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A COMPANION TO PHYSICAL AND INORGANIC CHEMISTRY

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ELECTRONIC THEORY AND CHEMICAL REACTIONS

A Companion to Physical and Inorganic Chemistry

BY

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PREFACE

I have long felt that text-books on elementary Physical Chemistry omit much valuable qualitative discussion. Doubtless this is necessitated by consideration of the amount of space available, but none the less such qualitative arguments lead to a much sounder understanding of the principles involved. In the first part of this book an effort has been made to provide such arguments. It is assumed that the student also has access to a more orthodox text-book in Physical Chemistry, and for this reason no examples or questions are given, and many standard topics have been omitted.

The second part of the book has a quite different aim in view. At the Scholarship level of the General Certificate of Education, and more particularly at the stage of University Scholarship and the first year at a university, the student of Chemistry is faced with the formidable task of memorizing a very large number of facts. Furthermore, he frequently fails to appreciate much relationship among these facts. In the second part of this book an effort has been made to provide a framework on which to hang the facts, and to show some relationships among them. Again, it is assumed that the reader already has an orthodox text-book on Inorganic Chemistry, but the summaries provided here should be helpful for revision and consolidation purposes. It is also assumed that the reader is familiar with the more elementary aspects of the Electronic Theory of Valency.

In order to conform to modern practice the sign conventions for Electrode Potentials and for Heats of

Formation are the reverse of those heretofore in use in England. The electrode potentials of the most active metals are given as positive, while those of the noble metals are negative. When heat is evolved in the formation of a compound its heat of formation is given as negative.

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CONTENTS

CHAPTER I

THE IONIC THEORY

In view of the importance of this theory, and also because it affords a good simple example of making a series of deductions from data, it is worth spending some time in considering the evidence for the Ionic Hypothesis. The evidence leading to the hypothesis comes from electrical experiments, but there is also much other evidence which supports it. This latter evidence will be found in Chapter II.

The Facts of Electrolysis

Substances can be divided into two classes: electrolytes, whose solutions in certain polar liquids, such as water, conduct electricity; and non-electrolytes, whose solutions do not conduct electricity. Electrolytes are confined to acids, bases, and salts, whereas non-electrolytes comprise all the other substances. Thus it will be seen at once that electrolytes are comparatively rare. We tend to get the opposite impression because most early work in Chemistry is done with electrolytes, but later on they are seen in their correct perspective.

When solutions of electrolytes in water are electrolysed, the following results are observed:

Liberated at the Cathode (*−ve pole*)	*Liberated at the Anode* (*+ve pole*)
The metal, or hydrogen.	The halogens, if present in the electrolyte as simple radicals; or oxygen; or else the metal of the anode may pass into solution.

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At first sight these facts are far from simple to explain, and further experiments are necessary. The phenomena at the cathode can be elucidated fairly easily, because it is quickly realized that the metal in solution is liberated unless it is one which, when free, attacks water. We can conclude, then, that the metal portion of a salt in solution is liberated at the cathode, unless it is too unstable to exist in contact with water. This fact can only be explained by supposing that the particles of metal in the solution carry a positive charge of electricity, and so are attracted to the cathode.

On the other hand the phenomena round the anode are clearly more complex, and it is far from simple to interpret them. A series of experiments with solutions containing different acid radicals and using different metals for the anode show that when the anode does not pass into solution either the radical or oxygen is liberated. This suggests that the way to attack the problem is to consider that the fundamental process at the anode consists in the liberation of the acid radical at an inert electrode. For instance, the halogens are liberated on a carbon anode.

When oxygen is liberated instead of the acid radical it is always found that the acid radical remains in solution, and this suggests that the oxygen is more likely to be derived from the water than from the acid radical, though at this stage it is not clear how the oxygen is liberated. Likewise it is not clear what mechanism is involved when the anode passes into solution. These two problems will eventually have to be solved, but to begin with it is best to develop a hypothesis to explain a simple case of electrolysis in which a metal is liberated at the cathode and an acid radical at the anode. A suitable example is the electrolysis of a solution of copper chloride, using a carbon anode. In this case copper is liberated at the cathode,

and chlorine at the anode, so that complications at either electrode are avoided. Having thus simplified the situation, however, it must be borne in mind that any resulting hypothesis must eventually be capable of modification so as to explain all cases of electrolysis.

In the case of the copper chloride solution the facts are very simple, namely, that copper is liberated at the cathode and chlorine at the anode. This being so, we conclude that in solution the particles of copper are positively charged while those of chlorine are negatively charged. This must be so at least in the immediate neighbourhood of the electrodes.

Before getting any further the results of quantitative experiments must be considered. Faraday was the first to carry out quantitative experiments, and the results of these experiments can be summarized thus:

FARADAY'S LAWS (IN MODERN WORDING)

1. The mass of any substance liberated at an electrode by electrolysis is proportional to the number of coulombs passed.

2. If the same number of coulombs of electricity is passed through solutions of different electrolytes, the masses of substances liberated are proportional to their chemical equivalents.

In addition to these two laws there is one other important fact about solutions of electrolytes: that they obey Ohm's Law. This is very important in that it shows, without doubt, that the passage of the current through the solution does not cause the molecules of solute to break up into charged particles. This is best seen by considering the problem graphically.

Since solutions of electrolytes obey Ohm's Law it means

that the current carried and the potential difference between the electrodes are related by the equation:

$$V = kI$$

where V = the potential difference between the electrodes,
I = the current,
and k is a constant.

The graph of this is a straight line *through the origin*, shown as (1) in Fig. 1.

Now suppose that the molecules of solute are dissociated into charged particles by the applied voltage (electric field). Since work must be done in this process of

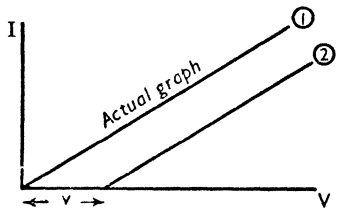


Fig. 1

separating charged particles, there clearly would be no separation of particles, and hence no current, unless a certain minimum potential difference were applied to the electrodes. The graph under these conditions is shown in Fig. 1, where v is the minimum potential difference required to separate the particles. This is graph (2) in Fig. 1.

Experiments carried out with voltameters, in which both electrodes are made of the same metal as that in the solution, always give graphs similar to (1). The conclusion from this is that v is zero, and therefore that the charged particles are not produced during electrolysis, but that they are there already. Further evidence for this conclusion will be found in Chapter II.

We can now visualize our solution of copper chloride as consisting of positively charged particles of copper and negatively charged particles of chlorine. When a potential difference is applied to electrodes in such a solution, the charged particles will migrate in opposite directions, so carrying electric charges through the solution and giving them up to the electrodes. However, we have as yet no evidence for either the sizes of the charges or the nature of the particles. That is the next step in developing the hypothesis, and it comes from interpreting Faraday's Laws.

The first of these laws is the easiest to interpret. The conclusion drawn is that all particles of the same kind carry the same sized charge, and are of the same mass. This conclusion may be reached by the following arguments:

Suppose that the positively charged particles consist of a mixture of particles carrying charges proportional to 1, 2, and 3. In an electric field these different types will have exerted on them forces proportional to the intensity of the field, and the magnitudes of the charges. Thus the various forces will be in the proportion of 1, 2, and 3, and these will cause the particles to drift through the water towards the cathode at speeds depending upon the sizes of the forces and the resistance to motion caused by the drag of the water. Now unless the sizes of the particles are so adjusted that in each case the drag of the water exactly corresponds to the force acting, the different types of particle will move at different speeds. If this is so, at an early stage of an electrolysis experiment the faster moving particles will predominate among those liberated at the cathode. Later on in the experiment, as the faster particles are used up, the slower ones will predominate. In that case the mass of metal liberated per coulomb carried will depend upon the length of time for which

electrolysis has been taking place. Since experiment reveals that the mass liberated per coulomb carried is constant throughout, we can only conclude that we are wrong to suppose that there is present more than one type of positively charged particle. A precisely similar argument shows that the same can be said of the negatively charged particles.

Faraday's second law shows that the charge carried by a particle is proportional to the valency of the radical concerned. This is at once obvious if we consider electrolysing two solutions, one containing a univalent metal X, and the other containing a divalent metal Y. Suppose that these solutions are connected in series, and that on passing through them a charge q the atomic weight of X (this is also its equivalent weight) is liberated. Then this charge also liberates the equivalent weight of Y, that is to say half its atomic weight. In order to liberate the atomic weight of Y, a charge of $2q$ is needed. Similarly in order to liberate the atomic weight of a trivalent metal a charge of $3q$ is necessary.

These results indicate that, in the case of metals, the particles concerned are probably atoms, and that each atom carries a charge proportional to its valency, though they afford no *proof* that they are atoms. Assuming this to be the case, it seems probable that the negative particles consist of the acid radicals carrying charges proportional to their valencies.

The theory so far, then, is that a solution of copper chloride consists of a mixture of chlorine atoms carrying a negative charge, and copper atoms carrying twice as much positive charge. In order to maintain electrical neutrality there must be twice as many charged chlorine atoms as there are charged copper atoms, as is suggested by the formula $CuCl_2$. The charged atoms are called ions.

When a current is passed through such a solution the

metallic ions move towards the cathode, while the acid radical ions move towards the anode. It seems reasonable to suppose that under the same electric field the two types of ion will move at different speeds, and the results of this must now be investigated.

Fig. 2 represents a solution containing univalent positive and negative ions, the portions A and B being the regions of solution round the cathode and anode respectively.

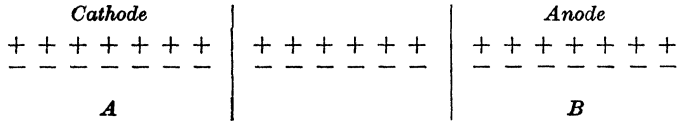


FIG. 2

The + and − signs represent the positive and negative ions respectively, and the number of each in compartments A and B being the same indicates that the concentrations are the same in these two compartments.

Now suppose that during electrolysis the speed of the positive ions is proportional to 2, and that of the negative ions to 3. This can be represented by supposing that in a given interval of time two positive ions enter the cathode chamber and leave the anode chamber, while three negative ions enter the anode chamber and leave the cathode chamber. The state of affairs after this is shown in Fig. 3, in which the new arrivals in each chamber are surrounded by a circle.

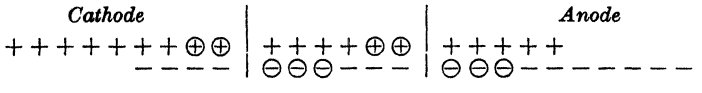


FIG. 3

Two things will be seen from this figure. In the cathode chamber there are five positive ions with no partners. Two of these result from the two new arrivals to the

chamber, and the other three were left behind by the three negative ions which left the chamber during electrolysis. That is to say the number of positive ions without partners is proportional to the sum of the velocities of the positive and negative ions. Likewise the number of negative free ions round the anode is also equal to the sum of the velocities of the positive and negative ions. It is these ions which are liberated at the electrodes, and Fig. 4 shows the state of affairs when they have been liberated.

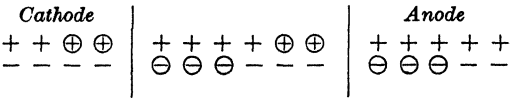


FIG. 4

It will be seen from Fig. 4 that round the cathode the concentration of the solution has dropped to four from the original concentration of seven (see Fig. 2): the drop in concentration is three, the velocity of the ions leaving the compartment. Likewise, in the anode compartment the concentration has dropped from seven to five, and the change is again equal to the velocity of the ions leaving the compartment. It should also be noted that the concentration of the solution remains unaltered in the middle portion of the solution (the portion between the vertical lines).

All the deductions made above can be verified experimentally in a suitable form of voltameter, which is illustrated in Fig. 5.

When electrolysis has been going on gently for some hours it is stopped, and the solutions round the anode, cathode, and central portions are run out and analysed. It is found that the concentration in the central portion remains unchanged, while those of the anode and cathode regions have decreased by different amounts.

Another experiment which shows that ions move at

different velocities is the one introduced by Lodge. As is shown in Fig. 6, two small beakers of solution are connected by a long tube containing jelly and one or more electrolytes.

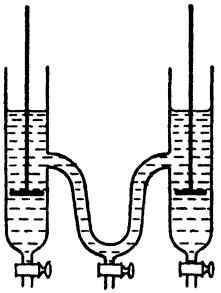


FIG. 5

For example, suppose that the tube AB contains some jelly with salt solution and litmus, while beakers A and B contain respectively alkali and acid. After electrolysis has gone on for some time the hydrogen ions leaving

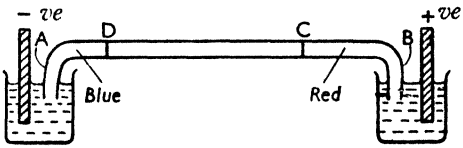


FIG. 6

beaker B will have advanced a certain distance along the tube, turning the portion BC red. In the same time hydroxyl ions will have advanced to D, turning the portion AD blue. By measuring the speeds of advancement of the boundaries of these colours it is possible to measure the speeds at which the ions move. Many experiments of this type can be devised, using various solutions in the

beakers and in the jelly. Such experiments reveal that different ions move at different speeds under the same potential gradient.

The following is a summary of the conclusions reached so far:

1. Solutions of electrolytes contain positive and negative ions.
2. The ions are not produced during electrolysis, but are always present in solution.
3. During electrolysis the ions move in opposite directions and thereby carry the current through the solutions.
4. The speeds of the ions vary with the type of ion, and this gives rise to changes in the concentration of electrolyte round the electrodes.

As yet it has not been possible to explain why sometimes hydrogen is liberated at the cathode, or why sometimes oxygen is liberated at the anode or the anode passes into solution. Nor is it clear why one metal is liberated in preference to another when a solution containing a mixture of salts of different metals is electrolysed. These problems will be considered in Chapter IV, and in the meanwhile some electrical properties of solutions will be considered quantitatively.

By using suitable Wheatstone-bridge circuits and alternating current it is possible to measure the resistance of a solution between two plates, and hence to calculate the Specific Resistance of the solution. As would be expected, the value of the specific resistance of a solution varies greatly with dilution, and little of value can be derived from such results. However, the reciprocal of the specific resistance is the specific conductivity of the solution, i.e. the conductivity per centimetre cube. If the specific conductivity is divided by the number of gram-

equivalents of electrolyte per cubic centimetre of the solution we obtain what is called the Equivalent Conductivity, and much valuable information can be obtained from these results.

For each electrolyte a number of measurements of specific conductivity are made at different concentrations. The values for the equivalent conductivity are calculated, and these values plotted against the dilution (i.e. the number of litres of solution which contain 1 gm.-equivalent of electrolyte). When this is done for a number of different

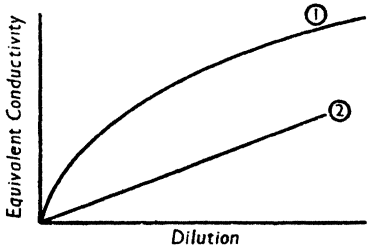


FIG. 7

electrolytes, the graphs obtained are found to be of two quite distinct types. The two types are illustrated in Fig. 7.

Salts, strong acids, and strong bases all give graphs similar to (1) in Fig. 7, whereas weak acids and weak bases give graphs similar to (2). These results show that electrolytes are of two types, which differ from one another fundamentally.

If the equivalent conductivity is plotted against the square root of the molecular concentration it is again found that electrolytes belong to two classes, as is shown in Fig. 8, in which the numbers refer to the same classes of electrolyte as they do in Fig. 7.

Electrolytes giving graphs of type (1) are called Strong

Electrolytes, and those giving graphs of type (2) are called Weak Electrolytes.

Weak electrolytes, such as acetic acid, have chemical properties which suggest that only a portion of the dissolved substance is dissociated into ions, so it seems likely that the change in degree of dissociation with dilution brings about the shape of the graphs given in Figs. 7 and 8. These will be considered first.

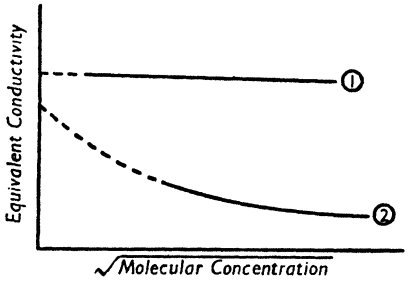


FIG. 8

WEAK ELECTROLYTES

Assuming that a weak electrolyte is partially dissociated, it should be possible to calculate from first principles the relation between the concentration of the solution, the degree of dissociation, and the equivalent conductivity.

Calculation of the Equivalent Conductivity of a Weak Electrolyte from First Principles

Specific conductivity can be regarded as the reciprocal of the specific resistance, but it is much clearer if it is regarded as the charge in coulombs carried per second *per unit potential gradient* across each square centimetre of the solution. Looked at in this way it is possible to calculate the specific conductivity in terms of the concentration of

the ions in solution and of their respective velocities under a potential gradient of 1 volt per cm.

Fig. 9 represents a tube in the electrolyte of cross-sectional area 1 sq. cm. Being a weak electrolyte, we suppose that of each gm.-molecule in solution a fraction α is

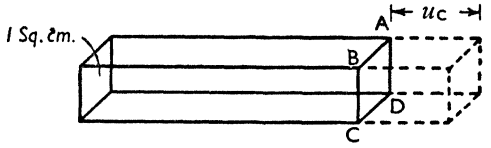


FIG. 9

dissociated into ions. It is these ions which carry the charge by migrating towards the electrodes.

Let: U_a=the velocity in centimetres per second of the anions under unit potential gradient,

U_c=the velocity in centimetres per second of the cations under unit potential gradient,

N=the number of gm.-molecules per cubic centimetre of solution,

F=the faraday (96,500 coulombs per gm.-equivalent),

V=the valency of the ions (the anion and cation are assumed to have the same valency),

and α=the degree of dissociation of the electrolyte, i.e. the fraction of each gm.-molecule which is dissociated into ions.

