closely resemble methane and ethane, being very little affected by most reagents, even sulphuric and nitric acids, whilst they all form substitution compounds with chlorine. The lower members are gases, but as the molecular weight rises the boiling and melting points rise, so that those containing from 5-15 carbon atoms are liquid and those of higher molecular weight are solid at the ordinary temperature.

The name, formula, and boiling and melting points of some of the series are given in the following table.

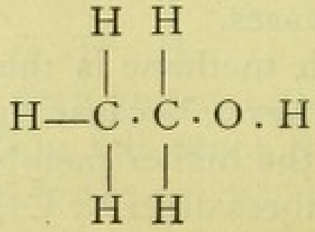
Name.	Formula.	Boiling Point.	Melting Point.
Methane . . .	CH_4	− 165°	...
Ethane . . .	C_2H_6	− 93°	...
Propane . . .	C_3H_8	− 45°	...
Butane . . .	C_4H_{10}	+ 1°	...
Pentane . . .	C_5H_{12}	+ 37°	...
Hexane . . .	C_6H_{14}	+ 69°	...
Hexadecane . .	$C_{16}H_{34}$	+ 287°	18°
Pentatriacontane . .	$C_{35}H_{72}$	331° at 15 mm.	75°

Similar series are known derived from ethylene, acetylene, benzene (C_6H_6), and many other hydrocarbons.

Ethyl Alcohol, C_2H_6O.—Ethane can be converted into an alcohol in precisely the same way as methane. Monochloroethane (or ethyl chloride), C_2H_5Cl, is formed by the action of chlorine in the light, and this when heated with water or potash yields ethyl alcohol,—

$$C_2H_5Cl + KOH = C_2H_5 \cdot OH + KCl.$$

Ethyl alcohol is the alcohol which is prepared by fermentation and is known as spirits of wine. It boils at 78° and closely resembles methyl alcohol in chemical properties. Precisely the same reasons lead to its formulation as $C_2H_5 \cdot OH$, as led to the analogous formula for methyl alcohol. When written more fully this becomes



$$\begin{array}{c} \quad\ \ H\ \ H \\ \quad\ \ |\ \ \ | \\ H—C \cdot C \cdot O\ .\ H \\ \quad\ \ |\ \ \ | \\ \quad\ \ H\ \ H \end{array}$$

or $CH_3 \cdot CH_2 \cdot O \cdot H$,

one of the hydrogen atoms of ethane having been replaced by the ·OH group.

Each hydrocarbon of the normal paraffin series is capable of yielding a similar alcohol, so that an homologous series of alcohols is also known, the members of which all possess similar chemical properties whilst the physical properties undergo a gradual and progressive change.

The Oxidation of Ethyl Alcohol.—Ethyl alcohol very readily undergoes oxidation when it is submitted to the action of oxidising agents. When the process is carefully examined it is found that it occurs in two stages.

1. When alcohol is slowly added to an oxidising mixture of potassium bichromate and sulphuric acid and the mixture kept cool, a volatile substance is produced the vapour of which distils over and may be collected in ether. This new substance combines with ammonia to form a compound insoluble in ether, and advantage is taken of this to obtain it in the pure state, the ammonia compound being dried and then distilled with dilute sulphuric acid. When pure the new compound is found to be a colourless liquid boiling at 21° and possessing a peculiar suffocating odour. It is known as *acetaldehyde* and has the molecular formula C_2H_4O. A small amount of it is formed when alcohol is burned in a limited supply of air.

2. When alcohol is more vigorously oxidised, as for example by a hot mixture of potassium bichromate and sulphuric acid, it is converted into acetic acid, which can be distilled, and converted into a salt from which the pure anhydrous acid can readily be prepared by treatment with concentrated sulphuric acid. Acetic acid boils at 119°, and solidifies at 17° to a crystalline mass. It has the molecular formula $C_2H_4O_2$. Acetic acid is also formed when acetaldehyde is further oxidised, so that the latter is an intermediate product between the alcohol and the acid. We are now able to see what change has been produced in composition by the successive stages of oxidation in passing from alcohol to acetic acid:

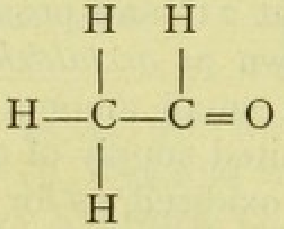
C_2H_6O	C_2H_4O	$C_2H_4O_2$
Alcohol.	Acetaldehyde.	Acetic Acid.

In the production of acetaldehyde two hydrogen atoms have been removed, and in the further production of acetic acid from this one atom of oxygen has been added. The question now arises as to how the constitution of these bodies differs from that of alcohol, and this can only be answered by a study of the properties of the two compounds.

Constitution of Acetaldehyde

1. Acetaldehyde does not contain a hydrogen atom which can be replaced by sodium.

2. The hydroxyl group (–OH) which was present in alcohol is no longer there. Phosphorus pentachloride instead of replacing hydroxyl by chlorine now exerts an entirely different action and replaces one atom of oxygen by two atoms of chlorine, producing a compound $C_2H_4Cl_2$.

These properties suffice to indicate the change that has occurred. In the removal of the two hydrogen atoms, the hydroxyl group has been destroyed and an oxygen atom left combined entirely with carbon. These facts lead to the constitutional formula  $H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-\overset{\displaystyle H}{\overset{|}{C}}=O$ for the aldehyde.

Constitution of Acetic Acid

1. Acetic acid, as its name implies, has acid properties, and is a monobasic acid. The silver salt, for example, which is only slightly soluble in water, has the formula $Ag \cdot C_2H_3O_2$.

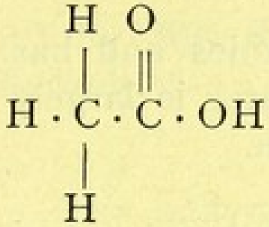
2. It contains an hydroxyl group which is replaced by chlorine when the acid is acted on by phosphorus pentachloride (see p. 327), yielding the compound C_2H_3OCl, known as acetyl chloride. This substance does not contain a hydrogen atom which can be replaced by sodium.

3. Acetic acid still contains the methyl group $\cdot CH_3$ which is present in ethyl alcohol. This is shown by many reactions, the simplest being that when an acetate is heated with an alkali, marsh gas is produced,—

$$CH_3 \cdot CO_2Na + NaOH = CH_3 \cdot H + Na_2CO_3.$$

It follows from this that the changes produced by oxidation have been confined to the atoms united with the carbon atom with which the ·OH group of the alcohol was combined.

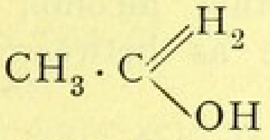
The formula which is in agreement with all these facts is



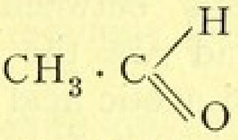
$$\begin{array}{l} \quad H\;\;O \\ \quad |\;\;\; \| \\ H\cdot C\cdot C\cdot OH \text{ or } CH_3\cdot CO\cdot OH. \\ \quad | \\ \quad H \end{array}$$

Acetyl chloride thus becomes $CH_3 \cdot CO \cdot Cl$.

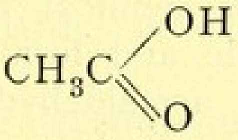
When the formulæ for alcohol, aldehyde and acetic acid are compared, the intermediate character of the aldehyde is well seen.



Ethyl Alcohol.



Acetaldehyde.



Acetic Acid.

This intermediate character is borne out by the behaviour of the aldehyde. When it is oxidised it is converted into acetic acid, and this occurs so readily that it reduces many metallic oxides. The formation of a silver mirror with an ammoniacal solution of silver oxide forms in fact one of the tests for aldehyde,—

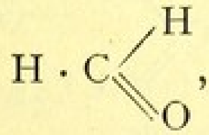
$$C_2H_4O + Ag_2O = C_2H_4O_2 + 2Ag.$$

On the other hand, when it is treated with sodium amalgam and water it is reduced back again to alcohol,—

$$C_2H_4O + 2H = C_2H_6O.$$

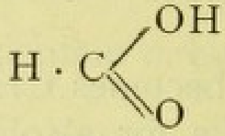
Acetic acid, on the other hand, cannot easily be either oxidised or reduced.

The Oxidation of Methyl Alcohol.—The oxidation of methyl alcohol also proceeds in two stages leading to the formation of first an aldehyde and then an acid.

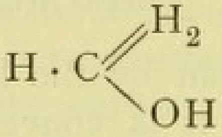
Formaldehyde,  , is prepared both on the large and small scale by the incomplete combustion of methyl alcohol, the vapour of which, along with the proper quantity of air, is passed through a heated tube containing copper, coke, or some other material, and the aldehyde obtained as a solution in water,—

$$2CH_3{\cdot}OH + O_2 = 2H{\cdot}CHO + 2H_2O.$$

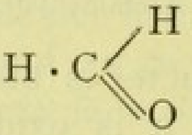
Like acetaldehyde it reduces many metallic oxides and has a pungent odour. A 40 per cent solution in water is largely used as a disinfectant under the name of formalin.

Formic Acid, H_2CO_2 or  is produced when formaldehyde is further oxidised, but this method is not suitable for its preparation.

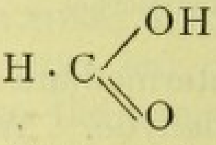
The chemical relations between methyl alcohol, formaldehyde and formic acid are the same as between ethyl alcohol, acetaldehyde and acetic acid :



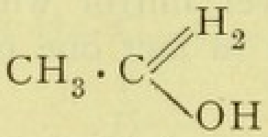
Methyl alcohol.



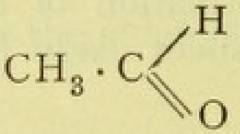
Formaldehyde.



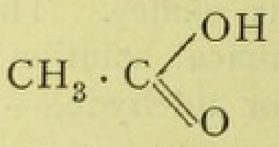
Formic acid.



Ethyl alcohol.

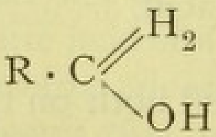


Acetaldehyde.

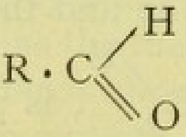


Acetic acid.

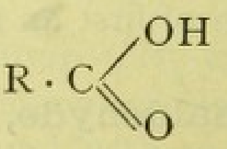
In every case the member of the ethyl series contains a methyl group, $\cdot CH_3$, in place of the hydrogen atom of the methyl series. A similar difference exists between the ethyl series and the next higher one and so on. It is therefore possible to express these relationships by a general formula in which R indicates a hydrogen atom or a univalent group such as methyl, $\cdot CH_3$, ethyl, $\cdot C_2H_5$, etc., these groups being known by the general term *alkyl* groups.



Alcohol.



Aldehyde.



Acid.

The salts of formic acid may be synthetically produced in two very simple ways: (1) By the direct union of carbon monoxide with caustic potash, which occurs very slowly,—

$$KOH + CO = H \cdot CO \cdot OK.$$

(2) By the direct union of carbon dioxide with sodium hydride,—

$$NaH + CO_2 = H \cdot CO \cdot ONa.$$

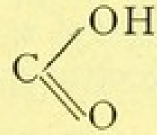
The anhydrous acid cannot be prepared in the same way as acetic acid, because strong sulphuric acid decomposes it into carbon monoxide and water,—

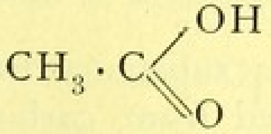
$$H \cdot CO \cdot OH = H_2O + CO.$$

This is one of the best methods for preparing pure carbon monoxide.

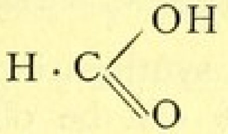
The pure acid is therefore prepared by decomposing lead formate with sulphuretted hydrogen, then distilling the acid,—

$$(H \cdot CO \cdot O)_2Pb + H_2S = 2H \cdot CO \cdot OH + PbS.$$

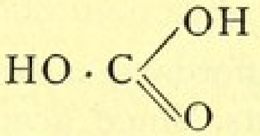
It boils at 101° and is a somewhat stronger acid than acetic. Formic acid differs in constitution from acetic acid only by having a single hydrogen atom combined with the group  , in place of the methyl group of acetic acid,—



Acetic Acid.



Formic Acid.



Carbonic Acid.

This makes it very closely allied with carbonic acid, as shown above. As a matter of fact, formic acid is much less stable than acetic acid and is very easily oxidised to carbonic acid. It is therefore a strong reducing agent and, like formaldehyde, produces a silver mirror with an ammoniacal solution of silver oxide,—

$$H \cdot CO \cdot OH + Ag_2O = HO \cdot CO \cdot OH + 2Ag = H_2O + CO_2 + 2Ag.$$

It also reduces mercuric chloride to mercurous chloride and can be estimated by means of this reaction, the mercurous chloride produced being weighed,—

$$2HgCl_2 + H_2CO_2 = 2HgCl + 2HCl + CO_2.$$

Formic acid, $H \cdot CO_2H$, and acetic acid, $CH_3 \cdot CO_2H$, are the first members of an homologous series of monobasic acids known as the fatty acid series, in which, as in those of the paraffin hydrocarbons and of the alcohols, the general chemical properties are analogous, whilst the physical properties undergo a gradual and progressive change. In this case as in the others the boiling point gradually rises as the molecular weight increases.

Compounds of Carbon with Nitrogen

Hydrocyanic Acid, HCN.—Carbon does not unite directly with nitrogen even at a high temperature, but combination can be indirectly effected in several ways. The formation of sodium cyanide from sodamide and carbon, and of potassium cyanide by heating potassium carbonate and carbon in ammonia are described elsewhere (pp. 162, 338), and the production of ferrocyanides is described later on (p. 389).

Hydrocyanic acid is also formed when a mixture of acetylene, C_2H_2, and nitrogen is subjected to a series of electric sparks,—

$$C_2H_2 + N_2 = 2HCN.$$

This affords a means of synthesising this substance from its elements, since acetylene can be obtained from carbon and hydrogen at a high temperature.

Part of the nitrogen of coal forms hydrocyanic acid when the coal is distilled, so that this compound is present in crude coal gas, which serves as a source of cyanides on the large scale (p. 389). The acid was formerly known as prussic acid because it was prepared from Prussian blue.

When potassium cyanide is treated with a dilute acid, it decomposes yielding the corresponding acid, hydrocyanic acid,—

$$KCN + H_2SO_4 = KHSO_4 + HCN.$$

The vapour of the acid is extremely poisonous and the pre-

paration of the anhydrous acid requires the greatest care and should only be undertaken by skilled persons. For this purpose a mixture of equal volumes of sulphuric acid and water is allowed to drop on to lumps of potassium cyanide. Hydrocyanic acid is evolved, is dried by being passed over warm calcium chloride, and is then condensed in a freezing mixture at -10°.

Pure hydrocyanic acid is a colourless, mobile liquid which boils at 26° and freezes at -15°. Its vapour has the normal density corresponding to the formula HCN.

It is inflammable and burns with a violet flame. The greatly diluted vapour of the acid possesses a characteristic smell and produces an irritation of the throat by which it can readily be recognised.

The acid mixes with water, yielding a solution which acts as a very weak acid (see p. 338).

The Cyanides.—The salts of the metals of the alkalis and alkaline earths are soluble in water and mercuric cyanide is also soluble, but those of the other metals are insoluble, although they are as a rule dissolved by potassium cyanide, soluble double cyanides being formed (see pp. 282, 389, 401). The soluble cyanides may be obtained by adding hydrocyanic acid to the hydroxides ; the insoluble ones by precipitation by means of sodium or potassium cyanide.

Concentrated sulphuric acid decomposes the cyanides with formation of ammonium sulphate and carbon monoxide,—

$$KCN + 2H_2SO_4 + H_2O = KHSO_4 + NH_4HSO_4 + CO.$$

When boiled with alkalis they slowly yield ammonia and formic acid (p. 334),—

$$KCN + 2H_2O = NH_3 + H \cdot COOK.$$

The acid is detected by the following reactions :—

1. Silver nitrate gives a white precipitate of silver cyanide, insoluble in cold dilute nitric acid, soluble on boiling.
2. When an alkaline solution is boiled with a mixture of a ferrous and ferric salt and then acidified, Prussian blue is formed. Ferrous cyanide is formed and is converted

into a ferrocyanide, which reacts in the acid solution with the ferric salt, forming Prussian blue (see p. 390).

3. When a cyanide is evaporated to dryness with a drop of yellow ammonium sulphide, it combines with sulphur, forming a thiocyanate, and this gives a characteristic red coloration with ferric chloride.

Potassium Cyanide, KCN, may be prepared on the large scale by heating potassium ferrocyanide, or by treating a fused mixture of potassium carbonate and charcoal with ammonia, but has now been largely superseded by the sodium salt (p. 162). It is a white crystalline salt, which, like hydrocyanic acid itself, is extremely poisonous. Hydrocyanic acid is a very weak acid, and a solution of potassium cyanide is always found to have an alkaline reaction (p. 161).

Potassium cyanide forms an excellent reducing agent, and is much used in the laboratory in this capacity. Thus, when fused with many metallic oxides it takes the oxygen from them, leaving the free metal, and forming a new salt, *potassium cyanate*, KCNO,—

$$KCN + PbO = KCNO + Pb.$$

Potassium Sulphocyanide, or Potassium Thiocyanate, KCNS.—This salt is formed when potassium cyanide is heated with sulphur, or when a solution of potassium cyanide is boiled with yellow ammonium sulphide. It crystallises in long prisms and is readily soluble in water, a considerable amount of heat being absorbed. It is used in analytical chemistry as a reagent for ferric salts, with which it gives a blood-red coloration, due to the formation of ferric thiocyanate.

Cyanogen $(CN)_2$.—When mercuric cyanide is heated it decomposes into metallic mercury and gaseous cyanogen, which may be collected over mercury,—

$$Hg(CN)_2 = Hg + (CN)_2.$$

It is most conveniently prepared by adding a concentrated solution of potassium cyanide to a solution of copper sulphate in twice its weight of water and warming. Cupric cyanide is first formed and then decomposes into cuprous cyanide, which is a white insoluble salt, and cyanogen,—

$$2Cu(CN)_2 = Cu_2(CN)_2 + (CN)_2.$$

This reaction is very similar to that which occurs when potassium iodide is added to copper sulphate solution (p. 272).

Cyanogen is a colourless gas, which is *very poisonous* and has an odour of peach kernels. It burns with a beautiful purple-mantled flame and readily forms explosive mixtures with air or oxygen,—

$$(CN)_2 + 2O_2 = 2CO_2 + N_2.$$

It is soluble in four volumes of water and condenses to a liquid which boils at $-21°$ and freezes at $-34°$. The vapour density corresponds with the molecular formula $(CN)_2$.

In its chemical properties cyanogen in many respects resembles a halogen element. Thus when it is passed over heated potassium it unites with it forming potassium cyanide, just as chlorine unites with potassium forming the chloride,—

$$2K + (CN)_2 = 2KCN,$$
$$2K + Cl_2 = 2KCl.$$

The group $-C \equiv N$, in other words, is able to act as a univalent acid radical, just as the group $-NH_4$ is able to act as a univalent metal. Thus two of these groups unite to form the molecule of the free gas, just as do two atoms of chlorine, bromine or iodine. This analogy is rendered evident when the formulæ of some of the compounds are placed side by side.

Chlorine, Cl_2	Cyanogen, $(CN)_2$
Hydrochloric acid, HCl	Hydrocyanic acid, $H(CN)$
Potassium chloride, KCl	Potassium cyanide, $K(CN)$
Mercuric chloride, $HgCl_2$	Mercuric cyanide, $Hg(CN)_2$

It is interesting to note that it was the study of the cyanogen compounds that first led to the recognition of compound radicals, capable of acting in many ways as an element (p. 198). The name cyanogen (producer of blue) refers to the fact that this group occurs in Prussian blue. The analogy between cyanogen and chlorine extends to the action of these substances on the alkalis. When cyanogen is passed into caustic potash solution, it is absorbed and a mixture of cyanide and cyanate is produced, just as a chloride and hypochlorite are formed from chlorine,—

$$2KHO + (CN)_2 = KCN + KCNO + H_2O.$$
$$2KHO + Cl_2 = KCl + KClO + H_2O.$$

Potassium Cyanate, KCNO.—This salt is also formed when potassium cyanide is melted with a reducible oxide (p. 338), but is best prepared by heating potassium ferrocyanide with potassium bichromate. It is soluble in dilute alcohol and in water. Acids produce a remarkable decomposition, as the unstable cyanic acid which is first produced is decomposed by the water present forming ammonium carbonate, which is then decomposed by the acid present,—

1. $KCNO + HCl = KCl + HCNO.$
2. $HCNO + 2H_2O = (NH_4)HCO_3.$
3. $(NH_4)HCO_3 + HCl = NH_4Cl + H_2O + CO_2.$

The cyanates therefore effervesce with acids like carbonates.

Pure *cyanic acid*, HCNO, is extremely unstable and is a colourless liquid having a very pungent smell.

Carbon and Sulphur

Carbon Bisulphide, CS_2.—When sulphur vapour is passed over red-hot charcoal, the two elements unite and form carbon bisulphide, CS_2. It is a colourless liquid which boils at 46° and is heavier than water, having the specific gravity 1.29. When pure it has a smell resembling that of chloroform, but usually contains impurities which give it a very unpleasant odour. It very easily takes fire in the air, even at 260°, and burns with a blue flame forming carbon dioxide and sulphur dioxide. A mixture of its vapour with nitric oxide burns with a brilliant blue flame and is highly explosive.

Carbon bisulphide is formed from its elements with absorption of heat and can be decomposed by a shock as already mentioned (p. 293).

Carbon bisulphide is almost insoluble in water; it is an excellent solvent for rubber and for oils and fats, and is industrially employed on account of these properties. It also readily dissolves iodine, forming a beautiful violet-coloured solution.

Carbon bisulphide corresponds in composition with carbon dioxide and is capable of combining with metallic sulphides to form salts, known as the thiocarbonates which correspond with the carbonates,—

$$CS_2 + Na_2S = Na_2CS_3$$

$$CO_2 + Na_2O = Na_2CO_3.$$

SUMMARY

Carbon forms an extremely large number of compounds with hydrogen, oxygen and nitrogen. In these it acts as a quadrivalent element and each atom of it is capable of combining with one or more other atoms of carbon.

Marsh gas is the first member of an homologous series of hydrocarbons, each of which is derived from the next lower by the substitution of hydrogen by the univalent methyl group $\cdot CH_3$.

These hydrocarbons form substitution products with chlorine and the other halogen elements. The monohalogen substitution derivatives can readily be converted into hydroxy-derivatives of the general formula $R \cdot CH_2 \cdot OH$, and these pass by oxidation into aldehydes, $R \cdot CHO$ and acids $R \cdot CO \cdot OH$.

Carbon unites with nitrogen to form cyanogen, $(CN)_2$, which contains the univalent radical $\cdot CN$, which in its chemical behaviour resembles chlorine and is present in hydrocyanic acid, HCN, and the cyanides.

Carbon unites with sulphur to form a bisulphide CS_2, which corresponds in composition with carbon dioxide.

EXERCISES ON LESSON XXX

1. Explain why the formula $CH_3 \cdot CH_2(OH)$ is given to ethyl alcohol.
2. What is the action of chlorine on marsh gas?
3. How could you obtain acetic acid from marsh gas?
4. Describe the chief properties of formic acid. How can (*a*) Carbon monoxide, (*b*) Carbon dioxide be prepared from it?
5. Describe the preparation and properties of cyanogen.
6. What is meant by (*a*) an homologous series, (*b*) substitution?
7. Describe the preparation of hydrocyanic acid from potassium cyanide. Compare the properties of this acid with those of hydrochloric acid.

LESSON XXXI

THE ELEMENTS OF THE CARBON GROUP (*Cont.*)

Silicon, Si, 28.3

THE element silicon does not occur in the free state, although it enters more largely than any other element, except oxygen, into the composition of the solid crust of the earth. It always occurs combined with oxygen, either in the form of silica (silicon oxide) or as a silicate of one or more metals.

Silicon Oxide, Silica, SiO_2, is found very widely distributed in the form of sand or sandstone, which consists almost entirely of particles of silica, more or less coloured by iron, and often cemented together by calcium carbonate or some other substance.

Sand has generally been produced by the disintegration of *quartz*, which is a crystalline variety of silica and is often found in well-developed six-sided prisms capped by pyramids (Fig. 17, p. 134). These crystals are usually transparent, and in this form quartz is known as rock-crystal, but they are sometimes coloured by a trace of oxide of manganese, which gives rise to the amethyst, or by other oxides. Quartz, however, occurs much more extensively as quartz rock or quartzite, which is found both alone and mixed with other minerals, forming rocks such as granite, gneiss, etc. It has a specific gravity of 2.65, and is very hard.

A second crystalline variety of silica also exists, which is known as *tridymite*; this crystallises in the asymmetric system, and is found in porphyry and other similar igneous rocks. This has the specific gravity 2.3 and is as hard as quartz.

The existence of these two crystalline varieties shows that silica, like calcium carbonate, is dimorphous (p. 142).

Silica is also found in the amorphous form, containing more or less water, as opal and flint. Agate and other similar stones, which are sometimes used for ornamental purposes, consist of amorphous silica, mixed with one or other of the crystalline varieties, and coloured by small amounts of various metallic oxides. The silica has probably been deposited in these forms from solution in water, in which it dissolves at a high temperature and under a high pressure. The different coloured concentric layers of the agate show that the rate of deposition varied at different times, and that impurities consisting of metallic oxides were sometimes present.

Silica also occurs in plants and animals, especially in the stems of cereals and the feathers of birds, and is also found in a very finely divided state in the form of *kieselguhr*, which consists of the skeletons secreted by diatoms. This material is largely used for making dynamite and filters for water.

Silica melts in the oxyhydrogen flame or the electric furnace to a thin glass, which is used for the production of quartz threads, which can be made extremely fine, and are employed for procuring a very delicate suspension in galvanometers, etc. Quartz can also be worked like glass into tubes and vessels of various forms, which are now frequently used for chemical purposes. Such vessels are unattacked by aqueous acids and alkalis. Moreover they withstand great variations of temperature without cracking, the coefficient of expansion of quartz being extremely small. Thus a tube of quartz may be safely heated in the blowpipe and immediately plunged into cold water.

Quartz has the property of transmitting ultra-violet light which is totally absorbed by ordinary glass, and it is therefore often employed in optical work.

Chemical Properties of Silica.—Silica is insoluble in water, and in all acids except hydrofluoric acid, which readily converts it into gaseous silicon fluoride (p. 349),—

$$SiO_2 + 4HF = SiF_4 + 2H_2O.$$

In its chemical properties it belongs to the group of acid-forming oxides. Thus, finely divided amorphous silica dissolves in caustic soda, forming sodium silicate, although quartz or even strongly ignited amorphous silica is only very slightly attacked. When silica is fused with sodium carbonate the latter is decomposed, carbonic acid gas is evolved, and sodium silicate is produced,—

$$2Na_2CO_3 + SiO_2 = Na_4SiO_4 + 2CO_2.$$

EXPERIMENT 145.—Make a bead of sodium carbonate on a piece of platinum wire. Dip the bead whilst hot into some sand and heat in the flame — the sand is dissolved with effervescence due to the escape of carbon dioxide.

Sodium silicate, Na_4SiO_4, is soluble in water, so that silica in all its forms, and even when present as an insoluble silicate, can be brought into solution by this process, which is much used in mineral analysis.

When concentrated hydrochloric acid is added to a strong solution of sodium silicate in water, a gelatinous precipitate of hydrated silica is formed. This substance does not appear to be silicic acid, H_4SiO_4, or indeed any definite acid, but contains a large amount of water, which is gradually lost on drying, and varies in amount according to the conditions under which the experiment is carried out. When it is strongly heated, after having been well washed, pure amorphous silica remains behind. On the other hand, when a dilute solution of sodium silicate is acidified with hydrochloric acid, no precipitate whatever is formed, a soluble form of silicic acid being produced.

Crystalloids and Colloids—Dialysis.—This solution has certain remarkable properties, which differ from those of a solution of an ordinary acid or crystalline salt, and more closely resemble those of a solution of glue or gelatine in water. When the solution is poured into a tube made of parchment paper, and this is plunged into water, it is found that only the excess of hydrochloric acid and the sodium chloride produced by the action of the hydrochloric acid diffuse through the parchment, whilst the whole of the soluble silicic acid remains behind. This fact was first discovered by Graham, who termed substances which refuse to pass through parchment in this way *colloids*, whereas substances which pass through the parchment are known as *crystalloids*. The process is known as *dialysis*, and the apparatus as a dialyser. This process requires a considerable time for its completion, and can be demonstrated by placing the solution in a tube of parchment, partially immersed in distilled water, which must be frequently renewed. As soon as the external water gives no reaction with silver nitrate, the solution of silicic acid may be removed and caused to coagulate by the addition of sodium carbonate.

The dialysed solution of silicic acid can be concentrated by boiling up to a certain point, but sets to a jelly when it is preserved for several days, or when a trace of sodium carbonate is added. Many other oxides can be obtained in solution by this process of dialysis, and closely resemble colloidal silica in their physical properties.

If a solution of silicic acid or a silicate be acidified, evaporated to dryness, and the residue then gently heated, moistened with concentrated hydrochloric acid, and finally treated with water, the whole of the silica remains behind in the insoluble form.

EXPERIMENT 146.—To a dilute solution of sodium silicate add dilute hydrochloric acid in excess—no precipitate occurs. Evaporate to dryness, heat gently on the sand bath, moisten with three drops of concentrated hydrochloric acid, and extract with boiling water—a gelatinous mass of silica is left.

The Silicates.—Although pure silicic acid has not itself been prepared, a very large number of silicates are known, many of which are crystallised minerals. These may be regarded as derived from acids containing different amounts of water, corresponding to some extent with the acids of phosphorus. The number of silicates known is very great, and only a few of the most important can even be mentioned here.

Sodium Orthosilicate, Na_4SiO_4, and **Sodium metasilicate**, Na_2SiO_3, are formed when sodium carbonate is fused with the requisite amounts of silica,—

$$2Na_2CO_3 + SiO_2 = Na_4SiO_4 + 2CO_2.$$

$$Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2.$$

These salts may be regarded as salts of orthosilicic acid, H_4SiO_4, and metasilicic acid, $H_2SiO_3 (= H_4SiO_4 - H_2O)$.

Sodium silicate is known commercially as soluble glass, and is made by fusing white sand with sodium carbonate. It is a brownish or greenish glass-like mass, which forms a thick solution in water. It is used as an addition to soap and as a cement.

The following may be taken as examples of naturally occurring silicates :—

Wollastonite . . .	$CaSiO_3$.
Leucite	$KAl(SiO_3)_2$.
Talc	$Mg_3H_2(SiO_3)_4$.
Potash mica (Muscovite) .	$KH_2Al_3(SiO_4)_3$.
Clay	$Al_2Si_2O_7 + 2H_2O$.
Meerschaum . . .	$Mg_2Si_3O_8$.
Asbestos	$(Mg, Ca)SiO_3$; a portion of the magnesium is here replaced by calcium.
Felspar	$KAlSi_3O_8$; a portion of the potassium is replaced by sodium, and if the latter be in excess the mineral is known as albite.