Now imagine the cations moving to the right in Fig. 9 during electrolysis under a potential gradient of 1 volt per centimetre. In one second there will emerge a rectangular sausage of length U_c and area of cross-section 1 sq. cm. This is shown in Fig. 9 in dotted lines. The ions within this sausage are the ones which have carried positive charge

across the area $ABCD$. We can, therefore, say that the number of coulombs carried per second by the cations across unit area of the solution ($ABCD$ in the figure) is $U_c VF\alpha N$,

where $U_c \times 1$ = the volume of the sausage,
αN = the number of ions per cubic centimetre in the solution,
and VF = the number of coulombs per gm.-ion.

The anions carry negative charge to the left, but this is equivalent to carrying positive charge to the right.

$\therefore$ coulombs carried per second by the anions $= U_a VF\alpha N$.
$\therefore$ total charge carried per second
$= (U_a + U_c)VF\alpha N$ coulombs.

Since this is the charge carried per second across each square centimetre of solution when the potential gradient is 1 volt per cm. we can say:

Specific conductivity $= (U_a + U_c)VF\alpha N$ reciprocal ohms.

Now the equivalent conductivity is the specific conductivity divided by the number of gm.-equivalents per cubic centimetre in the solution.

$\therefore$ equivalent conductivity

$$= \frac{(U_a + U_c)VF\alpha N}{VN} = (U_a + U_c)\alpha F.$$

At infinite dilution it is assumed, not unreasonably, that the degree of dissociation is unity, i.e. α is unity.

$\therefore$ equivalent conductivity at infinite dilution
$= (U_a + U_c)F.$

Several important points follow from the above calculation:

1. The symbol λ_v is used to denote the equivalent con-

ductivity at dilution v litres per gm.-molecule, and λ_∞ denotes the equivalent conductivity at infinite dilution.

$$\therefore \quad \lambda_v = (U_a + U_c)\alpha F$$

and $$\lambda_\infty = (U_a + U_c)F.$$

$$\therefore \quad \frac{\lambda_v}{\lambda_\infty} = \frac{(U_a + U_c)\alpha F}{(U_a + U_c)F} = \alpha.$$

This gives us a means of measuring α.

2. If the expression for λ_∞ is examined it will be seen that it is composed of two portions, one for each type of ion in the solution:

$$\lambda_\infty = FU_a + FU_c.$$

These quantities are called the Mobilities of the ions, for which the usual symbols are μ_a and μ_c respectively.

Thus $$\mu_a = FU_a \quad \text{and} \quad \mu_c = FU_c.$$

Thus, we may also say that:

$$\lambda_\infty = \mu_a + \mu_c.$$

Kohlrausch carried out the experimental work which established the Law of Independent Mobilities which was named after him. He found that the equivalent conductivity of an electrolyte at infinite dilution is the sum of terms which represent the separate contributions of each type of ion. These terms are called Ionic Mobilities, and the value of the mobility for any ion is the same in all its solutions. This can be proved by experiment, without finding the individual mobilities, in the following manner.

For potassium chloride, λ_∞ is 130·0 at 18°C. By hypothesis we may say, therefore:

$$\mu_{K^\cdot} + \mu_{Cl'} = 130{\cdot}0.$$

For sodium chloride, $\lambda_\infty = 108{\cdot}9$.

$$\therefore \quad \mu_{Na^\cdot} + \mu_{Cl'} = 108{\cdot}9.$$

For sodium nitrate, $\lambda_\infty = 105{\cdot}2$

$$\therefore \qquad \mu_{Na^\cdot} + \mu_{NO_3'} = 105{\cdot}2.$$

From these results it is possible to calculate the equivalent conductivity at infinite dilution of potassium nitrate solution. For:

$$\mu_{K^\cdot} + \mu_{NO_3'} = \mu_{K^\cdot} + \mu_{Cl'} + \mu_{Na^\cdot} + \mu_{NO_3'} - (\mu_{Na^\cdot} + \mu_{Cl'})$$
$$= 130{\cdot}0 + 105{\cdot}2 - 108{\cdot}9 = 126{\cdot}3.$$

Now when the equivalent conductivity at infinite dilution of potassium nitrate is measured it is found to come to 126·3 within experimental error, thus verifying the Law of Independent Mobilities for these solutions. Similar experiments verify it for other solutions.

If the velocity of an ion at unit potential gradient is measured directly in a Lodge tube it is possible to calculate that of another ion from the general relation:

$$\lambda_\infty = \mu_a + \mu_c$$

since, as was shown above theoretically, the following relationship would be expected to be true:

$$\mu_a = U_a F.$$

Thus if we divide an ionic mobility by the faraday (96,500) we should get the velocity of the ion in centimetres per second under unit potential gradient. If this velocity is checked by direct measurement in a Lodge tube it is found to agree with the predicted results, supporting the truth of the theoretical calculations made on page 13.

3. During electrolysis the fraction of charge carried by the cations is proportional to FU_c, that carried by the anions is proportional to FU_a, and the total charge carried is proportional to $FU_c + FU_a$, or $\mu_c + \mu_a$. It therefore follows that the cations and anions carry respectively the following fractions of the total charge carried:

$$\text{Fraction carried by the cations} = \frac{FU_c}{FU_c + FU_a} = \frac{\mu_c}{\mu_c + \mu_a}.$$

$$\text{Fraction carried by the anions} = \frac{FU_a}{FU_c + FU_a} = \frac{\mu_a}{\mu_c + \mu_a}.$$

These quantities are known as the Transport Numbers of the cations and anions respectively, and they can be measured in the apparatus illustrated in Fig. 5. It should be noted that the sum of the two transport numbers is always unity, so that it is usual to measure the transport number of the anion only in the following way.

The cathode is weighed, and a solution of measured concentration put into the apparatus. After a small current has been passed for some time the cathode is washed, dried, and again weighed. If the increase in weight is divided by the equivalent weight of the metal we get the number of equivalents deposited. This is proportional to $\mu_c + \mu_a$ (see argument on page 7).

The liquid in the cathode portion of the apparatus is then run out and analysed. So is some of that in the middle portion in order to check that its concentration is unchanged: this ensures that no convection currents have mixed the different portions of the solution.

The loss in concentration in the cathode liquid is converted to gm.-equivalents. From the argument on page 8 it will be realized that the loss in concentration in the cathode liquid is proportional to the mobility of the anion, so that the number of gm.-equivalents lost from the cathode compartment is proportional to μ_a. Thus we have:

$$\frac{\mu_a}{\mu_c + \mu_a} = \frac{\text{No. of gm.-equivalents lost from the cathode liquid}}{\text{No. of gm.-equivalents deposited on the cathode}}.$$

This is the transport number of the anion. That for the cation can then be obtained by subtracting this from unity.

The mobilities are calculated by multiplying the transport numbers by the equivalent conductivity at infinite dilution ($\lambda_\infty = \mu_c + \mu_a$). These agree with the values obtained by direct measurement in a Lodge tube.

Thus there is considerable experimental evidence for the results deduced theoretically on page 15, and for the reasoning leading to them. The next step is to summarize how values for the degree of dissociation of a weak electrolyte may be measured.

It has been shown on page 15 that $\alpha = \lambda_v/\lambda_\infty$. It is, therefore, necessary to measure λ_v and λ_∞. By means of a Wheatstone-bridge circuit, using alternating current, it is possible to measure the specific resistance of the solution at the dilution v litres per gm.-equivalent. From this the equivalent conductivity λ_v can be calculated. The next step is to measure λ_∞, which is not so easy. As an example we will suppose that the degree of dissociation for a solution of acetic acid is being measured.

As will be seen from Figs. 7 and 8, it is not possible to find λ_∞ for a weak electrolyte from either type of graph, because at great dilution readings are inaccurate, and so it is necessary to determine it by a roundabout method. We must work with strong electrolytes, and use the facts already discussed under ionic mobilities.

For acetic acid:

$$\lambda_\infty = \mu_{H^\cdot} + \mu_{Ac'}$$

where $\mu_{H^\cdot}$, and $\mu_{Ac'}$ stand for the ionic mobilities of hydrogen and acetate ions respectively. The sum of these two mobilities can be found by using Kohlrausch's Law of Independent Mobilities, and an outline of what must be done will now be given.

An inspection of Fig. 8 will make it clear that for strong electrolytes the graph of the equivalent conductivity plotted against the square root of the molecular concentration is a straight line, and where this line cuts the equivalent conductivity axis is λ_∞ for the solution.

The procedure for finding λ_∞ for acetic acid would be as follows:

1. Measure λ_v for a sodium acetate solution at a series of concentrations. If these readings are plotted against the square roots of the molecular concentrations a straight line is obtained, from which λ_∞ can be read. Now:

$$\lambda_{NaAc} = \mu_{Na^\cdot} + \mu_{Ac'}$$

where λ_{NaAc} stands for the equivalent conductivity at infinite dilution for sodium acetate.

2. The procedure is now repeated for solutions of sodium chloride, and of hydrochloric acid. These results give:

$$\lambda_{NaCl} = \mu_{Na^\cdot} + \mu_{Cl'}$$

and

$$\lambda_{HCl} = \mu_{H^\cdot} + \mu_{Cl'}$$

where λ_{NaCl} and λ_{HCl} stand for the equivalent conductivities at infinite dilution of sodium chloride and hydrochloric acid respectively.

3. The equivalent conductivity of acetic acid at infinite dilution can now be calculated by using Kohlrausch's Law of Independent Mobilities:

$$\lambda_{HAc} = \mu_{H^\cdot} + \mu_{Ac'} = \mu_{H^\cdot} + \mu_{Cl'} + \mu_{Na^\cdot} + \mu_{Ac'} - (\mu_{Na'} + \mu_{Cl'})$$
$$= \lambda_{HCl} + \lambda_{NaAc} - \lambda_{NaCl}.$$

It is important to realize that all the measurements mentioned above must be carried out at a constant temperature.

Having thus found λ_v and λ_∞ for acetic acid, we have for the degree of dissociation α:

$$\alpha = \frac{\lambda_v}{\lambda_\infty}.$$

It is now possible to verify the hypothesis that weak electrolytes are partially dissociated in solution. This was mentioned on page 12.

Consider a weak electrolyte HA, where A stands for some acid radical. If it is partially dissociated it would be expected that the undissociated molecules would be in equilibrium with the ions as follows:

$$HA \rightleftharpoons H^{\cdot}+A'.$$

If this is so the equilibrium will obey the Law of Mass Action, giving the equation

$$\frac{[H^{\cdot}]\times[A']}{[HA]}=K,$$

where K is a constant.

From this equation we can derive the relationship between the degree of dissociation and the degree of dilution, and this can be verified by measurements. The expression giving this relationship is known as Ostwald's Dilution Law, which will now be proved.

Ostwald's Dilution Law

Let the degree of dissociation of HA be α, and let one gm.-molecule of it be dissolved in v litres of solution.

In the equilibrium $HA \rightleftharpoons H^{\cdot}+A'$ we then have:

$$[H^{\cdot}]=[A']=\frac{\alpha}{v},$$

since of each gm.-molecule a fraction α is dissociated, and

$$[HA]=\frac{1-\alpha}{v},$$

since of each gm.-molecule a fraction $1-\alpha$ remains undissociated.

Applying the Law of Mass Action, we then get:

$$\frac{[H^{\cdot}]\times[A']}{[HA]}=K=\frac{(\alpha/v)\times(\alpha/v)}{(1-\alpha)/v}=\frac{\alpha^2}{v(1-\alpha)}.$$

This particular form of Ostwald's Dilution Law applies to a binary electrolyte. The results for other types can be calculated in a similar way.

If α is measured for a series of values for the dilution v, and the values for α and v are substituted in the above formula, it is found that the result is constant. This shows that the hypothesis that weak electrolytes are partially dissociated is correct.

Strong Electrolytes

The graphs for strong electrolytes shown in Figs. 7 and 8 show that their behaviour on dilution bears no resemblance to that of weak electrolytes, so it is not surprising to find that on being tested experimentally they do not obey Ostwald's Dilution Law. Apart from the strong acids, such as nitric acid and hydrochloric acid, strong electrolytes consist of salts. Now salts conduct electricity when fused, which indicates that their melts contain ions; and X-ray investigations of their crystals indicate that in the solid state they are ionic. It is, therefore, assumed that in solution all strong electrolytes are totally ionized at all concentrations, and that the change in equivalent conductivity with dilution is due to the effect on each ion of its neighbours. As yet, the mathematics of this inter-ionic interference has not been completely worked out, so that it can be described only qualitatively. As an example sodium chloride will be considered.

A crystal of sodium chloride consists of equal numbers of sodium and chloride ions arranged symmetrically as is shown in Fig. 10.

If this figure is carefully examined it will be seen that

each chloride ion is surrounded by six sodium ions: the chloride ion labelled *P* shows this clearly. Likewise each sodium ion is surrounded by six chloride ions. This close-packed structure is determined by the fact that in it the energy of the system is a minimum.

When sodium chloride dissolves in water the energy given out when the sodium and chloride ions are hydrated (for explanation see page 83) breaks down the ordered structure of the crystal, and the ions disperse among the

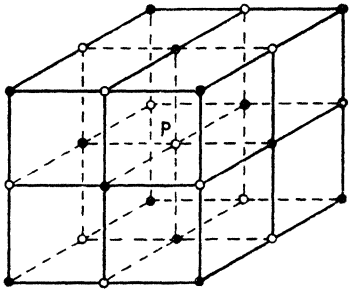


FIG. 10

water molecules and share their random thermal movement. However, since the sodium and chloride ions carry opposite charges there is still a slight tendency to form the ordered structure of the crystal. This tendency increases with increasing concentration of the solution, as would be expected, and of course it means that the ions are not completely free of each other. This lack of freedom, which decreases with dilution, accounts for the change in equivalent conductivity as the concentration is changed. The sodium ions experience a slight drag by the chloride ions, and vice versa, and this drag decreases with dilution.

This concludes the electrical evidence for the existence and behaviour of ions in solution. However, it is obvious that if electrolytes are ionized in solution we should be able to find evidence, other than electrical, for their presence. Such evidence comes from a study of the boiling-points, freezing-points, vapour pressures, and osmotic pressures of solutions of electrolytes. These phenomena will be considered in Chapter II.

CHAPTER II

VAPOUR PRESSURE AND RELATED PHENOMENA

The fact that liquids evaporate at all temperatures if left open to the air clearly indicates that molecules of the liquid escape from it from time to time and pass into the vapour state. For many reasons connected with Chemistry it is necessary to understand fairly thoroughly the mechanism by which this evaporation takes place, so that a fairly complete qualitative discussion of the mechanism must be given before dealing with the various phenomena which are related to it.

Mechanism of Evaporation

If clear thinking is to be achieved it is essential to consider a liquid as consisting of individual molecules, rather than just as a homogeneous fluid. A diagram such as Fig. 1 is a help, crude and out of scale though it is.

The dots shown in Fig. 1 (a) represent the individual molecules in the liquid. The Kinetic Theory of gases leads us to suspect that the molecules of a liquid are in a state of random movement similar to that in a gas, though the molecules in a liquid are much more closely packed and so the mean free path of the molecules will be much less than that for the gas at the same temperature and pressure. The fact that liquids diffuse into each other shows that this deduction is correct, and the Brownian Movement of small particles, observable under a microscope, is a direct proof of the random molecular movement. We must, therefore, visualize all the particles in

Fig. 1 (a) as moving entirely at random and colliding with each other.

When a molecule near to the surface of the liquid is moving in a suitable direction it may escape from the attraction of the neighbouring molecules and pass into the space above as a vapour molecule. For simplicity we will assume that the beaker is inside an evacuated bell jar, so as to avoid the complications arising from having air present. This being so, an enlarged picture of the molecules at the surface would be like Fig. 1 (b) in which are shown the forces acting on a particular molecule. It

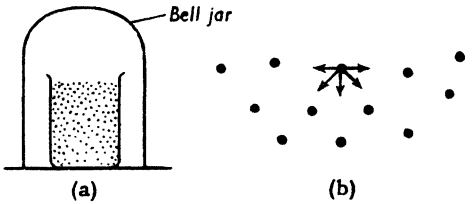


FIG. 1

should be noted that the forces on this molecule due to the attractions of its neighbours have their resultant acting downwards towards the liquid, thus impeding its escape. These forces, of course, are the same as those giving rise to the phenomena of Surface Tension.

If the molecule under consideration is to escape from the liquid it should now be clear that it must have sufficient kinetic energy to do work against the resultant of the forces shown till it is so far away from the liquid that the resultant is virtually zero. We could say that, on a molecular scale, the molecule has moved to an "infinite" distance[1] from the liquid, and so is free. The value of this minimum energy depends, very obviously, upon the

[1] The meaning of this is not precise, but in reality it can be taken as being quite a small fraction of a millimetre.

nature of the liquid, and this explains why, at the same temperature, some liquids evaporate more readily than others.

In case there is any difficulty in understanding why it is that for a molecule to move an "infinite" distance from the liquid against an attractive force, only a limited amount of work is needed an electrical analogy will be given.

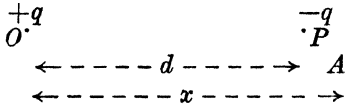


FIG. 2

In Fig. 2 O is a fixed charge of $+q$ e.s.u., and a charge of $-q$ e.s.u. is situated at P, d cm. from it. It is required to calculate the work needed to move the charge from P to an infinite distance.

Consider the charge to be at A, distant x cm. from O. Then the force acting on it is q^2/x^2 to the left. It follows from elementary calculus that:

Work done in moving charge from P to infinity

$$= \int_d^\infty \frac{q^2}{x^2} dx = q^2 \left[-\frac{1}{x} \right]_d = \frac{q^2}{d} \text{ ergs.}$$

Now in the case of the molecule we are considering we have to make a similar calculation for the vertical component of each force acting on it. The resulting integral is very complex, but, since inter-molecular forces obey an approximate inverse square law, the principle is similar to the electrical analogy. This should make it clearer that for the molecule to "escape" from the liquid only a finite amount of energy is needed.

In view of the fact that liquids evaporate only slowly it

is obvious that only a small fraction of the molecules at the surface have sufficient energy to escape. If the majority of the molecules had the required energy the liquid would burst into vapour explosively like a steam boiler bursting. We therefore conclude that the molecules which escape are the exceptional ones which happen to have had a series of collisions which have accelerated them in the right direction, and to understand this more intelligently and accurately it is necessary to consider the

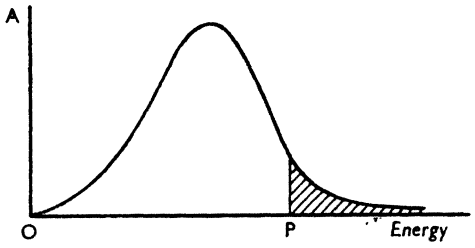


FIG. 3

Along the axis AO is plotted the number of molecules having a given kinetic energy, expressed as a fraction of the total number of molecules present.

way in which energy is distributed among a *large* community of molecules. This is a mathematical problem.

If a large collection of molecules is considered (many millions) the collisions between them will be completely random, and so will the distribution of kinetic energy, though the total energy in the whole collection of molecules will remain constant provided the temperature remains constant. The way in which the energy is distributed is thus seen to be a statistical problem, since the distribution will follow the laws of chance. The calculation of this distribution is too complex to introduce here, but it results in representing the distribution by a probability curve of the type shown in Fig. 3.

It is important to get clear what is plotted along the axis OA. Along the other axis is plotted the kinetic energy. The curve shows that exceedingly few molecules will be at rest at any instant, and that exceedingly few will have very high energies. The position of the maximum gives the most common energy for molecules to have at any instant, and it is this maximum which determines the temperature of the collection of molecules.

With the aid of this probability curve it is possible to gain more insight into the mechanism of evaporation. As was argued earlier, it is only those molecules with exceptionally high kinetic energy which have enough energy to escape. On the graph the minimum kinetic energy required for escape can be represented by the point P, which will be well to the right of the maximum. Of course any molecules with more than this minimum energy can escape also. Now it should be seen easily that the area under the probability curve to the right of the ordinate at P (shaded) gives the total number of molecules in the whole collection which have sufficient energy to evaporate. Obviously nearly all these are nowhere near the surface of the liquid, or they are moving in the wrong direction, but we can say that the rate of evaporation per square centimetre of surface is proportional to this area. The curve is asymptotic to the x-axis, so that the area extends to infinity: however, it is important to realize that in spite of this the shaded area is finite.

Before proceeding further it is necessary to investigate what happens to the probability curve when the temperature is raised. If the whole collection of molecules is heated it is obvious that the most common energy will increase, and also that more molecules than before will have the higher energies, and less will have the lower ones. Thus the maximum will move to the right, while the curve changes slightly in shape. This is shown in Fig. 4, in

which the curve shown in Fig. 3 has been reproduced as the solid curve, and the one for the higher temperature is dotted.

The new ordinate at P has increased greatly, and so has the area underneath the curve. The new area is shaded with vertical lines, whereas the old one is shaded as in Fig. 3. Since the rate of evaporation per square centimetre is proportional to this area, it is clear why a small

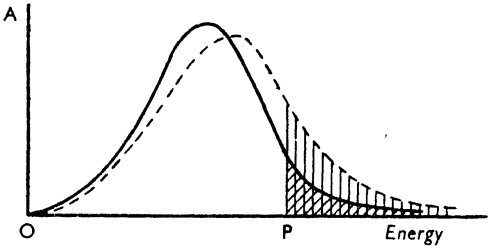


FIG. 4

rise in temperature produces a large increase in the rate of evaporation.

It is now possible to refer back to Fig. 1 (a) and consider what factors determine the rate of evaporation per square centimetre of surface.

FACTORS DETERMINING THE RATE OF EVAPORATION PER SQUARE CENTIMETRE OF SURFACE

1. The nature of the liquid. This operates by determining the position of P in Fig. 4.
2. The temperature. This operates by determining the position of the maximum in the probability curve, and hence the area under the curve to the right of the ordinate at P.

As evaporation proceeds molecules of vapour occupy the space above the liquid, and the random motion and collisions among themselves are exactly the same as for any

gas filling that space. Quite by chance a certain number of these vapour molecules will strike the surface of the liquid and enter it again. This process is called condensation, and the next thing is to consider what factors determine the rate of condensation.

Factors Determining the Rate of Condensation per Square Centimetre of Surface

1. The number of molecules per cubic centimetre of vapour.
2. The temperature, in that this determines the mean velocity of the vapour molecules, and hence the number striking the surface of the liquid per second.

It is important to realize that the rate of condensation has no direct connection with the rate of evaporation. The likelihood of a collision between a molecule emerging from the liquid and another one about to enter it is very small indeed, so that the processes of evaporation and of condensation proceed quite independently of each other.

Again, with reference to Fig. 1 (a) it is now possible to visualize what happens as the liquid evaporates into the vacuum above it. Initially there is no vapour, and so no condensation. However, as evaporation continues molecules of vapour accumulate in the space above the liquid, and so condensation begins. At first the rate of evaporation exceeds that of condensation, but as a result the number of molecules of vapour per cubic centimetre increases steadily. Finally, the concentration of vapour molecules reaches such a value that the rates of evaporation and of condensation become equal, and the liquid and vapour are then in equilibrium. *The pressure of vapour when it is in equilibrium with the liquid is known as the vapour pressure of the liquid.*

If the temperature of a liquid in equilibrium with its

vapour is raised, the rate of evaporation and that of condensation are both increased. However, owing to the behaviour of the probability curve already described, the increase in the rate of evaporation exceeds the increase in the rate of condensation. As a result the equilibrium between vapour and liquid is upset; the excess evaporation over condensation increases the concentration of vapour molecules, until finally equilibrium is re-established at a higher vapour pressure. Thus vapour pressure rises with temperature.

Effect on Vapour Pressure of Dissolved Substances

I. NON-VOLATILE SUBSTANCES

If a non-volatile solute is added to a liquid its vapour pressure is lowered, and if the solute is a non-electrolyte the lowering of the vapour pressure is proportional to the molecular concentration of the solute. All non-electrolyte solutes of the same molecular concentration in the same liquid produce the same lowering of vapour pressure, provided the temperature is constant.

The approximate reason for this is easy to see. In Fig. 1 (a) it will be seen that the effect of adding a solute is to replace a certain number of the molecules of the liquid by non-volatile solute molecules. Thus the number of molecules of the liquid exposed to a square centimetre of the surface is reduced in proportion to the number of solute molecules present at the surface. This means that the rate of evaporation of the liquid, and hence the vapour pressure also, are reduced in proportion to the number of solute molecules present, that is to say to the molecular concentration of the solute.

Raoult expressed this in the form:

$$\frac{p_0 - p}{p_0} = \frac{n_s}{n_0 + n_s}$$

where p_0=the vapour pressure of the pure solvent,
p=the vapour pressure of the solution,
n_s=the number of molecules of solute present,
and n_0=the number of molecules of solvent present.

This gives us a means of determining the molecular weight of a substance by measuring the drop in vapour pressure when a known weight of it is dissolved in a known amount of liquid. This is not a convenient method because it involves using a barometer with some of the liquid

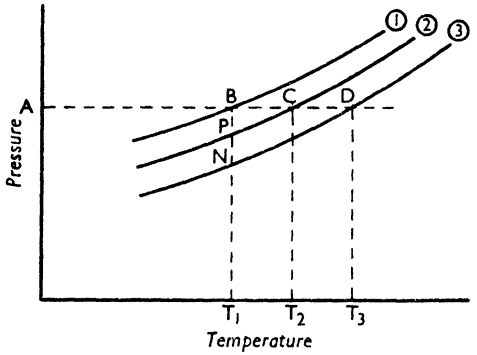


FIG. 5

above the mercury, while the temperature must be kept constant throughout. It is, therefore, preferable to take advantage of the fact that the drop in vapour pressure brought about by a solute produces an elevation in boiling-point and a depression in freezing-point of the liquid. These phenomena will now be considered.

Elevation of Boiling-points of Solutions

The boiling-point of a liquid is the temperature at which its vapour-pressure is equal to the pressure of the atmosphere: bubbles of vapour can then form freely, and this constitutes boiling. Curve (1) in Fig. 5 shows how the

vapour-pressure of a pure liquid changes with temperature, and curves (2) and (3) are the corresponding curves for two solutions of non-volatile solutes of different concentrations.

Suppose that the atmospheric pressure is A. Through A draw a line parallel to the temperature axis. The point at which this line meets the three curves gives the respective boiling-points T_1, T_2, and T_3, of the pure solvent and the two solutions. The elevations in boiling-points of the two solutions are now seen to be BC and BD.

Now, provided the curves do not deviate greatly from straight lines, in the "triangles" BCP and BDN we can say:

$$\frac{BC}{BD}=\frac{BP}{BN}.$$

Inspection of Fig. 5 will show that BP and BN are the depressions in vapour pressure for the two solutions, so that we can conclude that the elevation in boiling-point of a solution is *approximately* proportional to the lowering of vapour pressure. Since we know that the lowering of vapour pressure is proportional to the molecular concentration, we can say that the elevation in boiling-point is *approximately* proportional to the molecular concentration of the solute. Thus we have the well-known formula:

$$\text{Elevation in boiling-point}=K\times\frac{C}{M}$$

where C = the concentration of solute in grams per 100 gm. of solvent,

M = the molecular weight of the solute,

and K = a constant, known as the Molecular Elevation.

Provided we work with fairly dilute solutions, this gives as a convenient method for measuring molecular weights. The accuracy is not great, but it easily distinguishes between the values n, $2n$, $3n$, etc., which is usually what a

chemist needs for such measurements, since he knows the empirical formula of the substance by analysis.

The practical difficulties in the boiling-point method are to get a sensitive enough thermometer, to eliminate errors in the thermometer, and above all to avoid superheating of the liquid. The last of these raises an important and interesting phenomenon connected with vapour pressure, namely that the vapour pressure of a liquid depends upon the curvature of the surface.

Vapour Pressure and Curvature of Surface

It is found that for a convex surface of liquid its vapour pressure increases with the degree of curvature of the surface. Conversely, if the surface of the liquid is concave the vapour pressure decreases with increasing curvature. A qualitative explanation of the case of the convex surface is the easier to follow, and will now be given.

Reference to Fig. 1 (b) will reveal that for a molecule to get to the surface from the inner part of a liquid, some work must be expended, because as the molecule approaches the surface the resultant of the attractive forces exerted by its neighbouring molecules increases in size and acts against the motion of the molecule. Thus the molecules at the surface of a liquid have considerable potential energy relative to those in the bulk liquid: in other words part of the work needed to evaporate has already been done in getting them to the surface.

Now consider a spherical drop of liquid, and imagine a certain mass of the liquid to evaporate. If the radius of the drop is large only a small decrease in surface area of the drop will take place, whereas if the drop is small, there will be a larger decrease in surface area due to evaporation of the same mass of liquid. Thus in the second case a greater amount of surface energy is available to aid in evaporation than is available in the first case. This

results in a greater rate of evaporation, and hence a greater vapour pressure. A numerical example will help to make this clear.

Suppose that two drops of water are considered, one of radius 10^{-1} cm. and the other of radius 10^{-8} cm., and suppose that 10^{-25} gm. of water is evaporated. The surface energy of water is about 73 ergs per sq. cm. at 20°C. Let r be the radius in centimetres, and 1 the density in grams per cubic centimetre.

First drop

Initial area of drop $= 4\pi r^2 = 4\pi \times 10^{-2}$ sq. cm.

$$\text{Initial mass of drop} = \tfrac{4}{3}\pi r^3 \times 1 = \tfrac{4}{3}\pi \times 10^{-3}$$
$$= 0{\cdot}0041888 \text{ gm.}$$

Therefore after a loss of 10^{-25} gm. the change in surface area is almost incalculably small, and so is the change in surface energy.

Second drop

$$\text{Initial area of drop} = 4\pi r^2 = 4\pi \times 10^{-16}$$
$$= 12{\cdot}5664 \times 10^{-16} \text{ sq. cm.}$$

$$\text{Initial mass of drop} = \tfrac{4}{3}\pi r^3 \times 1 = \tfrac{4}{3}\pi \times 10^{-24}$$
$$= 4{\cdot}1888 \times 10^{-24} \text{ gm.}$$

After loss of 10^{-25} gm. mass of drop $= 4{\cdot}0888 \times 10^{-24}$ gm.

$\therefore$ Final volume, after loss $= 4{\cdot}0888 \times 10^{-24}$ c.c.

This gives final surface area after loss $= 12{\cdot}370 \times 10^{-16}$ sq. cm.

$\therefore$ loss in surface area $= 0{\cdot}1964 \times 10^{-16}$ sq. cm.

$\therefore$ change in surface energy $= 0{\cdot}1964 \times 73 \times 10^{-16}$
$= 1{\cdot}434 \times 10^{-15}$ ergs.

In the second case there is an appreciable reduction in area, and the surface energy thereby released increases the vapour pressure.

This accounts for the phenomenon of supersaturation of vapours. If the pressure on a vapour is increased till it exceeds the vapour pressure at the temperature concerned, and there is no liquid phase present, the vapour does not condense. The reason for this is that if by pure chance a relatively small number of molecules of vapour happen to congregate sufficiently close together to form a drop of liquid, this drop has such a small radius of curvature that it is not in equilibrium with the vapour. The equilibrium pressure for a drop of liquid of such small radius of curvature is greater than the pressure of the surrounding vapour, so the drop evaporates again. Thus the vapour does not condense unless there is introduced into it a surface with considerably greater radius of curvature, such as a dust particle.

Conversely a concave surface exerts a lower vapour pressure than does a flat one. When a liquid is heated to its boiling-point, if it is to boil a number of molecules (again by pure chance) have to form a small bubble of vapour. If the bubble is to be stable this vapour must be in equilibrium with the liquid, and it must exert a pressure equal to that of the atmosphere. However, since the liquid round the bubble has a very small radius of curvature its equilibrium pressure (vapour pressure) is much less than that for a flat surface, which at the temperature being considered is atmospheric. The small bubble, therefore, collapses, no boiling takes place, and if heating is continued the temperature of the liquid continues to rise, and so the liquid becomes superheated.

It is exceedingly difficult to avoid superheating when determining the boiling-point of a liquid, and partly for this reason the alternative method of finding mole-

cular weights is preferred, namely the freezing-point method.

Depression of Freezing-points of Solutions

The depression in freezing-point of a solution is proportional to the molecular concentration of the solute. Thus for freezing-point depression we have a formula similar to that for the elevation of the boiling-point:

$$\text{Depression of freezing-point} = K \times \frac{C}{M}.$$

K is known as the molecular depression, and C and M have the same meaning as they have on page 33.

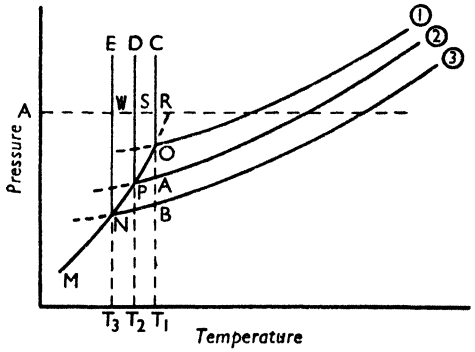


FIG. 6

The theoretical explanation of this is rather complex, and unsatisfactory, but it is worth considering. Fig. 6 is the same as Fig. 5, except that the vapour-pressure temperature curve for ice is included, whereas it was omitted from Fig. 5.

As for Fig. 5, curve (1) is the vapour-pressure temperature curve for the pure solvent, and (2) and (3) are the corresponding curves for two solutions of different concentrations. The curve *MNPO* is the vapour-pressure

temperature curve for ice. Where this curve meets the vapour-pressure curve for the pure solvent, is the triple point, O. Here, and here only, are the vapour, solid, and liquid, in equilibrium with each other. Likewise the triple points for the two solutions are P and N.

Now since the curves are nearly parallel, and only slightly curved, the triangles OAP and OBN are approximately similar.

$$\therefore \quad \frac{PA}{NB} \simeq \frac{OA}{OB}.$$

But approximately

$$\frac{PA}{NB} = \frac{T_1 - T_2}{T_1 - T_3}$$

and $T_1 - T_2$ is the depression in triple point for the first solution, while $T_1 - T_3$ is the depression in triple point for the second solution. OA and OB are the depressions in vapour pressure of the two solutions. Therefore, approximately:

Depression in triple point is proportional to the depression in vapour pressure, which in turn is proportional to the molecular concentration of the solution.

However, the triple points are not the freezing-points. The freezing-point is the temperature at which the *liquid* and *solid* are in equilibrium, and in general at atmospheric pressure no vapour is present. The curve OC shows the change in melting-point with pressure for the pure solvent, and PD and NE are the corresponding curves for the freezing-points of the solutions. The points R, S, and W, where these lines intersect the horizontal line through A (atmospheric pressure), are the freezing-points; the depressions in freezing-points are RS and RW. Now in practice the lines OC, PD, and NE are very nearly vertical: for instance at a pressure of 760 mm. of mercury the freezing-point of water is 0°C., while its triple point is

0·008°C. Thus the error in taking the depression in freezing-point instead of that of the triple point is negligible.

II. VOLATILE SUBSTANCES

When two liquids mix there are three possibilities: they may mix without having any effect on each other, they may form a compound with each other, or the liquids may be associated. These three types will be considered in turn.