Glass is a fused mixture of the silicates of the alkali metals with those of calcium or lead. It is amorphous, and is almost insoluble in water, and only very slightly attacked by acids. In these respects it differs from its constituents, for sodium silicate is readily soluble in water, whilst calcium silicate is easily attacked by acids, and is, moreover, crystalline. Glass, moreover, has the valuable property of passing through a viscid stage during cooling, so that it can be moulded or blown into any desired shape before it becomes hard and brittle. The chief varieties of glass are : *Window glass*, which is a mixture of the silicates of sodium and calcium ; *Bohemian glass*, which is a mixture of the silicates of potassium and calcium, and is much less fusible than window glass ; *Flint glass*, which is a mixture of the silicates of potassium and lead, and is very fusible and highly refractive.

Special forms of glass which are only very slightly attacked by acids and alkalis are made for chemical purposes and are known as Jena glass and resistance glass. They contain as a rule a certain amount of boron trioxide and the oxides of metals such as zinc and barium.

Glass is manufactured by fusing the constituents together in an earthenware pot. The silica is added in the form of sand or quartz, and with this is mixed carbonate or sulphate of potassium or sodium, and limestone. Special precautions have to be taken in making the finer kinds of glass that all the materials are free from iron, the presence of which results in the production of a green coloured glass.

When molten glass is allowed to cool quickly it forms a mass which readily flies to pieces when its surface is scratched. This is due to the fact that glass is a bad conductor of heat, and hence the outside of the mass cools long before the internal portions, and a state of strain is produced.

This is well seen in the so-called *Rupert's drops*, which consist of pear-shaped drops of glass which have been suddenly cooled by water. These are apparently quite stable, but fly to powder if the point be broken. All articles made of glass are therefore subjected to a process known as *annealing*, which consists in allowing them to cool very slowly, and prevents the unequal cooling of the different layers.

Porcelain consists of an infusible mass of aluminium silicate, which is penetrated and covered by a fusible glaze. Kaolin, or pure aluminium silicate, $Al_2Si_2O_7 + 2H_2O$, is made into a paste with water, worked into the required shape and then dried and baked. It is then covered with the material of the fusible glaze, which usually consists of felspar or a mixture of quartz and lime or gypsum; and the whole is strongly heated, so that the glaze melts and penetrates the entire mass of the porcelain.

Silicon itself is not easy to prepare in the pure state, since its compounds which occur in nature are all very stable, and hence are difficult to decompose.

It may be obtained by heating potassium fluosilicate with metallic potassium in an iron tube,—

$$K_2SiF_6 + 4K = 6KF + Si.$$

Impure silicon can readily be obtained by heating dried white sand with one-fourth of its weight of magnesium powder in a wide test-tube. This is best carried out by filling the test-tube to about half of its length with the mixture, supporting it in a slanting position in a clamp, and heating gradually from the top downwards. If heated too suddenly the action becomes almost explosive. The mass glows brightly when the reduction occurs, and after cooling is treated with dilute sulphuric acid to remove magnesia and unaltered magnesium, etc., and is then washed and dried.

Amorphous silicon is a brown powder which readily burns in the air to form silica,—

$$Si + O_2 = SiO_2.$$

It is insoluble in acids, with the exception of hydrofluoric acid, but dissolves in boiling alkalis, and combines with fluorine, chlorine, bromine, and iodine. Like boron it also exists in a crystalline form, which is obtained by heating the amorphous powder in a covered crucible with aluminium or zinc, and dissolving out the metal with dilute hydrochloric acid. It is prepared on the large scale by heating silica with the requisite amount of carbon in the electric furnace and forms lumps of metallic appearance, whereas small crystals are yellow coloured and transparent. It is used as a deoxidiser for castings of steel or bronze. Like boron, silicon has a very low atomic heat, which, however, increases with the temperature at which it is determined (p. 130).

Atomic Weight of Silicon and Formulæ of the Silicon Compounds.—The equivalent of silicon has been determined by decomposing the bromide with water, and estimating the amounts of silica and hydrobromic acid produced, and it has thus been found that in silicon bromide 7.075 parts of silicon are united with 79.92 of bromine, and are therefore equivalent to 1.008 of hydrogen.

The atomic weight has been settled, precisely as in the case of boron, by a comparison of the molecular weights and composition of the numerous volatile compounds of the element, and is about 28.

Hence $7.075 \times 4 = 28.3$ is taken as the correct atomic weight.

The bromide therefore has the formula $SiBr_4$, the atom of silicon being in this case quadrivalent.

Silicon Hydride, SiH_4. — Silicon forms two remarkable compounds with hydrogen—a gas, SiH_4, and a liquid Si_2H_6. When white sand is heated with an excess of magnesium powder, the silicon unites with magnesium to form a silicide of magnesium, and when this is treated with dilute hydrochloric acid silicon hydride is evolved. This gas, like phosphine, as ordinarily prepared, is spontaneously inflammable in the air, and burns, forming white clouds of silica,—

$$SiH_4 + 2O_2 = SiO_2 + 2H_2O.$$

The pure gas is not spontaneously inflammable, but takes fire very readily, and decomposes when heated, yielding an opaque mirror of silicon and two volumes of hydrogen. The formation of this gas may be demonstrated by heating sand with 1.5 part of magnesium, as described above (p. 348), and adding the cold product in small portions to hydrochloric acid. Hydrogen mixed with silicon hydride is evolved, and the bubbles take fire at the surface of the liquid.

Silicon also combines with many other metals forming *silicides*, which are decomposed by water or acids in a similar manner to the magnesium compound.

Silicon Fluoride, SiF_4.—Silicon takes fire when exposed to fluorine, forming the tetrafluoride, and this gas is formed whenever hydrofluoric acid acts on silica, the etching of glass by hydrofluoric acid being due to the formation of this compound. Silica is removed from the glass, and its transparency thus destroyed. It is prepared by heating sand and calcium fluoride with sulphuric acid in a flask,—

$$2CaF_2 + SiO_2 + 2H_2SO_4 = 2CaSO_4 + SiF_4 + 2H_2O.$$

The gas is colourless and fumes in the air, and is at once decomposed by water with formation of gelatinous silica and hydrofluosilicic acid, H_2SiF_6,—

$$3SiF_4 + 2H_2O = SiO_2 + 2H_2SiF_6.$$

This method serves for the preparation of amorphous silica.

Hydrofluosilicic acid forms a very sparingly soluble potassium salt, and is sometimes used in analytical work for the estimation of potassium.

The properties of silicon fluoride can be demonstrated by placing in a flask a mixture of powdered calcium fluoride with half its weight of sand, adding sufficient sulphuric acid to make the whole into a paste, mixing well and heating gently. The delivery tube of the flask dips into mercury placed in a cylinder, which is then partially filled with water. This arrangement prevents the tube being choked by the gelatinous silica formed by the action of water on the gas.

Silicon Chloride, $SiCl_4$, and **Silicon Bromide, $SiBr_4$,** are prepared by passing chlorine or bromine over heated silicon, but may also be obtained by heating a mixture of silica and carbon in a current of chlorine or bromine,—

$$SiO_2 + 2C + 2Cl_2 = SiCl_4 + 2CO.$$

They are both colourless fuming liquids, which are at once decomposed by water,—

$$SiBr_4 + 2H_2O = SiO_2 + 4HBr.$$

Silicon Carbide, SiC, is prepared by heating sand with coke in the electric furnace,—

$$SiO_2 + 3C = SiC + 2CO.$$

This substance crystallises in needles, which are colourless when pure, but are usually blue and iridescent. It is extremely hard, and is largely used for cutting and polishing purposes under the name of *carborundum*.

Detection of Silicic Acid.—Silica or silicic acid is detected by fusing the substance with sodium carbonate, and treating the resulting silicate with hydrochloric acid as described above. The gelatinous silica left causes effervescence when it is introduced into a bead of fused sodium carbonate, but does not dissolve in a bead of microcosmic salt.

Another test for the presence of silica is to heat the substance with calcium fluoride and concentrated sulphuric acid in a test-tube. If the gas evolved produces a white film on a drop of water held in it on the end of a glass rod, silica is present.

SUMMARY

Silicon exists both as a brown amorphous powder and as shining crystals of metallic appearance. It burns when heated in the air, forming silicon dioxide or silica, SiO_2, which is an acid-forming oxide, and is difficult to reduce.

The silicates are very numerous and often very complicated in composition. The simplest are the orthosilicates, R_4SiO_4, and the metasilicates, R_2SiO_3, but the acids from which these are derived have not been obtained pure.

Silica is acted on by hydrofluoric acid, gaseous silicon fluoride, SiF_4, being formed, and this is decomposed by water, yielding gelatinous silica and hydrofluosilicic acid. The chloride, $SiCl_4$, and the bromide, $SiBr_4$, are fuming liquids and are decomposed by water.

A soluble colloidal form of silica (or silicic acid) can be obtained by dialysing a dilute solution of sodium silicate to which hydrochloric acid has been added. Substances which diffuse through parchment paper are called crystalloids, those which do not are termed colloids.

Silicon forms an unstable volatile hydride, SiH_4.

Tin, Sn (Stannum), 119

Tin was one of the seven metals of the ancients and was associated with the planet Jupiter. The only important compound of this element which occurs largely in nature is the oxide, or *tin-stone*, SnO_2, and this is found in Cornwall, Austria, the island of Banca, the Malay Peninsula, and New South Wales.

Metallurgy of Tin.—The oxide is readily reduced when it is heated with carbon, and hence the manufacture of the metal can readily be carried out by simply heating the roasted ore with anthracite,—

$$SnO_2 + 2C = Sn + 2CO.$$

The ore usually occurs mixed with iron pyrites and arsenical pyrites, and on this account the roasting is carried out with great care in order to remove as much as possible of the arsenic and sulphur, the arsenious oxide being condensed in chambers. The roasted ore is then mixed with anthracite, and heated on the bed of a reverberatory furnace, the metal being run off into moulds.

Properties of Metallic Tin.—Tin is a white, lustrous metal, which has the specific gravity 7.3, and melts at 232°. It is crystalline in structure, and when it is bent emits a curious crackling sound, called the "cry of tin," this being due to the friction of the crystalline particles. The metal can be hammered or rolled into foil, but is too brittle for use as wire.

Tin, like sulphur, exists in two allotropic forms, one of which is only stable above 20° and the other below this temperature. Crystalline tin, therefore, at the ordinary temperature is really unstable, like the monosymmetric crystals of sulphur, and, like them but much more slowly, passes spontaneously into the second form, breaking up into a grey powder. The change takes place most rapidly at a low temperature, and like crystallisation, can be started by bringing the crystalline tin into contact with some of the powder.

Tin does not easily tarnish in the air, but when the molten metal is heated in the air it slowly takes up oxygen, finally forming the dioxide, SnO_2. Tin dissolves rapidly in concentrated hydrochloric acid, with evolution of hydrogen, and formation of the dichloride, $SnCl_2$,—

$$Sn + 2HCl = H_2 + SnCl_2.$$

It is not acted on by dilute sulphuric acid, but dissolves in the concentrated acid, sulphur dioxide being evolved. Nitric acid converts the metal into a white powder, which is a hydrated form of stannic oxide, a copious evolution of brown fumes taking place. The metal also dissolves in aqua regia, forming the tetrachloride, $SnCl_4$, and is slowly dissolved by alkalis.

EXPERIMENT 147.—Examine the behaviour of granulated tin to hydrochloric, nitric, and sulphuric acids.

Tin is largely used on account of its unalterability in the air for tinning iron, an operation which is carried out by dipping the clean hot iron into a bath of molten tin, a protecting layer of the metal being thus produced.

Alloys of Tin.—The alloys of tin are of great value, the most important being gun metal, bell metal, bronze, and solder, which have the composition shown in the following list:—

	Tin.	Lead.	Copper.	Zinc.	Antimony.
Britannia Metal	82	...	...	2	16
Gun Metal .	8	...	92	...	...
Bell Metal .	18	...	82	...	...
Bronze . .	9.2	.7	88.8	1.3	...
Solder . .	50	50	...	...	...

Equivalent and Atomic Weight of Tin.—Tin, like copper and mercury, forms two distinct series of salts, known as the stannous and the stannic salts.

The exact equivalent of tin in the stannic compounds has been determined by converting the metal into oxide, and by analysing the chloride, and has thus been found to be 29.75. The atomic weight is found by the atomic heat method, and by a study of the numerous volatile compounds of the element to be about 118, and hence $29.75 \times 4 = 119$ is taken as the atomic weight of the element.

It follows from this that in the stannic compounds each atom of tin replaces four atoms of hydrogen, and since the equivalent in the stannous compounds is 59.5, exactly double that which the metal has in the stannic compounds, it is seen that each atom of tin replaces two atoms of hydrogen in the stannous salts.

	Stannous.	Stannic.
Oxide . . .	SnO	SnO_2
Chloride . . .	$SnCl_2$	$SnCl_4$.

The stannic compounds correspond in composition with the compounds of silicon, whereas the stannous compounds correspond with the cupric and mercuric compounds.

Compounds of Tin

The same general relations hold between the two series of tin salts as between the cuprous and cupric or mercurous and mercuric salts. In presence of an excess of metal the stannous salts are formed, whilst in presence of an excess of a halogen element or any other oxidising agent, stannic salts are produced. The stannous salts very readily undergo oxidation and therefore act as reducing agents, whereas the stannic salts act as mild oxidising agents. This is well illustrated by the action of the chlorides of tin on different substances.

1. Stannous chloride readily reduces mercuric salts first to mercurous salts and then to metallic mercury,—

$$SnCl_2 + 2HgCl_2 = SnCl_4 + 2HgCl.$$

$$SnCl_2 + 2HgCl = SnCl_4 + 2Hg.$$

2. Stannous chloride reduces cupric and ferric salts to the corresponding cuprous and ferrous salts,—

$$SnCl_2 + 2CuCl_2 = SnCl_4 + Cu_2Cl_2.$$

$$SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2.$$

3. Stannous chloride reduces iodine to hydriodic acid,—

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI.$$

4. When it is treated with concentrated nitric acid, stannous chloride is converted into stannic chloride, and the nitric acid is reduced—oxides of nitrogen being evolved,—

$$3SnCl_2 + 6HCl + 2HNO_3 = 3SnCl_4 + 2NO + 4H_2O.$$

5. Stannic chloride is converted by boiling with metallic copper into stannous chloride,—

$$SnCl_4 + 2Cu = SnCl_2 + Cu_2Cl_2.$$

EXPERIMENT 148.—1. To a solution of mercuric chloride add a few drops of stannous chloride—a white precipitate of mercurous chloride is formed. Now add excess of stannous chloride and warm—a gray precipitate of metallic mercury is produced.

2. To a saturated solution of cupric sulphate add hydrochloric acid and a solution of stannous chloride, and warm—the green colour of the solution disappears and cuprous chloride is precipitated.

3. To a solution of stannous chloride add ferric chloride

solution drop by drop—the yellow colour of the ferric salt at first disappears, but finally remains even after warming. To this solution add mercuric chloride—no precipitate is produced, the whole of the stannous salt having been converted into stannic salt.

4. To a solution of iodine in potassium iodide add stannous chloride solution—the yellow colour of the iodine at once disappears.
5. To a solution of stannous chloride add concentrated nitric acid and warm—brown fumes are evolved.
6. Boil a solution of stannic chloride with copper turnings, pour off the solution and add mercuric chloride solution —a white precipitate of mercurous chloride is formed.

The Stannic Compounds

Stannic Oxide, SnO_2, occurs as *tinstone* or *cassiterite* in square prisms capped by pyramids, as well as in large masses. The oxide is best prepared by treating tin with nitric acid and heating the residue ; it then forms a white powder, which becomes brown at a high temperature, but regains its former appearance on cooling.

This oxide resembles silica very closely in its properties. Thus it is insoluble in hydrochloric and nitric acids, but can be brought into solution by fusion with sodium carbonate, sodium stannate, Na_2SnO_3, corresponding in composition with sodium metasilicate, Na_2SiO_3, being produced,—

$$Na_2CO_3 + SnO_2 = Na_2SnO_3 + CO_2.$$

This salt yields a gelatinous precipitate with hydrochloric acid, which, however, like gelatinous silica, cannot be regarded as a definite hydrate. The same gelatinous mass is obtained by adding an alkali to stannic chloride,—

$$Na_2SnO_3 + 2HCl = 2NaCl + SnO_2 + H_2O.$$
$$SnCl_4 + 4NaOH = 4NaCl + SnO_2 + 2H_2O.$$

A soluble colloidal form is also produced when a mixture of sodium stannate and hydrochloric acid, or of stannic chloride and caustic soda is dialysed.

The gelatinous oxide dissolves in alkalis, forming the stannates, which are soluble in water and are used as mordants in calico printing.

EXPERIMENT 149.—1. To a solution of stannic chloride add caustic soda solution—a gelatinous precipitate is produced which dissolves in excess of caustic soda.

2. To a solution of sodium stannate add hydrochloric acid —a gelatinous precipitate is produced. Filter off a portion of this, dry it in the air, and heat a part of it on a bead of sodium carbonate—effervescence occurs, just as in the case of silica (p. 344).

Metastannic Acid.—The white powder formed by the action of nitric acid on the metal is also a hydrated stannic oxide, and is known as metastannic acid. It does not dissolve in acids, but dissolves in alkalis, forming salts of complex composition known as the metastannates, such as sodium metastannate, $Na_2Sn_5O_{11}$, which differ in composition from the stannates. The prefix meta- is here used in a different sense from that which it bears in such names as metaphosphoric acid, etc.

Stannic Chloride, $SnCl_4$, is prepared by passing chlorine into melted tin, and is a colourless fuming liquid, which boils at 114° and produces a colourless vapour which has the normal density. It forms several crystalline hydrates with water, but decomposes when its solution is boiled, gelatinous stannic oxide being precipitated. The chloride is largely used as a mordant in dyeing, and is often prepared for this purpose by the action of nitric acid on stannous chloride.

Stannic Fluoride, SnF_4, is formed in solution by the action of hydrofluoric acid on stannic oxide, and unites with potassium fluoride to form potassium stannofluoride, K_2SnF_6, which is isomorphous with potassium silicofluoride, K_2SiF_6, with which it corresponds in composition (p. 349).

Stannic Sulphide, SnS_2, is best prepared by heating tin filings with sulphur and ammonium chloride; the sulphide then sublimes in golden yellow scales. It is known, from its appearance, as mosaic gold, and is used for bronzing various articles. It is also formed as a yellow precipitate when sulphuretted hydrogen is passed into a solution of stannic chloride. Like the sulphides of arsenic and antimony it dissolves readily in ammonium sulphide, forming thiostannates, which are again decomposed by acids,—

$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3.$$

EXPERIMENT 150.—Pass sulphuretted hydrogen into a warm acid solution of stannic chloride—a yellow precipitate of the sulphide is slowly formed. This dissolves in ammonium sulphide and is reprecipitated when an excess of hydrochloric acid is added.

The Stannous Compounds

Stannous Hydroxide, $Sn(OH)_2$, is precipitated as an amorphous white mass when an alkali is added to a solution of stannous chloride. In its behaviour towards acids and alkalis it closely resembles aluminium hydroxide, for like the latter it readily dissolves in acids, and is also soluble in caustic soda, but not in ammonia.

It absorbs oxygen from the air, but when it is carefully dried in a current of carbonic acid gas it yields stannous oxide, SnO, as a black powder, which burns when heated in the air, forming stannic oxide.

EXPERIMENT 151.—To a solution of stannous chloride add caustic soda drop by drop—a white precipitate of the hydroxide is produced which dissolves in excess of caustic soda, and is also soluble in hydrochloric acid.

Stannous Chloride, $SnCl_2$, is prepared by dissolving tin in hydrochloric acid and evaporating the solution. It crystallises in prisms containing two molecules of water, and these dissolve in a small quantity of water to form a clear solution, but when a large amount of water is added, a *basic chloride*, $Sn(OH)Cl$, is precipitated, soluble in hydrochloric acid.

The solution absorbs oxygen from the air, the stannous chloride being converted into stannic chloride if free hydrochloric be present, whilst, in the absence of acid, stannous hydroxide is precipitated, which gradually passes into stannic hydroxide.

EXPERIMENT 152.—Dissolve 10 grams. of granulated tin in warm concentrated hydrochloric acid (about 40 cc.), taking care that some metallic tin is left undissolved; evaporate to small bulk in the presence of the tin, allow to settle, and pour off the clear liquid. On standing, large transparent prisms of stannous chloride separate out.

Stannous chloride boils at 606°, and forms a vapour which at high temperatures has the density 95, corresponding with the molecular weight 190 and the formula $SnCl_2$. Stannous chloride is much used for the preparation of stannic chloride, as already described.

The reducing action of stannous chloride has already been sufficiently illustrated. The chloride combines with enough chlorine to convert it into stannic chloride, and this chlorine is derived either directly from the substance which is undergoing reduction, as in the case of mercuric chloride, or else from hydrochloric acid, the hydrogen of which acts as the direct reducing substance, as in the cases of iodine and nitric acid.

Stannous Nitrate, $Sn(NO_3)_2$, is formed by the action of very dilute nitric acid on metallic tin.

Stannous Sulphide, SnS, is formed as a dark coloured mass when the requisite amounts of tin and sulphur are fused together. When sulphuretted hydrogen is passed into an acid solution of stannous chloride a brown precipitate of the sulphide is formed, which is insoluble in hydrochloric acid. This precipitate is insoluble in colourless ammonium sulphide, but dissolves in the yellow sulphide which contains excess of sulphur. The stannous sulphide is converted by the sulphur into stannic sulphide, and this then dissolves in the usual way, forming a thiostannate.

Hence when acids are added to the solution of the brown sulphide in yellow ammonium sulphide, the yellow stannic sulphide is precipitated.

EXPERIMENT 153.—Pass sulphuretted hydrogen into stannous chloride solution and filter off the brown precipitate which is produced. Test the action of colourless and yellow solutions of ammonium sulphide on this. To the solution in yellow ammonium sulphide add hydrochloric acid—yellow stannic sulphide is precipitated.

Detection of Tin.—The tin compounds are all reduced to the metal when they are heated on charcoal with a reducing agent, such as a mixture of potassium cyanide and sodium carbonate. They do not colour the flame, or a borax bead, but when added to a bead coloured blue by a copper salt, change the colour to red.

The soluble salts of tin are detected by the characteristic sulphides and the action of stannous chloride on the mercuric salts.

SUMMARY

Tin is a white metal which slowly oxidises when heated in the air, and dissolves readily in hydrochloric acid, whilst nitric acid converts it into hydrated stannic oxide. The metal can easily be obtained by the reduction of its oxides.

Tin forms two series of salts, the stannic salts, in which it is quadrivalent, and the stannous salts, in which it is bivalent.

The stannic salts correspond in composition with the derivatives of carbon and silicon. The oxide is acid-forming, and the chloride is a fuming liquid.

The stannous salts are strong reducing agents and readily pass into the corresponding stannic salts. The chloride is formed when the metal dissolves in hydrochloric acid, and is a crystalline salt. The oxide has basic properties, but also acts towards strong bases as an acid-forming oxide.

EXERCISES ON LESSON XXXI

1. In what forms does silica occur in nature?

2. Describe the preparation of pure amorphous silica from quartz.

3. What occurs when silica is fused with sodium carbonate? Give an account of the properties of sodium silicate.

4. What is meant by the terms dialysis, crystalloid, colloid?

5. What is the composition of the following substances: porcelain, flint glass, felspar, meerschaum, asbestos?

6. Describe the preparation and properties of silicon fluoride and silicon chloride.

7. How is metallic tin obtained from its ores, and what are the chief physical properties of the metal?

8. Compare the stannic compounds with those of silicon.

9. Give instances of the action of stannous compounds as reducing agents, and point out the chemical changes which occur in these reactions.

10. How can the following substances be prepared from stannous chloride: stannic chloride, stannous oxide, stannic sulphide?

11. How would you attempt to prepare pure stannous chloride from bell-metal?

12. How much metallic mercury could be obtained from mercuric chloride by the action of 50 grams. of pure stannous chloride?

13. What reasons have we for supposing that tin is quadrivalent in the stannic compounds and bivalent in the stannous compounds?

LESSON XXXII

THE ELEMENTS OF THE CARBON GROUP (*Cont.*)

Lead, Pb, 207.1

LEAD, like tin, was well known to the ancients and was associated with the planet Saturn. The Latin name for the metal is *plumbum*, whence the symbol Pb is derived.

This metal is scarcely ever found in the free state, but usually occurs as the sulphide or *galena*, PbS, from which most of the lead of commerce is derived. It is also found in a number of other minerals, the most important of which are the carbonate, *cerussite*, $PbCO_3$, and the sulphate, *anglesite*, $PbSO_4$.

Properties of Metallic Lead.—Lead has a characteristic bluish colour, and is so soft that it can readily be cut with a knife. It has a specific gravity of 11.3, and is therefore by no means the heaviest of the metals, although the idea of great density is commonly associated with it. It melts at 328°, and only boils at the temperature of the oxyhydrogen flame.

When it is heated in the air it is slowly converted into the monoxide or litharge, PbO. The metal is not dissolved by hydrochloric or sulphuric acid but readily dissolves in nitric acid, lead nitrate being formed and oxides of nitrogen evolved. Lead also readily combines with chlorine and sulphur when heated with them.

EXPERIMENT 154.—Examine the action of hydrochloric, nitric, and sulphuric acids on metallic lead.

Lead is readily precipitated from a solution of the nitrate by metallic zinc, and separates out in long leaf-like crystals.

When the zinc is suspended in the solution the mass of crystals obtained is known as the lead tree.

EXPERIMENT 155.—Dissolve 5 grams. of lead nitrate in 100 cc. of water; place the solution in a cylinder or narrow beaker, and suspend in it near the top by means of cotton thread a piece of granulated zinc—crystals of lead are slowly formed around the zinc.

Lead is largely used in the form of sheet-lead and lead piping, since it is pliable and resists the action of water and acids. The metal enters into the composition of a large number of alloys, the composition of some of which is shown in the following list—

	Lead.	Tin.	Antimony.
Solder . . .	50	50	...
Pewter . . .	20	80	...
Type metal . .	50	25	25

The Atomic Weight of Lead.—The equivalent of lead was determined by Stas, who converted the metal into the nitrate by simply dissolving it in strong nitric acid, and then evaporating, drying and weighing the salt obtained. By this method it has been found that 1 part of lead yields 1.5988 part of lead nitrate. Now all the metallic nitrates are formed from nitric acid by the replacement of hydrogen, and we further know that 63.018 parts of nitric acid contain 1.008 part of hydrogen and 62.01 parts of nitrogen and oxygen. Hence, to obtain the equivalent of lead all that is necessary is to calculate how much lead unites with 62.01 parts of nitrogen and oxygen to form the nitrate.

0.5988 part of nitrogen and oxygen unite with 1 part of lead,
hence 1 part ,, ,, ,, $\frac{1}{0.5988}$,,
and 62.01 parts ,, ,, ,, $\frac{1 \times 62.01}{0.5988} = 103.55$

The atomic weight of lead has been settled in a precisely similar manner to that of tin, and has been found to be about 207, and hence 2 × 103.55 = 207.1 is taken as the exact atomic weight.

We thus learn that an atom of lead replaces two atoms of hydrogen, so that the formula of the nitrate is $Pb(NO_3)_2$.

Lead, like tin, forms two series of compounds, in one of which it replaces two atoms of hydrogen, and in the other four. This latter series comprises the dioxide, PbO_2, which has very feeble acid-forming and almost equally feeble basic properties, and a few unstable salts, such as the tetrachloride, $PbCl_4$. The lower series consists of a basic oxide, PbO, a chloride, $PbCl_2$, and a whole series of salts which are stable, and do not act as reducing agents like the stannous salts, with which they correspond in composition.

In addition to these lead also forms the oxides Pb_4O, Pb_2O_3, and Pb_3O_4, which do not yield salts of corresponding composition.

Metallurgy of Lead.—The smelting of lead is carried out in no less than three different ways. The simplest of these is the English process, which depends on the fact that when lead sulphide is heated with the necessary proportion of the oxide or sulphate, the oxygen of these compounds combines with the sulphur of the sulphide to form sulphur dioxide, which escapes, and metallic lead is left,—

$$2PbO + PbS = 3Pb + SO_2.$$

$$PbSO_4 + PbS = 2Pb + 2SO_2.$$

The ore, consisting mainly of galena, PbS, is therefore first roasted on the bed of a reverberatory furnace (B, Fig. 48), until the requisite quantities of the oxide and sulphate have been formed by the oxidation of the material. The temperature is then raised, so that the decomposition of the sulphide by the oxide and sulphate may take place and the molten lead is run off.

In order to refine the crude metal thus obtained, it is remelted, and the impurities which separate and the oxide formed on the surface are removed.

A second process for the production of lead consists in roasting the ore until it is converted into oxide, and then reducing this by means of carbon in a blast furnace, the construction of which somewhat resembles that of the blast furnace used in the manufacture of cast-iron (p. 375).

In some cases the sulphide is decomposed by the addition of metallic iron, which combines with the sulphur, but this process is usually employed in conjunction with one of the foregoing.

Separation of Silver from Crude Lead.—Much of the lead obtained by smelting galena contains a small amount of silver, which is derived from silver sulphide contained in the galena, and cannot be economically extracted by cupellation (p. 277). Two different methods are used for the extraction of this small amount of silver.

1. **The process of Parkes** depends on the fact that when lead containing silver is melted with zinc, nearly the whole of the silver dissolves in the zinc, which also takes up about 1.2 per cent of its weight of lead, forming an alloy which is insoluble in metallic lead and floats on the surface as a scum. This alloy, which is rich in silver, is removed and the silver extracted from it, whilst the residual lead, which only contains a small amount of dissolved zinc, is freed from this by partial oxidation and then brought into the market.