1. *Miscible Liquids which do not React with Each Other*

The vapour-pressure composition graph for a given temperature for this type of liquid is given in Fig. 7.

P is the vapour pressure of pure A, and Q that of pure B. If the liquids are closely similar to each other the line

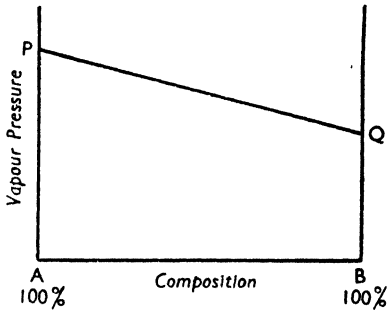


FIG. 7

joining P and Q, and giving the vapour pressures of mixtures of different composition, is a straight line. This type of vapour-pressure composition curve gives rise to a characteristic curve for boiling-point composition graphs, shown in Fig. 8.

The curve RST gives the boiling-points of the various

mixtures of A and B. However, when such mixtures are boiled the composition of the vapour is not the same as that of the liquid from which it comes: it is richer in the more volatile component. To express this on the graph the upper curve RNT is constructed in a way which is best explained by an example.

A mixture represented by M_1 boils at the temperature t, and gives off a vapour of composition M_2, the line tN being horizontal. When all points such as N are joined up we get the curve RNT. In other words any horizontal

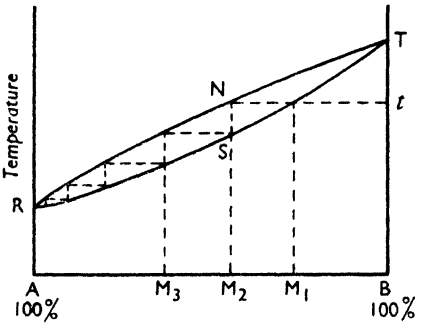


FIG. 8

line from curve RNT to curve RST represents the compositions of vapour and liquid which are in equilibrium with each other. The liquids give off the vapours when boiled, and the vapours condense to the corresponding liquids. For instance a vapour of composition M_2 first gives a liquid of composition M_1 on starting to condense. For this reason the curve RNT is sometimes called the condensation curve.

This type of mixture can be separated by fractional distillation, during which pure R will pass from the top of the fractionating column and pure T from its base. A crude picture of how the fractionating column works is as follows.

Liquid of composition M_1 gives off some vapour of composition approximating to M_2, leaving a liquid richer in B and so having a higher boiling-point. The latter runs down the column through regions of increasing temperature till eventually it runs out at the bottom as pure B. The vapour of composition M_2 is partially condensed by descending liquid in the column, and can be imagined as being redistilled, giving a vapour of composition M_3. This process is continued in steps, as shown in Fig. 8, till eventually pure A passes out of the column. However, it must be realized that in a column the individual steps

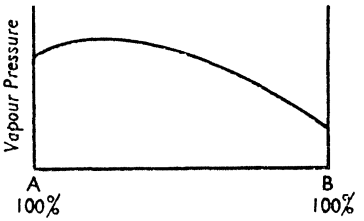


FIG. 9

are not as clearly defined as Fig. 8 suggests. Vapour is passing up the column, and liquid is streaming down, so that equilibrium between the two is never established.

Many mixtures of this type are encountered: examples are oxygen and nitrogen, benzene and toluene, chloroform and carbon tetrachloride.

2. *Two Liquids which are Associated*

Certain mixtures of liquids have a vapour-pressure curve with a maximum, as shown in Fig. 9. A common case is that in which one or the other is associated.

It will be seen that a vapour-pressure curve of this type will give rise to a boiling-point curve with a minimum

corresponding to the maximum in the vapour-pressure curve. As a result the diagram corresponding to that in Fig. 8 is similar to that shown in Fig. 10.

It will be seen at once that if a mixture whose composition is to the right of *M* is distilled in a fractionating column, pure *B* will emerge from the bottom of the column, and from the top will come a mixture of composition *M*. This is known as a constant-boiling mixture, and it will be seen from Fig. 10 that when this mixture boils it gives off a vapour of the same composition. It is

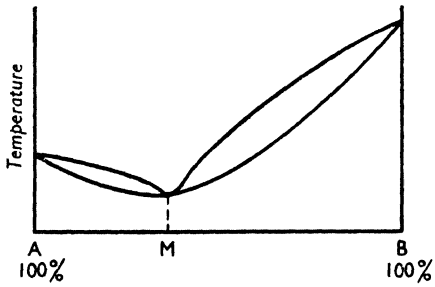


FIG. 10

therefore impossible to separate such a mixture further by simple distillation.

If a mixture whose composition lies to the left of *M* is fractionated it can be separated into pure *A* and the same constant-boiling mixture.

Mixtures of this type are common, examples being: ethyl alcohol and water, ethyl alcohol and ethyl acetate, ethyl acetate and water.

It is important to realize that Fig. 10 represents the state of affairs at a particular pressure. At a different pressure the graph changes, and so does the position of the point *M*. This fact is often used in commercial distillation processes.

3. *Two Liquids which Form a Compound*

If the two components of the mixture attract one another strongly, or form a compound, the vapour-pressure graph has a minimum, as shown in Fig. 11, and the boiling-point graph is as in Fig. 12.

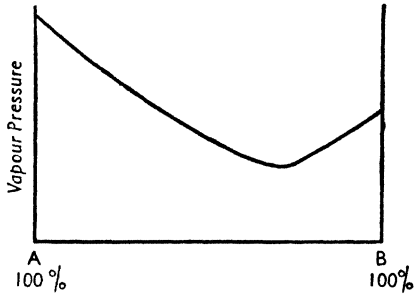


FIG. 11

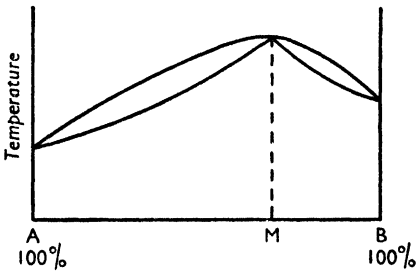


FIG. 12

As will be seen from Fig. 12, when such mixtures are fractionated the constant-boiling mixture emerges from the bottom of the column, and from the top comes either pure *A* or pure *B* according to whether the composition of the original mixture lies to the left or right of *M*. Nitric acid and water is an example of this type of mixture. Solutions of the halogen hydrides in water are also examples.

As in the previous type, the position of the maximum changes with pressure.

Osmotic Pressure

Certain membranes have the peculiar property of being permeable to a solvent, but impermeable to substances dissolved in the solvent. Such membranes are called semi-permeable.

It might be supposed that semi-permeable membranes act like a filter, through which the molecules of liquid can pass, whereas those of the solute are too large to do so. However, many cases are known where the solute molecules are almost certainly smaller than the solvent molecules. The more likely explanation of the semi-permeable nature of the membrane is that it forms a loose compound with the solvent molecules, but not with the solute ones. For instance many membranes which are semi-permeable to aqueous solution are made of cellulose or protein, both of which form hydrogen bonds with water. Thus free water molecules on both sides of the membrane are in dynamic equilibrium with those forming hydrogen bonds with the membrane, and so they also tend to get into dynamic equilibrium with each other.

Fig. 13 represents a vessel divided into two halves by a semi-permeable membrane *MN*. Pure water is in the left-hand half, and a solution in water is in the right-hand half. With this arrangement water diffuses into the solution steadily, the phenomenon being known as osmosis.

To understand how osmosis arises it is necessary to visualize the water and the solution as consisting of individual molecules, as is shown, very much out of scale of course, in Fig. 13. Assuming that the surface levels of the water and solution are the same, and that the densities of solution and water are also the same, the two liquids are in hydrostatic equilibrium at all levels. How-

ever, the rate of diffusion of the water from left to right is proportional to the concentration of water molecules in the pure water, whereas the rate of diffusion of water from right to left (remember that solute molecules cannot pass through the membrane) is proportional to the concentration of water molecules in the solution. Since in the solution the water has, so to speak, been "diluted" by the solute molecules, the concentration of water molecules in it is less than it is in the pure water in the left-hand section. As a result the rate of diffusion of water from

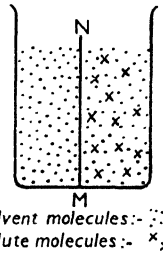


FIG. 13

left to right exceeds the rate of diffusion from right to left, and so there is a nett diffusion from left to right: this is osmosis.

By application of pressure to the solution it is possible to increase the rate of diffusion of water from the solution to the left-hand side, and when this rate has been made equal to the rate of diffusion from left to right, osmosis ceases. The extra pressure exerted on the solution is then known as the osmotic pressure of the solution.

From this theoretical explanation of osmosis it is to be expected that the osmotic pressure of a solution is proportional to the molar concentration of the solute. Experiments with many non-electrolytes show that this is so. In fact the osmotic pressures of dilute solutions obey the

Gas Laws, a fact which is usually stated by the expressions:

$$\pi V = RT$$

where π = the osmotic pressure,

V = the volume of solution containing 1 mole of solute,

T = the absolute temperature,

and R = the gas constant.

Thus calculations of osmotic pressures of dilute solutions can be made by assuming that the gm.-molecular weight of any non-electrolyte exerts an osmotic pressure of one atmosphere at 0°C. when it is dissolved in 22·4 litres of solution.

It should be obvious that osmosis takes place whenever a semi-permeable membrane separates any two solutions whose osmotic pressures differ.

Osmotic Pressures of Electrolytes

All electrolytes are found to give osmotic pressures considerably greater than is to be expected from calculations based on the assumption that no ionization has taken place. Pressures for binary electrolytes are nearly double the expected ones, those for ternary electrolytes nearly treble, etc.

From the theory of osmotic pressure outlined above, it is clear that the osmotic pressure of a solution is proportional to the number of *particles* of solute, irrespective of whether the particles are molecules or ions. In the case of sodium chloride, for instance, the molecular concentration is only half the ionic concentration, for each "molecule" of sodium chloride gives rise to two ions:

$$NaCl \rightarrow Na + Cl'.$$

Likewise, sodium sulphate gives rise to three ions per molecule:

$$Na_2SO_4 \rightarrow 2Na^{\cdot} + SO_4''.$$

Thus osmotic pressure measurements support the electrical evidence for the complete ionization of strong electrolytes.

The original work on the osmotic pressure of electrolytes was done by Van't Hoff, who expressed his results in the statement:

$$\pi V = iRT$$

where i is a constant for the particular electrolyte concerned. The significance of i, which is known as the Van't Hoff factor, is best brought out by the following statement:

$$i = \frac{\text{Measured osmotic pressure of a solution}}{\text{Calculated osmotic pressure, assuming no dissociation.}}$$

The same reasoning applies to depression of freezing-point and elevation of boiling-point, so that the constant can be regarded as any of the following:

$$i = \frac{\text{Observed osmotic pressure}}{\text{Calculated osmotic pressure}}$$

$$= \frac{\text{Observed depression of freezing-point}}{\text{Calculated depression of freezing-point}}$$

$$= \frac{\text{Observed elevation of boiling-point}}{\text{Calculated elevation of boiling-point}}$$

In all cases the "calculated" quantity assumes no dissociation.

For totally dissociated electrolytes the values for i should obviously be 2 for binary electrolytes, 3 for ternary ones, etc. However, owing to mutual interference between the ions of opposite sign the measured values of i

fall short of these theoretical values by amounts which vary with the concentration. The following table illustrates this[1]:

	Values of the Van't Hoff factor				
Salt	0·005*N*	0·02*N*	0·05*N*	0·1*N*	0·5*N*
KCl . .	1·96	1·92	1·89	1·86	1·80
NaCl . .	1·95	1·92	1·89	1·88	1·82
KBr . .	—	1·93	1·89	1·86	1·81
KNO_3 . .	—	1·88	1·84	1·78	—
HCl . .	1·99	1·96	1·93	1·92	—
$CaCl_2$ . .	—	2·76	2·67	2·63	—
$Ba(NO_3)_2$.	2·83	2·71	—	—	—
K_2SO_4 . .	2·86	2·71	2·57	2·46	2·14
Na_2SO_4 . .	—	2·73	2·59	2·47	2·13
$MgSO_4$ . .	1·69	1·54	1·42	1·32	1·08
$CuSO_4$ . .	1·62	1·46	1·32	—	—
$K_3Fe(CN)_6$.	3·68	3·34	—	—	—

Relation Between the Van't Hoff Factor and the Degree of Dissociation of a Weak Electrolyte

As before, consider a weak acid HA, for which the equilibrium will be:

$$HA \rightleftharpoons H^{\cdot} + A'.$$

If a fraction α of each gm.-molecule ionizes, for each gm.-molecule of HA which is being considered there will be the following amount after equilibrium has been attained:

$(1-\alpha)$ undissociated gm.-molecules

α hydrogen gm.-ions

α A′ gm.-ions.

Total number of particles present $= 1-\alpha+2\alpha = 1+\alpha$.

[1] Results of freezing-point experiments: see Noyes and Falk, *J. Amer. Chem. Soc.*, **34**, 454.

Without dissociation there would have been only 1 gm.-molecule, so we can say:

$$i = \frac{\text{Actual number of particles present}}{\text{Number of particles, assuming no dissociation}} = \frac{1+\alpha}{1}$$

$$\therefore \quad \alpha = i - 1.$$

For ternary or quaternary electrolytes a similar calculation is easily made.

By working with osmotic pressures for finding the Van't Hoff factors of solutions at different concentrations, *and at constant temperature*, it is possible to confirm that weak electrolytes obey Ostwald's Dilution Law. However, this is not as convenient as the conductivity method because of the difficulties of measuring osmotic pressures accurately. Nevertheless the fact that electrolytes have abnormal freezing-points, boiling-points, and osmotic pressures, supports the electrical evidence for the Ionic Theory.

CHAPTER III

WATER

Its familiarity frequently causes us to overlook the fact that water is a very peculiar liquid with rather exceptional properties. Also, since we ourselves are water-resistant, and since most common substances round us are also more or less inert towards it, we are liable to overlook the fact that chemically water is frequently very reactive. In view of its interesting properties and of its great importance in Chemistry, it is worth some discussion.

The Physical Properties of Water

When considering the physical properties of water it is best to compare it with hydrogen sulphide, its neighbour in the same group of the Periodic Table. The corresponding properties are shown below:

	Water	*Hydrogen sulphide*
Melting-point	0°C.	−82·9°C.[1]
Boiling-point	100°C.	−61·8°C.[1]
Difference between melting- and boiling-points	100°C.	21·1°C.[1]
Dielectric constant	81·07	5·93[1]
Molecular weight	18	34·08
Dipole moment	$1{\cdot}84\times10^{-18}$ e.s.u.-cm.	$1{\cdot}10\times10^{-18}$ e.s.u.-cm.

[1] Figures taken from *Handbook of Chemistry and Physics*, 29th edition.

From these figures it will be noticed at once that there are four outstanding ways in which the properties of water differ from those of hydrogen sulphide:

1. The temperature range between the melting- and boiling-points is very great.
2. The dielectric constant is very high.
3. The dipole moment is very high.
4. The melting-point and boiling-point are both very much higher than the corresponding values for hydrogen sulphide.

Of these the fourth will be considered first. The discussion in Chapter I should have made it clear that when a liquid vaporizes the molecules must be given sufficient energy to escape from their neighbours. It is not surprising, then, that in the case of most liquids the boiling-point rises with molecular weight. To put it crudely, it is easier to throw a brick over a wall than it is to do the same to a large rock. This analogy is not strictly accurate, but it may help to produce the right picture. For similar reasons the melting-points usually rise with molecular weight. The data below illustrate these points.[2]

	M.p. (°C.)	*B.p.* (°C.)		*M.p.* (°C.)	*B.p.* (°C.)
Methane	−184·0	−161·5	$SiCl_4$	−70	57·6
Ethane	−172	−88·3	$SiBr_4$	5	153
Propane	−189·9	−42·17	SiI_4	120·5	290
Butane	−135	−0·6	CCl_4	−23	76·8
Pentane	−131·5	36·2	CBr_4	48·4	189·5
Hexane	−94·3	69·0	CI_4	171	decomp.

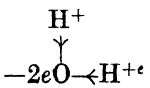
[2] Figures taken from *Handbook of Chemistry and Physics*, 29th edition.

The fact that both the melting-point and the boiling-point of water are so much above the corresponding data for hydrogen sulphide, indicates that we are not dealing with simple H_2O molecules. Water must be associated both in the solid and in the liquid. X-ray investigation

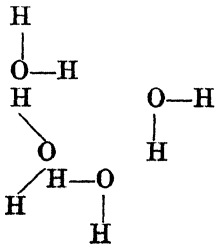
of ice reveals that there are aggregates of H_2O molecules. These aggregates change on melting, and as the temperature is raised, and these changes account for the extraordinary facts that water is more dense than ice at the melting-point, and that water reaches its maximum density at 4°C. They also account for the large difference between the freezing-point and boiling-point.

The explanation of this behaviour lies in the structure of water, which electronically is:

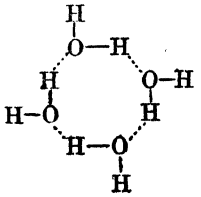
Now the dipole moment of water and, of course, its dielectric constant indicate that the molecule has considerable electric polarity. This is indicated in the following diagram, in which the arrows represent slight displacements of the electrons in the bonds towards the oxygen atom, giving a small residual charge of $+e$ on each hydrogen atom, and two corresponding negative ones of $-e$ on the oxygen atom.



These small charges will cause the molecules to be attracted by each other in small groups, whose size depends upon the violence of the thermal movement, i.e. upon the temperature:



However, the bonding between these water molecules is not only electrostatic; it involves hydrogen bonds as well. Thus the bonding is stronger than what would result from electrostatic attraction only. A better representation of the aggregate is:



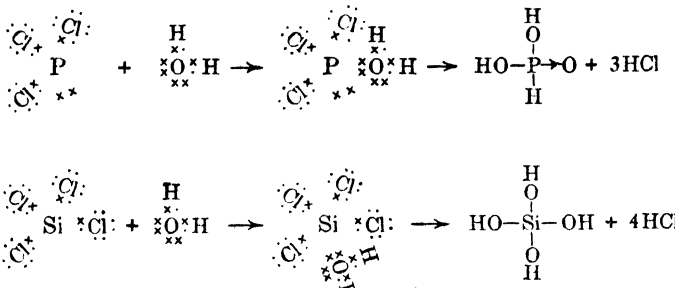
The Chemical Properties of Water

The fact that water is an oxidizing agent is of no particular interest so far as this discussion is concerned. The interesting properties are that it can form hydrogen bonds, and that it is a strong donor of electrons. These two facts account for its most common and interesting reactions.

Hydrogen bonds are formed between any pairs of atoms of the following elements: oxygen, fluorine, sulphur, and nitrogen. As a result of this, water molecules form hydrogen bonds with many compounds containing hydroxyl groups, oxygen atoms, or nitrogen atoms. Examples are carbohydrates, proteins, amines, amides, alcohols, aldehydes, ketones, alcohols, phenols, and carboxylic acids. It also combines with many hydroxides, such as metallic hydroxides and silicic acid. Thus hydrated substances are very common.

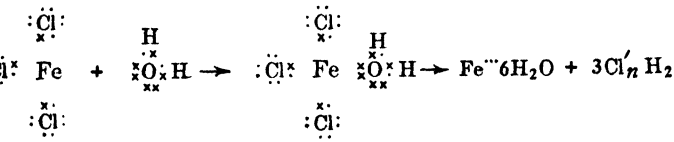
As a result of having two lone pairs of electrons, water will act as a donor to any compound which can take the lone pair of electrons. Some of the resulting compounds are unstable, and decompose; others are stable. Examples of the former type are many non-metal halides, such as

phosphorus trichloride, and silicon tetrachloride, which probably react as follows:



In both the above cases it is possible that more than one water molecule forms a co-ordinate link, since both phosphorus and silicon have a covalency maximum of six. However, the resulting compounds are unstable, and immediately decompose to give respectively phosphorous acid and silicic acid, both of which are heavily hydrated if excess of water is present.

The covalent chlorides of weak metals behave similarly initially, but the intermediate compound breaks up into hydrated ions:



Most reactions of this kind are quite violent, considerable heat being given out.

The last example of water acting as a donor is the case where it breaks down the crystal lattice of a salt and hydrates the ions finally produced. The hydration of the ions provides the energy necessary to break up the crystal lattice, and this type of reaction probably occurs whenever

a salt dissolves in water. Hydration of ions is, therefore, a very important reaction, though it is frequently glossed over in elementary work. Owing to its high dielectric constant the water reduces the electrostatic forces between the ions, and enables them to disperse easily.

It is probable that the bond between an ion and a water molecule varies between two extreme types: a co-ordinate link, and an electrostatic attraction.

There seems little doubt that in solution all ions are hydrated, and of course many are hydrated in the crystal. The positions of the water molecules in the crystals of hydrated salts can only be found by means of X-rays. These reveal that some water molecules are held in the crystal lattice between the positive and negative ions: these are probably held partly by hydrogen bonds, and partly by electrostatic attraction by the positive and negative ions. The majority of water molecules, however, are held round the cations, and the resulting complex ion is much larger in diameter than the metallic ion alone: as a result the crystal of a hydrated salt has a structure different from that of the anhydrous salt. Metallic ions in solution are hydrated to a degree which is determined by the solid geometry of spheres. The relative sizes of the metallic ion and the water molecule determine the number of molecules of water which can be packed round the ion. However, additional molecules of water can be attached to this nucleus by hydrogen bonding or electrostatic forces. Ionic mobilities indicate that the smallest ions carry the largest number of water molecules in solution, as is shown in the table on page 56.

The probable explanation of this is that the smaller the ion the greater is the electric field in its neighbourhood, and therefore the greater is the number of molecules of water held round the ion by electrostatic attraction. Also, the molecules of water nearest to the ion are held

	Mobility at 18°C.	*Ionic radius Ångström Units*[1]
Li	33	0·6
Na	43·5	0·95
K	64·6	1·33
Rb	68	1·48
Cs	68	1·69

[1] An Ångström Unit $= 10^{-10}$ metre.

more firmly, and as a result they may be included in the crystal structure involving the ions, whereas the corresponding salt of a similar metal with larger ionic radius may be anhydrous. An example of this is that several sodium salts are hydrated in the crystal, whereas the corresponding potassium ones are anhydrous.

Differences in the stabilities of hydrated ions are often revealed when crystals of hydrated salts are heated. Some give the anhydrous salts, others decompose to give the metallic oxides. Examples of this will be encountered in Chapter VI. The stability of hydrated ions is also important when Electrode Potentials are being considered, as will be found in Chapter IV.

Another important reaction arising from the donor properties of water is that in which it reacts with itself:

$$H_2O + H_2O \rightleftharpoons H_3O^{\cdot} + OH'.$$

The ionic product for water, $[H_3O^{\cdot}] \times [OH']$, comes to only $0{\cdot}6 \times 10^{-14}$ at 18°C., but nevertheless this reaction means that water always contains both hydroxonium ions (hydrogen ions) and hydroxyl ions, and it is very important in several ways.

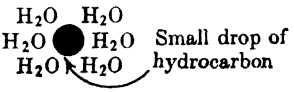
Water as a Solvent

Solutions consist of homogeneous mixtures of liquids and the dissolved material. Water dissolves a very large

number of substances, but for the most part these substances consist of electrolytes, or compounds containing atoms of oxygen or nitrogen. Other substances are either insoluble or only very slightly soluble. The explanation of this lies in the highly polar nature of water, and the fact that it forms hydrogen bonds with compounds containing oxygen or nitrogen atoms.

When these substances meet water they all react with it in a sense. The ions of the electrolytes are hydrated, and those substances which contain oxygen or nitrogen atoms form hydrogen bonds with the water. In either case, when once the "reaction" has taken place the ions, or molecules as the case may be, are covered with water molecules, and as a result they are miscible with the remaining water molecules. They are, as it were, disguised as water, and so are of a similar nature to water.

To understand this process more fully it is necessary to consider what happens when a substance "insoluble" in water is forced into "solution", as small droplets by shaking. For instance a very fine emulsion of a hydrocarbon in water can be considered. Each drop of hydrocarbon is surrounded by polar water molecules, as illustrated crudely below:



Now the hydrocarbon is not polar, so that there is no electrostatic attraction between its surface and the water molecules. On the other hand the water molecules attract each other strongly, since they are polar, and so tend to expel the particle of hydrocarbon. As a result the hydrocarbon settles out into a separate layer.

Particularly interesting cases arise if a substance is composed of molecules which have one or more groups which

are miscible with water, while the remainder of the molecule is not miscible. Fatty acids are examples of this type of compound, and their behaviour will be described. Consider the case of stearic acid:

$$CH_3 \cdot (CH_2)_{16} \cdot C(=O) - OH.$$

Owing to the fact that it contains oxygen atoms, the carboxyl group is miscible with water, forming hydrogen bonds with it. On the other hand the long hydrocarbon chain is hydrophobic, i.e. repelled by the water. Since the repulsion of the hydrocarbon chain exceeds the attraction of the carboxyl group, the molecule as a whole is insoluble in water. However, at the surface of the water a compromise arrangement is possible. The carboxyl groups form hydrogen bonds at the surface of the water, and the hydrocarbon chains stick up away from the water thus:

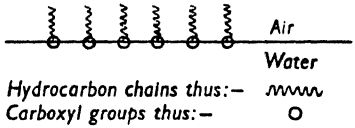


FIG. 1

By this means there is formed a mono-molecular layer in which the molecules of fatty acid are all orientated the same way. Such molecules stabilize emulsions of oil in water by arranging themselves so that the hydrophilic groups (carboxyl groups in the above case) are in the water, and the hydrophobic portions are in the oil.

Substances of this type are known as surface-active agents, and are very important in industry as detergents. They are also important in living organisms.

CHAPTER IV

ELECTRODE POTENTIALS AND EQUILIBRIUM POTENTIALS

The Electromotive Series of the metals is of considerable value even in elementary Chemistry, because it is appreciated that the order of the metals in this series bears a fairly close resemblance to their order of chemical activity. However, the correlation between the order of chemical activity and that in the electromotive series is far from complete; and also it is valuable to have some quantita-

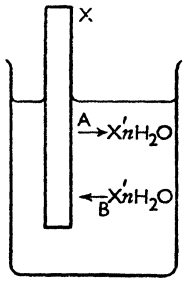


FIG. 1

tive, as distinct from mere qualitative idea of the relative activities. This can be gained to some extent from the values of the electrode potentials of the metals. It is desirable, therefore, to discuss the equilibrium between a metal and a solution of its own ions.

Fig. 1 represents a univalent metal X immersed in a solution of its own ions. The thermal movement[1] of the

[1] By thermal movement is meant the molecular movement already discussed on page 24.

metal and water causes ions of the metal to pass into solution, leaving the electrons behind on the metal rod. At the same time the thermal movement of the ions in the solution causes them to hit the metal rod. If these ions strike the rod with sufficient energy to remove the water molecules attached to them (water of hydration) they will enter the metal crystal lattice of the rod, and so be "discharged". In this connection it is important to realize that the structure of a metal consists of ions of the metal held together by a kind of "electron gas" composed of the valency electrons from the metallic atoms. When we are

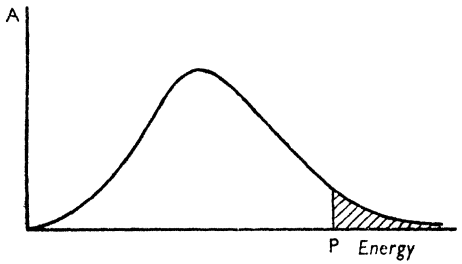


FIG. 2

considering the removal of an ion from the metal, therefore, we are dealing with its removal from a crystal lattice, and not merely the ionization of an isolated atom of metal. The other important points to realize are that in solution the ions are hydrated, and that the process of forming ions is quite independent of that of discharging them.

As in the case of evaporation of a liquid, the rate of removal of ions is determined by a probability curve similar to that on page 27. This curve is reproduced in Fig. 2, and the value of the energy at the point *P* is the minimum required to remove an ion from the crystal lattice of the metal. Thus the rate of formation of ions is proportional to the area beneath the curve to the right of

P—the shaded area. Also, as in the case of evaporation, rise in temperature will increase the rate by increasing this area.

Similarly, the rate at which ions leave the solution and re-enter the crystal lattice of the metal composing the rod is determined by a similar probability curve, only the area concerned is determined by the minimum energy required to remove the water of hydration from the ion. Thus the two factors are respectively the stability of the crystal lattice, and the stability of the hydrated ions. We are now in a position to consider all the factors which determine the rates of the two processes A and B, shown in Fig. 1.

The rate of formation of hydrated ions, process A, depends upon:

1. The nature of the metal concerned.
2. The temperature.
3. The potential difference between the metal and the solution.

The rate of liberation of ions, process B, depends upon:

1. The stability of the hydrated ion, i.e. the energy required to remove the water of hydration.
2. The temperature.
3. The potential difference between the metal and the solution.
4. The concentration of the ions in solution.

When a metal is dipped into a solution of its own ions, it is exceedingly unlikely that initially the rates of the two processes A and B will be equal. Suppose that the rate of A is greater than that of B. In that case a negative charge will build up on the metal, producing an increasing potential difference between the rod and the solution.

This potential difference decreases the rate of A, and increases that of B, until finally the two rates become equal. There is then a state of equilibrium, and the potential difference between the metal and the solution is called the Equilibrium Potential of the metal concerned.

By working with the same ionic concentration for each solution and measuring the equilibrium potential for every metal in turn we shall obviously have a set of values which would give us the relative activities of the metals *so far as forming ions is concerned.* Unfortunately it is impossible to do this, because in order to measure the potential difference between any metal and the solution it is necessary to get an electrical contact with the solution, and for this purpose another metal must be put into the solution. This at once introduces an equilibrium between the second metal and the solution, and all that we measure is the algebraical difference between the equilibrium potentials of the two metals.

The only way to get out of this difficulty is to use a standard reference electrode and measure the potential difference between this standard and each of the metals in turn. The standard electrode is hydrogen on platinum black, dipping into a normal solution of a strong acid at 25°C., the hydrogen being at a pressure of one atmosphere. When measurements are made each metal concerned is dipping in a molar solution of its own ions at 25°C., and this solution and that of the acid are connected by a tube full of jelly containing a strong solution of potassium chloride. The potential difference between the hydrogen electrode and the metal under these conditions is known as the Standard Electrode Potential, or more usually just the electrode potential. It must always be borne in mind that these values refer to metals dipping in molar solutions of their own ions. If the concentration of the solution is changed the potential changes also, as can be seen from

the theory outlined above. The equation relating the new potential with the standard electrode potential is:

$$E = E_0 - \frac{RT}{VF} \log C$$

where E_0 = the standard electrode potential,

E = the potential for ionic concentration C,

V = the valency of the ions,

R = the gas constant,

T = the temperature in degrees absolute,

and F = the faraday (96,500 coulombs per gm.-equivalent).

If this is worked out it will be found that at room temperature a change in concentration by the factor 10 changes the potential by about 0·029 volts for divalent ions, and by twice as much for monovalent ones. This change is important in connection with electrolysis, in particular when solutions containing more than one type of ion are concerned.

Deductions from Electrode Potentials

Electrode potentials explain many chemical reactions satisfactorily, and they enable correct predictions to be made in some cases. In other cases, however, this is not so, for there is bad correlation between electrode potential and many chemical properties.

The graphs of electrode potential and of atomic volume plotted against atomic numbers are shown in Fig. 3, and from this figure certain interesting points arise.

The high electrode potentials of lithium, sodium, potassium, rubidium, and cæsium correspond to the high atomic volumes of these elements. The electrode potentials of magnesium, calcium, strontium, and barium also corre-

spond to their atomic volumes. In all these cases this is probably explained by the fact that only a comparatively small amount of energy is needed to bring about the ionization of these atoms, though lithium has a higher electrode potential than its atomic volume would indicate:

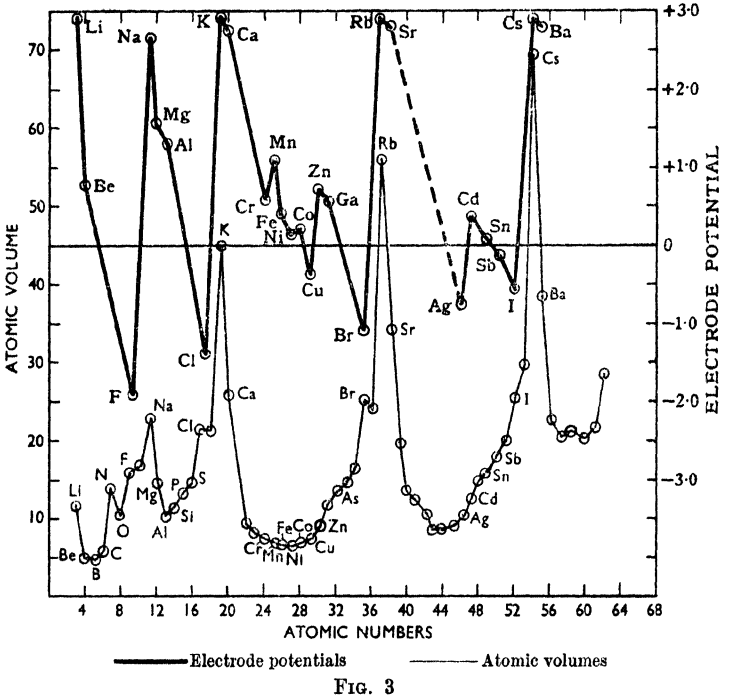


FIG. 3

the probable explanation of this property of lithium is the stability of its hydrated ion.

Likewise, the low atomic volumes of oxygen, the halogens, copper, and silver correspond to their negative electrode potentials, presumably because considerably more energy is required to bring about their ionization than is the case for the elements mentioned previously.

However, the surprising elements are: beryllium; aluminium; the transition elements, such as cobalt, manganese, iron, nickel, and chromium; zinc; cadmium; and tin. All these elements have positive electrode potentials, while having low atomic volumes. The low atomic volume would be expected to involve the expenditure of a relatively large amount of energy in order to bring about ionization, thereby giving rise to negative electrode potentials comparable to those of copper, silver, and the halogens. The explanation of this anomaly is probably the high heat of hydration of the ions of these metals. The resulting stability of the ions increases the energy required to remove the water of hydration when an ion from the solution enters the crystal lattice of the metal, and this decreases the rate of process *B* referred to in Fig. 1 and on page 61. So far as reactions involving the ionization of these metals are concerned they are fairly reactive; for instance they displace hydrogen from acids, and displace from solution all the metals with lower electrode potentials. In many other respects, however, they are weak metals, having in most cases covalent chlorides, and low heats of formation of the oxides (except aluminium). These latter properties would not be predicted from the electrode potentials.

A completely safe prediction, of course, is that any metal will displace from solution any other metal with a lower positive, or more negative, electrode potential *provided the solution of the other metal is sufficiently concentrated*. This will be mentioned again.

There is a rough correlation between electrode potentials and the heats of formation of the oxides, though there is no obvious explanation of this fact, since the energy of hydration of the ions is involved in electrode potentials, but not in the formation of the oxides.