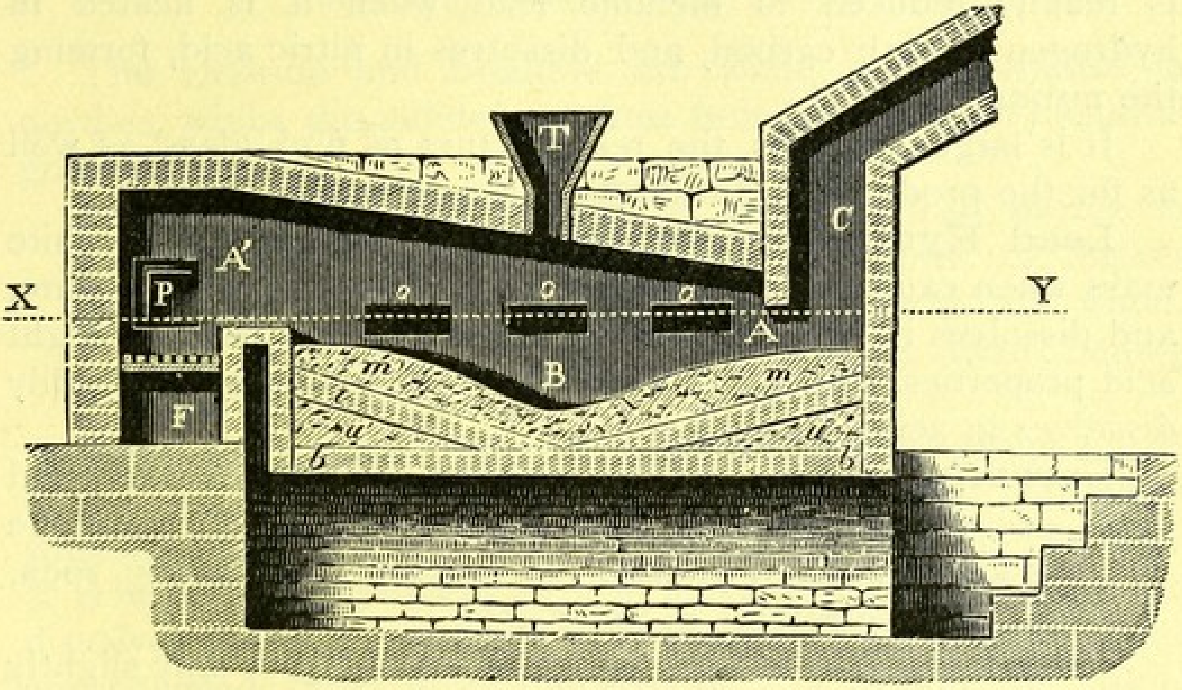


Fig. 48

2. **Pattinson's Process.**—When molten lead containing a small amount of silver is allowed to cool slowly it behaves in the same manner as a dilute solution of a salt in water (p. 16). Just as the latter first deposits ice, so the alloy of lead and silver first deposits crystals of pure lead. These are removed from the mass by perforated ladles, and the residue is thus

left considerably richer in silver. This process is repeated systematically, and the rich lead which is finally left is cupelled.

The Compounds of Lead

Lead Monoxide, Litharge, PbO, is formed, as already mentioned, when the metal is heated in the air. It is a yellow scaly mass, which undergoes further oxidation when heated to redness in the air, red lead, Pb_3O_4, being formed. Litharge is readily reduced to metallic lead when it is heated in hydrogen or with carbon, and dissolves in nitric acid, forming the nitrate.

It is largely used in the manufacture of flint glass, as well as for the production of the other salts of lead.

Lead Hydroxide, $Pb(OH)_2$, is precipitated as a white mass when caustic soda is added to a solution of lead nitrate, and dissolves in excess of the alkali, so that it possesses slight acid properties. It, however, turns red litmus blue and readily dissolves in acids, forming salts.

EXPERIMENT 156.—To a solution of lead nitrate add caustic soda solution drop by drop—a white precipitate is formed, which redissolves in excess of caustic soda, and is also soluble in nitric acid.

Most of the salts of lead are either insoluble or only slightly soluble in water, the two most important exceptions being the nitrate and the acetate, or sugar of lead, so that when a solution of a lead salt is spoken of, one or other of these is almost always meant.

Lead Nitrate, $Pb(NO_3)_2$, is prepared by dissolving litharge in nitric acid, evaporating, and allowing the salt to separate out. It crystallises in milk-white anhydrous octahedra, and is freely soluble in water, 100 parts of which dissolve 44.4 parts of the salt at 10°. When it is heated gently it yields red lead, Pb_3O_4.

EXPERIMENT 157.—Dissolve 5 grams. of litharge in dilute nitric acid, filter, evaporate to small bulk, and allow to cool. Lead nitrate crystallises out in octahedra, often resembling in shape the distorted crystals formed by alum.

Lead Acetate, Sugar of Lead, $Pb(C_2H_3O_2)_2 + 3H_2O$,

so called from its sweet taste, is prepared by dissolving litharge in acetic acid, and crystallises in prisms, which are soluble in 1.5 part of water.

Lead Chloride, $PbCl_2$, Lead Bromide, $PbBr_2$, and **Lead Iodide, PbI_2,** are all soluble in hot water, but only sparingly soluble in cold water. They are prepared by precipitating lead nitrate with the corresponding acid or its sodium or potassium salt, filtering and recrystallising from hot water,—

$$Pb(NO_3)_2 + 2KI = PbI_2 + 2KNO_3.$$

The chloride and bromide are white and crystallise in needles, whilst the iodide separates from hot water in beautiful golden spangles.

EXPERIMENT 158.—Dissolve 1 gram. of lead nitrate in water, add potassium iodide solution until no further precipitate is produced, filter and wash with cold water. Recrystallise a portion of the product from boiling water.

Lead Sulphide, PbS, occurs as the mineral galena; it is formed when lead is heated in sulphur vapour, and when sulphuretted hydrogen is passed into a solution of a lead salt. It is insoluble in hydrochloric acid and ammonium sulphide, but dissolves in hot dilute nitric acid, forming lead nitrate, whilst concentrated nitric acid converts part of it into the white insoluble sulphate, and part into lead nitrate. The precipitated sulphide is readily converted into the white sulphate by hydrogen peroxide,—

$$4H_2O_2 + PbS = 4H_2O + PbSO_4.$$

EXPERIMENT 159.—Pass sulphuretted hydrogen into lead nitrate solution, and treat separate portions of the washed precipitate with (*a*) dilute nitric acid, (*b*) concentrated nitric acid, (*c*) hydrogen peroxide.

A piece of paper soaked in lead nitrate or lead acetate solution is often used to test for the presence of sulphuretted hydrogen, since very small quantities of this gas suffice to produce a brown stain on the paper.

When sulphuretted hydrogen is slowly passed into an acid solution of lead chloride, a red precipitate is formed. This is a compound of lead sulphide with lead chloride, and is analogous to the white compound formed by mercuric chloride under similar circumstances.

Lead Sulphate, $PbSO_4$, is a white powder which is precipitated when sulphuric acid or a sulphate is added to a solution of a lead salt. It is almost insoluble in water, requiring no less than 21,739 parts for solution, but it dissolves easily in caustic soda solution, and is also soluble in concentrated sulphuric or hydrochloric acid.

The natural sulphate, known as anglesite, is isomorphous with barium sulphate. The sulphate is used to some extent as a white paint, but is not so satisfactory as white lead.

EXPERIMENT 160.—To a solution of lead nitrate add dilute sulphuric acid. Show that the precipitate is soluble in caustic soda and in hydrochloric acid.

Lead Carbonate, $PbCO_3$, occurs as cerrussite, which is isomorphous with arragonite. It is formed when ammonium carbonate is added to a solution of lead nitrate, and is slowly soluble in water containing carbonic acid in solution. The **basic carbonate,** $2PbCO_3 + Pb(OH)_2$, is known as **white lead,** and is very largely used as a white paint, since it is very dense and opaque. It is made by a variety of methods, the simplest of which consists in grinding litharge with water and sodium bicarbonate.

The Dutch process, which yields white lead of an excellent quality, is carried out by placing spirals of sheet-lead in pots, at the bottom of which is vinegar, and allowing the whole to stand for four or five weeks covered with tan or dung. The vinegar evaporates and attacks the lead, forming a basic acetate, which is converted into white lead by the carbonic acid evolved from the decaying tan, etc. The acetic acid thus liberated attacks a fresh portion of the lead, and this series of changes is repeated until the whole of the metal has been converted into white lead.

Red Lead, Pb_3O_4, is formed when litharge is heated in the air, and also when the carbonate or nitrate is gently heated. It is a heavy, red crystalline powder, and loses oxygen when it is strongly heated,—

$$2Pb_3O_4 = 6PbO + O_2.$$

Red lead is an instance of an oxide which is neither basic nor acid-forming, and in fact yields no corresponding series of salts. In many respects it behaves as a mixture or compound of lead dioxide and litharge, $2PbO + PbO_2$; thus when it is treated with nitric acid, the lead dioxide is left behind and lead nitrate formed by the action of the acid on the litharge,—

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

EXPERIMENT 161.—1. Heat 0.5 gram. of red lead in a test-tube—oxygen is evolved (test by splint).

2. To 10 grams. of red lead add 10 cc. of water and 10 cc. of concentrated nitric acid. Filter and evaporate the filtrate—lead nitrate crystallises out. Wash the brown residue with cold water, dry in the air, and use for the experiments on lead dioxide.

Lead Dioxide or Lead Peroxide, PbO_2, is most easily prepared by the reaction just mentioned, and is also formed when a lead salt is heated with a solution of bleaching powder. It is a heavy brown or puce-coloured powder, and decomposes when it is heated, forming litharge and oxygen,—

$$2PbO_2 = 2PbO + O_2.$$

It also acts as a powerful oxidising agent.

Lead dioxide does not yield hydrogen peroxide when treated with acids, and hence it differs from barium peroxide, BaO_2, in this respect.

Hydrochloric acid is at once oxidised, chlorine being evolved and lead chloride formed,—

$$PbO_2 + 4HCl = PbCl_2 + 2H_2O + Cl_2.$$

This reaction with hydrochloric acid is given by the higher oxides of many metals, and is used for estimating them. (See chromium and manganese.)

EXPERIMENT 162.—1. Heat a small quantity of lead dioxide in a test-tube—oxygen is evolved and a residue of litharge left.

2. Heat some lead dioxide with hydrochloric acid—chlorine is evolved and lead chloride formed.

Lead dioxide is used in accumulators or secondary batteries, which can be charged by the current produced by a dynamo, and then serve to generate a current for a considerable time, after which they can again be charged. These contain lead plates, immersed in dilute sulphuric acid, and one of the plates is coated with lead peroxide. When the plates are connected by a wire a current is produced, during the passage of which the lead peroxide is reduced to litharge, whilst the surface of the other lead plate becomes oxidised to litharge. During recharging, the litharge on one plate is oxidised to the dioxide, whilst that on the other is reduced to metallic lead.

Lead peroxide possesses both acid-forming and basic properties, although only to a slight extent. Thus when it is fused with caustic potash, an unstable soluble salt, known as *potassium plumbate*, K_2PbO_3, is formed, which loses oxygen when it is heated. On the other hand, when the dioxide is dissolved in well-cooled hydrochloric acid, *lead tetrachloride* is formed,—

$$PbO_2 + 4HCl = PbCl_4 + 2H_2O.$$

This substance is a yellow fuming liquid and is decomposed by water, forming hydrochloric acid and the dioxide, so that it closely resembles stannic chloride, $SnCl_4$, in its properties.

Poisonous Action of Lead Salts—Action of Water on Lead.—The salts of lead act as very powerful poisons, and even when only very small amounts are regularly taken into the system distressing symptoms soon appear, a characteristic sign of lead poisoning being a blue line along the gums. All persons who handle preparations of lead, even although these are almost insoluble, such as white lead, are liable to be attacked. Thus in the potteries, the dippers, who coat the earthenware, etc., with the materials for the glaze, which contain lead carbonate, sometimes suffer from the poisoning known as lead colic, and in aggravated cases they become blind. On this account glazes free from lead are now being employed.

Since lead is largely used for water pipes it is very important that the water thus supplied should be incapable of dissolving the metal. Pure water only acts slowly on lead, but waters containing small amounts of ammonium salts, or of chlorides or nitrates, as well as water containing organic acids, act much more vigorously. Waters containing dissolved calcium carbonate do not as a rule attack lead, whereas soft and peaty waters, which are often acid, frequently, but not invariably, dissolve the metal. In many districts where the only water which is available is of this kind, filters of limestone are employed so as to impregnate the water with calcium carbonate and thus prevent the solution of the lead. Water containing large amounts of soluble sulphates is liable to act on lead pipes to a dangerous extent, and this can be also prevented by the addition of calcium carbonate.

Detection of Lead.—All the compounds of lead can readily be reduced to the metal on charcoal, and the salts all impart a grayish tinge to the flame.

Lead is precipitated from solutions of its salts by hydrochloric acid as the sparingly soluble chloride, and by sulphuretted hydrogen as the black sulphide. The chloride readily dissolves in hot water, and this solution gives a white precipitate of the sulphate with sulphuric acid.

Thorium, Th, 232

Thorium is a comparatively rare element which occurs in the mineral monazite, which is found in Brazil. The oxide thoria which has the composition ThO_2, is an acid-forming oxide and yields a nitrate $Th(NO_3)_4$, a chloride $ThCl_4$, and a sulphate $Th(SO_4)_2$, all of which are soluble. The nitrate is now largely used for the manufacture of the Welsbach incandescent gas mantles, which consist of thoria containing a little oxide of cerium.

The compounds of thorium are all radio-active (see p. 462).

SUMMARY

Lead is a soft, bluish-white metal, which can readily be obtained by the reduction of its oxides. It dissolves readily in nitric acid.

Lead forms two series of salts, the plumbic salts and the plumbous salts, which correspond in composition with the stannic and stannous salts.

The plumbic compounds are very unstable and readily decompose, forming the plumbous compounds. Plumbic chloride, $PbCl_4$, is a fuming liquid, whilst the dioxide is a brown powder which has feeble acid-forming and weak basic properties.

The ordinary stable lead salts are plumbous compounds, but unlike the stannous salts, these do not act as reducing agents. Only the nitrate and acetate are readily soluble in water. The hydroxide dissolves both in acids and bases.

Lead also forms an oxide, Pb_3O_4, red lead, which acts in many respects as a mixture of the monoxide and dioxide, $2PbO + PbO_2$.

General Properties of the Elements of the Carbon Group

The gradual change from non-metal to metal as the atomic weight increases is seen very clearly in this group, both in the properties of the elements themselves and in those of their compounds.

The oxides, RO_2, only possess weak acid-forming properties, and the chlorides, RCl_4, are liquids or volatile solids. The group also contains a rare element, Germanium, Ge, which is intermediate both in properties and atomic weight between silicon and tin.

The compounds of lead, which correspond in composition with silica, silicon chloride, etc., are very unstable, whilst the compounds in which the metal is bivalent are stable. Tin is in this respect intermediate between lead and silicon. The stannic compounds are much more stable than the plumbic salts, whilst the stannous salts are unstable and are converted by oxidising agents into the more stable stannic salts, so that they act as reducing agents.

Carbon and silicon both unite with many of the metals to form stable carbides and silicides.

Exercises on Lesson XXXII

1. Describe the preparation of lead from galena.
2. How can crude lead be desilverised?
3. How would you attempt to prepare pure lead nitrate from solder?
4. Give an account of the preparation and properties of red lead.
5. What are the chief chemical properties of lead dioxide? How does this substance differ from barium dioxide?
6. How can the following substances be prepared and what are their properties: (*a*) lead dichloride, (*b*) lead sulphide, (*c*) lead tetrachloride, (*d*) lead dioxide?
7. How much zinc is required to precipitate 100 grams. of lead from a solution of the nitrate?

8. Compare the properties of the dioxides of carbon, silicon, tin, and lead.

9. Compare the properties, chemical and physical, of mercury, lead, and bismuth.

10. Why are carbon, silicon, tin, and lead classed together in one group?

LESSON XXXIII

THE METALS OF THE IRON GROUP

Iron. Nickel. Cobalt.

Iron (Ferrum), Fe, 55.85

Iron, of all the metals, is by far the most useful to man, and it has been used during historic times among nearly all nations, although in prehistoric times, when iron seems not to have been known, flint and then bronze were successively employed for the purposes for which iron is now used. It was one of the seven metals known to the alchemists, and was associated with the planet Mars, sacred to the god of war.

Iron is readily converted into the oxide by moist air, and hence is rarely found in the metallic state. Masses of metallic iron are, however, occasionally found in the form of meteorites, which fall on to the surface of the earth from regions beyond the limits of our atmosphere. Meteoric iron always contains a considerable amount of nickel, and is usually crystalline in structure. Some meteorites are of great size and weight, masses weighing as much as 21,000 kilos. having been found off the coast of Greenland, whilst meteoric iron is also found as a fine dust consisting of minute rounded particles on the snowfields of the far North, and in the deposits accumulating in mid-ocean at the bottom of the sea. The compounds of iron which occur most abundantly are the oxides, the carbonate, and the sulphides, although small amounts of iron are very commonly present in other minerals. Of these the oxides and the carbonate are employed for the manufacture of the metal, whilst the sulphides are chiefly valuable for the sulphur which they contain. Iron is also present in plants, and is a constituent of hæmoglobin, the red colouring matter of the blood.

The properties of metallic iron are greatly influenced by the presence of small quantities of other substances, especially carbon (p. 374), and hence although it is such a common metal, special precautions have to be adopted in preparing it in the pure state.

Properties of Metallic Iron.—Iron is a silver white metal and has a specific gravity of 7.8. It becomes soft at a red heat, but only melts at a very high temperature (about 1600°). Iron differs from all the metals which we have hitherto considered by being attracted by the magnet. It also has the power of becoming magnetic, but pure iron soon loses its magnetic properties, whereas steel is capable of retaining them permanently. Iron does not become oxidised in perfectly dry air or in water from which all air has been expelled. It is, however, attacked by moist atmospheric air or aerated water, and is gradually converted into rust (see p. 386). When iron is strongly heated in the air or oxygen, it burns brilliantly, emitting showers of sparks, and forms the magnetic oxide, Fe_3O_4 (p. 388). This can readily be demonstrated by burning a piece of steel watch spring in a jar of oxygen. The combustion is best started by attaching a small piece of string to the steel and setting fire to this; the heat produced is then sufficient to start the combustion of the steel. A more vivid combustion may be obtained by placing some cast-iron nails on a piece of firebrick, and then strongly heating them by means of a large oxyhydrogen blowpipe.

When steam is passed over heated iron, hydrogen is liberated, and the same oxide formed as when the iron burns in oxygen. All the oxides of iron are reduced to the metal when they are heated with carbon, or in a current of hydrogen. Iron also readily unites with chlorine, bromine, iodine, sulphur, and phosphorus.

Metallic iron dissolves both in dilute hydrochloric and sulphuric acids, hydrogen being evolved. When iron containing carbon is employed for this purpose the gas evolved has an extremely unpleasant odour, which is due to the presence of volatile hydrocarbons.

Passive Iron.—When a clean piece of iron is dipped into highly concentrated nitric acid (sp. gr. 1.45) no action appears to take place at first, but if the iron be removed and washed, and then plunged into a solution of copper sulphate, no copper is precipitated on to the metal, whereas ordinary iron is at once covered with a layer of copper. If the iron whilst still immersed in the copper sulphate solution be scratched with a file, the passive state is destroyed and a deposit of copper is at once formed. It seems probable that a layer of oxide is formed by the action of the nitric acid, which protects the metal from the further action of the acid and also from the action of copper sulphate.

The same condition is produced by many other oxidising agents, such as chromic acid, and occurs when the iron is made the + pole in a bath of sulphuric acid.

Less concentrated nitric acid readily acts on the metal, converting it into ferric nitrate, whilst red fumes are evolved.

Atomic Weight of Iron—Formulæ of the Iron Salts.—Iron forms very few volatile compounds, and hence its atomic weight has been settled by the atomic heat method, according to which it is about 56. The metal forms two well-marked series of salts, known as the ferric and the ferrous salts. It has been found by analysis of the chlorides, according to the usual method (p. 67), that in ferric chloride the equivalent of the metal is 18.617. From this it follows that the correct atomic weight is $18.617 \times 3 = 55.85$, and that in this compound one atom of iron has replaced three atoms of hydrogen, the empirical formula of ferric chloride being therefore $FeCl_3$.

In ferrous chloride, on the other hand, the equivalent of iron is 27.925, and in this compound, therefore, one atom of iron replaces two of hydrogen, and the formula of the chloride is $FeCl_2$.

Metallurgy of Iron

The properties of iron are, as already mentioned, greatly influenced by the presence of small amounts of foreign substances, especially carbon, phosphorus, and silicon, which the metal takes up during the process of reduction from its ores. Three varieties of iron are usually distinguished :—

1. **Cast-Iron.**—This contains from 2.2 to 4.5 per cent of carbon and fuses readily, but is brittle when cold. On this

account it cannot be worked under the hammer, but is very valuable for castings.

2. **Wrought-Iron or Malleable Iron** contains less carbon than cast-iron. It is produced in a pasty state without having been melted and consequently contains particles of slag. It does not fuse readily and does not become hard when suddenly cooled.

3. **Steel** also contains less carbon than cast-iron and fuses less readily, and includes all malleable alloys of carbon and iron which have at any time been actually melted. It possesses the valuable property of becoming hard and capable of taking an edge when it is suddenly cooled from a high temperature. It is, moreover, permanently magnetic, whereas the other varieties of iron, although they can easily be rendered magnetic, soon lose their magnetism.

The process to be adopted for the preparation of metallic iron from its ores depends on the nature of the product which is desired, whether cast-iron, steel, or wrought-iron. The most usual process, however, is to make cast-iron directly from the ore in a blast furnace, and then to convert this into wrought-iron or steel. Only the more important processes for effecting this are here shortly described. For further details a work on metallurgy must be consulted.

I. Manufacture of Cast-Iron in the Blast Furnace.—The ores chiefly employed for this purpose are the various oxides, such as magnetic iron ore and red and brown hæmatite; clay iron stone, which is a variety of spathic iron ore containing sand or clay; and spathic iron ore itself. These ores are first of all calcined in order to drive off water and carbonic acid gas and to render the mass more porous for the succeeding operations. The ore is then reduced in a blast furnace with carbon, lime or limestone being added in order to form a fusible silicate, termed slag, with the silica present. The furnace employed for this purpose is from 50-100 feet in height, and 14-24 feet in diameter, the construction being shown in Fig. 49. It consists of a shaft A, which is built up of wrought-iron plates lined with fire bricks, and has the shape shown in the figure, the top of the shaft, B, being known as the *throat*, the widest portion as the *belly* or *bosh*, and the lower portion, C, as the *hearth*.

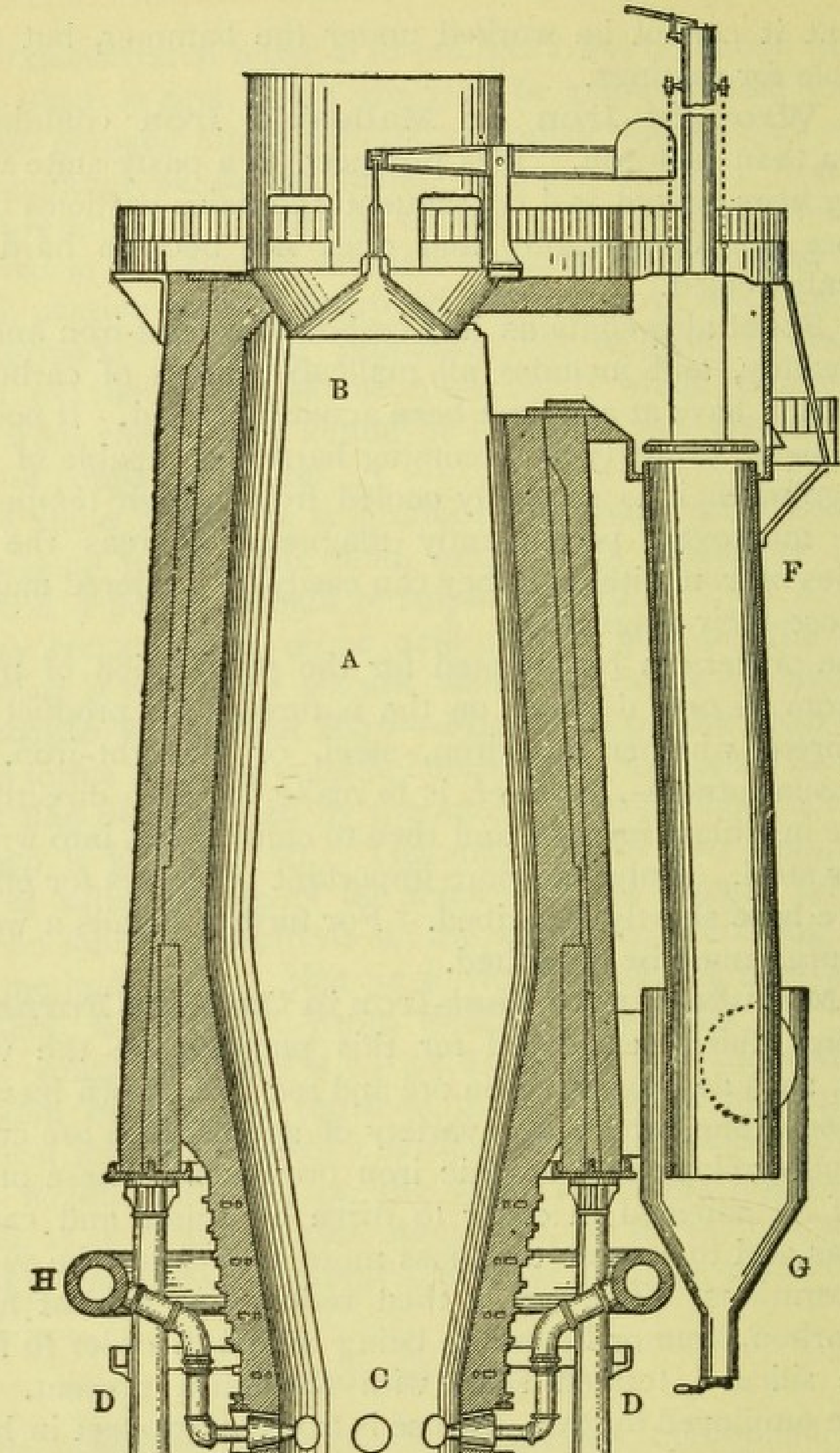


Fig. 49.

The throat is closed by a cast-iron cone which can be raised or lowered at will. At the lower portion of the furnace the walls are pierced with holes, C, through which a blast of heated air is driven from jets, known as tuyères, which are supplied with air, which is heated and sometimes dried, from the pipe H, which surrounds the furnace. A hole is also pierced at E, known as the tapping hole, through which the molten iron is withdrawn at intervals, whilst the lighter slag flows out at another hole, not shown in the figure, which is placed at a somewhat higher level.

When the furnace is in full work the mixture of calcined ore, coke, and limestone is introduced at the top of the furnace, whilst the iron and slag are drawn off at the bottom, so that the process is rendered continuous, and is carried on for long periods without cessation.

Near the top of the furnace the ore and fuel meet the carbon monoxide produced from the coke by the action of the blast. Reduction takes place and the ore is almost completely converted into a spongy mass of metallic iron,—

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$

The reduction becomes quite complete as the mass passes down the furnace, and becomes heated to a higher temperature, and finally, when the hottest part, just below the "bosh," is reached the iron takes up carbon from the fuel and melts. The molten mass runs down into the hearth, and is drawn off at intervals by the hole at E, whilst the slag, consisting chiefly of calcium silicate, floats upon the metal and is allowed to run in a continuous stream from the slag hole. In addition to carbon the iron also takes up small amounts of phosphorus, silicon, sulphur, and manganese from the materials present in the furnace. The gases which reach the top of the furnace are combustible and contain about 25 to 30 per cent of carbon monoxide. They are allowed to pass out at a side tube and removed by the pipe F, and are finally utilised for heating the air with which the blast is maintained.

The molten iron is run into moulds in sand, and thus obtained in the form of bars, flat on one side and rounded on the other, which are known as "pigs."

The carbon in such iron is present in two forms, partly combined with the iron and partly free in the form of graphite. *Gray iron* contains most of its carbon free in the form of graphite, whilst *white iron* contains it nearly all in the combined form. The graphitic carbon is left behind in the form of black scales when the metal is dissolved in acids, whilst the combined carbon is evolved in the form of hydrocarbons, to the presence of which the characteristic smell of hydrogen prepared from iron is due.

II. Manufacture of Wrought or Malleable Iron from Cast-Iron by the Puddling Process.—The object of this process is to remove the greater portion of the carbon, silicon, phosphorus, and sulphur which are present in the cast-iron, and this is accomplished by exposing the molten iron to ferric oxide, which acts as an oxidising agent upon the carbon,—

$$Fe_2O_3 + 3C = 2Fe + 3CO.$$

For this purpose the cast-iron is melted on the bed of a puddling furnace which is lined with ferric oxide, and the molten mass is then well stirred up so that it is exposed to the action of the air and to that of the oxide of iron present. Carbon monoxide is evolved, whilst the silicon, phosphorus, manganese and sulphur are also oxidised and fusible slags are formed. The cast-iron is thus converted into a mass of porous iron, which is then removed from the furnace, hammered to squeeze out as much as possible of the slag and thus to obtain a coherent mass and finally rolled.

A distinguishing feature of malleable iron is that in the process of preparation it is never fused after the removal of the carbon.

III. Manufacture of Steel from Cast-Iron.—Steel is now usually made from cast-iron by the removal of carbon and other impurities by the Bessemer process, which consists in removing a portion of the carbon and other constituents by means of a blast of air blown through the molten metal. The process is carried out in a "converter," which is shown in Fig. 50. This is an egg-shaped vessel made of wrought-iron plates lined with a silicious material, and provided at the bottom with tuyères through which air can be blown. The whole is mounted on pivots, so that it can be turned over and the molten steel run out into moulds. The melted cast-iron is run into this converter, and air is then blown through it, carbon monoxide being formed which burns at the mouth of the converter. The blast is continued until all the carbon has been removed, and a small amount of "spiegeleisen" is then added. This is a variety of white cast-iron which contains a large amount of manganese, and is added to the mass in the converter in order to introduce the carbon which is required to be present in the finished steel. The liquid steel is then poured out into a ladle and cast in ingots.