Application of Electrode Potentials in Electrolysis

In Chapter I the problem of why some acid radicals are liberated at the anode during electrolysis, whereas others are not, was not solved. This can now be done, for the key to its solution is a consideration of the discharge potentials for the anions. As an example the electrolysis of a cupric sulphate solution with a copper anode will be considered. At the anode any of three things may happen: sulphate ions be discharged, hydroxyl ions be discharged, or copper ions pass into the solution from the anode. The potentials for these three processes are approximately 2·0, 1·2, and 0·34 volts respectively. Hence, since least energy is thereby involved, the copper anode passes into solution in preference to either of the two alternative processes. On the other hand, if the anode is made of platinum, hydroxyl ions are liberated, with the ultimate formation of oxygen and water:

$$4OH' \rightarrow 2H_2O + O_2 + 4 \text{ electrons.}$$

It is interesting that the hydroxyl ions are discharged in spite of their very low concentration: cupric sulphate solution is slightly acidic so that the concentration of hydroxyl ions is less than 10^{-7} gm.-ions per litre.

An instructive example of electrolysis is that of hydrochloric acid at various concentrations. At a platinum anode the results are as follows:

Very dilute acid: hydroxyl ions are liberated, giving oxygen.

Medium concentration of acid: hydroxyl ions and chloride ions are liberated, giving a mixture of chlorine and oxygen.

Concentrated acid: chloride ions only are liberated.

In the very dilute acid (nearly pure water) the chloride

ions are so dilute that the potential required to liberate them is greater than that required to liberate hydroxyl ions. In the medium concentration of acid the discharge potential is approximately the same for both ions, and in the concentrated acid it is less for the chloride ion than for the hydroxyl ion.

The above example illustrates the effect of concentration on discharge potentials for anions. The same principle can be used for discharging two different metals at a cathode, forming alloys. As an example the formation of brass will be considered.

The electrode potentials for copper and zinc are respectively $-0{\cdot}34$ and $+0{\cdot}76$ volts, from which it is obvious that in solutions of copper and zinc salts of any reasonable concentrations only copper will be liberated at the cathode by electrolysis. If the concentration of the copper ions were to be reduced by dilution sufficiently to bring the discharge potential to that for zinc there would be virtually no copper in solution. However, if a soluble cyanide, such as sodium cyanide, is added to mixed solution of copper and zinc salts, complexes of both metals are formed. These complex ions are in equilibrium with cyanide and metallic ions:

$$Cu^{\cdot} + 2CN' \rightleftharpoons Cu(CN)_2'$$
$$Zn^{\cdot\cdot} + 4CN' \rightleftharpoons Zn(CN)_4''.$$

Of the two complex ions that of copper is the more stable, and this makes it possible to add sufficient excess cyanide to bring the discharge potentials of copper and zinc nearly to the same value. By mass action the excess of cyanide ions displaces both equilibria towards the formation of the complex ions, but that for copper is displaced much more than that for zinc. The resulting reduction in concentration of copper ions relative to that of zinc ions increases the discharge potential of copper

relative to that of zinc, until they both become comparable. If the two discharge potentials are nearly the same, copper and zinc are deposited together to give a brass, and by altering the concentration of cyanide it is possible to control the composition of the brass deposited. The anode in such plating baths is brass, from which both metals pass into solution.

In these cyanide solutions the discharge potentials of copper and zinc are not quite equal to each other, but in electrolysis change in current density brings about a further change in their relative values. This effect is shown by the following figures.[1]

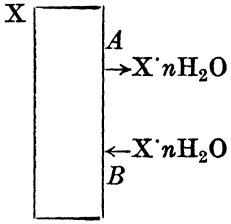
Current Density amps. cm.$^{-2}$	*Deposition Potential in Volts*			
	$N.CuSO_4$	$0{\cdot}1N.KCu(CN)_2$	$N.ZnSO_4$	$0{\cdot}1N.K_2Zn(CN)_4$
0	−0·302	+0·61	+0·795	+1·033
0·001	−0·273	+0·77	+0·829	+1·12
0·003	−0·262	+1·12	+0·838	+1·25

The above table shows that the discharge potential rises with current density, which is a common phenomenon. The probable explanation of this is that during electrolysis the concentration of the ions being liberated falls in the immediate neighbourhood of the electrode. As a result of the concentration gradient thereby set up the supply of ions to the electrode is maintained by diffusion from the remainder of the electrolyte, but inevitably the concentration adjacent to the electrode surface is considerably reduced. This, of course, raises the discharge potential (i.e. makes it more positive, or less negative). This phenomenon is frequently important in electrolysis: for

[1] See Spitzer, *Zeit. Electroc.*, **11**, 345.

instance it partly accounts for the liberation of sodium at the mercury cathode in the Castner–Kellner cell for manufacturing sodium.

Finally, it is important to get a correct mental picture of the state of affairs at an electrode where ions are being liberated during electrolysis. As was described earlier, at any metal surface there is set up an equilibrium between the two opposite processes, the formation and liberation of ions:



During electrolysis the applied potential difference between the solution and the electrode upsets the equilibrium by increasing the rate of process *B*, and decreasing that of process *A*. This results in the *nett* liberation of ions. It is important to realize that the direct cause of the liberation of the ions is the thermal movement, *not* the migration of the ions due to their carrying the current through the solution. The migration of the ions no doubt causes some of them to be liberated, but the thermal movement probably causes by far the greater number. Thus the *nett* liberation is probably due to a relatively slight upset of the rates of the two processes *A* and *B*.

Strictly speaking, therefore, it is probably incorrect to say that, for instance, during the electrolysis of a solution of a sodium salt no sodium ions are liberated at the cathode. Owing to thermal movement presumably a number of sodium ions are momentarily liberated, but they immediately pass back into solution. Hydrogen ions are also liberated by thermal movement. However, when

the voltage is applied to the electrode it is sufficient to alter the equilibrium of the hydrogen ions in favour of nett liberation, but in the case of the sodium ions it is not great enough to do so. Similar reasoning applies to the anode when considering the liberation of anions.

Electrode Potentials and Heats of Formation of Oxides

	* *Electrode Potentials Volts at 25°C.*	† *Heat of Formation of Oxide K.cal. per 8 gm. of oxygen*
Li	+3·01	−71·2
Rb	+2·98	−39·9
Cs	+2·92	−37·9
K	+2·92	−43·2
Ba	+2·92	−66·7
Sr	+2·89	−70·5
Ca	+2·84	−75·9
Na	+2·71	−49·7
Mg	+2·38	−71·8
Be	+1·7	−73·0
Al	+1·66	−66·7
Mn	+1·06	−46·0 (MnO)
Zn	+0·76	−41·5
Cr	+0·71	—
Fe	+0·44	−32·7
Cd	+0·40	−30·4
Co	+0·27	−28·6
Ni	+0·23	−29·2
Sn	+0·14	—
Pb	+0·13	—
Cu	−0·34	−18·5 (CuO)
Hg	−0·80	−10·8
Ag	−0·80	−3·6
Pt	−1·2	—
Au	−1·42	—
OH′	−0·40	
I′	−0·54	
Br′	−1·07	
Cl′	−1·36	
F′	−2·85	

* Bockris *et al.*, *Discussions of the Faraday Society*, 1947.

† National Bureau of Standards, Circular 500, Washington.

CHAPTER VI

CLASSIFICATION OF ELEMENTS AS METALS AND NON-METALS

The study of Chemistry inevitably involves a large number of facts being assimilated. In any case this is a very great burden on the memory, but this burden can be greatly reduced by having clearly in mind a scheme for the study of any group of elements in the Periodic Table. The student then knows the main points to consider when he is studying the Chemistry of any particular element or group of elements. On this framework he can hang his facts. It is the object of this chapter to provide such a framework, and it will be used in later chapters when some of the individual groups of elements in the Periodic Table are being considered.

Obviously there is very little difficulty in distinguishing between a very definite and strong non-metal and a strong metal. Not only are the physical properties entirely different, but also the chemical ones are too, and little confusion can arise. However, when metalloids or very weak metals are being considered the problem is very much greater, and this summary is intended mainly for the purpose of sorting out these difficult metals.

Elementary though it may seem, the physical properties are well worth considering, for they frequently help to give the right picture of an element in the mind. However, by themselves they are wholly inadequate, and it is necessary to consider certain compounds of the element quite carefully. By far the most important compounds to consider are the oxides, chlorides, hydrides, sulphides, and any

complex ions which the element may form. These will now all be considered in turn.

Physical Properties

Metals are malleable, ductile, conduct electricity and heat well, and have what we call a metallic sheen. In addition the density is usually high. Definite non-metals have properties opposite to all of these, though the metalloids have some of the properties of metals and some of non-metals. On the other hand metals which one would call weak, such as aluminium and zinc, have the physical properties of good metals, but some of their chemical properties are those of non-metals. For instance aluminium and zinc both have covalent chlorides, and zinc readily forms complexes as negative ions.

Chemical Properties

By far the most important chemical property to be investigated is the electrode potential. With certain exceptions, a high positive electrode potential indicates a vigorous metal, and a low positive potential, or a negative one, indicates either a weak metal, or of course a non-metal. However, as was explained when electrode potentials were being discussed, there are certain outstanding exceptions to this. For instance, aluminium and zinc both have high positive electrode potentials, and yet a lot of their chemistry suggests that they are comparatively weak metals: in fact in many ways they are weaker than the transition elements such as iron, nickel, cobalt, and manganese, most of which have lower electrode potentials.

Oxides

So far as oxides are concerned the elements can be divided into four types as follows:

Elements whose Oxides are entirely Basic

These oxides react with acids to form salts and water, and they are the oxides of the strongest metals, which in the Periodic Table comprise Groups 1A and B, 2A and magnesium, and a number of the transition elements, for instance nickel and cobalt.

Elements whose Oxides are Acidic

Acidic oxides are characteristic of non-metallic elements, and they are the anhydrides of acids. They are the oxides of boron, the elements in Group 4 except for tin and lead, the elements in Group 5 except for antimony and bismuth, and all the elements in Groups 6 and 7 of the Periodic Table.

Elements whose oxides are Amphoteric

The oxides of this group react with acids to form salts, and with bases (fused if necessary) also to form salts. Thus under certain circumstances they are acidic, and under other circumstances they are basic. The elements which form these oxides are all called metals, and they are those metals which were left out of the list in the first category of oxides, namely: Group 2B, aluminium, tin, lead, antimony, and bismuth.

Elements which have Oxides of Two or more Kinds

In the case of those transition elements which have only two oxides the lower one is basic and the higher one amphoteric. For example ferrous oxide is basic, and ferric oxide is amphoteric.

In the case of those transition elements which have more than two oxides the lowest ones are basic, the next higher

ones are amphoteric, and the highest are acidic. For example manganous and chromous oxides are basic, manganic and chromic oxides are amphoteric, and the higher oxides of both these elements are acidic.

Hydrides

There are three main groups of hydrides as follows:

Saline Hydrides

Very strong metals react with gaseous hydrogen to form white solids with high melting-points, in which the metallic ions are positive and the hydrogen ions are negative. Thus in these compounds hydrogen is resembling a halogen. They conduct electricity when fused, and hydrogen is liberated at the anode. They all react very violently with water, but in other respects they are stable. The metals which form these hydrides are the whole of Group 1A, the elements calcium, strontium, and barium, and the rare earths.

Covalent and Acidic Hydrides

This group of hydrides is by far the largest. The elements which form them are Groups 3, 4, 5, 6, and 7, in the Periodic Table. As is well known, the hydrides of the elements in Group 7 are all strongly acidic, and those of Group 6 are weakly acidic (e.g. water and hydrogen sulphide). The hydrides of nitrogen, phosphorus, arsenic, silicon, tin, and boron, and some of the hydrides of carbon, are derived from metallic compounds of these elements by hydrolysis. This reaction suggests that the metallic compounds are of the nature of salts of these hydrides. On the other hand the hydrides are not acidic in water: in fact most of them are insoluble. Some nitrides and phosphides give on hydrolysis, respectively, ammonia and

phosphine, and these compounds also behave as though they are salts of ammonia and phosphine respectively, yet the hydrides ammonia and phosphine are basic.

Hydrides Which are Like Alloys

The best-known metal to form an alloy with hydrogen is of course palladium, but a number of the transition elements together with copper, silver, gold, cadmium, and zinc, will also do the same thing. The properties of this type of alloy are not very interesting or important.

Chlorides

Though the properties of the chlorides are very varied, they can be divided into two main groups with a somewhat complicated transitional type between them. The two main groups consist respectively of the chlorides of strong metals, and those of the non-metals. The chlorides of transitional type are those of the weak metals.

Ionic Chlorides

The chlorides of strong metals are all ionic in the solid state, and in solution. The solids have high melting-points and boiling-points, and the majority of them are soluble in water to give solutions which are neutral. The metals whose chlorides are of this type are those in Group 1A, together with lithium and sodium, and the elements in Group 2A, together with magnesium. With the exception of copper, silver, and gold all these can be described as strong metals. Being ionic, all these chlorides conduct electricity when fused.

Covalent Chlorides

The elements whose chlorides are covalent are all the non-metals, together with beryllium, those in Group 2B,

some of the transition elements, and aluminium. Thus it will be seen that this group of chlorides contains non-metals on the one hand and certain weak metals on the other, and for this reason the group can be sub-divided into two sections: the covalent chlorides of the non-metals, and those of the weak metals.

Chlorides of the Non-metals

Most of the chlorides of the non-metals are liquids or gases at room temperature. With the exception of those of carbon, all of them are hydrolysed by water to give hydrogen chloride and an oxy-acid of the non-metal. For example phosphorus trichloride and silicon tetrachloride hydrolyse as follows:

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl.$$

Chlorides of Weak Metals

Some weak metals have covalent chlorides only in the anhydrous state, some being liquids, and others being solids due to co-ordinate links being formed between the molecules themselves. This type of chloride reacts, usually violently, with water, to give a hydrated salt consisting of hydrated metallic ions and chloride ions. In solution in water these hydrated metallic ions are acid due to the fact that they ionize to give hydrogen ions. Examples of this type are the chlorides of aluminium, zinc, and cadmium. The result of hydrolysis in the case of aluminium is given below:

$$AlCl_3 + 6H_2O \rightarrow Al^{\cdots}6H_2O + 3Cl'.$$

Another type of weak metal has two kinds of chloride: the lower chloride is ionic and neutral in solution, and the higher chloride is covalent, and with water behaves like

the type mentioned above. This type of metal is found among the transition elements (for instance iron), and tin and lead behave in the same way.

Another characteristic of the weak metals which have covalent chlorides is that the hydrated chlorides when heated to dryness suffer complete hydrolysis and give either an oxychloride or the oxide of the metal, and hydrogen chloride. For example, this happens when the hydrated chlorides of aluminium, zinc, cadmium, ferric iron, and tin are heated strongly. This fact is particularly useful because it can be tested for in the laboratory in a few minutes, merely by heating some of the hydrated chloride in a test-tube. This does not happen with the hydrated chlorides of strong metals, i.e. those in Groups 1 or 2A: in the case of these chlorides strong heating gives rise to the anhydrous chlorides and water. On the other hand the hydrated higher chlorides of some of the transition elements, on being strongly heated, do two things: part of the salt decomposes to anhydrous chloride and water, and some of it is hydrolysed to give the oxide and hydrogen chloride.

Sulphides

For the most part the sulphides of the elements do not provide very much information about the strength of metals. The sulphides of Groups 1 and 2A are all soluble in water, whereas the sulphides of the rest of the metals are insoluble, and the majority are entirely neutral. However, the sulphides of arsenic, antimony, and tin are acidic in that they react with alkalis and dissolve, or will react with ammonium sulphide, and pass into solution as thiosalts. For instance the two sulphides of tin react in the following way with ammonium sulphide, and ammonium polysulphide respectively.

In the case of stannous sulphide:

$$SnS + (NH_4)_2S_2 \rightarrow (NH_4)_2SnS_3$$

or

$$SnS + S_2'' \rightarrow SnS_3''.$$

And in the case of stannic sulphide:

$$SnS_2 + (NH_4)_2S \rightarrow (NH_4)_2SnS_3$$

or

$$SnS_2 + S'' \rightarrow SnS_3''.$$

This property is of value in distinguishing between the sulphides of arsenic, antimony, and tin, and the rest of the sulphides in Group 4 of the Analysis Tables.

Formation of Complex Ions

Another property to look for when dealing with weak metals is whether or not the metals form complex ions in the negative radicals. Common ones to look for are complexes with chlorides and cyanides, and the following examples illustrate what is meant:

$$CuCl_2 + 2Cl' \rightleftharpoons CuCl_4''$$

$$Zn(CN)_2 + 2CN' \rightleftharpoons Zn(CN)_4''$$

$$Mg'' + 3Cl' \rightleftharpoons MgCl_3'$$

$$Cu(CN) + CN' \rightleftharpoons Cu(CN)_2'.$$

For convenience a summary of these facts is given opposite.