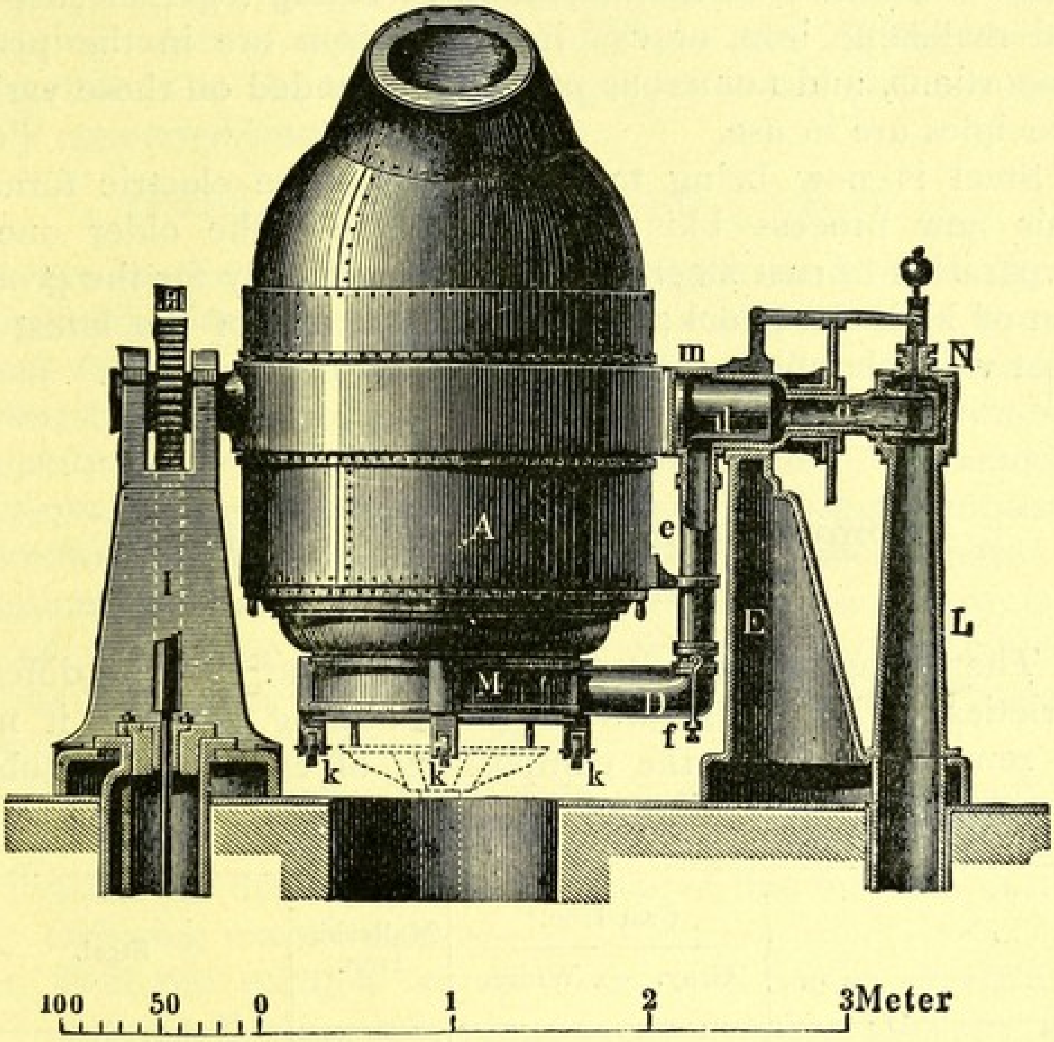


Fig. 50.

It is found that when a converter is lined with a basic material, such as calcined dolomite, the phosphorus of cast-iron is also removed, calcium and magnesium phosphates being formed and retained in the slag.

Steel can also be made from malleable iron by introducing the necessary carbon. This was invariably done before the introduction of the Bessemer process by the *cementation process*, which consists in simply heating bars of wrought-iron in steel crucibles packed with powdered charcoal for about ten days. Under these circumstances wrought iron takes up carbon and is converted into steel.

Steel can also be manufactured by fusing together cast-iron and malleable iron, or cast-iron and iron ore in the proper proportions, and numerous processes founded on these various principles are in use.

Steel is now being manufactured in the electric furnace. This new process bids fair to supersede the older one of preparation of cast steel in crucibles, especially for the production of high-class tool steel, and this is one of the latest and most valuable applications of electricity to metallurgy.

Composition of Cast-Iron, Malleable Iron, and Steel

The composition of samples of some of the different varieties of iron is shown in the following list, but it must be remembered that the composition of each kind is subject to considerable variation—

	Cast-Iron.		Malleable Iron.	Steel.	
	Gray.	White.			
Graphite	3.90	...	...	...	1.18
Combined Carbon	0.39	4.10	0.15	0.234	
Silicon	1.07	0.23	0.14	0.033	0.33
Sulphur	0.08	0.10	0.04	trace	...
Phosphorus	0.07	0.07	0.47	0.044	0.02
Manganese	0.30	0.30	0.14	0.139	trace
Iron	94.19	95.20	99.06	99.550	98.47
	100.00	100.00	100.00	100.000	100.00

Compounds of the Ferrous Series

The ferrous salts are usually colourless when pure and free from water, but they form greenish solutions in water and separate out, as a rule, in greenish coloured hydrated crystals containing water of crystallisation. These salts rapidly absorb oxygen from the air, and in the presence of an acid are completely converted into ferric salts,—

$$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O.$$

In the absence of an acid ferric hydrate or a basic salt is precipitated, since there is not enough acid present to form a normal ferric salt. The ferrous salts are also very readily converted into ferric salts by oxidising agents, and can indeed be quantitatively estimated by the determination of the amount of oxygen which they absorb from some oxidising compound of known composition, such as potassium bichromate or potassium permanganate (p. 422). The most convenient way of converting a ferrous into a ferric salt is to boil the solution with nitric acid, or hydrochloric acid and potassium chlorate, or to pass chlorine into it.

EXPERIMENT 163.—Prepare 25 cc. of a saturated solution of ferrous sulphate by shaking the powdered salt with water in the cold, and take 5 cc. of this for each of the following experiments :—

1. Boil the solution for some time—a brown precipitate of basic ferric salt is formed and a yellow solution produced.
2. Repeat this experiment with 5 cc. of the solution to which 5 cc. of dilute sulphuric acid have been added—a yellow solution is formed as before, but no precipitate is formed.
3. Boil the solution with 5 cc. of hydrochloric acid and a crystal of potassium chlorate—a yellow solution of a ferric salt is produced, which remains yellow after all the chlorine has been boiled off.
4. Add 5 cc. of dilute sulphuric acid and then 2 cc. of concentrated nitric acid, and shake up — the liquid

becomes almost black and then yellow, and the tube becomes filled with brown fumes.

The action of nitric acid is very characteristic, and is used as a test for this acid. The reactions which occur are the following:—

1. The nitric acid acts on the ferrous sulphate as follows,—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O.$$

2. The nitric oxide which is at first produced dissolves in the excess of ferrous sulphate still present, forming a dark coloured solution containing a compound of this gas with ferrous sulphate.

3. As the ferrous sulphate becomes more and more completely converted into ferric salt, the nitric oxide is driven out of solution into the air, where it at once unites with oxygen, whilst the liquid shows the characteristic yellow colour of the ferric salts. If no sulphuric acid be added a certain amount of ferric nitrate is produced.

Ferrous Oxide, FeO, is prepared by heating ferric oxide to about 300° in hydrogen, and is a black powder.

Ferrous Hydroxide, $Fe(OH)_2$, is a white mass, and is precipitated when an alkali is added to a ferrous salt in the absence of oxygen. The precipitate usually obtained has a greenish tinge, and gradually turns brown when exposed to the air, ferric hydroxide being produced.

The oxide is insoluble in alkalis, but readily dissolves in acids, forming the ferrous salts.

EXPERIMENT 164.—To 5 cc. of ferrous sulphate solution add excess of caustic soda solution—a greenish precipitate is formed. Divide into two portions: (1) To the first add dilute sulphuric acid—the precipitate dissolves, forming ferrous sulphate. (2) Allow the remainder to stand in a test-tube, shaking up at intervals—brown ferric hydroxide is produced.

Ferrous Sulphate, $FeSO_4$.—When iron is dissolved in dilute sulphuric acid ferrous sulphate is formed, and separates out when the solution is evaporated in presence of excess of iron, filtered, and allowed to cool. The crystals are green and contain 7 molecules of water, $FeSO_4 + 7H_2O$. This salt is also formed when iron pyrites is allowed to oxidise in the air in presence of moisture, and it is prepared in this way on the large scale. It has long been known to chemists, and was formerly termed copperas or green vitriol, and employed for the manufacture of sulphuric acid, which is produced when it is distilled.

When gently heated the salt loses water and leaves a residue of anhydrous ferrous sulphate, which is white, like most of the anhydrous ferrous salts.

Ferrous sulphate readily forms crystalline double salts with the alkali sulphates. The most important of these is ferrous ammonium sulphate, $FeSO_4 + (NH_4)_2SO_4 + 6H_2O$, which does not oxidise so readily in the air as ferrous sulphate itself, and is therefore often used instead of the pure sulphate for analytical purposes.

EXPERIMENT 165.—Heat 30 cc. of water to 80° in a beaker, add to it 28 grams. of powdered ferrous sulphate and stir until dissolved. Make a solution of 13 grams. of ammonium sulphate in 20 cc. of hot water and add this to the warm solution of ferrous sulphate. Ferrous ammonium sulphate crystallises out on standing. Pour off the clear liquid, drain the crystals and dry them between layers of filter paper. A further quantity of the salt may be obtained by adding 25 cc. of alcohol to the filtrate and filtering off the salt which is precipitated. About 35 grams. of the salt should be obtained.

Ferrous Chloride, $FeCl_2$, is prepared in the anhydrous state by heating iron wire in hydrochloric acid gas,—

$$Fe + 2HCl = FeCl_2 + H_2.$$

It is a colourless crystalline substance and readily dissolves in water, from which it separates in bluish crystals, $FeCl_2 + 4H_2O$.

Ferrous Carbonate, $FeCO_3$, occurs in nature as spathic iron ore, which usually also contains the isomorphous carbonates of calcium, magnesium, and manganese, and does not oxidise in the air. This salt is found dissolved probably in the form of bicarbonate in natural waters containing carbonic acid, which are known as *chalybeate waters.* When such a water is exposed to the air the excess of carbonic acid gas escapes from the solution, and oxidation at the same time occurs, so that a reddish mass of ferric hydroxide is deposited.

Ferrous Sulphide, FeS, is formed when iron filings and sulphur are heated together. A hard, dark coloured mass is thus obtained, which readily dissolves in dilute hydrochloric or sulphuric acid, with evolution of sulphuretted hydrogen, and the sulphide is therefore much used in the laboratory for the preparation of this gas,—

$$FeS + 2HCl = FeCl_2 + H_2S.$$

The sulphide usually contains free iron, which gives rise to hydrogen in the gas obtained.

Ferrous sulphide is precipitated as a black mass when ammonium sulphide is added to a solution of a ferrous salt,—

$$FeSO_4 + (NH_4)_2S = FeS + (NH_4)_2SO_4.$$

It is readily soluble in dilute hydrochloric or sulphuric acid, and is therefore not precipitated when sulphuretted hydrogen is passed into a solution of ferrous sulphate in water. It is also formed when ammonium sulphide is added to a solution of ferric salt, this being reduced to the ferrous state by part of the ammonium sulphide (p. 206),—

$$2FeCl_3 + (NH_4)_2S = 2FeCl_2 + 2NH_4Cl + S.$$

EXPERIMENT 166.—1. Pass sulphuretted hydrogen into a solution of ferrous sulphate—no precipitate is produced.

2. To a solution of ferrous sulphate add ammonium sulphide—a black precipitate is produced which is readily soluble in hydrochloric acid.

Compounds of the Ferric Series

The ferric salts usually form yellow solutions in water. They can readily be converted into ferrous salts by reducing agents, and therefore act themselves as oxidising agents. This reduction to the ferrous state can be effected in a great number of ways, as, for example, by the use of zinc and dilute sulphuric acid, sulphuretted hydrogen, stannous chloride (p. 357), sulphur dioxide, potassium iodide, etc., the changes produced by these reagents being represented by the following equations,—

(1) $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$.

(2) $Fe_2(SO_4)_3 + Zn = 2FeSO_4 + ZnSO_4$.

(3) $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$.

(4) $2FeCl_3 + 2KI = 2FeCl_2 + 2KCl + I_2$.

(5) $Fe_2(SO_4)_3 + H_2SO_3 + H_2O = 2FeSO_4 + 2H_2SO_4$.

EXPERIMENT 167.—1. Pass sulphuretted hydrogen into 5 cc. of ferric chloride solution—the solution becomes colourless and sulphur is precipitated.

2. To a solution of ferric chloride add potassium iodide solution—iodine is at once liberated.

This property is utilised for the volumetric estimation of iron, which is present in the ferric state. The solution is treated with zinc and sulphuric acid, or with sulphurous acid, so that the whole of the iron present is brought into the ferrous state, and the amount of oxygen which is required to reoxidise it to the ferric state is then ascertained, a standard solution of potassium permanganate or potassium bichromate being employed as the source of the oxygen (p. 423).

Ferric Oxide, Fe_2O_3, occurs very largely as a mineral and is one of the purest and most important ores of iron. The anhydrous oxide is known as *hæmatite*, and is found in red, kidney-shaped masses, or in distinct crystals, in which form it is termed *specular iron ore*. A hydrated form of the oxide is found as a brown or yellow mass known as *brown hæmatite*, *limonite*, *yellow ochre*, or *bog iron ore*. The oxide is prepared artificially by heating the hydroxide, and is a brownish-red powder which is readily reduced by hydrogen or carbon on heating. Finely divided ferric oxide, such as that left when ferrous sulphate is distilled, is known as colcothar, and is used for polishing, the finest portion being known as rouge.

Ferric Hydroxide, $Fe(OH)_3$, is precipitated as a brownish-red mass when caustic soda or ammonia is added to a ferric salt. It dissolves in ferric chloride to form a dark red solution, which deposits the excess of hydroxide on boiling. When this dark coloured solution is dialysed almost all the ferric chloride is removed, and a solution of the colloidal hydroxide is left which gelatinises on standing. This solution is used in medicine under the name of dialysed iron. The hydroxide readily dissolves in acids, forming the ferric salts.

The Rusting of Iron.—When a clean surface of iron is exposed to moist air or aerated water it becomes rusty. It was at one time thought that the rust was formed by direct combination of the iron with the oxygen of the air, in presence of moisture, but it has since been found that this is not the case. The active agent in the production of rust is the carbon dioxide always present in the air and in water. This acts on the iron like a dilute acid, forming ferrous carbonate and free hydrogen,—

$$(1)\ Fe + CO_2 + H_2O = FeCO_3 + H_2.$$

The ferrous carbonate is then oxidised by the oxygen of the air, in presence of water, forming ferric hydroxide,—

$$(2)\ 2FeCO_3 + 3H_2O + O = 2Fe(OH)_3 + 2CO_2.$$

A clean surface of iron remains without rust when exposed to air and water, both freed from carbon dioxide. It is, however, extremely difficult to remove the last traces of this gas from water, and this can only be done by distilling it with baryta. Fresh rust contains both ferrous hydroxide and ferrous carbonate. The equations given above also explain why it is that iron cannot rust in dry air or in water free from air (p. 373).

Ferric Chloride, $FeCl_3$, is formed when iron wire is heated in dry chlorine, and sublimes in black plates. The solution is best prepared by dissolving iron in hydrochloric acid and passing in chlorine, or boiling with a small quantity of nitric acid and then evaporating. It is a deliquescent yellow mass, and is very soluble in water, with which it unites to form several crystalline hydrates. The aqueous solution has an acid reaction to litmus.

Ferric Sulphate, $Fe_2(SO_4)_3$, is prepared by boiling a solution of ferrous sulphate with sulphuric and nitric acids and then evaporating. The reaction which occurs has already been discussed. The salt forms colourless crystals and, like aluminium sulphate, combines with the sulphates of the alkali metals to form "alums."

Ammonium Iron Alum, $(NH_4)_2SO_4 + Fe_2(SO_4)_3 + 24H_2O$, is prepared by adding ammonium sulphate to a solution of ferric sulphate and evaporating. It crystallises in violet octahedra, and is isomorphous with ordinary ammonium alum and with chrome alum (p. 319).

EXPERIMENT 168.—Dissolve 28 grams. of ferrous sulphate in 30 cc. of water, add 5 grams. of concentrated sulphuric acid and 5 cc. of concentrated nitric acid, and boil until no more brown fumes are evolved. Then add a solution of 7 grams. of ammonium sulphate in 10 cc. of water, and allow to cool—iron alum crystallises out in characteristic distorted octahedra (p. 142).

Ferric Nitrate, $Fe(NO_3)_3$, is prepared by dissolving iron in nitric acid and forms colourless crystals, containing 9 molecules of water. It yields a brown solution in water, which is rendered colourless by strong nitric acid.

Ferric Acetate.—When a solution of sodium or ammonium acetate is added to ferric chloride a blood-red solution is formed which contains ferric acetate. Ferric acetate is largely used in calico printing as a mordant, giving a black dye with alizarin. When this liquid is boiled an insoluble basic ferric acetate is precipitated and acetic acid liberated, the precipitation of the iron being quantitative.

Ferric Phosphate, $FePO_4$, is precipitated as a yellowish-white amorphous mass when ordinary sodium phosphate is added to a solution of ferric chloride, and is insoluble in acetic acid, but soluble in hydrochloric acid. The formation of this salt is used for the analytical separation of phosphoric acid from solutions of the phosphates of the metals, such as bone ash. The solution is made neutral, and a slight excess of ferric chloride is added, which precipitates the whole of the phosphoric acid as ferric phosphate. The excess of ferric chloride is then removed by boiling with ammonium acetate, and the liquid is then filtered. The whole of the phosphate remains in the precipitate, whilst the filtrate contains the calcium.

The *arsenate* is similar to the phosphate.

EXPERIMENT 169.—1. To 5 cc. of a 10 per cent solution of sodium phosphate add ferric chloride—a yellowish-white precipitate is produced.

2. To 5 cc. of a 10 per cent solution of sodium acetate add a few drops of ferric chloride solution—a deep-red coloration is produced. Boil the solution—a brown

precipitate is formed and the liquid becomes colourless.

Basic Ferric Arsenite is formed when freshly precipitated ferric hydroxide is shaken with arsenious acid. It is insoluble in water, and hence ferric hydroxide is sometimes used as an antidote in cases of arsenic poisoning.

Ferric Thiocyanate, $Fe(CNS)_3$, is present in the blood-red solution produced when potassium thiocyanate is added to a ferric salt (p. 338). It crystallises in almost black cubes, and is very readily soluble in water. The formation of this salt is often used as a test for ferric salts, since pure ferrous salts give no coloration with potassium thiocyanate.

Other Compounds of Iron

Magnetic Oxide of Iron, Fe_3O_4, is found as the mineral magnetite, which attracts iron, and was formerly known on this account as loadstone. It is a very valuable ore of iron, and occurs largely in Sweden and Norway, and near Lake Superior. It is produced when iron burns in oxygen or is heated in steam.

This oxide does not form a corresponding series of salts, but when dissolved in acids yields a mixture of ferrous and ferric salts, as though it were itself a mixture of the corresponding oxides, $Fe_2O_3 + FeO$.

$$Fe_3O_4 + 8HCl = 2FeCl_3 + FeCl_2 + 4H_2O.$$

When caustic soda is added to the solution, however, a black precipitate is produced, which, after drying, has the composition $Fe_3O_4 + H_2O$.

Ferric Acid, H_2FeO_4.—When ferric hydroxide is suspended in caustic potash and chlorine passed through the solution a purple liquid is obtained, and this is also formed when reduced iron is heated with potassium nitrate and the mass extracted with water. This solution contains potassium ferrate, K_2FeO_4, and gives with barium chloride a red precipitate of barium ferrate, $BaFeO_4$. The solution decomposes on boiling, oxygen being evolved.

The ferrates are probably derived from an acid of the formula H_2FeO_4, which would correspond with an oxide FeO_3, but neither the acid nor the oxide has been prepared.

Iron Carbonyl, $Fe(CO)_5$, is a liquid, boiling at 102.5°, which is formed by the direct union of metallic iron with carbonic oxide. It decomposes when heated into metallic iron and carbonic oxide in a similar manner to the nickel compound (p. 396).

Iron Pyrites, Iron Disulphide, FeS_2, occurs in nature to a very large extent, and is much used as a source of sulphur for the manufacture of sulphuric acid. It forms a yellow, brass-like mass, which is not attacked by dilute hydrochloric or sulphuric acid, but dissolves in nitric acid. On exposure to air and moisture it forms ferrous sulphate, as already mentioned. It is frequently found in carbonaceous shale, and is then known as coal brasses.

The Cyanogen Compounds of Iron

Potassium Ferrocyanide (Yellow Prussiate of Potash), $K_4Fe(CN)_6$, is formed when ferrous sulphate is treated with an excess of potassium cyanide. Ferrous cyanide is first formed, but this dissolves on boiling with excess of potassium cyanide to form the ferrocyanide,—

$$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6.$$

This salt is not a simple salt of hydrocyanic acid, but of a complex acid containing iron, which is termed ferrocyanic acid, $H_4Fe(CN)_6$. This is shown by the fact that when hydrochloric acid is added to a solution of the salt no hydrocyanic acid is evolved, as would be the case were the salt an ordinary cyanide, but a white precipitate of free ferrocyanic acid is formed, which becomes blue in the air. The iron, moreover, is not precipitated by ammonia or ammonium sulphide.

EXPERIMENT 170.—1. To a saturated solution of potassium ferrocyanide add a few drops of concentrated hydrochloric acid — a white precipitate is formed which rapidly becomes green in the air.

2. To a solution of potassium ferrocyanide add excess of ammonia—no precipitate is produced.

Potassium ferrocyanide is now prepared from the hydrocyanic acid which is present in small quantity in crude coal gas, and is absorbed by passing the gas through an alkaline liquid, such as caustic potash or milk of lime, containing ferrous hydroxide in suspension. If lime be used the resulting calcium salt is decomposed by potassium carbonate. It was formerly manufactured by heating potassium carbonate in an iron pot with nitrogenous organic matter, such as clippings of horn, and this process is still used to some extent. Potassium ferrocyanide crystallises in yellow quadratic tablets containing 3 molecules of water, and readily dissolves in water. Although it may be prepared from potassium cyanide, which is a powerful poison, it is not poisonous.

Potassium Ferricyanide, $K_3Fe(CN)_6$. When a solution of potassium ferrocyanide is treated with chlorine, one atom of potassium is removed and a new salt is produced, which crystallises in red prisms, and is sometimes known as red prussiate of potash,—

$$2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl.$$

These two salts give characteristic reactions with the iron salts, and are often used to distinguish ferric salts from ferrous salts in analytical work.

Ferric Salts give with potassium ferrocyanide at first a blue precipitate of *potassium ferric ferrocyanide*, $FeKFe(CN)_6$, and then, when an excess of the ferric salt is added, and without any change in appearance, Prussian blue, $Fe_7(CN)_{18}$.

$$(1)\ K_4Fe(CN)_6 + FeCl_3 = FeKFe(CN)_6 + 3KCl.$$

$$(2)\ FeCl_3 + 3FeKFe(CN)_6 = 3KCl + Fe_7(CN)_{18}.$$

With potassium ferricyanide, the ferric salts give a dark brown solution, containing soluble ferric ferricyanide.

Ferrous Salts give, with potassium ferrocyanide, a white precipitate, rapidly becoming blue, which consists of potassium ferrous ferrocyanide, $FeK_2Fe(CN)_6$.

With potassium ferricyanide the ferrous salts give first a blue precipitate which is identical with that produced from a ferric salt and potassium ferrocyanide. Potassium ferrous ferricyanide is probably first formed, as might be expected, but immediately changes into potassium ferric ferrocyanide. Excess of a ferrous salt converts this without any change in appearance into a blue compound $Fe_5(CN)_{12}$, which rapidly oxidises in moist air, forming Prussian blue and other compounds,—

$$(1)\ FeSO_4 + K_3Fe(CN)_6 = FeKFe(CN)_6 + K_2SO_4.$$
$$(2)\ 2FeKFe(CN)_6 + FeSO_4 = Fe_5(CN)_{12} + K_2SO_4.$$

The commercial substances known as Prussian blue and Turnbull's blue are usually mixtures; they are used as pigments.

EXPERIMENT 171.—To a solution of potassium ferrocyanide add: (1) Ferrous sulphate—a white precipitate rapidly becoming blue is formed. (2) Ferric chloride—a deep blue precipitate is formed.

To a solution of potassium ferricyanide add: (1) Ferrous sulphate—a deep blue precipitate is formed. (2) Ferric chloride—a dark coloration is produced.

Detection of Iron

All iron compounds are reduced to metal when they are heated before the blowpipe on charcoal with potassium cyanide. The temperature obtained is rarely high enough to melt the metal, and it is therefore usually obtained as a magnetic powder, which dissolves in nitric acid, forming a solution which gives the reactions of ferric iron and leaves a yellow stain when evaporated. Iron compounds also impart a yellowish-brown colour to the borax bead in the oxidising flame, due to the presence of ferric oxide, whilst in the reducing flame ferrous oxide is produced, which colours the bead green.

Iron is precipitated from its solutions by ammonium sulphide as the black ferrous sulphide, ferric salts being first reduced. The sulphide dissolves readily in hydrochloric acid, and yields a solution which after oxidation gives with caustic soda a reddish-brown precipitate of ferric hydroxide, insoluble in excess and in ammonia.

Iron is usually estimated gravimetrically by precipitating it as ferric hydroxide, heating strongly and weighing the resulting ferric oxide; it is estimated volumetrically by means of potassium permanganate or potassium bichromate (pp. 408-423).

SUMMARY

Iron is a white metal melting at a high temperature, it is slowly oxidised in moist air containing carbon dioxide, but is not altered by dry air in the cold. When strongly heated in oxygen it burns vigorously.

The properties of metallic iron are greatly influenced by the presence of small amounts of foreign substances, especially of carbon, the three varieties, cast-iron, steel, and wrought or malleable iron being distinguished partly by the proportions of this substance which are present.

Iron forms two series of salts, the ferrous salts, in which each atom of the metal replaces two atoms of hydrogen, and the ferric salts, in which each atom of the metal replaces three of hydrogen. The *ferrous salts* are, as a rule, light green in colour and are readily converted by oxidation into the yellow *ferric salts*, which, on the other hand, can easily be reduced to ferrous salts. In both series the chloride, nitrate, and sulphate are easily soluble in water.

Iron also forms an oxide of the formula Fe_3O_4, which when treated with acids yields a mixture of ferrous and ferric salts. The cyanides of iron readily combine with other cyanides to form complex cyanogen compounds, such as the ferrocyanides.

EXERCISES ON LESSON XXXIII

1. What are the chief compounds of metallic iron which occur in nature?

2. What are the most important properties of cast-iron, steel, and wrought-iron? How do these three varieties differ in composition?

3. Describe one method for the manufacture of (*a*) cast-iron, (*b*) wrought-iron, and (*c*) steel.

4. How can the following substances be prepared from metallic iron: (*a*) magnetic oxide of iron, (*b*) ferrous chloride, (*c*) ferric chloride?

5. How is ferrous sulphate obtained on the large scale? Describe the preparation of ferrous ammonium sulphate and iron alum from this salt.

6. What occurs when a solution of ferric chloride is treated with (*a*) sulphuretted hydrogen, (*b*) ammonia, (*c*) ammonium sulphide, (*d*) potassium iodide, (*e*) stannous chloride?

7. Describe the preparation and properties of potassium ferrocyanide and potassium ferricyanide.

8. How can a ferrous salt be distinguished from a ferric salt?

9. How much metallic iron would be required to precipitate the copper from one kilo. of crystallised copper sulphate?

LESSON XXXIV

THE METALS OF THE IRON GROUP (*Cont.*)

Nickel, Ni, 58.68

THE salts and some of the ores of nickel are green, and were at first mistaken by miners and chemists for compounds of copper, but of course did not yield the expected copper when smelted. Hence arose the name nickel, from the old German *kupfer-nickel* or false copper.

Nickel nearly always occurs in nature together with cobalt, which it resembles very closely in many of its properties. It occurs chiefly as sulphide, which is usually mixed with other sulphides, especially those of iron and copper. Thus the nickel ores of Canada consist of sulphide of iron, containing 2-3 per cent of nickel and the same amount of copper. In New Caledonia the nickel occurs largely as silicate, and finally, as has already been mentioned, this metal is invariably found as a constituent of meteoric iron.

The smelting of nickel is usually carried out in a somewhat similar manner to that of copper (p. 265), the ore being alternately roasted and melted to remove the iron and sulphur. The residual nickel oxide is then mixed with charcoal, pressed into cubes, and strongly heated. The oxide is thus reduced and cubes of the metal containing a certain amount of carbon are formed,—

$$NiO + C = Ni + CO.$$

Nickel somewhat resembles iron in appearance, and like it is strongly magnetic; it has a specific gravity of 8.9, and only melts at a very high temperature (1484°), which is, however, rather lower than the melting-point of iron.

It does not oxidise on exposure to moist air, and even when heated in the air is only slowly converted into the oxide. It also slowly decomposes steam at a red heat, the monoxide being formed (compare iron, p. 373).

The metal dissolves slowly in hydrochloric acid, readily in dilute nitric acid.

Metallic nickel is largely used for plating iron and steel in order to protect them from rust. It also forms a constituent of several valuable alloys; thus *nickel-steel* contains 3-15 per cent of nickel, and is largely used for armour plate for war vessels, since it is extremely tough and difficult to penetrate. *German silver* is an alloy composed of about 3 parts of copper, 1 of nickel, and 1 of zinc, and is largely used for coins and a variety of other purposes, since it retains its lustre well and may be worked like brass.

Atomic Weight of Nickel and Formulæ of its Compounds.—The equivalent of nickel has been found by the analysis of the bromide to be 29.34. Its atomic weight as determined by the atomic heat method appears to be about the same as that of iron, and this agrees with the value deduced from the molecular weight and composition of nickel carbonyl (p. 396), the only readily volatile compound of nickel which is known. Hence the correct atomic weight is 58.68, and it is thus seen that in the bromide each atom of nickel replaces two atoms of hydrogen.

Nickel only forms a single series of salts, which are derived from the monoxide, NiO, and therefore correspond in composition with the ferrous salts. They differ from these, however, by not possessing reducing properties, since no salts corresponding with the ferric salts are known, although the corresponding oxide to ferric oxide, nickel sesquioxide, Ni_2O_3, exists.

The salts are generally yellow in the anhydrous state, but form brilliant green crystals, containing water of crystallisation.

Compounds of Nickel

Nickel Monoxide, NiO, is prepared by strongly heating the sesquioxide or nitrate, and is also formed when the metal is strongly heated in the air. It is a light green powder and is easily reduced when heated in hydrogen or with carbon.

Nickel Hydroxide, $Ni(OH)_2$, is formed as an apple green precipitate when caustic soda is added to a nickel salt; it forms a blue solution with ammonia. The hydroxide dissolves readily in acids, but is insoluble in caustic soda. It is, however, soluble in ammonia, forming an ammoniacal compound resembling that formed by copper under similar circumstances.

Nickel Chloride, $NiCl_2$.—Nickel is readily acted on by chlorine, the anhydrous yellow chloride being produced, which sublimes in shining plates. The green crystalline salt obtained by dissolving the carbonate in hydrochloric acid and evaporating the solution has the composition $NiCl_2 + 6H_2O$, and is readily soluble in water.

Nickel Sulphate, $NiSO_4$, is prepared by dissolving nickel or its carbonate in dilute sulphuric acid and evaporating. Green crystals of the composition $NiSO_4 + 7H_2O$ are deposited, which are readily soluble in water. Like ferrous sulphate it readily forms crystalline double salts, such as **nickel ammonium sulphate,** $NiSO_4 + (NH_4)_2SO_4 + 6H_2O$, which is prepared by mixing the two constituent salts, and is used for nickel plating.

EXPERIMENT 172.—Dissolve 28 grams. of nickel sulphate and 13 grams. of ammonium sulphate in the smallest possible quantity of hot water and allow to cool. The salt may be obtained in large crystals by a process similar to that employed for alum.