	Strong Metals	Non-Metals	Weak Metals
Electrode Potentials	Large positive values. Form positive ions. Examples: alkali metals, and alkaline earths.	Form negative ions.	The majority of the transition elements have small positive values, though manganese is an exception. Other weak metals may have large positive values (e.g. aluminium), or negative ones (e.g. copper, silver, gold).
Oxides	Entirely basic. Examples: alkali and alkaline earth metals.	Entirely acidic, or neutral. Examples: sulphur, phosphorus, nitrogen, chlorine, carbon.	Usually amphoteric. Examples: aluminium, zinc, tin. Sometimes basic. Examples: copper, silver, gold, nickel, cobalt. Some transition elements have lower oxides basic, higher ones amphoteric or acidic. Examples: iron, chromium, manganese.
Hydrides	Saline. Ionic, with hydrogen as negative ions. Examples: alkali and alkaline earth metals.	Covalent. The hydrides of the strongest non-metals are acidic. Examples: HCl, SiH_4, NH_3, H_2O.	Absent, or of an alloy type. Examples: iron, copper, palladium.
Chlorides	Ionic. Soluble in water to give neutral solutions. Hydrated solids give anhydrous chlorides on heating. Examples: alkali and alkaline earth metals.	Covalent. Most are hydrolysed to oxy-acids of the non-metal and hydrochloric acid. Examples: NCl_3, PCl_3, $SiCl_4$.	*Type A:* Covalent. Hydrolyse to hydrated ions, which are soluble to give an acid solution. Solid hydrated salts give oxide or oxychloride of the metal and hydrogen chloride on heating. Examples: aluminium, zinc. *Type B:* Lower chlorides are ionic, and give neutral solutions. Higher chlorides are covalent, and behave like those of Type A. Examples: iron, chromium, tin, lead. *Type C:* Ionic, but form acid solutions. Examples: copper, silver, nickel, cobalt.
Complex Ions	Do not form complex ions.	Do not form complex cations, but they form many complex anions. Examples: S_2'', SO_4'', CO_3'', SiF_6'', SiO_4''''.	Form complex anions, commonly with Cl′, and CN′. Examples: $SnCl_6''$, $PbCl_4''$, $CuCl_4''$, $Zn(CN)_4''$, $MgCl_3'$. Also form ammines with ammonia, and hydrated ions with water. When heated many of these hydrated salts decompose to the oxide of the metal. Examples: $Cu''4NH_3$, $Cu''4H_2O$, $Fe'''6H_2O$, $Al'''6H_2O$.

CHAPTER VII

THE PERIODIC TABLE

As is well known, the Periodic Table results from arranging the elements in groups. The first person to do this was Mendeleev, but the most convenient form of it is the one introduced by Bohr, which is given below. In the first series the *L* level of electrons is going from 1 in lithium to 8 in neon. These elements are usually peculiar relative to the other elements in the same group because they have low atomic volumes, and also the maximum number of covalent and co-ordinate links which any of these elements can form is 4, whereas in all other elements it is at least 6 and sometimes 8. This last fact sometimes makes a very considerable difference to the reactiveness of the compounds of these elements, compared with those of the corresponding elements in series 1. One result of the low atomic volumes is that there is an oblique relationship which will be explained later.

In the second series the *M* level of electrons rises from 1 in sodium to 8 in argon, and these are known as typical elements of the groups. Their atomic volumes are considerably larger than those of the corresponding elements in series 1, and as a result all these elements are more metallic than the corresponding ones in series 1, or alternatively weaker as non-metals, as the case may be.

These two series constitute the first type of elements, in which the outer group of electrons is being built up from 1 to 8, ending in each case with an inert gas. The inner levels of electrons are complete in all these atoms.

In series 3 and 4 there is a different thing happening.

Two levels of electrons are incomplete and are being filled in these series: to explain this we will consider series 3. Potassium and calcium add respectively one and two electrons to the *N* level. However, scandium, instead of adding a third electron to the *N* level, adds one more to the *M* level. This process continues right through until copper is reached, by which time the *M* level has been built from 8 to 18, and the *N* level has gone back to 1. In the rest of the elements from zinc to krypton this *N* level is built up to 8, as in the previous two series. In the fourth series corresponding things are happening to the *N* and *O* levels, and these elements are very similar to the corresponding ones in series 3. Those elements in which the outer but one level of electrons is being built up are the transition elements, and of course their best-known characteristic is the variable valency, which usually varies from 2 to 3; they also have many other characteristics in common, including the fact that their salts are coloured.

In series 5 exactly the same thing happens as far as lanthanum. However, from cerium to lutecium, instead of the inner level of electrons being increased, the inner but one is increased from 18, which it attained in silver, to 32, which is attained in lutecium. After this, starting with hafnium and ending with gold, the outer level but one is again built up to 18. Then, finally, from mercury to radon the outermost level of electrons is built up to 8. The elements from cerium to lutecium are known as the Rare Earths, and the chemistry of all these elements is exceedingly similar: this constitutes a special type on its own.

The transition elements, which are the ones in which the outer group but one of electrons is being increased from 8 to 18, are enclosed in a framework in the table. These also constitute a special type.

Throughout this table similar elements are joined by

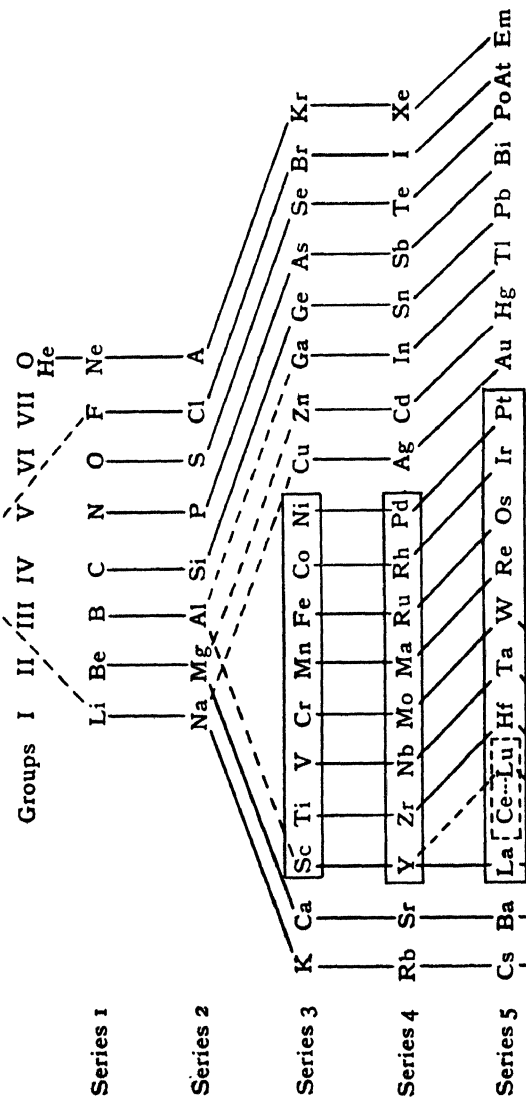

Groups I II III IV V VI VII O
Series 1
Series 2
Series 3
Series 4
Series 5
Series 6
H
He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Ma Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La [Ce...Lu] Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi PoAt Em
Fr Ra Ac Th Pa U Np Pu Am Cm

Fig. 1

lines, some of which are solid, and others dotted. The solid lines join the elements which are most closely related to each other; the dotted lines indicate less close resemblances. For instance, in Group 1 the main relationship runs lithium, sodium, potassium, rubidium, and cæsium, and there is a less close relationship between sodium and copper, silver, and gold. The portion potassium, rubidium, cæsium is known as the A sub-group, and that containing copper, silver, and gold as the B sub-group. This nomenclature is used throughout the table, i.e. the portion of the group which is to the right of the typical element is called the sub-group B, and the elements which are to the left are known as sub-group A.

Trends in the Periodic Table

The valencies increase with the groups from left to right until Group 4 is reached: after this the valency decreases again. Thus Group 1 is monovalent, Group 2 divalent, Group 3 trivalent, Group 4 tetravalent, Group 5 trivalent, Group 6 divalent, and Group 7 monovalent. Group 0, consisting of the inert gases, has the valency of zero.

With the exception of sub-groups 1B and 2B, the elements increase their vigour as metals, or decrease their vigour as non-metals, which amounts to the same thing, on going from the top of any group to the bottom. For example, in Group 2, beryllium, magnesium, calcium, strontium, and barium all have positive electrode potentials, and the values of these potentials increase steadily in that order. On the other hand in Group 7, which consists entirely of non-metals, the vigour of these elements as non-metals decreases progressively through fluorine, chlorine, bromine, and iodine: this is shown not only by the energy involved in their reactions with other elements, but also in their electrode potentials. As Groups 1B and 2B are descended the elements in them become less

vigorous as metals, and all these elements are much weaker as metals than the members of their respective A sub-groups. Two other definite examples of this trend are worth noting. Group 4 consists of the non-metals carbon, silicon, germanium, followed by the two weak metals tin and lead. Likewise in Group 5 we have the non-metals, nitrogen, phosphorus, and arsenic, followed by an exceedingly weak metal antimony, and a less weak one in bismuth.

The Trends on Going Across the Series

The trends here differ in different parts of the Periodic Table. First of all we can consider series 1 and series 2. In series 1 we have first two metals, lithium and beryllium, followed by the non-metals boron, carbon, nitrogen, oxygen, and fluorine, all of which are increasingly vigorous as non-metals. Thus we can say that across this series we go from a fairly strong metal in lithium to a very vigorous non-metal in fluorine; i.e. the trend is decreasing strength of metal, or increasing strength of non-metal.

Series 2 behaves in almost exactly the same way as series 1, except that in Group 3 we still have a metal in aluminium, though a weak one, and the first non-metal that we meet is in silicon. Furthermore, the metals in this series are stronger as such and the non-metals weaker than the corresponding elements in series 1.

In series 3 we have the same trend as is found above, except that in the middle we get the transition elements. Omitting these for the moment, the trend is increasing strength as non-metals, or decreasing strength as metals through potassium, calcium, copper, zinc, gallium, germanium, arsenic, selenium, bromine. The transition elements, which occur in the middle of this series, are all very closely similar in their main characteristics, and they

are all weak metals. However, as will be seen later they are rather characteristic of themselves only, and as weak metals they are not very similar to other weak metals in the Periodic Table.

Series 4 is very similar to series 3, and in most respects so is series 5, except that in this case towards the left-hand end of the transition elements we have the rare earths extending from cerium to lutecium.

The Oblique Relationship

In the first two series, at the left-hand end, there is a peculiar oblique relationship as follows: lithium resembles magnesium, beryllium resembles aluminium, and boron resembles silicon. These pairs of elements resemble each other in their general chemistry, though of course they have not got the same valencies. This oblique relationship ceases with boron and silicon. There is little resemblance between carbon and phosphorus or between nitrogen and sulphur.

The Transition Elements

It is not necessary at this stage to go into any detailed chemistry of these elements, but it should be noted that they all have common characteristics of variable valency and coloured salts. Furthermore, they are all what would be called weak metals. Several of them, such as iron, chromium, and manganese, have two chlorides, the lower of which is ionic and the higher covalent. They also have their lower oxides basic and their higher ones either amphoteric or entirely acidic. The detailed chemistry of each of these elements must be considered carefully on its own, but it is worth noting these general properties in passing.

It is now proposed to summarize the main chemical

characteristics of each group of elements in turn. These summaries, of course, will cover only the main characteristics without giving undue detail, but they will be done on the lines laid down in Chapter VI, that is to say the main subjects considered will be: electrode potentials, oxides, hydrides, chlorides, formation of complex ions, and the solubility of the sulphates and sulphides. Since all nitrates are soluble, there is no need to mention this again.

The real object of these summaries is to try to arrange the main data in the same order for each group of metals, so that the task of committing to memory the facts will be reduced to a minimum. A number of properties are common to all the elements in the same group, and it is a complete waste of effort to learn these separately for each element in turn, because it simply means a repetition and a corresponding burden on the memory.

It is proposed first of all to consider Group 1A, since this is characteristic of the really strong metals. This will be followed by a consideration of Group 7, which is a group of very strong non-metals: thus these two will form a great contrast with each other, and it makes better sense when the other groups are considered afterwards. Throughout these summaries only the common elements will be considered; the unusual ones, which are usually not studied at an early stage, will be omitted. Thus, for instance, only boron and aluminium will be considered in Group 3, and of the transition elements only iron, manganese, and chromium will be considered. It is not proposed to include much detail on boron.

CHAPTER VIII

GROUP 1: THE ALKALI METALS

These metals are all so very similar that it is not necessary to include a very great deal of information in the summary. They form a family of active metals whose activity increases in the order: lithium, sodium, potassium, rubidium, and cæsium. This is shown by the electrode potentials, all of which are high positive values, and also by the vigour with which these metals react with other elements. The most important metals from a practical point of view are, of course, sodium and potassium. Lithium, rubidium, and cæsium are very much less important and also rarer, so very little need be said about them. Table I gives a summary of the most important properties of this group.

The main points concerning respectively the metals, oxides, hydrides, and chlorides are as follows:

Metals

All these have very high positive electrode potentials, and this means, of course, that they displace hydrogen from all acids, including water. Sometimes the reaction is so vigorous that the hydrogen is ignited in the air and the metal itself catches fire. Likewise these metals react very vigorously with other elements; for instance with chlorine and oxygen.

Uses of Metals

Cæsium has a small use in photo-electric cells, but apart from this the only important metal from a practical point of view is sodium. Sodium metal is made in considerable

TABLE I.—SUMMARY OF GROUP 1

	Atomic Volume	*Electrode Potential*[1]	*Melting-point of Chloride*[2] °C.	
Li	11·8	+3·01	610	Differs from the other alkali metals in that its carbonate, fluoride, and phosphate are not very soluble in water. Also the hydroxide goes to the oxide on heating, and the chloride is soluble in some organic liquids. The nitride is formed readily direct from nitrogen.
Na	22·9	+2·71	808	The salts of all common acids are soluble in water. None of the hydrated ions is acidic in solution, no complexes with ammonia or with negative ions are formed. The carbonates do not decompose unless they are heated very strongly; nor do the hydroxides. Potassium salts are essential for plants, and they are adsorbed by soil: sodium salts are not adsorbed by soil. Rubidium and cæsium are relatively rare.
K	45·3	+2·92	772	
Rb	56·2	+2·98	717	
Cs	70·4	+2·92	645	

All the metals in this group form two oxides: X_2O and X_2O_2. They all form hydrides and nitrides.

[1] From Bockris *et al.*, *Discussions of the Faraday Society*, 1947.
[2] Data taken from National Bureau of Standards, Circular 500, Washington.

quantities, and a great deal of it is used in organic syntheses: for instance it is used for making acetoacetic ester. The other important use is for making sodium cyanide, which is needed in large quantities for the extraction of gold, and also for organic syntheses.

Experiments have been tried in which metallic sodium is inside a metal tube used as an electrical conductor, but

so far this has not reached a large-scale commercial production. Metallic sodium is also used in the hollow stems of the valves of aero-engines, in order to conduct the heat from the head of the valve down to the stem. In use the sodium melts and swishes up and down the stem as the valve oscillates, thereby cooling the valve head and conveying the heat to the stem. This enables the valves to be run safely at a temperature which would be impossible without the aid of the sodium.

Oxides

All these metallic oxides are basic, and soluble in water to give alkaline solutions of hydroxides.

All the metals will form peroxides, which are salts of hydrogen peroxide: this is liberated from them by acid. Sodium peroxide is used to a certain extent for bleaching.

Hydrides

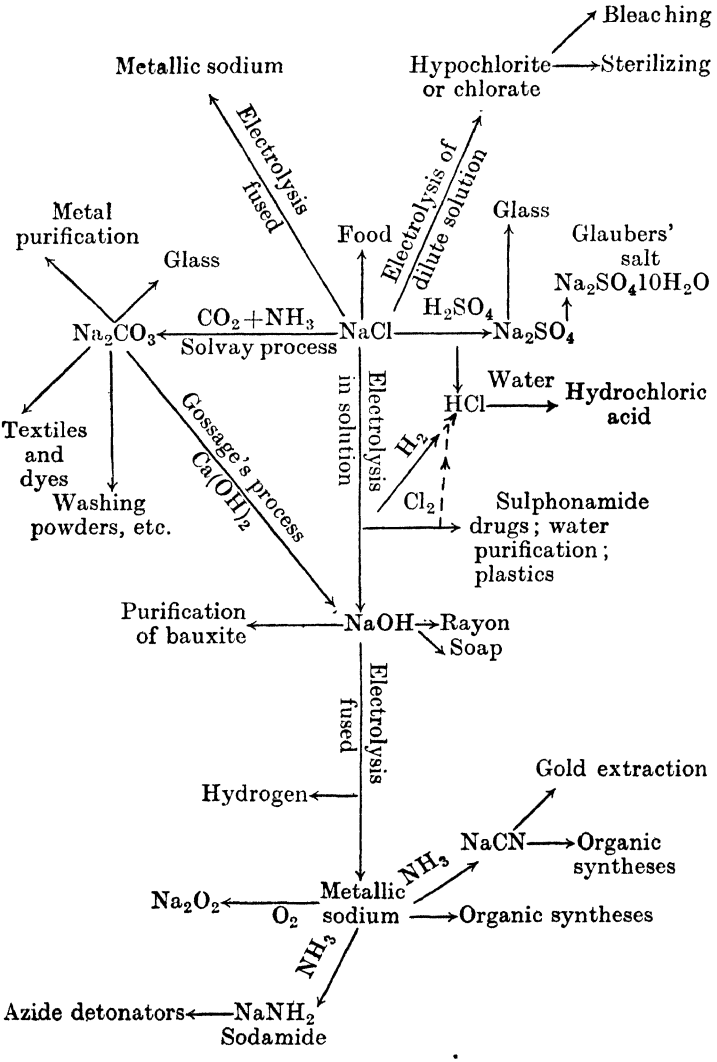
All of these metals form hydrides in which the hydrogen is a negative ion. They are all ionic compounds with high melting-points, and decompose readily with water to give off gaseous hydrogen, leaving behind the metal hydroxide.

Chlorides

All the chlorides of these elements are ionic, and they are soluble in water to give neutral solutions. On evaporation these solutions give the anhydrous salt in all cases except that of lithium chloride, which to a small degree is hydrolysed to give a small proportion of lithium hydroxide and hydrogen chloride.

The following table shows diagrammatically the products from sodium chloride and their uses.

INDUSTRIAL USES FOR SODIUM CHLORIDE, AND DERIVATIVES



N.B.—Most sodium is now manufactured by the electrolysis of fused sodium chloride.