Nickel Sulphide, NiS, is formed when nickel and sulphur are heated together, and is precipitated as a black powder when ammonium sulphide is added to a solution of a nickel salt. It is insoluble in dilute hydrochloric acid, but is not precipitated when sulphuretted hydrogen is passed into a solution of a nickel salt containing hydrochloric acid. It dissolves in nitric acid, and in hydrochloric acid to which a crystal of potassium chlorate has been added, and is slightly soluble in ammonium sulphide, a dark coloured solution being formed.

Nickel Sesquioxide, Ni_2O_3.—The residue left when nickel nitrate is gently heated in the air is black, and consists of the sesquioxide. When this is more strongly heated it loses oxygen and passes into the monoxide,—

$$2Ni_2O_3 = 4NiO + O_2.$$

This oxide does not yield a corresponding series of salts, when it is treated with acids, but always forms the ordinary nickel salts and loses oxygen, which is either given off as gas or acts on the acid. Thus, when it is heated with sulphuric acid nickel sulphate is formed and oxygen evolved, whilst hydrochloric acid yields nickel chloride and free chlorine,—

$$Ni_2O_3 + 6HCl = 2NiCl_2 + Cl_2 + 3H_2O.$$

When a solution of a nickel salt is heated with sodium hypochlorite a black precipitate of the **trihydroxide**, $Ni(OH)_3$, is formed, which behaves towards acids like the oxide.

Nickel Carbonyl, $Ni(CO)_4$.—When nickel oxide is reduced by hydrogen and the finely divided metal is then exposed to a current of carbon monoxide at 80°, the nickel combines with this gas and forms a compound which condenses on cooling to a colourless liquid boiling at 43°. This compound is the only easily volatile derivative of nickel, and forms a vapour which has the density corresponding with the formula given above. The vapour is very poisonous, and explodes when heated to 60°, but when it is mixed with hydrogen and passed through a hot tube, it decomposes into carbon monoxide and metallic nickel, which is deposited as a mirror on the walls of the tube,—

$$Ni(CO)_4 = Ni + 4CO.$$

The vapour burns in the air with a very bright flame, carbon dioxide and nickel monoxide being produced. The formation and decomposition of this compound have been utilised for the extraction of nickel from its ores. The crude nickel oxide is reduced to metal by water gas (a mixture of hydrogen and carbon monoxide), and is then exposed to the action of carbon monoxide at 80°, the resulting vapour being decomposed in heated chambers in which the metallic nickel is deposited, whilst the carbon monoxide is used over again.

Detection of Nickel.—Nickel compounds are reduced to a magnetic black powder of metallic nickel when they are heated with potassium cyanide on charcoal in the reducing flame of the blowpipe. This powder dissolves in nitric acid, forming a solution which leaves a bright green stain on evaporation. The compounds of nickel colour the borax bead brown in the oxidising flame, but in the reducing flame the bead becomes gray and opaque owing to the formation of metallic nickel, which is insoluble in borax. Nickel is separated from all other metals except cobalt by removing the metals which are precipitated by sulphuretted hydrogen in presence of hydrochloric acid, and then adding ammonia and ammonium sulphide. When the resulting precipitate is treated with dilute hydrochloric acid, only the sulphides of nickel and cobalt are left undissolved. These are then treated as described under cobalt (p. 401).

SUMMARY

Nickel is a white magnetic metal, which does not readily oxidise in the air.

Only one series of salts is known, and in these the metal is bivalent. The chloride, nitrate, and sulphate are green soluble salts, and do not become oxidised on exposure to the air.

Nickel forms a black oxide, Ni_2O_3, which decomposes when heated into the green oxide, NiO, and does not yield a corresponding series of salts when treated with acids. The metal forms a very characteristic volatile compound with carbon monoxide, which decomposes when heated, metallic nickel being deposited.

Cobalt, Co, 58.97

Cobalt, like nickel, was first found in a false copper or ore resembling one of copper, and received its name from the German word for a spirit or ghost (*kobold*). It is usually found along with nickel, and resembles this element very closely in its chemical properties. Physically, however, the salts of the two elements differ very much from one another, those of cobalt being, as a rule, blue in the anhydrous state, and pink in solution or in the form of hydrated crystals.

Cobalt occurs chiefly as *speiss cobalt*, an arsenide of cobalt $CoAs_2$, in which part of the latter is replaced by iron and nickel.

Metallic Cobalt is not manufactured on the large scale, and is usually prepared by reducing the oxide or chloride in hydrogen. It resembles iron in appearance and is strongly magnetic. It has a specific gravity of 8.8, is harder than iron, and melts at 1530°.

Atomic Weight of Cobalt and Formulæ of its Salts.—No volatile compounds of cobalt are known, and its atomic weight has therefore been settled by the atomic heat method, and has thus been found, like that of nickel, to have about the same value as that of iron. The equivalent of the metal has been ascertained to be 29.485 by the analysis of the bromide, and hence the atomic weight is $29.485 \times 2 = 58.97$. It follows from this that each atom of the metal replaces two atoms of hydrogen to form the bromide, so that the formula of this salt is $CoBr_2$.

All the stable cobalt salts have analogous formulæ, and therefore correspond in composition with the ferrous salts and those of nickel, with which they are also isomorphous. Cobalt, however, forms a series of unstable salts which correspond in composition with the ferric salts, and may be regarded as derived from the oxide Co_2O_3.

In order to prepare the salts of cobalt, speiss cobalt is roasted, a process which yields a crude arsenate of cobalt. This is then dissolved in hydrochloric acid and treated with sulphuretted hydrogen to precipitate copper, bismuth, etc. The filtrate from these is then precipitated with bleaching powder, and the crude oxide filtered off, washed, and dried. In order to obtain cobalt salts this oxide, which always contains iron and nickel, is redissolved in acid and purified by special methods.

Compounds of the Cobaltous Series

Cobaltous Oxide, CoO, is formed when the higher oxide, Co_3O_4, is gently heated in hydrogen, and is a light brown powder, which is reconverted into the higher oxide by being heated in the air.

$$6CoO + O_2 = 2Co_3O_4.$$

This behaviour shows that cobaltous oxide is much more easily oxidised than nickel oxide, NiO, and the same is true of the cobaltous salts, which yield unstable cobaltic salts on oxidation, whereas no such salts of nickel are known.

Cobaltous Hydroxide, $Co(OH)_2$.—When caustic soda is added to a solution of a cobalt salt, a blue basic salt is thrown down, which becomes converted into the pink hydroxide on boiling. This absorbs oxygen from the air and becomes brown on standing.

EXPERIMENT 173.—To a solution of cobalt nitrate add caustic soda solution—a blue precipitate is formed, which becomes pink on heating and then gradually becomes brown.

Cobaltous Chloride, $CoCl_2$, is obtained by heating the metal in chlorine and sublimes in blue crystalline scales. When the carbonate is dissolved in hydrochloric acid a pink solution is formed which deposits pink crystals, $CoCl_2 + 6H_2O$, on evaporation, and when these are dried at 110°-120° the blue anhydrous chloride is left. The blue crystals form a blue solution in alcohol, which becomes pink when water is added to it. The pink aqueous solution, on the other hand, becomes blue when concentrated sulphuric or hydrochloric acid or alcohol is added. Solutions of cobalt salts have been used as sympathetic inks, since they become blue when dried, but are a faint and almost invisible pink when moist. The change is so delicate that in dry weather a piece of paper impregnated with cobalt chloride becomes blue and in damp weather pink.

EXPERIMENT 174.—Evaporate a solution of cobaltous chloride to dryness—a blue mass is obtained. When concentrated hydrochloric acid is added to this or to the aqueous solution, a blue liquid is obtained which becomes pink on the addition of water.

Cobaltous Nitrate, $Co(NO_3)_2 + 6H_2O$, is prepared by dissolving the carbonate in nitric acid and evaporating. When it is strongly heated the oxide, Co_3O_4, is left, whilst when gently heated the sesquioxide, Co_2O_3, is formed.

Cobaltous Sulphate, $CoSO_4 + 7H_2O$, is also a pink salt, and, like the sulphates of iron and nickel, forms double salts with the sulphates of the alkalis.

Compounds of the Cobaltic Series

Cobaltic Oxide, Co_2O_3.—When a solution of bleaching powder or sodium hypochlorite is added to a solution of a cobalt salt a black precipitate is produced. If the liquid be heated it froths up and oxygen is evolved, until the whole of the hypochlorite present has been reduced to chloride. This is a case of so-called catalytic action, which is very similar to that of manganese dioxide on potassium chlorate, and probably depends on the successive formation and decomposition of an unstable higher oxide of cobalt. The oxide left at the close of the reaction is probably a mixture of the sesquioxide, Co_2O_3, and the dioxide, CoO_2. Cobaltic oxide is a black powder, which behaves towards acids like the corresponding oxide of nickel (p. 396).

EXPERIMENT 175.—To a solution of cobaltous nitrate add caustic soda and then bleaching powder. A black precipitate is formed. Heat the liquid gently—oxygen is evolved with effervescence.

Cobaltic Sulphate, $Co_2(SO_4)_3 + 18H_2O$, is the best known of the unstable cobaltic salts, and is formed when a solution of cobaltous sulphate is electrolysed, the salt in the neighbourhood of the positive pole being oxidised. The sulphate crystallises in blue needles, and like ferric sulphate forms an alum.

Cobalto-cobaltic Oxide, Co_3O_4, corresponds in composition with the magnetic oxide of iron, and is the most stable oxide of cobalt, being formed when the other oxides are strongly heated in the air. When heated with hydrochloric acid it yields cobaltous chloride and chlorine (compare the behaviour of magnetic oxide of iron, p. 388),—

$$Co_3O_4 + 8HCl = 3CoCl_2 + Cl_2 + H_2O.$$

Smalt.—This name is given to an intensely blue silicate of cobalt which is prepared by fusing roasted cobalt speiss with sand and pot-ashes. It is much used for colouring glass and as a blue paint, which is not affected by acids and can be fired.

Zaffre, an impure arsenate of cobalt, and **Thenard's blue,** which is formed by heating a salt of cobalt with alumina, are also used as blue colouring matters. The formation of the latter substance is employed as a test for alumina.

The Cyanogen Compounds of Cobalt

Potassium Cobalticyanide, $K_3Co(CN)_6$. — Cobalt closely resembles iron in its behaviour to potassium cyanide, and in this respect differs very markedly from nickel. When a solution of potassium cyanide is added to one of a salt of cobalt a precipitate of the cyanide is produced, which readily dissolves in excess of potassium cyanide solution. This solution still shows the properties of an ordinary cobalt salt, and yields a black precipitate of the higher hydroxide with sodium hypochlorite solution, whilst when a drop of hydrochloric acid is added, the excess of potassium cyanide is decomposed and the cobaltous cyanide precipitated.

A solution of a nickel salt behaves in precisely the same manner. If, however, a drop of acetic acid be added to each of the solutions and the liquids boiled, an important difference is manifested. The cobalt salt absorbs oxygen from the air and is converted into potassium cobalticyanide, $K_3Co(CN)_6$, which corresponds in composition with potassium ferricyanide,—

$$2Co(CN)_2 + 8KCN + O + H_2O = 2K_3Co(CN)_6 + 2KHO.$$

Like the latter substance it must be regarded as the salt of a complex acid, since it has reactions which differ entirely from those of cobaltous cyanide. Thus its solutions do not give a precipitate with dilute hydrochloric acid nor with sodium hypochlorite. The salt crystallises in yellowish prisms and is isomorphous with potassium ferricyanide.

The nickel solution, on the other hand, is not altered by boiling, so that when a mixture of the two salts is treated as described above, the whole of the nickel can be precipitated by bleaching powder, whereas the cobalt remains in solution. This method is therefore frequently used for the analytical separation of cobalt from nickel, and also for the purification of cobalt salts from nickel. The cobalt can be obtained from the clear liquid from which the nickel hydroxide has been filtered, by evaporating down to dryness, heating strongly, and then washing with water and redissolving the residue in hydrochloric acid.

Cobalt Carbonyl, $Co(CO)_4$, is only formed when cobalt is heated with carbon monoxide under a high pressure. It is solid at the ordinary temperature, forming red crystals which melt at 42°. Like nickel carbonyl it decomposes when heated into the metal and carbon monoxide.

Detection of Cobalt.—Cobalt, like nickel and iron, is obtained as a magnetic powder when its compounds are reduced on charcoal with potassium cyanide. The powder dissolves in nitric acid, forming a solution which leaves a pink stain on evaporation. All compounds of cobalt colour a borax bead an intense blue both in the oxidising and reducing flames.

Cobalt sulphide is obtained in the ordinary analytical process along with that of nickel as described above (p. 397). The two sulphides are then dissolved in a mixture of hydrochloric acid and potassium chlorate, the acid removed by evaporation and the solution treated with potassium cyanide as just described.

EXPERIMENT 176.—To a solution of cobalt nitrate add an excess of potassium cyanide. To two small portions of this solution add (1) dilute hydrochloric acid—cobalt cyanide is precipitated; (2) caustic soda and sodium hypochlorite—a black precipitate of the trihydroxide is produced on boiling.

(3) Boil the remainder of the solution with a drop of acetic acid, and again test with hydrochloric acid and with caustic soda and sodium hypochlorite—no precipitate is produced in either case. Repeat these experiments with a solution of nickel sulphate, and compare the results obtained.

SUMMARY

Cobalt, like iron and nickel, is a white magnetic metal and unites with carbon monoxide. It forms two series of salts, the *cobaltous salts,* which correspond in composition with the ferrous salts, and the *cobaltic* salts, which correspond with the ferric salts. The cobaltous salts yield pink solutions, but are blue in the anhydrous state, and are stable in the air. The chloride, nitrate, and sulphate are all soluble in water.

The cobaltic salts are extremely unstable, and can only be obtained with difficulty.

In addition to the oxides CoO and Co_2O_3, cobalt forms an oxide Co_3O_4, which is produced when either of the other oxides is heated in the air.

Like iron, cobalt readily forms complex cyanogen compounds, the most important of which is potassium cobalticyanide, $K_3Co(CN)_6$.

General properties of the Metals of the Iron Group

Iron, nickel, and cobalt resemble each other very closely, especially in their physical properties. Thus these three metals are all magnetic, and are the only metals which possess this property. They are, moreover, all white metals, melt at a high temperature when pure, and have nearly the same specific gravity. In their chemical properties, also, these metals show a close analogy; they all form a series of salts of the formula MR'_2, the sulphates and chlorides being readily soluble in water. The ferrous salts, however, are very readily converted by oxidation into the ferric salts, FeR'_3, whilst the cobaltous salts can only be converted into the corresponding cobaltic salts, CoR'_3, with considerable difficulty, and no nickel salts of the formula NiR'_3 are known. All three metals unite with carbon monoxide to form characteristic volatile carbonyl compounds.

Both iron and cobalt form complex cyanogen derivations, whilst nickel forms no compounds of this class.

A remarkable fact is that these three metals, which are so similar in general properties, have almost the same atomic weight, and do not, like the members of other groups of elements, such as silicon, tin, and lead, etc., differ considerably in atomic weight (see p. 444).

Exercises on Lesson XXXIV

1. Describe the mode of occurrence and the manufacture of metallic nickel. For what purposes is the metal used?

2. How would you prepare a specimen of pure nickel ammonium sulphate from German silver?

3. What occurs when the following substances are added to a solution of cobalt chloride: (*a*) concentrated hydrochloric acid; (*b*) caustic soda; (*c*) bleaching powder solution; (*d*) ammonium sulphide?

4. Give a short account of the chief oxides of nickel and cobalt, stating the action of hydrochloric acid on each of them.

5. Describe a method for the separation of nickel from cobalt.

6. 5.109 grams. of cobaltous bromide were found to yield 1.377 grams. of metallic cobalt on reduction in hydrogen. Calculate the equivalent of cobalt, the equivalent of bromine being 79.92.

7. Describe the preparation and properties of nickel carbonyl.

8. Compare the physical and chemical properties of iron, nickel, and cobalt.

LESSON XXXV

Chromium, Cr, 52.0

CHROMIUM belongs to a group of elements which also contains the metals molybdenum, tungsten, and uranium, all of which are described in this work. In its chemical relations it shows considerable resemblance to manganese and iron, whilst, like sulphur, it combines with three atoms of oxygen to yield an acid-forming oxide (see p. 406).

Nearly all the compounds of this element have a brilliant colour, and hence the metal has received its name from the Greek word for colour (chroma).

The chief source of the chromium compounds is a heavy black mineral known as *chrome iron ore*, which is a compound of ferrous oxide and chromium sesquioxide, and has the formula $FeCr_2O_4$. When the finely powdered mineral is mixed with potassium carbonate and lime, and heated strongly and well stirred in a current of air—a process which is usually carried out on the bed of a reverberatory furnace—a yellow mass is obtained. When this is extracted with water a yellow solution is formed, whilst a residue of ferric hydroxide and other insoluble matter is left behind. This solution on evaporation yields a salt, which crystallises in pyramids of exactly the same shape as those of potassium sulphate, and this is known as potassium chromate. This substance may serve as the starting-point for our study of the chromium compounds, although for practical reasons, which will shortly be explained, it is not actually manufactured directly from chrome iron ore.

The following experiments may serve to give a general idea of the behaviour of the chromium compounds.

1. Potassium chromate is a salt derived from chromic acid, which is decomposed by sulphuric acid, yielding an acid-forming oxide, chromium trioxide.

EXPERIMENT 177.—Dissolve 25 grams. of potassium chromate in 100 cc. of water, and use 10 cc. for each of the following experiments:—

1. Add caustic soda—no change occurs.
2. Gradually add 10 cc. of concentrated sulphuric acid, shaking after each addition and then cool—red crystals separate out, which must be drained on a porous plate or filtered through asbestos.
3. Dissolve the crystals in water, neutralise with caustic potash and evaporate—potassium chromate is left.

2. Potassium chromate is a strong oxidising agent, and is converted by reducing agents into green salts, which are derived from a basic oxide.

EXPERIMENT 178.—1. Heat some crystals of potassium chromate with concentrated hydrochloric acid—chlorine is evolved and a green solution formed.

2. Add to a solution of potassium chromate 5 cc. of dilute sulphuric acid and a crystal or two of sodium sulphite and boil—the solution becomes green. To this liquid add caustic soda gradually until just alkaline—a greenish precipitate is formed which is readily soluble in dilute acids.

3. The basic oxide is stable in the air, but can be reconverted by oxidation into the acid-forming oxide or the salts derived from it.

EXPERIMENT 179.—Filter off a little of the hydroxide obtained above, dry it in a small crucible over the flame, add some potassium carbonate and nitrate, and fuse—a yellow mass soluble in water containing potassium chromate is formed.

Atomic Weight of Chromium—Formula of the Chromium Compounds.—The composition of the salts of chromium which are derived from the basic hydroxide has been ascertained by analysing the chloride in the usual way by means of silver nitrate, and it has thus been found that the equivalent of the metal in this salt is 17.33. The atomic weight of chromium is found by the specific heat method to be about $\frac{6.4}{0.1208} = 53$, and hence the correct atomic weight is taken to be $3 \times 17.33 = 52.0$. The empirical formula of the chloride is therefore $CrCl_3$, whilst that of the hydroxide is $Cr(OH)_3$, and that of the oxide obtained by heating it is Cr_2O_3.

The composition of the acid-forming oxide is ascertained by determining how much oxygen it loses when it passes into the lower oxide, and it has been found that in this change it loses exactly half of its oxygen. The acid-forming oxide must therefore have the composition $[Cr_2O_3 + 3O]$ or Cr_2O_6, or more simply CrO_3. The corresponding acid, chromic acid, is H_2CrO_4, and from this the chromates are derived.

Metallic Chromium

Metallic chromium is formed when the sesquioxide is very strongly heated with carbon, the process being best carried out in the electrical furnace. It may also be prepared by the "thermite" process (p. 315), the oxide being mixed with an equivalent amount of finely divided aluminium and ignited,—

$$Cr_2O_3 + 2Al = Al_2O_3 + 2Cr.$$

When once started the reduction proceeds rapidly with great evolution of heat and produces a fused mass of almost pure metallic chromium. An alloy with iron, known as ferro-chrome, is made on the large scale from chrome iron ore by one of the above methods, and is used for the production of a very hard chrome steel which is specially suitable for the manufacture of projectiles.

Chromium is a white metal, which has the specific gravity 6.92, is extremely hard, and only melts at a very high temperature. It dissolves readily in hydrochloric acid, hydrogen being evolved and chromic chloride, $CrCl_3$, being produced.

Chromium Trioxide and the Chromates

Chromium Trioxide, CrO_3, is prepared by acting on potassium bichromate with strong sulphuric acid,—

$$K_2Cr_2O_7 + 2H_2SO_4 = 2KHSO_4 + 2CrO_3 + H_2O.$$

EXPERIMENT 180.—Powder 30 grams. of potassium bichromate, add 50 cc. of water and 42 grams. of concentrated sulphuric acid; allow to stand and pour off the solution from the potassium hydrogen sulphate which separates out. Warm the clear liquid and add 15 grams. of concentrated sulphuric acid, allow to stand and decant the clear liquid. The red crystals attack paper, and must therefore be drained through asbestos or a porous plate. They may be purified by being washed on an asbestos filter with fuming nitric acid, and then placed in a tube and gently warmed in a current of air dried by sulphuric acid to expel the nitric acid.

Chromium trioxide forms red crystals which decompose on heating, oxygen being evolved, and the basic green sesquioxide, Cr_2O_3, being produced,—

$$4CrO_3 = 2Cr_2O_3 + 3O_2.$$

The trioxide acts as a very powerful oxidising agent, and several instances of this have already been given. When absolute alcohol is allowed to drop on to the pure trioxide, the alcohol takes fire and a green mass of the lower oxide, Cr_2O_3, is left.

EXPERIMENT 181.—Heat a few crystals of chromium trioxide in a test-tube—oxygen is evolved (test by glowing splint), and the green sesquioxide is left.

Chromic Acid, H_2CrO_4, is formed when the trioxide is warmed with a small amount of water, and like the oxide crystallises in red needles.

The *chromates* are derived from this acid and are yellow or reddish coloured, those of the alkali metals being the only ones which are soluble in water, More complex salts are also known which are termed *bichromates*, and are derived from bichromic acid, $H_2Cr_2O_7$, which has not, however, been isolated.

The bichromates are formed by the addition of the requisite amount of an acid to the chromates, chromium trioxide being thus formed which unites with the excess of the chromate,—

$$H_2SO_4 + 2K_2CrO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

They are converted by the action of alkalis into the chromates,—

$$2KHO + K_2Cr_2O_7 = 2K_2CrO_4 + H_2O.$$

When hydrogen peroxide and sulphuric acid are added to a solution of potassium chromate, a deep blue coloured solution is formed, which contains an acid derived from a peroxide of chromium. The blue compound dissolves in ether and its production may be used as a test for the presence either of chromic acid or hydrogen peroxide.

EXPERIMENT 182.—To 10 cc. of potassium chromate solution (p. 405) add 1 cc. of concentrated sulphuric acid. Notice the change in colour from yellow to red. Cool and stir—a thick precipitate of yellowish-red crystals of potassium bichromate is produced. Filter, dissolve the precipitate in water, and add caustic potash—the colour changes back to yellow, potassium chromate being reformed.

Potassium Chromate, K_2CrO_4, is prepared by the action of caustic potash on potassium bichromate, and forms readily soluble yellow crystals, which are isomorphous with those of potassium sulphate.

Potassium Bichromate, $K_2Cr_2O_7$, is prepared directly from chrome iron ore by adding sulphuric acid to the solution obtained by extracting the fused mass of chrome iron ore and potassium carbonate with water (p. 404). It is only sparingly soluble in water, and hence can readily be purified by re-crystallisation. It is for this reason, and because it contains a higher percentage of chromium, that this salt is manufactured instead of potassium chromate.

When heated with concentrated hydrochloric acid it yields chlorine and a mixture of potassium chloride and chromic chloride,—

$$K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2.$$

It is largely used as an oxidising agent. In all such reactions the chromium may be regarded as passing from the state of trioxide to that of sesquioxide,—

$$2CrO_3 = Cr_2O_3 + 3O$$

so that 3 atoms of oxygen become available for oxidising purposes when two molecules of CrO_3 or one of $K_2Cr_2O_7$ are employed.

Ammonium Bichromate, $(NH_4)_2Cr_2O_7$, resembles the potassium salt in appearance. When it is heated a remarkable decomposition occurs, the ammonia being oxidised to nitrogen and water, whilst green chromium sesquioxide is left behind as a very bulky mass.

Lead Chromate, $PbCrO_4$, is a yellow precipitate which is obtained by adding lead acetate to potassium bichromate solution,—

$$2Pb(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2PbCrO_4 + 2K(C_2H_3O_2) + 2C_2H_4O_2.$$

It is used as a paint under the name of *chrome yellow*. The salts of zinc and bismuth are also used as yellow paints.

Silver Chromate, Ag_2CrO_4, is a red powder.

Estimation of Iron by Means of Potassium Bichromate.—A solution of potassium bichromate is often employed for the estimation of iron in the ferrous state. When a solution of a ferrous salt is acidified with hydrochloric acid and treated with potassium bichromate solution, the latter is reduced and the ferrous salt is converted into a ferric salt,—

$$K_2Cr_2O_7 + 6FeCl_2 + 14HCl = 2KCl + 2CrCl_3 + 6FeCl_3 + 7H_2O.$$

When the oxidation is complete the solution no longer contains a ferrous salt, and therefore gives no blue coloration with potassium ferricyanide, so that this substance can be used as an indicator.

A standard solution of potassium bichromate is made, 1 litre of which is capable of oxidising 5.585 grams. of iron from the ferrous to the ferric state, and therefore, as is seen from the following equation,—

$$2FeO + O = Fe_2O_3,$$

contains 0.8 grams. of available oxygen.

Since the molecule of potassium bichromate weighing 294.2 contains, as we have seen, 3 atoms of available oxygen weighing 48, it is necessary for this purpose to weigh out

$\frac{294.2 \times 0.8}{48} = 4.903$ grams. of potassium bichromate, dissolve it in water and make it up to 1 litre of solution.

The ferrous solution is then placed in a beaker, hydrochloric acid is added, and the potassium bichromate is then run in slowly from a burette. The potassium ferricyanide is not added to the solution, but drops of a dilute solution of the salt are placed on a white tile, and a drop of the liquid which is being titrated is removed from time to time on the end of a glass rod and added to one of them. As long as any ferrous salt is still present a blue coloration is produced. As soon as this is no longer the case the oxidation is complete.

Thus, supposing that 25 cc. of a solution of an iron salt require 20 cc. of the bichromate solution for complete oxidation, it follows that $20 \times 0.005585 = 0.1170$ grams. of iron are present in the ferrous state in the 25 cc. taken for the experiment.

EXPERIMENT 183.—Prepare a standard solution of potassium bichromate, and by its aid ascertain the percentage of iron in ferrous ammonium sulphate.

Chromium Oxychloride, or **Chromyl Chloride**, **CrO_2Cl_2**, is formed when a chromate is distilled with common salt and concentrated sulphuric acid,—

$$K_2CrO_4 + 4HCl = CrO_2Cl_2 + 2KCl + 2H_2O.$$

It is a dark-red liquid which boils at 115.9°, and has the vapour density 77.5, which corresponds with the molecular formula given above. It is a very powerful oxidising agent, and is at once decomposed by water, with formation of chromic and hydrochloric acids, whilst alkalis form the corresponding salts,—

$$CrO_2Cl_2 + 4NH_4HO = (NH_4)_2CrO_4 + 2NH_4Cl + 2H_2O.$$

Bromine and iodine do not form similar compounds, the elements themselves being set free when a bromide or iodide is distilled with sulphuric acid and potassium bichromate. The formation of chromium oxychloride is therefore often used as a test for the presence of a chloride in presence of a bromide or iodide. If a chloride be present, the distillate yields a yellow solution of a chromate when excess of caustic soda is added, whereas bromine and iodine dissolve, forming colourless solutions.

EXPERIMENT 184.—Place a well-ground mixture of 5 grams. of potassium chromate and 2.5 grams. of sodium chloride in a small retort, add 10 grams. of concentrated sulphuric acid and heat gently, collecting the distillate in a small dry flask. A dark-red fuming liquid passes over. Pour a drop of this on a glazed tile and add a drop or two of alcohol. The latter takes fire and burns with a bright flame. To the remainder add water, and test the yellow solution produced for chromic and hydrochloric acids.

Chromium Sesquioxide, Cr_2O_3, and the Chromic Salts

Chromic sesquioxide and the chromic salts correspond in composition with the ferric salts of iron, but can only be reduced with great difficulty. They are prepared by the reduction of the chromates. The salts have a blue or violet colour.

Chromium Sesquioxide, Cr_2O_3, is usually prepared by heating solid potassium bichromate with a reducing agent such as sulphur or ammonium chloride, and washing the residue. It is a green powder, which like alumina is practically insoluble in acids after it has been strongly heated, and thus rendered crystalline, but dissolves when it has only been gently heated. It is used as a green paint and in the preparation of green glass, etc.

Chromic Hydroxide, $Cr(OH)_3$, is formed as a pale-blue precipitate when ammonia is added to a solution of chrome alum in cold water. Caustic soda produces a green precipitate soluble in excess, forming a sodium compound analogous to sodium aluminate (p. 317).

Chromic Chloride, $CrCl_3$, is prepared by heating a mixture of the oxide and charcoal in a stream of chlorine,—

$$Cr_2O_3 + 3C + 3Cl_2 = 2CrCl_3 + 3CO.$$

It forms peach-blossom coloured plates, and volatilises at a very high temperature; the density of its vapour at 1200° is 79.2, and its molecular formula therefore is $CrCl_3$. The anhydrous chloride is almost insoluble in water, but a soluble crystalline hydrated salt, $CrCl_3 + 6H_2O$, may be prepared by dissolving the hydroxide in hydrochloric acid and evaporating the green solution, or by heating chromium trioxide with hydrochloric acid,—

$$2CrO_3 + 12HCl = 2CrCl_3 + 3Cl_2 + 6H_2O.$$

Chromic Sulphate, $Cr_2(SO_4)_3 + 18H_2O$, crystallises in blue octahedra, and is formed by dissolving the hydroxide in sulphuric acid. Like aluminum sulphate and ferric sulphate it forms an alum with potassium sulphate.

Chrome Alum, $K_2SO_4 + Cr_2(SO_4)_3 + 24H_2O$, is best prepared by acidifying a solution of potassium bichromate with sulphuric acid and treating it with methylated spirit, which is oxidised at the expense of the oxygen of the bichromate. The reduction may also be carried out by passing sulphur dioxide into the solution,—

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O.$$

EXPERIMENT 185.—Dissolve 10 grams. of potassium bichromate in 50 cc. of water and add 50 cc. of dilute sulphuric acid. Cool and gradually add alcohol, cooling after each addition. Chrome alum crystallises out on standing in flat distorted octohedra.

Chrome alum forms violet crystals, and yields a violet solution in cold water, which becomes green on heating. It is often produced in the preparation of certain colouring matters by the reduction of potassium bichromate, and is also found in the cells of exhausted bichromate batteries (p. 304).

Chromic Sulphide, Cr_2S_3, is formed when the metal is heated with sulphur. It is not produced by the action of ammonium sulphide on a chromic salt, the hydroxide being precipitated and sulphuretted hydrogen liberated, exactly as occurs with aluminium salts,—

$$2CrCl_3 + 3(NH_4)_2S + 6H_2O = 6NH_4Cl + 2Cr(OH)_3 + 3H_2S.$$

The Chromous Salts

Chromium forms a second series of salts, CrR'_2, corresponding in composition with the ferrous salts. These are formed by the reduction of the chromic salts, and are known as the chromous salts, being derived from the oxide CrO. They are very unstable and rapidly absorb oxygen from the air, chromic salts being produced.

Chromous Chloride, $CrCl_2$, is prepared by reducing potassium bichromate with zinc and hydrochloric acid. It is a bright-blue crystalline salt, which instantly absorbs oxygen when it is exposed to the air, and can be used for removing the last traces of oxygen from nitrogen or hydrogen. In presence of hydrochloric acid it is at once converted by oxygen into chromic chloride,—

$$4CrCl_2 + 4HCl + O_2 = 4CrCl_3 + 2H_2O.$$

This can readily be demonstrated by placing 30 grams. of zinc in a flask fitted for the preparation of hydrogen, adding 50 cc. of a saturated solution of potassium bichromate, and then pouring in 50 cc. of concentrated hydrochloric acid. As soon as the first violence of the reaction has moderated insert an india-rubber stopper fitted with a tube-funnel and delivery tube, so as to prevent the access of oxygen to the flask. After about five minutes the liquid in the flask becomes bright blue and then contains chromous chloride. If another 50 cc. of the potassium bichromate be reduced to chromic salt with sulphurous acid and the two be compared, the contrast between the green chromic salt and the blue chromous salt is well seen. When a few cc. of the blue solution are poured into a test-tube and shaken in the air the liquid rapidly becomes green.

Detection of Chromium

All chromium compounds impart a green colour to the borax bead both in the oxidising and reducing flames.

Chromic acid is recognised by the formation of the characteristic salts of lead and silver, and by the fact that it is readily reduced to the green chromic salts.

The chromic salts give a precipitate of the hydroxide with ammonia and ammonium sulphide. The hydroxide is converted by a boiling solution of sodium hypochlorite into sodium chromate, which is also formed when it is fused with sodium carbonate and sodium nitrate.

Molybdenum, Mo, 96.0; Tungsten, W, 184.0; and Uranium, U, 238.5

These three elements, which all belong to the chromium group, can only be very briefly mentioned here.

Molybdenum occurs chiefly as the *sulphide*, MoS_2. The *trioxide*, MoO_3, is a white powder and like chromium trioxide is an acid-forming oxide and yields an *acid*, H_2MoO_4, and a series of *molybdates*.

Ammonium molybdate is largely used as a reagent for phosphoric acid, with which it produces a yellow precipitate of complex composition. The molybdates are reduced by zinc and hydrochloric acid with formation of blue lower oxides.

Tungsten occurs as iron tungstate in the mineral *wolfram*, from which the symbol of the element is derived. The metal melts at a very high temperature, 2800°, and conducts electricity badly, and is on account of these properties used for the production of filaments for incandescent electric lamps. The *oxide*, WO_3, yields *tungstic acid*, H_2WO_4, and a series of tungstates. The sodium salt is soluble and is employed for rendering various textile fabrics non-inflammable.

Uranium occurs in *pitch-blende* as an oxide, U_3O_8. It also yields a trioxide, UO_3, which forms a series of uranates with bases, whilst with acids it yields the yellow fluorescent *Uranyl* salts, such as the *nitrate*, $UO_2(NO_3)_2$. The *acetate*, $UO_2(C_2H_3O_2)_2$, is employed for the volumetric estimation of phosphates. Uranium has the highest atomic weight of the known elements and is radio-active (see p. 462).

SUMMARY

Chromium is a white metal which fuses at a high temperature and forms stable compounds which are not easy to reduce.

It forms several oxides, the highest of which, chromium trioxide, CrO_3, is an acid-forming oxide, whilst chromic oxide, Cr_2O_3, and chromous oxide, CrO, are basic oxides.

Chromic acid yields numerous stable salts, the *chromates*, R'_2CrO_4, and the *bichromates*, $R'_2Cr_2O_7$.

The *chromic salts*, CrR'_3, are formed by the reduction of the chromates, and can be reconverted into these by oxidation. They are usually green or violet; the sulphate forms "alums" with the alkali sulphates.

The *chromous salts*, CrR'_2, are blue in colour and are formed by the reduction of the chromic salts. They readily absorb oxygen and are reconverted into chromic salts.

EXERCISES ON LESSON XXXV

1. Describe the preparation of potassium bichromate on the large scale.

2. How can metallic chromium be prepared, and what are its properties?

3. What is the action of (*a*) hydrochloric acid, (*b*) sulphurous acid, (*c*) ferrous sulphate and hydrochloric acid, on potassium bichromate?

4. How would you prepare the following substances from potassium bichromate: (*a*) chromium trioxide, (*b*) chromium oxychloride, (*c*) chromous chloride, (*d*) chrome alum, (*e*) lead chromate?

5. Give a short account of the chief chromic salts.

6. How much chrome alum could be obtained from 1 ton of chrome iron ore containing 70 per cent of chromium sesquioxide?

7. How much potassium bichromate is contained in a litre of solution of which 1 cc. contains 0.0008 gram. of available oxygen?

8. 1 gram. of a substance containing iron in the ferrous state is dissolved in water and diluted to 100 cc. 25 cc. of this solution require 10 cc. of potassium bichromate solution (1 cc. = 0.0008 gram. available oxygen) for titration. Calculate the percentage of iron present as ferrous salt in the original substance.

9. 50 cc. of a solution containing 7 grams. of ferrous ammonium sulphate in 500 cc. are required to reduce 25 cc. of a solution of chromic acid. How much chromic trioxide is present in a litre of the latter solution?

10. How would you attempt to prove experimentally that chromium trioxide loses half its oxygen when it is reduced to chromium sesquioxide?

11. Contrast the properties of compounds of chromium with those of the compounds of iron.

LESSON XXXVI

Manganese, Mn, 54.93

THE chemistry of manganese is even more complicated than that of chromium since the metal forms a large number of oxides, some of which act as basic oxides, others as acid-forming oxides, and others again as peroxides.

The element occurs chiefly in the form of the dioxide or black oxide of manganese, MnO_2, as the mineral *pyrolusite*, but is also found as a compound of this with baryta, as the mineral *psilomelane*, $BaMnO_3$, and in the form of the oxides *braunite*, Mn_2O_3, and *hausmannite*, Mn_3O_4.

The black oxide actually serves as the source of nearly all the manganese compounds, and may, therefore, be taken as the starting-point in our study of these.

1. The black oxide is not strongly acid-forming or strongly basic, and is, therefore, not dissolved either by dilute acids or alkalis.

EXPERIMENT 186.—In this and the following experiments the finely divided artificial oxide should be used, as it is more readily acted on than the denser mineral.

Treat small separate portions of the oxide with dilute hydrochloric and nitric acids and with dilute caustic soda solution—no action occurs.

2. When the oxide is treated with concentrated hydrochloric acid part of the oxygen oxidises the acid, free chlorine being produced along with a chloride of manganese corresponding to a lower oxide.

EXPERIMENT 187.—Heat about 0.5 gram. of the oxide in a test-tube with concentrated hydrochloric acid and test the gas evolved for chlorine. Boil off all the chlorine, filter, and add caustic soda. A white precipitate insoluble in excess is produced, which consists of the hydroxide, $Mn(OH)_2$, corresponding with the lower oxide, MnO. This soon becomes brown on standing from absorption of oxygen. In the presence of iron, a frequent impurity of manganese dioxide, the precipitate contains ferric hydroxide and is slightly brown to commence with.

3. The black oxide of manganese is capable of further oxidation and thereby yields an acid-forming oxide, which forms green salts with solutions of caustic potash. These salts correspond with the trioxide, MnO_3.

EXPERIMENT 188.—Place 2 grams. of caustic potash and 0.25 gram. of the black oxide in a crucible, heat over the flame and add a few crystals of potassium nitrate or potassium chlorate at intervals to act as an oxidising agent. When cold extract with 10 cc. of cold water, and notice the dark-green alkaline solution which is obtained.

4. This green salt is very unstable, and is readily converted into a pink salt, known as potassium permanganate, $KMnO_4$, which corresponds with a still higher oxide, Mn_2O_7.

EXPERIMENT 189.—1. To a few drops of the clear green solution add 100 cc. of water—a pink solution is formed.

2. Allow some of the solution to stand in the air for some time—the liquid becomes pink and a dark-brown precipitate is formed.

3. Acidify some of the solution with dilute sulphuric acid —the liquid becomes pink.

These changes are described in detail later on (p. 421), but without discussing their nature at present, it is sufficient to notice that these experiments afford evidence that whilst the black oxide of manganese itself is not possessed of strong acid-forming or basic properties, the lower oxide is basic and forms salts with acids, and the higher oxides are acid-forming and yield salts with bases.

Metallic Manganese and the Manganous Salts

Metallic manganese is not prepared on the large scale, although its alloys with iron, *ferromanganese* and *spiegeleisen* or *spiegel iron*, are largely used in the manufacture of steel (p. 379). The oxides are reduced when they are heated with carbon to whiteness or when mixed with aluminium and ignited, whilst the chloride is decomposed by sodium or magnesium, so that the metal can be prepared on the small scale by both of these methods as well as by electrolysis.

Manganese has a gray colour, is very hard and brittle, has a specific gravity of about 8, and melts at 1245°. It oxidises easily in the air when pure, decomposes water very slowly in the cold, and readily dissolves in dilute acids, forming the manganous salts. These salts are almost colourless, but possess a faint pink tint, whilst in their general properties they resemble the salts of nickel and cobalt or ferrous iron. The chloride, nitrate and sulphate are readily soluble in water, whilst the carbonate and phosphate are insoluble in water.

Equivalent of Manganese and Formulæ of the Manganous Salts.—The analysis of manganous chloride shows that the equivalent of the metal in this salt is 27.465, whilst the atomic weight is found from the atomic heat to be about 52. Hence the correct atomic weight is taken as 54.93, and the formula of the chloride is $MnCl_2$, the corresponding oxide being MnO.

Manganous Oxide, MnO, is a grayish powder, and is formed by heating any one of the other oxides in a current of hydrogen. When heated in the air it forms the oxide Mn_3O_4, which is the final product when any of the other oxides is submitted to this treatment.

Manganous Hydroxide, $Mn(OH)_2$, is produced as a white precipitate when caustic soda is added to a manganese salt, and is insoluble in excess of caustic soda, but easily soluble in acids. It readily absorbs oxygen from the air, the sesquioxide, Mn_2O_3 being produced. In the presence of ammonium salts the hydroxide is not immediately precipitated by alkalis, so that in this respect manganese resembles magnesium.

EXPERIMENT 190. — 1. To 5 cc. of a 10 per cent solution of manganous sulphate, add excess of caustic soda solution. A white precipitate is produced which rapidly becomes brown, especially when shaken up in the air. The best result is obtained by boiling both solutions before mixing them, so as to remove dissolved oxygen.

2. To 1 cc. of a solution of manganous sulphate add a large excess of ammonium chloride solution, and then add caustic soda solution drop by drop. No precipitate is at first produced, but the hydroxide gradually separates out.

Manganese Chloride, $MnCl_2$, is formed in solution when the black oxide, or any of the other oxides, is boiled with hydrochloric acid,—

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O.$$

It is best prepared from the residual liquid obtained in the preparation of chlorine. This always contains iron, which may be removed by precipitating a portion of the manganese as carbonate and leaving it in contact with the solution. Under these circumstances the iron is precipitated as ferric hydroxide, whilst some of the manganese carbonate is redissolved.

EXPERIMENT 191.—Evaporate the residual liquid obtained in the preparation of chlorine from manganese dioxide and hydrochloric acid to dryness. Dissolve in hot water, filter and remove one-tenth of the clear solution. To this tenth add sodium carbonate in slight excess, filter and wash the precipitated manganous carbonate, and then add it to the bulk of the solution and warm gently for some time on the sand-bath. As soon as a few drops of the clear liquid no longer produce a black precipitate with ammonium sulphide all the iron has been precipitated. Filter, evaporate to small bulk, and allow to crystallise.

The chloride crystallises from water in pink crystals of the formula, $MnCl_2 + 4H_2O$.

Manganese Sulphate, $MnSO_4$, is formed when manganese dioxide is heated with concentrated sulphuric acid, oxygen being evolved,—

$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

It is a pink salt, and crystallises with five molecules of water. Like the sulphates of nickel, cobalt, and iron, it forms double salts with the alkali sulphates.

Manganous Sulphide, MnS, is formed as a pink or flesh-coloured precipitate when ammonium sulphide is added to a solution of a manganous salt, and is easily soluble in hydrochloric acid.

Manganous Nitrate, $Mn(NO_3)_2$, resembles the sulphate and chloride in appearance.

Manganese sesquioxide, Mn_2O_3, and the Manganic Salts.

When manganous hydroxide is exposed in the moist state in the air it is converted into manganic hydroxide, $Mn(OH)_3$, which is a brown mass resembling hydrated manganese dioxide in appearance. The corresponding oxide, Mn_2O_3, occurs as the mineral braunite, and is formed when manganese dioxide is heated in an atmosphere of oxygen. It acts as a feebly basic oxide, but the salts derived from it are extremely unstable.

Manganic Chloride, $MnCl_3$, probably exists in the dark-coloured solution which is produced when manganese dioxide is dissolved in concentrated hydrochloric acid. When this liquid is heated the salt decomposes and manganous chloride and free chlorine are formed,—

$$2MnO_2 + 8HCl = 2MnCl_3 + Cl_2 + 4H_2O$$
$$2MnCl_3 = 2MnCl_2 + Cl_2.$$

Manganic Sulphate, $Mn_2(SO_4)_3$, is formed by the action of sulphuric acid on manganese dioxide at 138°. It is a green powder and is extremely unstable.

Red Oxide of Manganese, Mn_3O_4, is formed as a red powder when any of the other oxides is heated in the air. It does not form any corresponding salts, but behaves towards acids in many respects like red lead. Thus nitric acid produces manganese dioxide and manganous nitrate,—

$$Mn_3O_4 + 4HNO_3 = MnO_2 + 2Mn(NO_3)_2 + 2H_2O,$$

whilst with hydrochloric acid it yields chlorine and manganous chloride.

Manganese Dioxide, MnO_2, occurs as the mineral pyrolusite, which serves as the source of nearly all the manganese compounds. It is best prepared by heating manganous nitrate at 150°-160°, and then forms a hard lustrous black mass. The *hydrated dioxide* is formed whenever potassium permanganate acts as a reducing agent in neutral or alkaline solution.

EXPERIMENT 192.—To a dilute solution of potassium permanganate add caustic soda and a few drops of methylated spirits, and warm. A brown precipitate of the hydrated dioxide is produced.

It does not form salts when treated with acids, but loses oxygen, which either escapes as gas or acts on the acid,—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$
$$2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2.$$

Manganese dioxide therefore resembles lead dioxide in its chemical behaviour, and differs from barium dioxide.

The dioxide, however, acts as a weak acid-forming oxide and yields salts, termed the *manganites*, with lime and other alkalis. The manganese mud obtained in the treatment of chlorine residues in Weldon's process (p. 177), contains a manganite of calcium, and is not free manganese dioxide.

The Manganates and Permanganates

It has already been mentioned that when manganese dioxide is heated with caustic potash and an oxidising agent, a green salt known as potassium manganate is formed,—

$$MnO_2 + 2KHO + O = K_2MnO_4 + H_2O.$$

This salt is extremely unstable, and can only exist in the presence of a large amount of caustic alkali. When this is removed the salt undergoes a remarkable decomposition, a portion of the manganese being precipitated as manganese dioxide, whilst the remainder is converted into potassium permanganate, which is purple coloured,—

$$3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KHO.$$

This change occurs, therefore, whenever a sufficient quantity of an acid is added to the green alkaline solution; such weak acids as carbonic acid and acetic acid being capable of bringing about the change. The green solution also becomes pink when largely diluted with water (Experiment 189).

Potassium Manganate, K_2MnO_4, can be obtained in crystals by evaporating the green solution in a vacuum, and these have the same form as those of potassium sulphate, with which they are isomorphous. The manganates are also formed by the partial reduction of the permanganates in alkaline solution, and are produced when potassium permanganate is heated gently,—

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2.$$

EXPERIMENT 193.—1. To a strongly alkaline solution of potassium permanganate gradually add dilute sodium thiosulphate solution. A green solution of potassium manganate is formed.

2. Heat some crystals of potassium permanganate in a test-tube, cool, and extract with cold water. A green solution is obtained.

The manganates are derived from manganic acid, H_2MnO_4, which has not been prepared in the free state. The corresponding oxide, **manganese trioxide, MnO_3,** is a pink deliquescent mass obtained by dropping a solution of potassium permanganate in sulphuric acid on to potassium carbonate. When brought into contact with water it does not form manganic acid as might have been expected, but yields permanganic acid and manganese dioxide,—

$$3MnO_3 + H_2O = 2HMnO_4 + MnO_2.$$

Potassium Permanganate, $KMnO_4$, is prepared by heating caustic potash with manganese dioxide and an oxidising agent, such as potassium chlorate. The green mass is extracted with water, and the resulting green solution is allowed to stand until it becomes pink, and is then poured off from the deposit of manganese dioxide and evaporated. It is also possible to neutralise partially with sulphuric acid and evaporate the clear liquid.

The salt is isomorphous with potassium perchlorate, $KClO_4$, and crystallises in long, almost black prisms having a metallic lustre and forming a purple-coloured solution in water. When this solution is acidified no change occurs in appearance, but the liquid now contains **permanganic acid, $HMnO_4$** which decomposes slowly with formation of manganese dioxide and liberation of oxygen.

Potassium permanganate is a very powerful oxidising agent, and is often used as a disinfectant, although it is not so efficacious as some others because it is so easily reduced. Condy's fluid, much used for the above purpose, is a solution of sodium manganate and permanganate made by heating manganese dioxide with sodium carbonate in shallow vessels and extracting with water.

Potassium permanganate is largely employed in volumetric analysis. When acted on by a reducing substance in presence of sulphuric acid it is reduced to a manganous salt. Thus when a solution of ferrous sulphate containing free sulphuric acid is treated with potassium permanganate, the whole of the iron is converted into ferric sulphate, whilst the manganese and potassium of the permanganate appear as potassium sulphate and manganese sulphate,—

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O.$$

Potassium permanganate acts in an analogous way on oxalic acid, the latter being converted into carbon dioxide and water,—

$$2KMnO_4 + 5C_2H_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O.$$

It also liberates iodine from hydriodic acid and oxidises many organic compounds. In all these oxidations in acid solution, the manganese may be regarded as passing from the state of Mn_2O_7 to that of MnO,—

$$Mn_2O_7 = 2MnO + 5O,$$

so that five atoms of oxygen become available for oxidising purposes when two molecules of potassium permanganate are employed.

A standard solution of potassium permanganate is usually prepared by dissolving the salt in water and then standardising the solution by means of a ferrous salt or pure oxalic acid. The best method of employing iron is to weigh out a known amount of pure iron wire, and dissolve this in dilute sulphuric acid in the absence of oxygen. This is effected by placing the iron and dilute acid in a flask provided with a conducting tube which dips under water, and adding a small amount of sodium carbonate before putting in the cork. The air is thus expelled and the iron dissolved without any danger of the formation of a ferric salt.

The reaction is carried out by placing the iron solution in a beaker and adding the permanganate from a burette until the pink colour is no longer discharged. Thus the permanganate solution acts as its own indicator. The strength of the solution is usually expressed in terms of the amount of oxygen which is available for oxidising purposes, or of the amount of iron which it can oxidise from the ferrous to the ferric state.

Two atoms of iron in the ferrous state require one atom of oxygen to convert them into the ferric state, as is seen from the following equation, which relates to the oxides,—

$$2FeO + O = Fe_2O_3$$

Hence if 10 cc. of a solution are required to oxidise 0.01 gram. of iron from the ferrous to the ferric state, each cc. is equivalent to 0.001 gram. of ferrous iron, or $\frac{0.001 \times 8}{55.85} =$ 0.000143 gram. of available oxygen.

Oxalic acid is titrated in a similar manner, but the action proceeds very slowly unless the liquid is heated.

EXPERIMENT 194. — 1. Gradually add a solution of potassium permanganate to one of ferrous sulphate acidified with dilute sulphuric acid; the pink colour at first disappears, but finally remains, whilst a ferric salt is produced (test by ferricyanide of potassium).

2. Dissolve 1 gram. of oxalic acid in 50 cc. of water, add 10 cc. of dilute sulphuric acid, and add two or three drops of potassium permanganate solution. No change occurs at first, but when the liquid is heated the colour slowly disappears. Continue adding the permanganate

solution, and notice that carbonic acid gas is evolved as the oxidation proceeds.

Standard pemanganate is used for the estimation of iron and oxalic acid, and in water analysis for determining the amount of dissolved organic matter.

A remarkable reaction occurs when an acid solution of potassium permanganate is mixed with hydrogen peroxide. Both of these powerful oxidising agents are reduced, free oxygen being evolved, one-half of which is derived from the potassium permanganate, and the other half from the hydrogen peroxide,—

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5O_2 + 8H_2O.$$

This reaction is often used for the estimation of hydrogen peroxide, the oxygen which is evolved being collected and measured, or the volume of a standard solution of potassium permanganate, which is required for the change, being ascertained.

In alkaline or neutral solution potassium permanganate is not converted into a manganous salt, but is reduced to manganese dioxide, so that only three atoms of oxygen are rendered available from two molecules of the salt (Experiment 193), whereas in acid solution five atoms are available (p. 423). The manganese in this case may be regarded as passing from the state of Mn_2O_7 to that of MnO_2,—

$$Mn_2O_7 = 2MnO_2 + 3O$$

EXPERIMENT 195.—Add 10 cc. of dilute sulphuric acid to 5 cc. of a solution of hydrogen peroxide, and then add potassium permanganate solution slowly — oxygen is vigorously evolved and the pink colour disappears.

Potassium permanganate yields free oxygen when the solid salt is heated alone. When treated with hydrochloric acid it yields chlorine and manganous chloride.

EXPERIMENT 196.—1. Heat some crystals of potassium permanganate in a test-tube and test for oxygen by a glowing splint.

2. Heat some crystals of potassium permanganate with hydrochloric acid and test for chlorine.

The manganous salts, into which the permanganates are converted by reduction in acid solution, can be retransformed by oxidising agents into permanganates. Thus manganese nitrate is at once converted into *permanganic acid*, when its solution is boiled with lead dioxide and strong nitric acid. A deep purple coloured solution is formed, and this reaction is often used for the detection or estimation of manganese salts,—

$$6HNO_3 + 2Mn(NO_3)_2 + 5PbO_2 = 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O.$$

Permanganic acid is derived from the very unstable *heptoxide*, Mn_2O_7, which is formed by the action of sulphuric acid on potassium permanganate, but very readily decomposes with evolution of oxygen.

Detection of Manganese

Manganese compounds do not yield the metal when they are heated on charcoal with reducing agents. They impart an amethyst colour to the borax bead in the oxidising flame (manganic oxide), but the bead becomes colourless in the reducing flame (manganous oxide). When fused with sodium carbonate and potassium nitrate they yield a green mass of a manganate.

The manganous salts yield no precipitate with sulphuretted hydrogen in acid solution, but the sulphide is precipitated as a buff coloured mass when ammonium sulphide is added to the solution. Caustic soda added to the solution of the sulphide in hydrochloric acid produces a white precipitate of the hydroxide, which rapidly becomes brown. In the presence of ammonium salts no precipitate is produced at first by caustic soda or ammonia, but after standing some time the hydroxide is slowly deposited.

General Relations of the Manganese Compounds

Manganese is closely related both to iron and chromium, as is seen by the physical properties of the metal and the formation of the manganous and manganic salts and the manganates. On the other hand, in its higher oxides it has some analogy with the halogen elements, the permanganates, $RMnO_4$, being isomorphous with the perchlorates $RClO_4$.

SUMMARY

Manganese is a gray metal which melts at 1245° and can be prepared by reducing the oxides with carbon.

It forms a number of oxides, the higher ones being acid-forming and the lower basic.

Manganese heptoxide is very unstable, and the permanganates which are derived from the corresponding acid are powerful oxidising agents.

Manganese trioxide is also unstable, whilst the manganates can only exist in the presence of excess of alkali.

Manganese sesquioxide, Mn_2O_3 is a basic oxide, but the corresponding salts are unstable and readily pass into the manganous salts.

Manganese monoxide, MnO, is a basic oxide and yields stable pink salts, whilst the oxide itself absorbs oxygen from the air. The sulphate and chloride are soluble in water.

Manganese also forms the oxides MnO_2 and Mn_3O_4, which do not yield stable salts, although the dioxide has weak acid-forming properties. All the oxides are converted into Mn_3O_4 when they are heated in the air.

EXERCISES ON LESSON XXXVI

1. Describe the chief compounds of manganese which occur in nature.

2. How would you prepare pure manganese sulphate from pyrolusite?

3. What is the effect of adding the following substances to a solution of manganese nitrate:—(*a*) caustic soda, (*b*) sulphuretted hydrogen, (*c*) potassium sulphide, (*d*) sodium hypochlorite.

4. How can potassium permanganate be prepared? What is the effect of an acid solution of this substance on (*a*) ferrous sulphate, (*b*) potassium iodide, (*c*) hydrogen peroxide?

5. Give a short account of the reactions of potassium manganate.

6. Describe the preparation of manganese dioxide. What is the action of (*a*) sulphuric acid, (*b*) hydrochloric acid, (*c*) caustic potash on this substance?

7. How much potassium permanganate is required to convert 10 grams. of ferrous sulphate into ferric sulphate?

8. 25 cc. of a solution of potassium permanganate, of which 1 cc. = .0008 grams. of available oxygen, are required to oxidise the iron in 0.5 gram. of a salt. Calculate the percentage of iron present in the salt.

9. How would you prepare (*a*) oxygen, (*b*) chlorine from potassium permanganate?

LESSON XXXVII

PLATINUM; THE GASES OF THE HELIUM GROUP

Platinum, Pt, 195.2

PLATINUM was not known to the alchemists, but was first clearly recognised as a new metal in the middle of the eighteenth century. It occurs in the free state in nature, and is found in the same way as gold, and often along with it, in alluvial deposits and in beds of rivers, from which it is obtained by washing. The chief localities in which it occurs are the Ural Mountains, Borneo, New South Wales, and Canada. The native platinum is by no means pure, but contains iron, copper, gold, and a number of other metals, called the platinum metals, which resemble platinum very closely in properties and are only present in small quantities.

Properties of Platinum.—Pure platinum has a tin-white appearance and is one of the heaviest of metals, its specific gravity being 21.4. It is soft and extremely ductile, so that it can be drawn out into very fine wire. It only melts at a very high temperature, about 1710°, and is therefore much used for vessels which have to be exposed to great heat, such as crucibles for use in the laboratory, etc. In order to melt masses of the metal the oxyhydrogen flame is employed, the operation being usually carried out by fusing the metal in a cavity between two blocks of lime, or the electric furnace is used.

Platinum precisely resembles gold in its behaviour towards acids and oxygen; it only dissolves in aqua regia or in liquids in which free chlorine is present, and it is not oxidised when heated in the air or oxygen. It is, however, acted on by alkalis, and readily forms fusible alloys with metals such as lead, antimony, zinc, etc. Substances containing these elements should therefore not be heated in platinum crucibles, especially if there is any chance of reduction taking place.

Metallic platinum has a remarkable power of bringing about the combustion of many gases and vapours at a lower temperature than that at which combustion occurs when the gases are simply heated with oxygen or air. This is well illustrated by the apparatus known as the Davy glow lamp. A spiral of platinum wire is warmed in the flame and then brought into a small beaker containing a few cc. of methyl alcohol or ether. The vapour of the latter, mixed with air, comes in contact with the warm platinum and becomes oxidised, and the heat thus liberated maintains the platinum wire at a red heat. If the supply of air be properly regulated by means of a card placed over the mouth of the beaker the wire may be made to glow continuously for a long period. Finely divided platinum has this property in a much higher degree than the wire. The platinum prepared by heating ammonium chloroplatinate, $(NH_4)_2PtCl_6$, is known as *spongy platinum*, whilst that obtained by the reduction of various salts of platinum by chemical means is called *platinum black*, and both these varieties are extremely active. If a jet of hydrogen or coal gas be simply directed on to some spongy platinum the gas is at once ignited, and this device was applied by Döbereiner in his hydrogen lamp in the days before the invention of lucifer matches. This lamp consisted of a small apparatus for generating hydrogen, on the same principle as that of Kipp, a small quantity of spongy platinum being so placed that when the tap was turned the hydrogen impinged upon the platinum and became ignited.

The part actually played by the platinum in this action is difficult to understand. Spongy platinum is capable of absorbing more than 100 times its volume both of oxygen and hydrogen, and it is possible that when it is exposed to a mixture of both, the gases are absorbed and so brought into more intimate contact with each other, and are thus enabled to combine. Exactly the same amount of heat is evolved during the oxidation in presence of platinum as in ordinary combustion, the only difference being that the process begins at a lower temperature.

Platinum resembles gold not only in many of its physical properties, but also in its chemical properties, with the important exception that it replaces a different number of hydrogen atoms. It forms two series of compounds, the analyses of which show that in the platinous compounds the element is bivalent, whilst in the platinic compounds it is quadrivalent,

Platinous chloride.	Platinic chloride.
$PtCl_2$	$PtCl_4$

Like the chlorides of gold these compounds unite with hydrochloric acid to form acids, and with metallic chlorides to form the salts of these acids.

The atomic weight has been settled by the atomic heat method, and is 195.2

Chloroplatinic Acid, $H_2PtCl_6(PtCl_4 + 2HCl)$, is formed when platinum is dissolved in aqua regia and evaporated repeatedly with hydrochloric acid in order to remove the nitric acid. It forms brownish-red, deliquescent crystals, $H_2PtCl_6 + 6H_2O$, and yields a yellow solution in water. This solution is often spoken of simply as platinic chloride, and is much used in testing for potassium and ammonium salts, which form sparingly soluble salts of the acid.

Potassium Chloroplatinate, or **Potassium Platinochloride, K_2PtCl_6,** is formed when a potassium salt is added to the solution described above,—

$$H_2PtCl_6 + 2KNO_3 = K_2PtCl_6 + 2HNO_3.$$

It forms yellow crystals, and is soluble in about 100 parts of cold water, but is insoluble in alcohol. In order to test for potassium, therefore, the solution is concentrated, and chloroplatinic acid and then an equal volume of alcohol added. On stirring, a yellow precipitate is produced if potassium be present. When it is heated the salt decomposes, yielding potassium chloride, finely divided platinum, and chlorine.

Ammonium Chloroplatinate, $(NH_4)_2PtCl_6$, closely resembles the potassium salt, but when it is heated leaves behind pure platinum in the form of spongy platinum. This salt is often made use of for the purification of platinum, the metal being dissolved in aqua regia and precipitated by means of ammonium chloride in the form of ammonium chloroplatinate, which is carefully washed and then decomposed by heat. This is done, for example, in the separation of platinum from many of the metals which accompany it in the native state.

Platinic Chloride, $PtCl_4$, is prepared by heating platinum gently in chlorine, or by boiling chloroplatinic acid with the proper quantity of silver nitrate solution,—

$$H_2PtCl_6 + 2AgNO_2 = 2AgCl + 2HNO_3 + PtCl_4.$$

It crystallises in red crystals which are not deliquescent, and readily unites with hydrochloric acid to reform chloroplatinic acid, and with potassium chloride to form the potassium salt. When it is strongly heated it decomposes completely into chlorine and platinum.

Platinous Chloride, $PtCl_2$, is formed when chloroplatinic acid is carefully heated at 300°,—

$$H_2PtCl_6 = 2HCl + Cl_2 + PtCl_2.$$

It is a greenish powder which is insoluble in water, and decomposes when it is strongly heated. It forms a compound with hydrochloric acid, H_2PtCl_4, and a corresponding series of salts.

Platinic Hydroxide, $Pt(OH)_4$, is formed as a white precipitate when caustic potash is added to platinic chloride, $PtCl_4$. Like gold trihydroxide it has weak acid properties, and also dissolves in acids. When it is gently heated it yields *platinum dioxide*, PtO_2, which is a black powder and decomposes into platinum and oxygen when it is more strongly heated.

Platinic Sulphide, PtS_2, is formed as a black precipitate when sulphuretted hydrogen is passed through a solution of chloroplatinic acid. It dissolves in alkali sulphides, and platinum is therefore found along with arsenic, antimony, and tin in the ordinary course of qualitative analysis.

Potassium Platinocyanide, $K_2Pt(CN)_4 + 12H_2O$, is formed when ammonium chloroplatinate is boiled with caustic potash and potassium cyanide. It forms yellow crystals and becomes luminous when exposed to the Röntgen rays. The barium salt has this property in a still higher degree, and is therefore used for covering screens on which "radiograms" may be projected.

The rare metals which are usually classed with platinum are iridium, Ir; osmium, Os; ruthenium, Ru; rhodium, Rh; palladium, Pd.

SUMMARY

Platinum is a very dense white metal, is not attacked by the simple acids, and does not unite with oxygen when it is heated in the air.

It forms two series of compounds: the platinous compounds, PtR_2, and the platinic compounds, PtR_4, the later being the most stable.

The chlorides readily combine with hydrochloric acid to form complex compounds such as K_2PtCl_4 and K_2PtCl_6.

Both the oxide and the chlorides decompose on heating, metallic platinum being left.

The Gases of the Helium Group

Discovery of Argon.—In determining the density of nitrogen, Rayleigh noticed that the gas prepared from the atmosphere by the absorption of the oxygen was decidedly heavier than that prepared from ammonia and other nitrogenous substances, the difference amounting to about 0.5 per cent.

On careful examination it was found that this was due to the presence in the atmospheric nitrogen of a new gas heavier than nitrogen having a density of 19.94. This gas is left behind when nitrogen derived from the atmosphere is passed over heated magnesium, which unites with the nitrogen, forming magnesium nitride (p. 239), whilst the new gas is not affected. This gas can also be isolated from atmospheric nitrogen by mixing the latter with oxygen, and submitting the mixture to the action of a stream of sparks from an induction coil in the presence of caustic soda solution. The nitrogen is oxidised by this treatment, the resulting oxide being absorbed by the caustic soda, and the new gas left behind, mixed with oxygen, which can easily be removed. Air contains about 1 per cent of this gas, which is characterised by the remarkable property of not forming a compound with any known substance, and has therefore received the name *Argon* (Greek, inactive) and the symbol A. It has the density 19.94 ($H = 1$) and its molecular weight is therefore 39.88. Since the gas does not form any compounds it has been found impossible to determine its atomic weight in the usual way, but since it closely resembles mercury vapour in certain of its physical properties, it seems probable that the molecules of argon, like those of mercury, consist of a single atom ; if this be the case, the atomic weight is 39.88.

Continued investigation, however, soon revealed the fact that argon was a member of a whole group of gaseous elements which resembled it in its most striking property of forming no compounds with other elements.

Discovery of Helium.—The name of *helium* (Greek, the sun) was given to the unknown element which, it was conjectured, gave rise to a line in the spectrum of the outer layer of the sun's atmosphere. This line was situated near the yellow sodium line, and was not present in the spectrum of any substance of terrestrial origin which had up to that time been examined.

After the discovery of argon it was however found that a gas which yields a spectrum containing this line, but had previously been mistaken for nitrogen, can be obtained by heating certain minerals (such as cleveite or pitch-blende, impure forms of uranium oxide) in a vacuum, and that the same gas is present in the water of many springs, and in extremely small quantity in the atmosphere.

This new gas, helium, is much lighter than air, having a density of only 1.995 and therefore a molecular weight of 3.99. As in the case of argon it is probable that the molecules consist only of one atom, the atomic weight being therefore also 3.99.

Discovery of Neon, Krypton, and Xenon.—The existence of two such remarkable gases of atomic weight 3.99 and 39.88, rendered it very probable that a similar element of intermediate atomic weight also existed, forming a group of three similar elements, analogous to those already known among the other elements (Ramsay). This new element was discovered by the careful examination of liquid argon obtained from the air. It was found that this liquid was not pure. The most volatile part contained helium and a new gas of density 10.1 and molecular and atomic weight 20.2, which was named *Neon* (Greek, new). Finally, by the fractional evaporation of a large volume of liquid air, two other analogous gases were found, *Krypton* (Greek, hidden), of molecular and atomic weight 82.9, and *Xenon* (Greek, stranger) 130.2.

Helium, He, 3.99

Helium, as already mentioned, occurs in many minerals, from which it can be obtained by heating in vacuum, and in the water of many springs. About 1000 litres of helium are brought to the surface annually by the water of the King's well, Bath, whilst other springs are known which yield 10 times this amount. The solubility of the gas in water is, however, very slight, 100 of water at 25° dissolving only 1.4 cc. of pure helium.

Helium is the most difficult of all gases to condense, owing to the fact that its critical temperature is only about 5° absolute temperature (– 268° C.), or 8° below the lowest temperature attainable by the rapid evaporation of liquid hydrogen. The condensation was effected by Onnes in a similar manner to that of air or hydrogen. The strongly compressed gas was cooled first with liquid air and then with liquid hydrogen and was finally allowed to expand through a Linde-Hampson valve. About 60 cc. of liquid were obtained from 200 litres of pure helium. It has a density of 0.15 and is therefore twice as dense as liquid hydrogen. It boils at 4.5° absolute temperature (– 268.5° C.), but has not yet been solidified, although its temperature has been reduced by rapid evaporation to – 270.5° C., the lowest temperature ever reached.

Helium is one of the products of disintegration of radium (p. 465).

Argon, A, 39.88

Argon is more soluble in water than nitrogen, 100 cc. of water dissolving 4 cc. of argon and 1.7 of nitrogen when shaken up with the pure gases at 12°. Liquid argon forms a colourless liquid which boils at – 186°, and freezes at – 189.6°. The gas also gives a characteristic spectrum.

The physical properties of the gases of the helium group are summarised in the following table :

Name.	Symbol.	Atomic Weight.	Boiling Point.	Critical Temperature.	Density of Liquid at the Boiling Point.	cc. dissolved by 100 cc. of Water at 0°.	Per cent by Weight in the Atmosphere.
Helium	He	3.99	−268.5°	−268°	0.15	1.3	0.000056
Neon .	Ne	20.2	about −240°	...	...	1.1	0.00086
Argon .	A	39.88	−186.1°	−117°	1.40	5.6	1.3
Krypton	Kr	82.9	−151.7°	−72.5°	2.155	12.0	0.028
Xenon .	X	130.2	−109.1°	+14.8°	3.52	21.9	0.005

The boiling point of the liquid and its density rise regularly with the atomic weight. They form a well marked family of elements and, on account of their remarkable property of forming no chemical compounds, are sometimes known as the noble gases, from analogy with the noble metals, gold, platinum, etc., which are not changed in the air or dissolved by simple acids.

Exercises on Lesson XXXVII

1. How does platinum occur in nature, and what are its most important physical properties?

2. Give a short account of the chief compounds of platinum.

3. Describe the preparation of chloroplatinic acid. How is this substance used in testing for potassium?

4. Compare the compounds of platinum with those of gold.

5. 2.493 grams. of potassium chloroplatinate yield 1 gram. of platinum. Calculate the equivalent of platinum. What equivalents are required in the calculation?

6. How was argon discovered, how can it be isolated from the air, and what are its chief properties?

7. In what respects do the gases of the helium group resemble other families of elements?

LESSON XXXVIII

CLASSIFICATION—THE PERIODIC SYSTEM

THE study of the most common elements and their compounds at once reveals the fact that these can be arranged in groups or families, the members of which are closely related to each other both in chemical and physical properties. Numerous instances of this have been met with in the course of the systematic study of the metals and non-metals mentioned in the foregoing pages, and it is found that the remaining elements also fall into and complete the same groups. Thus the group of the alkali metals, the most common members of which are potassium and sodium, contains three less common metals, lithium, rubidium, and caesium, which closely resemble potassium and sodium in chemical and physical properties. These elements are all univalent, and all readily oxidise in the air and decompose water in the cold, forming a strongly alkaline hydroxide, and liberating hydrogen. Physically they are all soft metals, and melt at comparatively low temperatures, the melting-point becoming lower as the atomic weight becomes higher.

If we consider another group, such as that containing nitrogen, phosphorus, arsenic, antimony, and bismuth, we find that the properties of these elements are strikingly different from those of the alkali metals. In this group, as has already been pointed out, the elements are usually tervalent or quinquevalent, and yield acid-forming oxides, whilst they show a progressive change from the non-metallic to the metallic character as the atomic weight rises. Iron, nickel, and cobalt form a third well-marked group of elements, the atomic weights, specific gravities, and melting points of which are almost equal, whilst the chemical properties are also very similar.

The question at once arises, What is the connection between these various groups of similar elements? Do they form part of a general scheme, or is each group quite independent of all the others?

After many attempts had been made by various chemists, this question was answered in 1869 by the Russian chemist, Mendeléeff. It has been noticed in the foregoing lessons that in most of the groups or families of elements, the properties of the individual elements vary in a regular manner with the atomic weight. The elements of the chlorine and nitrogen groups form excellent examples of this, and the same thing has been observed in greater or less degree in nearly all the chief families. Mendeléeff extended this idea to include not only the members of a single group of elements, but the whole of the known elements. When these are arranged in a list in the order of their atomic weights, certain regularities are at once seen, which can be illustrated by examining the first sixteen elements excluding the elements of the helium group. The following is such a list, the elements being represented by their symbols:—

1	2	3	4	5	6	7
H						
Li	gl	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K						

Of these only lithium, Li, and glucinum, gl, are in any way uncommon, and it may be said in brief that lithium closely resembles sodium and potassium, and that glucinum as closely resembles magnesium.

It is at once seen that, starting from and including lithium, there are seven elements, each of which belongs to a different group, and then follows sodium, which belongs to the group of the alkali metals, and is therefore placed under lithium. When the list is continued it is found that each element falls below one in the first row which belongs to the same chemical group, and this continues until chlorine is reached, after which comes potassium, another alkali metal.

A study of these "rows" at once brings out relations of great importance.

1. The valency of the elements undergoes a regular change. This may be expressed in two ways, by considering the stable compounds with hydrogen, or, for those elements which do not unite with hydrogen, chlorine, on the one hand, and by considering the highest salt-forming oxide on the other.

1	2	3	4	5	6	7
$NaCl$	$MgCl_2$	$AlCl_3$	SiH_4	PH_3	SH_2	ClH
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7

These may be expressed in general formulæ, in which R represents an atom of the element, and X an atom of hydrogen (or chlorine).

1	2	3	4	5	6	7
RX	RX_2	RX_3	RX_4	RX_3	RX_2	RX
R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7
	$(2RO)$		$(2RO_2)$		$(2RO_3)$	

The valency to hydrogen becomes a maximum at group 4, and then decreases, whereas the valency to oxygen steadily increases as far as the seventh group, and then suddenly drops again to that of the first group.

As we have already seen, the valency of an element is not a constant quantity, so that the above relations only hold when we confine our attention to certain particular series of the compounds of these elements, and it is on this account that the highest salt-forming oxide is taken in each case.

2. The physical properties undergo a somewhat similar variation, which is well illustrated by the atomic volumes of the elements. The *atomic volume* is found by dividing the atomic weight by the specific gravity of the solid element, and may, therefore, be taken as representing the volume in cc. occupied by a weight of the element equal to its atomic weight expressed in grammes. Thus sodium has the specific gravity 0.97, and the atomic weight 23, so that its atomic volume is $\frac{23}{0.97} = 23.7$. In other words, 23 grams. of solid sodium

occupy 23.7 cc. Potassium, again, has the atomic weight 39.1, and the specific gravity 0.875, so that its atomic volume is $\frac{39.1}{0.875} = 44.7$.

In the accompanying diagram the atomic volume of each element is measured along the vertical lines, and its atomic weight along the horizontal lines, a dot being placed at the intersection of the two lines corresponding to these two values. These dots are then joined, and the result is a line showing how the atomic volume changes as the atomic weight increases. It will be observed that whilst the atomic weight steadily increases the atomic volumes of the elements at first decrease, until carbon is reached, after which they increase again up to sodium, which has a higher atomic volume than lithium. After sodium an analogous change again occurs, the atomic volume decreases until silicon is reached, an element which belongs to the same group as carbon, and it then again rises to potassium, the atomic volume of which is higher than that of sodium, just as that of the latter is higher than that of lithium. The curve thus falls into sections which resemble each other in general shape.

A variation of the kind shown by the valency and the atomic volumes of these elements is called a *periodic variation*, because the elements are thus divided into a number of sets or periods, within each of which the variation is of the same kind.

The law discovered by Mendléeff can, therefore, be expressed in the words, *the properties of the elements vary periodically with their atomic weights.*

The result of this is that each element is not only to be considered as a member of a *group*, but also as a member of a *period.* Thus magnesium must not only be considered as a member of the zinc group, but also as intermediate between sodium and aluminium, whilst aluminium is intermediate between magnesium and silicon, and so on with the others. Thus whilst sodium is univalent, and aluminium is tervalent, magnesium is bivalent. Sodium oxide is strongly basic, alumina is only a weak basic oxide and possesses feeble acid-forming properties ; magnesia, on the other hand, is less basic than sodium oxide, and more basic than alumina. The

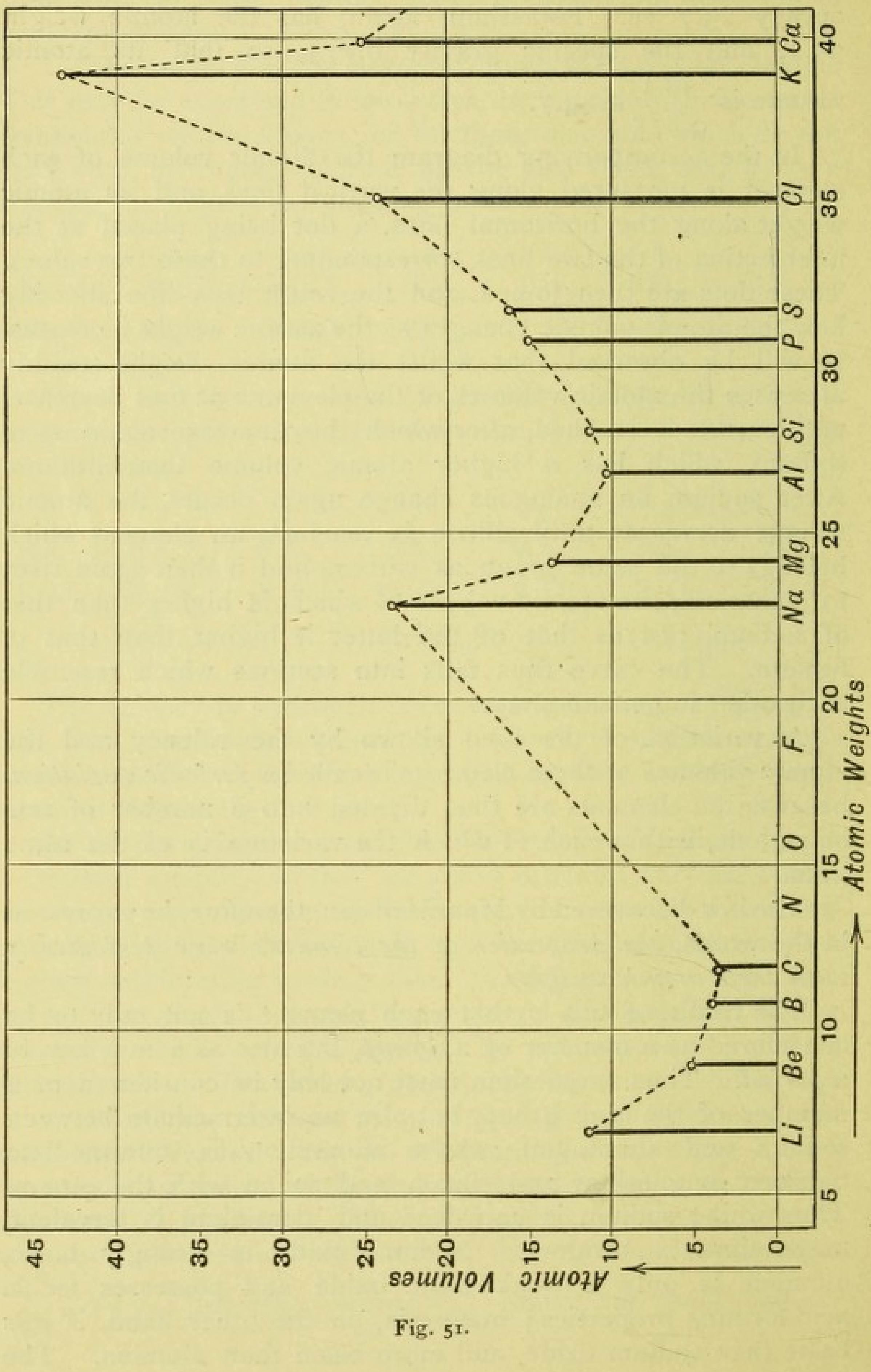

Atomic Weights
5
10
15
20
25
30
35
40
Li
Be
B
C
N
O
F
Na
Mg
Al
Si
P
S
Cl
K
Ca
Atomic Volumes
0
5
10
15
20
25
30
35
40
45

Fig. 51.

atomic volume of magnesium is also intermediate between those of sodium and aluminium, and so on with many other of its characteristic properties.

When a complete table of the elements is made it is seen that each element is surrounded by four others, two in the same *group* and two in the same *period*, and is intermediate in properties between them, so that from the properties of these four those of the element in question can be deduced. In fact, Mendeléeff actually foretold in this way the properties of several elements (germanium, scandium, and gallium), which had not been discovered when he drew up his periodic system, and were represented in his original table by empty spaces. It will be seen that in the table of the system many gaps still exist, and it is possible that some or all of these may be filled by elements still to be discovered.

The elements of the helium group form no compounds with each other or with other elements and may therefore be regarded as of zero valency. They fall into place as a group 0 preceding the alkali metals. The only irregularity is that the atomic weight of argon, 39.9, is greater than that of potassium, 39.1.

A complete table of the elements arranged on the periodic system is given on page 442, containing the symbols and atomic weights of all the well-known elements. For the sake of reference an alphabetical list of the names is also given. In both lists the elements described in this book are printed in thicker type.

The positions of the following elements in the periodic system have not yet been definitely settled.

Dysprosium	Dy	162.5	Praseodymium	Pr	140.6
Erbium	Er	167.4	Samarium	Sa	150.4
Europium	Eu	152.0	Terbium	Tb	159.2
Gadolinium	Gd	157.3	Thulium	Tm	168.5
Lutecium	Lu	174.0	Ytterbium (Neoyt-terbium)	Yb	172.0
Neodymium	Nd	144.3			

Group.	O.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Series 1.	...	H 1.008							
,, 2.	**He** 3.99	Li 6.94	Gl 9.1	**B** 11.0	**C** 12.00	**N** 14.01	**O** 16.00	**F** 19.0	...
,, 3.	**Ne** 20.2	23.00 **Na**	24.32 **Mg**	27.1 **Al**	28.3 **Si**	31.04 **P**	32.07 **S**	35.46 **Cl**	...
,, 4.	**A** 39.88	**K** 39.10	**Ca** 40.09	Sc 44.1	Ti 48.1	V 51.06	**Cr** 52.0	**Mn** 54.93	**Fe** 55.85 **Co** 58.97 **Ni** 58.68
,, 5.	...	63.57 **Cu**	65.37 **Zn**	69.9 Ga	72.5 Ge	74.96 **As**	79.2 Se	79.92 **Br**	...
,, 6.	**Kr** 82.9	Rb 85.45	**Sr** 87.63	Y 89.0	Zr 90.6	Cb 93.5	**Mo** 96.0	...	Ru 101.7 Rh 102.9 Pd 106.7
,, 7.	..	107.88 **Ag**	112.40 **Cd**	114.8 In	119.0 **Sn**	120.2 **Sb**	127.5 Te	126.92 **I**	...
,, 8.	**Xe** 130.2	Cs 132.81	**Ba** 137.37	La 139.0	Ce 140.25	...	...	...	...
,, 9.	...	...	...	...	...	..	...	...	...
,, 10.	...	...	...	...	...	Ta 181.0	**W** 184.0	...	Os 190.9 Ir 193.1 **Pt** 195.2
,, 11.	...	197.2 **Au**	200.0 **Hg**	204.0 **Tl**	207.10 **Pb**	208.0 **Bi**	...	...	...
,, 12.	...	...	**Ra** 226.4	...	**Th** 232	...	**U** 238.5	...	...
Oxygen Compounds	...	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	R_2O_8

LIST OF ELEMENTS

		O = 16			O = 16
Aluminium	**Al**	27.1	**Molybdenum**	**Mo**	96.0
Antimony	**Sb**	120.2	Neodymium	Nd	144.3
Argon	**A**	39.88	**Neon**	**Ne**	20.2
Arsenic	**As**	74.96	**Nickel**	**Ni**	58.68
Barium	**Ba**	137.37	**Nitrogen**	**N**	14.01
Bismuth	**Bi**	208.0	Osmium	Os	190.9
Boron	**B**	11.0	**Oxygen**	**O**	16.00
Bromine	**Br**	79.92	Palladium	Pd	106.7
Cadmium	**Cd**	112.40	**Phosphorus**	**P**	31.04
Cæsium	Cs	132.81	**Platinum**	**Pt**	195.2
Calcium	**Ca**	40.09	**Potassium**	**K**	39.10
Carbon	**C**	12.00	Praseodymium	Pr	140.6
Cerium	Ce	140.25	**Radium**	**Ra**	226.4
Chlorine	**Cl**	35.46	Rhodium	Rh	102.9
Chromium	**Cr**	52.0	Rubidium	Rb	85.45
Cobalt	**Co**	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.5	Samarium	Sa	150.4
Copper	**Cu**	63.57	Scandium	Sc	44.1
Dysprosium	Dy	162.5	Selenium	Se	79.2
Erbium	Er	167.4	**Silicon**	**Si**	28.3
Europium	Eu	152.0	**Silver**	**Ag**	107.88
Fluorine	**F**	19.0	**Sodium**	**Na**	23.00
Gadolinium	Gd	157.3	**Strontium**	**Sr**	87.63
Gallium	Ga	69.9	**Sulphur**	**S**	32.07
Germanium	Ge	72.5	Tantalum	Ta	181.0
Glucinum	Gl	9.1	Tellurium	Te	127.5
Gold	**Au**	197.2	Terbium	Tb	159.2
Helium	**He**	3.99	Thallium	Tl	204.0
Hydrogen	**H**	1.008	**Thorium**	**Th**	232.0
Indium	In	114.8	Thulium	Tm	168.5
Iodine	**I**	126.92	**Tin**	**Sn**	119.0
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	**Fe**	55.85	**Tungsten**	**W**	184.0
Krypton	**Kr**	82.9	**Uranium**	**U**	238.5
Lanthanum	La	139.0	Vanadium	V	51.06
Lead	**Pb**	207.10	**Xenon**	**Xe**	130.2
Lithium	Li	6.94	Ytterbium (Neoytterbium)	Yb	172.0
Lutecium	Lu	174.0			
Magnesium	**Mg**	24.32	Yttrium	Y	89.0
Manganese	**Mn**	54.93	**Zinc**	**Zn**	65.37
Mercury	**Hg**	200.0	Zirconium	Zr	90.6

Several points in this extended table require some explanation.

1. The first point to be noticed is that in the fourth period or horizontal row, after manganese, the three elements, iron,

cobalt, and nickel are found. These three elements (together with the platinum metals) fall in an eighth group, which differs in many respects from the other seven. Thus iron, nickel, and cobalt have nearly the same atomic weights and specific gravities, and are very closely related both in chemical and physical properties ; thus they all form oxides of the formulæ RO and R_2O_3, and are all magnetic and melt at high temperatures. In the other groups, elements which closely resemble one another, such as antimony and arsenic, sodium and potassium, etc., belong not to the same *horizontal period*, but to the same *vertical group*, and differ considerably in atomic weight. The elements of the eighth group, therefore, form an exception in this respect.

2. After the first two horizontal periods the elements of each group fall into two distinct sub-groups, and the members of these often differ considerably in properties, although they have the same valency and bear a general resemblance to each other.

This is well seen in group II., where, neglecting the first two elements, glucinum and magnesium, the two sub-groups are calcium, strontium, barium, and radium on the one hand, and zinc, cadmium, and mercury on the other. Thus the metals calcium, strontium, and barium all oxidise in the air and decompose water in the cold ; their hydroxides are soluble in water, and their sulphates almost insoluble in water. The other metals, zinc, cadmium, and mercury remain bright in the air, and do not act on cold water ; their hydroxides are insoluble in water and their sulphates soluble. The metals of both series, however, are bivalent and form soluble chlorides, but insoluble carbonates, phosphates, and sulphides. In a similar manner the metals copper, silver, and gold are found in the first group, which also contains the alkali metals. These two sub-groups are in many respects dissimilar, particularly in the physical properties of the metals themselves. They agree, however, in forming a series of salts in which each atom of the metal replaces one atom of hydrogen, such as potassium chloride, silver chloride, aurous chloride, etc. On the other hand, it is seen that copper, silver, and gold are respectively related in many ways with the elements which immediately precede them in the system, nickel, palladium, and platinum.

Thus copper, like nickel, forms a series of salts in which it is bivalent, whilst the salts themselves are coloured. Gold, again, like platinum, is insoluble in simple acids, and forms a chloride, $AuCl_3$, which resembles platinic chloride, $PtCl_4$, in many of its chemical properties, especially in its power of forming complex salts with the chlorides.

Comparing groups I. and II. it is seen that the alkali metals, sodium, potassium, etc., immediately precede calcium, strontium, and barium, which they also resemble in many respects, such as their action on water, etc.; whilst copper, silver, and gold precede zinc, cadmium, and mercury.

The only other instances of this to which reference can here be made are chromium and manganese. Chromium falls in the same group as sulphur, with which at first sight it seems to have little in common. These two elements, however, both yield an acid-forming oxide, RO_3, and the salts produced from the corresponding acids, sulphuric acid and chromic acid, are isomorphous. On the other hand, chromium forms a series of salts in which it is tervalent, as are the elements of the nitrogen group, which immediately precedes the sulphur group, and a series in which it is bivalent, in this respect resembling manganese. Manganese, again, is related to the elements of the chlorine sub-group in much the same way as chromium to sulphur. Thus the permanganates and the chlorates are derived from oxides of the same general formulæ, Cl_2O_7 and Mn_2O_7, and these salts are isomorphous. On the other hand, manganese is in many respects related to iron, which immediately follows it, and like this metal forms two series of salts, the manganous and manganic salts, which correspond with the ferrous and ferric salts. The relations of manganese to chromium have been already mentioned.

The fact that the elements when arranged in the order of their atomic weights fall into a system of this kind may be used as an argument in settling the atomic weight in any doubtful case. Thus, let us suppose that the equivalent of strontium is known from the analysis of its chloride to be 43.8, but that it is not known whether its atomic weight is 43.8, 87.6, or some other multiple of 43.8. If the atomic weight were 43.8 the element would immediately follow calcium in the periodic system, and thus fall in the aluminium group. Here it would be quite out of place, because the other elements of this group do not decompose water or form soluble basic hydroxides and insoluble sulphates, etc., whereas strontium has all these properties. Moreover, the members of the aluminium group are tervalent, whereas the formula of strontium chloride would be SrCl if the atomic weight of strontium were 43.8. Similar considerations show that only the atomic weight 87.6 and the formula $SrCl_2$ for the chloride bring strontium into its proper place as a member of the calcium and barium group. Considerations such as these have often been of great value in deciding the atomic weights of various little known elements at the time of their discovery.

One or two unexplained irregularities exist in the table. In addition to argon, which has already been mentioned, two other elements are made by the table to precede elements of lower atomic weight, viz. tellurium, which precedes iodine, and cobalt, which precedes nickel.

The position of hydrogen is also altogether anomalous as it is the sole occupant of Series 1. Some authorities place it in Group VII. instead of Group I. on account of its non-metallic character and power of combining with metals to form hydrides (p. 159).

It is thought by many chemists that the possibility of arranging the elements according to the periodic system indicates that the elements are in reality complex substances, forming series which are related to each other in composition. The recent discoveries concerning the radio-active elements (p. 462) give some support to this idea, but at present it can only be considered as an extremely interesting speculation.

EXERCISES ON LESSON XXXVIII

1. Explain what is meant by the periodic system.
2. What is meant by the atomic volume of an element? A mass of iron weighing 10 grams. has a volume of 1.25 cc. What is the atomic volume of iron?
3. How do (*a*) the specific, (*b*) the atomic volumes of the elements vary with their atomic weights?
4. How does the valency of the elements vary with their atomic weights?

5. Point out the relationship of the metals of the alkaline earths to (*a*) the alkali metals, (*b*) the metals of the zinc group.

6. Point out the relations of iron, nickel, and cobalt to (*a*) manganese, (*b*) copper.

7. In what respects does lead resemble carbon and silicon in chemical properties?

8. How do the properties of the elements of the zinc group alter as the atomic weight rises?

9. In what respect does chromium resemble sulphur, and manganese resemble chlorine?

10. How can the existence and properties of unknown elements be foretold?

11. In what way can the atomic weight of an element be confirmed by means of the periodic system?

LESSON XXXIX

DETERMINATION OF THE MOLECULAR WEIGHTS OF DISSOLVED SUBSTANCES

In the foregoing lessons reference has only been made to the vapour density method of determining the molecular weight of a substance. This method can only be applied to bodies which can be converted into gas without undergoing decomposition, and is not capable of application to solid or liquid substances which cannot be volatilised. Several methods have, however, been found by which the molecular weight of a *dissolved substance* can be ascertained, and these can be applied to any substances which can be brought into solution in a suitable solvent.

Determination of the Molecular Weight of a Dissolved Substance.—We have already seen that when a dilute solution of a substance is cooled, the freezing-point of the solvent is lowered (p. 16), so that a portion of the solvent separates out in the solid form, but at a temperature below the freezing-point of the pure solvent. Careful experiments have shown that the amount by which the freezing-point is lowered depends on two things.

In the first place, it is directly proportional to the amount of the dissolved substance present. Thus 2 grams. of sugar lower the freezing-point of a given weight of water exactly twice as much as one gram.

In the second place, it depends on the molecular weight of the dissolved substance, to which it is *inversely proportional.* In other words, if two compounds be taken, the molecular weight of the first of which is exactly twice that of the second, it is found that 2 grams. of the first produce exactly the same effect on the freezing-point of the solvent as 1 gram. of the second. If, on the other hand, *equal* weights of the two be dissolved in the same weight of water, the depression of the freezing-point produced by 1 gram. of the substance of high molecular weight will only be half that produced by the 1 gram. of the substance of lower molecular weight. If, then, equal weights of a series of compounds be dissolved in equal quantities of a liquid, the depressions of the freezing-point thus produced are inversely proportional to the molecular weights of the dissolved substances. If, therefore, these depressions be multiplied by the molecular weights of the compounds a constant number is obtained, and this is known as the *molecular depression* of the freezing-point for the solvent in question. This is shown by the following results obtained with substances dissolved in acetic acid :—

Substance.	Formula.	Molecular Weight.	D.	MD.
Carbon tetrachloride .	CCl_4	154	0.252°	38.8
Carbon disulphide . .	CS_2	76	0.505°	38.4
Sulphur chloride . .	S_2Cl_2	135	0.284°	38.3
Arsenious chloride . .	$AsCl_3$	181.5	0.232°	42.1
Stannic chloride . .	$SnCl_4$	261	0.157°	41.0
Sulphur dioxide . .	SO_2	64	0.601°	38.5
Sulphuretted hydrogen .	H_2S	34	1.047°	35.6

In this table D is the depression in degrees Centigrade produced by 1 gram. of substance dissolved in 100 grams. of acetic acid, whilst MD is the product of this number with the molecular weight of the compound. It will be seen that the molecular depression is nearly constant, the numbers varying a little on either side of 39.

Upon these facts a very simple method for determining the molecular weight of a soluble substance has been based. A weighed quantity of a suitable solvent is placed in a wide test-tube provided with a stirrer, and this is surrounded by a freezing mixture, and the freezing-point of the liquid determined by means of an accurate thermometer graduated to .01 of a degree. A weighed amount of the substance is then added, and when this has dissolved completely the freezing-point is again carefully ascertained in the same way as before. Thus 1.35 gram. of carbon tetrachloride dissolved in 55 grams. of acetic acid lowered the freezing-point of the latter from 16.750° to 16.132°. The depression produced is therefore the difference between these temperatures, $16.750° - 16.132° = 0.618.°$

Since 1.35 gram. lowers the freezing-point of 55 grams. of acetic acid by 0.618°, it would lower that of 100 grams. by $\frac{0.618 \times 55}{100}$. 1 gram. would therefore lower the freezing-point of 100 grams. of acetic acid by $\frac{0.618 \times 55 \times 1}{100 \times 1.35} = 0.252°$. Now the molecular depression (MD) for acetic acid is 39, and hence the molecular weight must be $\frac{39}{0.252} = 154$.

The number agrees with that obtained by the vapour density method, viz. 154.

The addition of a soluble substance to a liquid not only lowers the freezing-point of the latter, but also diminishes its vapour pressure and raises its boiling-point, and the changes in both these respects are found to depend on the quantity and molecular weight of the dissolved substance. Several methods for the determination of the molecular weights of dissolved substances have been based upon these facts, for the details of which a work on physical chemistry must be consulted.

It is important to remember that these methods can only be applied to *dilute* solutions, and do not give correct results with concentrated solutions, just as the law of Boyle does not apply without modifications to gases under high pressures or at low temperatures.

These relations hold for solutions in all solvents, but a very important class of exceptions exists in the case of all solutions in water which contain electrolytes, a class of bodies which, as we have seen, includes acids, alkalis, and almost all metallic salts. When an attempt is made to determine the molecular weight of one of these substances in aqueous solution by the freezing-point or other method, the number obtained is found to be some fraction of that which was to be expected, generally about $\frac{1}{2}$ or $\frac{1}{3}$. On the other hand, non-electrolytes, such as sugar or alcohol, give perfectly good results, the molecular depression for water being about 18. This anomalous result may be compared with that obtained by the vapour density method with such substances as undergo dissociation, and it seems probable that something of an analogous nature also occurs in dilute aqueous solutions of electrolytes. As we have already seen (p. 301), many facts make it appear probable that in such solutions the ions of the electrolyte exist already separated in the liquid. According to this view, then, a dilute solution of hydrochloric acid only contains very few molecules of HCl, but a large proportion of separated and charged ions $H^{\cdot}$ and $Cl^{\prime}$. Each one of these ions behaves like a molecule of a non-electrolyte, and therefore produces its own effect in lowering the freezing-point, etc., the total depression being due to the sum of those produced by the ions, each considered as an independent molecule, together with that due to the unaltered molecules. Since the depression is inversely proportional to the molecular weight, the result obtained by this method seems to show that hydrochloric acid has about one-half of the molecular weight corresponding with the formula HCl. In general, salts or acids, such as hydrochloric acid, common salt, silver nitrate, which are broken up into two ions ($H^{\cdot}$ and $Cl^{\prime}$, $Na^{\cdot}$ and $Cl^{\prime}$, $Ag^{\cdot}$ and NO'_3), appear to have about half the calculated molecular weight. Dibasic acids and salts of the type represented by sodium sulphate, Na_2SO_4, and calcium chloride, $CaCl_2$, appear to have a molecular weight which is less than the half of the calculated, these substances being to some extent broken up into three ions ($Na^{\cdot}$, $Na^{\cdot}$, $SO_4^{\prime\prime}$; $Ca^{\cdot\cdot}$, $Cl^{\prime}$, $Cl^{\prime}$).

The ordinary reactions of double decomposition which are employed so widely in analytical chemistry are in reality reactions of the *ions*, and this explains many facts which are otherwise somewhat difficult to understand. It is a matter of common experience that the reactions of a metallic element are as a rule the same, whatever be the particular salt of the metal which is taken. Thus, the salts of zinc give a white precipitate with ammonium sulphide, whether the sulphate, nitrate, or chloride of the metal be taken. This is because in each case it is the zinc ion which reacts, as shown in the following equations, it being understood that when a positively charged ion combines with one which is negatively charged, the charges are neutralised,—

$$(1)\ Zn^{++} + Cl^{-} + Cl^{-} + NH_4^{+} + NH_4^{+} + S^{--} = ZnS + NH_4^{+} + NH_4^{+} + Cl^{-} + Cl^{-}.$$

$$(2)\ Zn^{++} + SO_4^{--} + NH_4^{+} + NH_4^{+} + S^{--} = ZnS + NH_4^{+} + NH_4^{+} + SO_4^{--}.$$

In these two cases it is seen that the only change which occurs is the union of the zinc ion with the sulphur ion. The ammonium chloride formed in reaction 1, and the ammonium sulphate formed in reaction 2, are both electrolytes and remain dissociated. The same considerations hold for the acid radicals. What are usually termed the tests for a sulphate are in reality tests for the sulphate ion, SO_4^{--}, and are the same whatever soluble salt of sulphuric acid is used.

On the other hand, the ferrocyanides do not give the ordinary reactions for iron, although they contain a large amount of this element. This is because the ordinary reactions for iron apply to the ferrous ion, $Fe^{\cdot\cdot}$, or the ferric ion, $Fe^{\cdot\cdot\cdot}$, neither of which is present in a solution of potassium ferrocyanide. This salt yields as ions $K^{\cdot}$ and the complex group $Fe(CN)_6''''$, which has its own special reactions and properties.

It has been found that what are called *acid properties* are peculiar to substances of which one of the positive ions is $H^{\cdot}$, whilst *basic substances* are characterised by the negative ion OH'. Weak acids and bases, such as acetic acid, boric acid, ammonia, etc., are found to be only very slightly dissociated, whilst strong acids and bases, such as hydrochloric and nitric acids, caustic soda and caustic potash, are very largely dissociated even in moderately strong solution. The percentage of dissociated molecules in solutions which contain the molecular weights of the various substances expressed in grams. in one litre of liquid is 60-90 for strong acids and bases, and 0-20 for weak acids and bases. The salts of weak acids are dissociated to a much greater extent than the acids themselves.

When a strong acid such as hydrochloric acid and a strong base such as caustic soda are brought together in dilute solution the reaction which occurs is usually written,—

$$HCl + NaOH = NaCl + H_2O.$$

When the ions are considered, however, it is seen that what happens is more accurately represented by the equation,—

$$H^+ + Cl^- + Na^+ + OH^- = H_2O + Na^+ + Cl^-.$$

The ions Na^+ and Cl^- do not unite, but remain unaltered, whilst the only change which occurs is the union of the ions H^+ and OH^- to form water. Precisely the same change occurs when any other strong acid is neutralised by any other strong base, nitric acid by caustic potash for example,—

$$H^+ + NO_3{}^- + K^+ + OH^- = H_2O + K^+ + NO_3{}^-.$$

In agreement with this it is found that the amount of heat evolved in these two cases is exactly the same and represents the heat of union of the ions H^+ and OH^-. These relations only hold for strong acids and bases in dilute solutions because in concentrated solutions the molecules of these substances are not completely dissociated into their ions, whilst weak acids and bases are not completely dissociated even in very dilute solution.

Exercises on Lesson XXXIX

1. How does the depression of the freezing-point produced by dissolving a solid in a liquid vary (*a*) with the amount of the solid, (*b*) with the molecular weight of the solid?

2. What is meant by the term molecular depression of the freezing-point?

3. If 1 gram. of alcohol, C_2H_6O, dissolved in a certain weight of water produces a depression of 0.3°, what depression will be caused by the same weight of cane sugar, $C_{12}H_{22}O_{11}$?

4. 0.75 gram. of arsenious chloride lowers the freezing-point of 50 grams. of acetic acid by 0.351°. Calculate the molecular weight of arsenious chloride. The molecular depression for acetic acid is 39.

5. What substances produce abnormal depression of the freezing-point when dissolved in water, and to what is this supposed to be due?

6. 0.75 gram. of sodium chloride lowers the freezing-point of 75 grams. of water by 0.615°. Calculate the apparent molecular weight of sodium chloride. The molecular depression for water = 18.

LESSON XL

SPECTRUM ANALYSIS

AN entirely new branch of chemical analysis, of great delicacy, simplicity, and importance, has been developed within the last fifty years, based upon the researches of Bunsen and Kirchhoff, the principles of which may here be shortly stated.

It has long been known that certain chemical substances, especially the salts of the alkalis and alkaline earths, when strongly heated in the blowpipe, or other nearly colourless flame, impart to that flame a peculiar colour, by the occurrence of which the presence of the substance may be detected. If many of these substances are present together, the detection of each by the naked eye becomes impossible, owing to the colours being blended, and thus interfering with each other. Thus, for instance, the sodium compounds colour the flame an intense yellow, whilst the potassium salts tinge the flame violet: the yellow soda colour is, however, so much more intense than the purple potash tint, that a small trace of soda prevents the eye from detecting the purple, even if large quantities of potash salts are present. This difficulty is altogether overcome, and the method of observation rendered extremely sensitive, if, instead of regarding the flame with the naked eye, it is examined through a prism. This consists of a triangular piece of glass, in passing through which the light is refracted, or bent out of its course, each differently coloured ray being differently refracted: so that if a source of white light, such as the flame of a candle, be thus regarded, a continuous band of differently coloured rays is observed; the compound white light being resolved into all its variously coloured constituents. This coloured band is termed a *spectrum;* and each source of pure white light gives the same *continuous spectrum*, stretching from red (the least refrangible) to violet (the most refrangible), identical, in fact, with the colours of the rainbow.

If these coloured flames are examined by means of a prism, the light being allowed to fall through a narrow slit upon the prism, it is at once seen that the light thus refracted differs essentially from white light, inasmuch as it consists of only a particular set of rays, each flame giving a spectrum containing a few *bright bands*. Thus the spectrum of the yellow soda flame contains only one fine bright yellow double line, whilst the purple potash flame exhibits a spectrum in which there are two bright lines, one lying at the extreme red, and the other at the extreme violet end. These peculiar lines are always produced by the same chemical element, and by no other known substance; and the positions of the lines always remain unaltered. When the spectrum of a flame tinted by a mixture of sodium and potassium salts is examined, the yellow ray of sodium is found to be confined to its own position, whilst the potassium red and purple lines are as plainly seen as they would have been had no sodium been present.

The coloured flames which are exhibited by the salts of lithium, barium, strontium, and calcium, likewise each give rise to a peculiar spectrum, by means of which the presence or absence of very small quantities of these substances in a mixture can be ascertained with certainty, simply by observing the presence or absence of the peculiar bright bands characteristic of the particular body.

The advantage which this method of analysis possesses over other processes lies in the extreme delicacy as well as in the great facility with which the presence of particular elements can be detected with certainty. Thus a portion of sodium salt less than the $\frac{1}{180,000,000}$ part of a grain in weight can be detected; and compounds are found to be most widely disseminated throughout the earth which were supposed to occur very seldom. The extreme delicacy of the method is seen when we learn that every substance which has been exposed to the air even for a moment gives the sodium line, every minute speck of dust containing sodium compounds in sufficient quantity to produce the characteristic reaction, when placed in a colourless flame. Thus, too, the lithium compounds, which were formerly supposed to be contained in only four minerals, have by aid of spectrum analysis been found to be substances of most common occurrence, being observed in almost all spring-waters, in tea, tobacco, milk, and blood, but existing in such minute quantities as to have altogether eluded recognition by the older and less delicate analytical methods. A portion of lithium less than the $\frac{1}{6,000,000}$ part of a grain can thus be detected.

A still more striking proof of the value of spectrum analysis lies in the fact of the discovery of many new elementary bodies by its means: two new alkali-metals, rubidium and cæsium, having been found, together with potash and soda, in certain mineral springs; and three metals, thallium, indium, and gallium having been respectively detected in iron pyrites and zinc ores. The new alkali-metals, discovered by Bunsen in 1860, resemble potassium so closely in their properties that it would be nearly impossible to have detected them by the ordinary analytical methods, although their spectra exhibit very distinct bright bands not seen in the spectrum of potassium or any other known element. The metal thallium was discovered by Sir Wm. Crookes, who observed a splendid green line which did not belong to any known substance; whilst indium, first noticed by Reich and Richter, was recognised by the presence of a hitherto unobserved fine dark blue line, and another new metal termed gallium was discovered by Lecoq de Boisbaudran in some French blendes, being detected by the presence of two characteristic blue lines in its spectrum.

It is not only those bodies which have the power of imparting colour to a flame which yield characteristic spectra, for this property belongs to every elementary substance, whether metal or non-metal, solid, liquid, or gas; and it is always observed when such an element is heated to the point at which its vapour becomes luminous, for then each element emits the peculiar light given off by it alone, and the characteristic bright lines become apparent when its spectrum is observed. Most metals require a much higher temperature than the common flame in order that their vapours should become luminous; but they may be easily heated up to the requisite temperature by means of the electric spark, which in passing between two points of the metal in question volatilises a small portion, and heats it so intensely as to enable it to give off its peculiar light. Thus all the metals, among others iron, platinum, silver, and gold, may each be recognised by the peculiar bright lines which their spectra exhibit.

The permanent gases also yield characteristic spectra when they are strongly heated, as by the passage of an electric spark; thus, if the spark be passed through an atmosphere of hydrogen gas, the light emitted is bright red, and its spectrum consists of one bright red, one green, and one blue line; whilst in nitrogen gas the spark has a purple colour, and the peculiar and complicated spectrum of nitrogen is observed when this spark is examined with a prism.

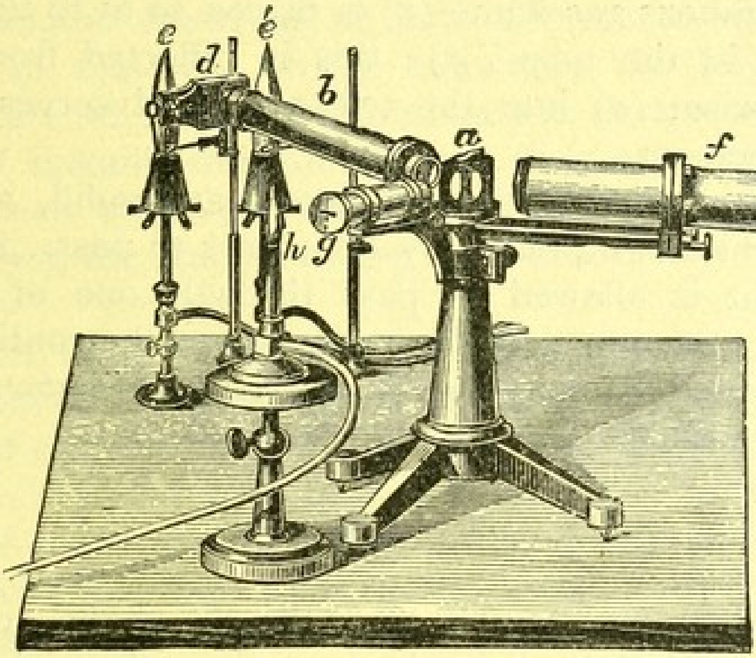


Fig. 52.

The instrument used in these experiments is termed a *spectroscope*, and this has now become, next to the balance, the most important instrument possessed by the chemist. It consists of a prism (*a*, Fig. 52) fixed upon a firm iron stand, and a tube (*b*) carrying the slit, seen on an enlarged scale in Fig. 53 (*b*), through which the rays from the coloured flames (*e* and *e*) fall upon the prism, being rendered parallel by passing through a lens. The light, having been refracted, is received by the telescope (*f*), and the image magnified before reaching the eye. For exact experiments the number of

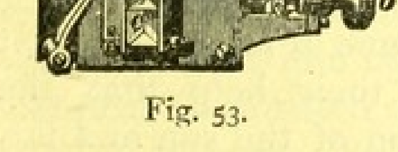


Fig. 53.

prisms and the magnifying power are increased. The rays from each flame are made to pass into the telescope (*f*), one set through the upper uncovered half of the slit, the other by reflection from the sides of the small prism (*c*, Fig. 53) through the lower half; thus bringing the two spectra into the field of view at once, so that any wished-for comparison of the lines may be made.

The small luminous gas flame (*h*) is placed so as to illuminate a fixed scale in the tube (*g*); this is reflected from the surface of the prism (*a*) into the telescope, and serves as a means of measurement.

Many substances, both gaseous, liquid, and solid, absorb certain rays of white light, but allow the others to pass. Hence when white light is allowed to pass through one of these bodies, and is then examined by the spectroscope, the continuous spectrum is found to be interrupted by dark bands, an *absorption spectrum* being thus produced.

Solar Chemistry

If sunlight be allowed to fall upon the slit of the spectroscope it is observed that the solar spectrum thus obtained differs essentially from the spectra which we have hitherto considered, inasmuch as it consists of a band of bright light, passing from red to violet, but intersected by a very large number of *fine black lines* of different degrees of breadth and shade, which are always present, and always occupy exactly the same relative position in the solar spectrum. These lines indicate the absence in sunlight of particular rays, and they may be considered as shadows, or spaces where there is no light; they are called "*Fraunhofer's lines*," after a German optician who first satisfactorily mapped and described them.

The existence of these lines has become a matter of great importance and interest, as it is by their help that the determination of the chemical constitution of the sun and far-distant fixed stars has become possible. The spectra of the moon and planets (reflected sunlight) are found to exhibit these same lines in unaltered position, and hence the conclusion has long been drawn that the Fraunhofer's lines are in some way produced in the body of the sun itself.

If the positions of these dark lines in the solar spectrum be carefully compared in a powerful spectroscope with those of the bright lines in the spectra of certain metals, such as sodium, iron, and magnesium, it is seen that each of the *bright* lines of the particular metal coincides, not only in position, but also in breadth and intensity with a *dark* solar line; if the apparatus be so arranged that a solar and metallic spectrum be both allowed to fall, one below the other, in the field of the telescope, the bright lines of the metal are *all* seen to be continued in dark solar lines. In the case of metallic iron alone more than sixty such coincidences have been observed; and the higher the magnifying power employed, the more striking and exact does this coincidence appear.

With other metals — such, for instance, as gold and antimony—no single coincidence can be noticed, whilst all the lines of certain other metals have their dark representatives in the sun. From these facts it is clear that there must be some kind of connection between the bright lines of these metals and the coincident dark solar lines, as such coincidences cannot be the result of mere chance. Is the coincidence of the *dark* solar lines with the *bright* iron lines caused by the presence of iron in the sun? And if so, how do the lines come to appear *dark* in the solar spectrum?

The explanation of this is given by an experiment, in which the bright metallic lines are *reversed*, or changed into dark lines. Thus the bright yellow soda lines (coincident with Fraunhofer's lines D) can be made to appear as dark lines, by allowing the rays from a strong source of white light (such as the oxyhydrogen light) to pass through a flame coloured by soda, and then to fall upon the slit of the spectroscope. Instead of then seeing the usual sodium spectrum of a *bright* yellow double line upon a dark ground, a double *dark* line, identical in position and breadth with the sodium line, will be seen to intersect the continuous spectrum of the white light. Here then the yellow flame has absorbed the same kind of light that it emits, a consequent diminution of intensity in that part of the spectrum has occurred, and a dark line has made its appearance. In like manner the spectra of many other substances have been *reversed*, each substance in the state of vapour having the power of absorbing the same rays as it emits, or being opaque for such rays.

The explanation of the existence of dark lines in the solar spectrum, coincident with bright metallic lines, now becomes evident: these dark lines are caused by the passage of white light through the glowing vapour of the metals in question present in the sun's atmosphere, and these vapours absorb exactly the same kind of light which they are able to emit. The sun's atmosphere, therefore, contains these metals in the condition of glowing gases, the white light proceeding from the strongly heated solid or liquid mass of the sun which lies in the interior.

By observing the coincidences of these dark lines with the bright lines of terrestrial metals, we arrive at a knowledge of the occurrence of such metals in the solar atmosphere with as great a degree of certainty as we are able to attain in any question of physical science. The elements hitherto detected in the sun's atmosphere are more than thirty-six in number, among them being iron, sodium, magnesium, calcium, chromium, nickel, barium, copper, zinc, strontium, cadmium, cobalt, manganese, aluminium, lead, titanium, and hydrogen. This last element is found to exist in large quantity surrounding the luminous portion of the sun's body as a zone of incandescent gas, termed the solar *chromosphere*, whilst masses of ignited hydrogen thrown still higher form the red protuberances seen during a total eclipse. The rapidity with which the ignited hydrogen moves on the sun's surface is enormous; solar cyclones or circular storms have been shown to blow with a velocity compared with which our most violent terrestrial tornadoes are mere summer breezes.

The subject of solar chemistry is still in its infancy, but the results already obtained lead to the belief that our knowledge of the chemical composition of those far distant bodies will become more intimate as the methods of experiment and observation are gradually perfected.

[For fuller information on this subject see Roscoe's *Lectures on Spectrum Analysis*, and Lockyer's *Lessons in Elementary Astronomy*.]

Exercises on Lesson XL

1. Describe the spectroscope.
2. How can the spectra of the metals be examined?
3. What is meant by the terms (*a*) spark spectrum, (*b*) absorption spectrum, (*c*) reversed lines?
4. What are Fraunhofer's lines? What information do they give us concerning the chemical composition of the sun?

LESSON XLI

THE RADIOACTIVE ELEMENTS

IN 1896 it was discovered by Becquerel that the compounds of uranium (p. 414) are radioactive, *i.e.* are constantly emitting radiations which have the power of affecting a photographic plate, causing phosphorescence in certain substances, such as the platinocyanides (p. 431) and crystalline zinc sulphide, and discharging a charged electroscope. This discovery was followed in 1898 by the observation that pitch-blende, an impure oxide of uranium which occurs as a mineral, was much more strongly radioactive than the pure uranium oxide contained in it (Mons. and Mme. Curie), and that this was due to the presence of two new strongly radioactive elements which were named *radium* (Latin, shining) and *polonium* (after the Polish nationality of one of the discoverers). Subsequently a third new element, termed *actinium* (Greek, a ray) was also obtained from the same source.

Radium, Ra, 226.4

In its chemical properties radium closely resembles barium, forming a soluble chloride and bromide and an insoluble sulphate, and it is separated from pitch-blende along with the barium which this mineral always contains. Extremely little of the new element is present, the amount obtainable from a ton of pitch-blende being less than 1 gram. of the chloride. It can be separated from barium by the recrystallisation of the mixed chlorides or bromides, and its salts are thus obtained pure. The metal itself has been isolated by the electrolysis of a solution of the chloride in presence of mercury, and like its salts is strongly radioactive. It is a white lustrous metal, which melts at 700°. It becomes black in the air, and decomposes water vigorously. Less than 0.1 gram. has so far been obtained (1910). Its spectrum has also been examined and found to be of the same general character as those of the elements of the calcium group. In all these respects radium appears to be an elementary substance belonging to the calcium group, having the atomic weight of 226.4 and finding a position in the periodic system in complete accord with these properties.

All the compounds of the element are very strongly radioactive and possess very remarkable properties. The power which the emitted radiations possess of discharging a charged electroscope provides a method by which their intensity and variation with time can be very accurately measured, as well as affording an extremely delicate mode of detecting the presence of a radioactive element. This process of detection indeed far exceeds in delicacy the methods of spectrum analysis, and must be regarded as the most sensitive yet discovered

Among the most remarkable and interesting properties of the radium compounds are the following :—

1. They constantly evolve heat and maintain themselves at a temperature 3-5° above that of the surrounding atmosphere. This extraordinary process goes on even at the temperature of liquid hydrogen, and the amount of heat emitted each day is sufficient to decompose a weight of water equal to 1.3 times that of the radium in the radioactive salts, or in other words is equal to 118 gram.-calories per hour per gram. of radium. The significance of this enormous loss of energy is discussed later on (p. 465).

When dissolved in water the salts produce a slow decomposition of the water into hydrogen and oxygen, and they are capable of bringing about other similar chemical changes.

2. They give off radiations of three different kinds, known as α, β, and γ rays. The investigation of these radiations has shown that the α and β rays consist of particles of matter projected with a high velocity from the mass of radium salt. The α *particles* consist of positively charged atoms of helium,

moving at a velocity of 200,000 kilometres a second. Owing to their high rate of motion these can penetrate thin layers of glass or metal, although they are stopped by thicker layers. The helium produced from radium has actually been collected (Ramsay and Soddy), and the rate at which it is produced has been determined and been found to be about 0.46 cubic millimetres of helium per gram. of radium per day. The helium in rocks and mineral springs has probably been formed in this way from radium. When the α particles fall on screens dusted with crystals of zinc sulphide they cause a series of flashes and it has been found that each such flash is caused by the impact of a single atom of helium. It is therefore possible in this way to see the effect produced by a single atom of matter and to count the number of atoms of helium given off in a certain time by a known weight of radium. The instrument devised to render this effect visible is called a spinthariscope (Greek, a spark). The number of helium atoms emitted can also be counted by an electrical method.

The *β particles* are negatively charged, and very much lighter than the α particles and move with a much higher velocity, approaching that of light. They are able to penetrate considerable thicknesses of glass and metals. Their mass is about $\frac{1}{2000}$ part of that of a hydrogen atom and they seem to be identical with the particles given off from the cathode in the discharge of electricity through gases and known as the cathode rays. Similar particles are intimately concerned with the passage of electricity through conductors of all sorts, and they have therefore also received the name of electrons. The *γ-rays* are still more penetrating in character than the β-rays and appear to resemble the Röntgen-rays in their properties.

3. They evolve a gaseous substance known as the *radium emanation*, which can be removed by a mercury pump, liquefied and examined, but has only been obtained in quantities of about 0.1 cubic millimetre at a time. It is a colourless gas, probably belonging chemically to the argon series, and its atomic weight is about 220. Its spectrum has been observed and many of its physical properties ascertained. When cooled it forms a colourless liquid boiling at − 62°. It freezes at − 71°, forming a solid which glows with great brilliancy, at first appearing steel blue, but at a lower tempera-

ture becoming brilliant orange. This emanation is itself radioactive and evolves heat in the same manner as radium itself and also gradually decomposes, evolving helium and forming another new substance known as radium A (Rutherford). It appears in fact that a long series of changes of this character occurs, radium A changing into another substance and so on, each change being accompanied by the emission either of α or β particles and sometimes of γ-rays.

The amount of heat evolved during the complete decomposition of 1 cubic centimetre of the emanation has been calculated to be nearly 7,000,000 gram.-calories, or about $2\frac{1}{2}$ million times as much heat as 1 cc. of detonating gas yields on explosion. This evolution of heat is therefore of quite a different order of magnitude from that observed in an ordinary chemical decomposition, and this fact renders it very unlikely that radium, the emanation and the other radioactive products derived from radium are compounds in the ordinary sense of the word. Similar emanations are given off by the salts of thorium and actinium.

The most probable explanation of these remarkable phenomena seems rather to be that the atoms of these radioactive elements are unstable and a certain proportion of them decompose in every unit of time. The first products are themselves also unstable and these decompose in their turn but at a different rate, and so on until a substance is finally produced of which the atom is no longer unstable and the radioactive properties disappear. All the radioactive elements, therefore, are to be regarded as having only a temporary existence under the conditions in which they are now found, and the length of time required for their spontaneous decomposition can be calculated from the rate at which they give off their radiations. Thus one-half of any given quantity of radium would decompose in about 2000 years, whilst the emanation requires only about 4 days for half of it to be decomposed.

Of the elements previously known, only uranium and thorium have been found to be radio-active and they undergo changes very similar to those described for radium. Indeed it has now been proved that radium is actually formed from uranium, and this is probably the reason why all uranium minerals contain a certain definite very small proportion of radium. Of the other radioactive elements mentioned above as being found in pitch-blende, polonium forms one of the chain of products derived from radium, whilst the relations of actinium to the other elements are not known.

The explanation just given of these phenomena introduces the idea of the atom as a highly complicated structure possessing an enormous store of potential energy. Certain atoms decompose spontaneously, whereas others appear to be perfectly stable. At present we are unable to influence this decomposition in any way, but are only able to observe the phenomena which accompany it, and to gather from these observations some ideas as to the nature and relations of the elements.

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THE END

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