USES OF OTHER SODIUM AND POTASSIUM SALTS

Other sodium salts which are of commercial value are the following:

Sodium nitrate

This occurs naturally in Chile, from which a large quantity is exported for agricultural purposes in order to provide nitrate in the soil. It is also made artificially at the works where the ammonia is synthesized from atmospheric nitrogen. This is done by reacting dilute nitric acid with sodium hydroxide, the resulting sodium nitrate being transported to places where nitric acid is required. From it concentrated nitric acid is generated by distillation with concentrated sulphuric acid. This avoids the dangerous procedure of transporting concentrated nitric acid. This artificial sodium nitrate is also used as a fertilizer.

Sodium nitrite

This is made entirely as a by-product of the manufacture of nitric acid by the oxidation of ammonia. At the end of the process for making dilute nitric acid the gases contain nitric oxide and nitrogen dioxide in equimolecular proportions. This mixture is washed with dilute caustic soda from which the sodium nitrite is recovered. It is used for making nitrous acid for synthesis of dyes.

Sodium thiosulphate

This is used for washing chlorine out of substances which have been bleached, and for photography.

Potassium Salts

Potassium perchlorate is used for flash-powders and explosives. Potassium iodide and bromide are used mainly for photography, and some bromide is used for medical purposes.

CHAPTER IX

GROUP 7: THE HALOGENS

Such properties of these elements as can be summarized in a tabular form are given in Table II.

This table shows that by and large chlorine, bromine, and iodine are extremely similar to each other. They all react very vigorously with most of the elements, and this activity increases in the order iodine, bromine, and chlorine, as is shown by the heats of formation.

On the other hand fluorine differs in many ways. The vigour with which fluorine takes on an extra electron is the cause of these differences, and also of the extreme activity of fluorine itself. It always causes other elements to exert their highest possible valency, and fluorine compounds as a whole are extremely stable. Apart from the fact that it does not form any oxy-acids, and that its action with water is quite different from that of the rest of the group, the other most important fact about fluorine is that it can form hydrogen bonds: it does so, for instance, in gaseous hydrogen fluoride, and even in solution much H_2F_2 is present. The solution is a weaker acid, and it ionizes to one hydroxonium ion and one ion consisting of HF_2': the dissociation of this ion is extremely small. Presumably the weakness of this acid is also due to the strength of the hydrogen–fluorine bond. Hydrofluoric acid is the only halogen acid which attacks silicates: it forms SiF_4, and to a certain extent the acid H_2SiF_6.

The other properties of these elements are best summarized under the following headings:

Electrode Potentials

All these elements form negative ions, and in the case of fluorine, chlorine, and bromine, as can be seen from the

TABLE II

	Atomic Volume	*Electrode Potential Volts*[1]	*Heat of Formation of HX in kilo.cal.*[2]	*Boiling-point of Hydride*[3]	*Action of element with water*	*Hydroxy Acids*	*Complexes*
F	16·7	−2·85	−64·20 Reaction explosive.	19·9°C.	$3F_2+3H_2O \rightarrow 6HF+O_3$ Equilibrium Constant for first stage of hydrolysis.[3]	None	None with oxygen. Forms many with weak metals, and with non-metals. Examples: SiF_6'', AlF_6''', BF_4'.
Cl	21·4	−1·36	−22·06 Reaction explosive in ultra-violet light.	−85·05°C.	$4{\cdot}5\times10^{-4}$	HClO $HClO_2$ $HClO_3$ $HClO_4$	Very common. Examples: ClO', ClO_2', ClO_3', ClO_4', $CuCl_4''$, $SnCl_6''$, $PtCl_6''$, $ZnCl_3'$, $MgCl_3'$.
Br	25·1	−1·06	−8·66 Reaction not explosive.	−66·73°C.	$5{\cdot}2\times10^{-9}$	HBrO $HBrO_3$	BrO', BrO_3'. Metal complexes similar to those of chlorine.
I	25·9	−0·54	+6·20 Reaction slow, unless at high temperature	−35·36°C.	3×10^{-13}	HIO HIO_3 HIO_4	IO', IO_3', IO_4', I_3'. Metal complexes similar to those of chlorine.

↑ Increasing stability to heat

↑ Hydrolysis similar ↓ $X_2+H_2O \rightleftharpoons H'+X'+HXO \rightleftharpoons 2H'+X'+XO'$.

[1] Figures taken from Bockris *et al.*, *Discussions of the Faraday Society*, 1947.
[2] National Bureau of Standards, Circular 500, Washington.
[3] *Z. physikal Chem.*, 1899.

electrode potentials, these ions are very stable. The stability of the iodide ion is smaller, and, as is well known, it is quite easily oxidized to iodine. Of these elements any one will displace from their solutions the elements which have lower electrode potentials. Most of the metals form ionic compounds with all of these elements, unless the metals are weak, in which case they form covalent chlorides, bromides, and iodides, but even then the fluorides are usually ionic.

Oxides

All four elements have oxides of formula X_2O. Chlorine and bromine also have oxides formula XO_2, which are the anhydrides of the acids HXO_3. With the exception of F_2O, which is not acidic, the oxides X_2O are the anhydrides of the acids HXO, namely: hypochlorous, hypobromous, and hypoiodous acids.

There are other oxides of these elements, but they are not very important.

Hydrides

All these elements form hydrides of the general formula HX, though in the case of hydrogen fluoride it is associated, even in solution, to at least H_2F_2. In the pure form at room temperature hydrogen fluoride is a liquid. In solution hydrofluoric acid dissociates mainly according to the following equilibrium, $H_2F_2+H_2O \rightleftharpoons H_3O^{\cdot}+HF_2'$. This is a weak acid for which the dissociation constant is approximately $2{\cdot}3\times10^{-5}$ at room temperature.

All the other hydrides are exceedingly soluble in water and are strong acids, that is to say they are totally dissociated in solution. The reaction with water can be represented by the general equation:

$$HX+H_2O \rightleftharpoons H_3O^{\cdot}+X'.$$

The hydrides of all the elements in this group in the

pure state are covalent, and with the exception of hydrogen fluoride are gases at room temperature. As will be seen from the table, all these hydrides, except hydrogen iodide, are exothermic.

Being endothermic, hydrogen iodide is not stable at room temperature, but at this temperature it decomposes only very slowly. If the temperature is raised slightly, for instance by putting into it a hot wire, the gas immediately decomposes with the evolution of a considerable amount of heat, sometimes causing the resultant hydrogen to ignite in the air. At first sight this appears to contradict Le Chatelier's principle, which would lead us to suppose that an increase in temperature would increase the yield of hydrogen iodide from hydrogen and iodine, whereas when warmed with the wire it quite obviously decomposes. The explanation of this is that the rise in temperature due to the hot wire increases the speed at which the gas attains equilibrium with hydrogen and iodine. Since at that temperature the amount of hydrogen iodide in the equilibrium mixture is negligible, the gas virtually decomposes, leaving only a very small proportion of hydrogen iodide in the mixture. If, as usually happens, the iodine itself condenses, of course this displaces the equilibrium still further, almost to completion.

Complexes

From the examples given in the table it is obvious that all of these elements form complexes with non-metals, and with weak metals such are innumerable. Chlorine, bromine, and iodine also form a number of complexes with oxygen, but fluorine does not do this.

The Lowest Oxyacids

With the exception of fluorine, all these elements react with water to give the hydroxy acids, hypochlorous, hypo-

bromous, and hypoiodous respectively. All of these acids, presumably in the unionized state, are strong oxidizing agents, and bring about many oxidations, including those which lead to bleaching of certain dyes.

If chlorine is passed into a solution of a strong alkali, the equilibrium between chlorine and the water is continuously displaced to the right:

$$Cl_2 + H_2O \rightleftharpoons H^{\cdot} + Cl' + HClO \rightleftharpoons 2H^{\cdot} + Cl' + ClO'.$$

The alkali neutralizes the hydrogen ions, giving finally a solution containing a mixture of chloride and hypochlorite. Since hypochlorous acid is a weak acid, the hypochlorite ions react with hydrogen ions from the water to form the equilibrium with unionized hypochlorous acid. Thus even in an alkaline solution there is a small concentration of unionized hypochlorous acid, and this slowly brings about the oxidation of hypochlorite ions to chlorate ions, according to the equation:

$$2HClO + ClO' \rightleftharpoons ClO_3' + 2H^{\cdot} + 2Cl'.$$

If the solution is near boiling-point this reaction takes place fairly quickly, and is virtually complete in about a quarter of an hour.

Corresponding reactions take place between alkalis and bromine, and also iodine. However, the rate of oxidation to bromate is considerably greater than that of oxidation to chlorate, and the rate of oxidation to iodate is even greater still. In solutions of the same strength, the rate of production of bromate is about a hundred times as great as that of the formation of chlorate, and the rate of production of iodate is nearly three million times as great. For this reason it is practically impossible to have a solution of hypoiodite for any practical purposes: such solutions invariably become iodate in a few moments.

Uses of Fluorine, Chlorine, Bromine, and Iodine

Fluorine

Fluorine is now used quite extensively. Polytetrafluoroethylene is a useful plastic in that it is self-lubricating, and other fluoro-hydrocarbons are useful where a very inert material is required, and as the working substance in refrigerators. Other fluorine compounds are used in insecticides and in dyes. Fluorine is also used for making boron trifluoride, which is much used as a catalyst in organic chemistry.

A solution of hydrofluoric acid is used for finishing glassware after it has been "cut" or etched. The acid dissolves off the surface of the glass and leaves it smooth and bright.

Large quantities of calcium fluoride are used as a flux in steel-making. It lowers the melting-point of the slag, and so "thins" it. Calcium fluoride is also used in "blooming" lenses, when a thin film of it on the surface of the lens reduces by interference the loss of light by reflection. Cryolite, $Na_3\ AlF_6$, is essential in the production of aluminium.

Chlorine

The largest present-day use for chlorine is for making the large range of sulphonamide drugs; considerable quantities are also used for making the phosphorus halides for use in organic syntheses, and also for making silicon tetrachloride, most of which is subsequently converted to silicones, which are very valuable for many purposes. Large quantities are also used for making plastics, the principal one being polyvinyl chloride.

A smaller but very essential use for chlorine is in the purification of drinking-water. The chlorine is mixed with the water in sufficient concentration to kill the

bacteria, and then after a sufficient time has elapsed for this to have been done the excess chlorine is neutralized by the required amount of sulphur dioxide, leaving finally an exceedingly dilute solution of sulphuric and hydrochloric acids.

$$HClO + H_2SO_3 \rightarrow HCl + H_2SO_4.$$

A certain amount of chlorine is used for bleaching purposes. The fabric to be bleached is put into a very dilute solution of chlorine in water, and the resulting hypochlorous acid brings about the bleaching action. An alternative bleaching solution, which is often used on a smaller scale, is produced by the electrolysis of a very dilute sodium chloride solution. If the products of electrolysis at the cathode and anode are properly mixed by good stirring this leads to a solution of sodium hypochlorite and sodium chloride. Hydrolysis of the hypochlorite ion gives rise to sufficient hypochlorous acid to act as a bleaching agent, and when the solution is exhausted it is simply re-electrolysed.

Bromine

The largest use for bromine is in making ethylene dibromide, which is mixed with petrols containing lead tetra-ethyl. During the combustion of the fuel in the engine the lead is removed as volatile lead bromide. If this were not done lead oxide would be formed and this would choke up the valves and exhaust ports of the engine. Smaller amounts of bromine are used for making bromides for organic syntheses and metallic bromides for use in medicine and photography.

Iodine

The uses for iodine are very numerous, but they are all comparatively small and most of them are connected with medicine.

CHAPTER X

GROUP 2: THE ALKALINE EARTH METALS, ZINC, CADMIUM, AND MERCURY

The main properties of these elements are summarized in Table III (pp. 128, 129).

From this table it will at once be seen that there is a very great change in properties between calcium and beryllium. There is a large drop in electrode potential, and in the melting-points of the chlorides, but above all in the equivalent conductivity of the fused chlorides. This is also shown by the fact that the chlorides of barium, strontium, calcium, and magnesium are ionic, whereas those below them in the table are covalent. Magnesium is peculiar in that for the most part it is similar to calcium, strontium, and barium, but in some respects it resembles beryllium, zinc, and cadmium, though this resemblance is never very close.

Mercury is so different from all other elements in this group that it is best thought of as being separate. In any case its chemistry is very much more complicated than that of any other element in this group.

There follows a very short summary of the properties of the main compounds of these elements. The properties of the compounds of barium and strontium are so similar to those of calcium that no special mention is made of them.

The Compounds of the Elements

Metals

With the exception of mercury all these metals have high, or very high, positive electrode potentials. As a

TABLE

	Atomic Volume	*Electrode Potential in volts*	*Melting-Point of Chloride*[1]	*Equivalent Conductivity of Fused Chloride*	*Heat of Formation of Oxide per gm.-atom of Oxygen (kilo cals.)*[1]	*Nature of Oxide*	*Hydrides*
Ba	39·0	+2·92[1]	962°C.	64·6	−133·4	↑ Basic ↓	BaH_2 ionic
Sr	34·5	+2·89[1]	875°C.	55·7	−141·1		SrH_2 ionic
Ca	25·9	+2·84[1]	782°C.	51·9	−151·9		CaH_2 ionic
Mg	14·0	+2·38[1]	714°C.	28·8	−143·7		MgH_2 Probably covalent.
Be	4·92	+1·70[1]	Sub-limes	0·086	−146	↑ Amphoteric ↓	BeH_2 Probably covalent.
Zn	9·2	+0·76[1]	275°C.	0·08	−83·17		ZnH_2 Structure uncertain
Cd	13·0	+0·40[1]	568°C.	0·08	−60·86		CdH_2 Structure uncertain.
Hg	13·9	−0·80 ($Hg^{\cdot\cdot}_2$)	277°C. ($HgCl_2$)	$2·5 \times 10^{-8}$ ($HgCl_2$) 40 (Hg_2Cl_2)	−21·68 (HgO)	Basic	HgH_2 Structure uncertain.

[1] National Bureau of Standards, Circular 500, Washington.

III.

Nitrides	*Chloride Structure*	*Solubility of Sulphides in Water*	*Solubility of Sulphates in Water*	*Solubility of Fluoride in Water*	*Solubility of Hydroxide in Water*	*Complex Ions*
Ba_3N_2	Ionic	Yes	No	No	↑ Increasingly soluble. Alkaline solution.	
Sr_3N_2	Ionic	Yes	No	No		$Sr^{\cdot\cdot}6H_2O$.
Ca_3N_2	Ionic	Yes	Very slight	No		$Ca^{\cdot\cdot}6H_2O$; $Ca^{\cdot\cdot}8NH_3$; $Ca^{\cdot\cdot}4C_2H_5OH$.
Mg_3N_2	Ionic	Yes	Yes	No		$Mg^{\cdot\cdot}6H_2O$; $Mg^{\cdot\cdot}6NH_3$; $MgCl_4''$.
Be_3N_2	Covalent	No	Yes	Yes		$Be^{\cdot\cdot}4H_2O$; BeF_4''; $Be^{\cdot\cdot}4NH_3$; and innumerable other complexes.
Zn_3N_2	Covalent	No	Yes	Yes	All *slightly* soluble to give alkaline solution.	$Zn^{\cdot\cdot}6H_2O$; $Zn^{\cdot\cdot}6NH_3$; $ZnCl_3'$; $Zn(CN)_4''$; and many other complexes.
Cd_3N_2	Covalent	No	Yes	Yes		$Cd^{\cdot\cdot}6H_2O$; $Cd^{\cdot\cdot}6NH_3$; $CdCl_3'$; $Cd(CN)_4''$; and many other complexes.
Hg_3N_2	Covalent $HgCl_2$ Ionic Hg_2Cl_2	No	Yes	Yes		Innumerable complexes.

result they all displace hydrogen from acids, and the majority of them displace it from water, under certain circumstances. Barium, strontium, and calcium, all displace hydrogen from water with considerable vigour. Magnesium and beryllium do so slowly, and zinc will only do so when the oxide film has been dissolved by alkali; thus zinc will dissolve in fairly strong alkali. Cadmium does not do this, and mercury does not attack water at all; nor does it displace hydrogen from any acids. When mercury reacts with nitric acid it is a case of oxidation of the metal by the nitric acid, and it has nothing to do with the displacement of hydrogen.

All these metals react fairly readily with the halogens, oxygen, and sulphur.

Hydrides

Calcium, strontium, and barium all form hydrides of the saline type in which the metallic ions are positive and the hydrogen ions are negative. The hydrides of the other metals in this group have only recently been discovered, and there is still some uncertainty about them.[1]

CHLORIDES

The chlorides of barium, strontium, calcium, and magnesium are all ionic, and they are all soluble in water to give neutral solutions. On evaporating to dryness the chlorides of barium, strontium, and calcium give the anhydrous salt; but in the case of magnesium, hydrolysis takes place leaving magnesium oxide and hydrogen chloride.

The chlorides of zinc, cadmium, and beryllium are all covalent in the anhydrous state; they dissolve in water to give hydrated ions, and when these solutions are

[1] See *J. Amer. Chem. Soc.* (1951), **73**, 4585; *Z. Naturforsch.* (1950), **5b**, 396, and (1951), **6b**, 461.

evaporated to dryness, hydrolysis takes place, giving rise to hydrogen chloride and usually the oxy-chloride on the way to forming th oxide. For example, in the case of zinc chloride, at the end of the evaporation the following reaction probably takes place:

$$ZnH_2O^{\cdot\cdot} + 2Cl' \rightarrow ZnO + 2HCl.$$

These three chlorides dissolve in quite a number of organic liquids, which would be expected in view of their covalent nature.

Mercurous chloride is ionic, and mercuric chloride is covalent in the solid state, and in solution in water it is a weak electrolyte. Both these chlorides sublime on being strongly heated. In the case of mercuric chloride this is because, being covalent, it is volatile; but in the case of mercurous chloride the action is considerably different. The salt splits up to a mixture of mercury and mercuric chloride, which on condensing recombines to form mercurous chloride.

$$Hg^{\cdot\cdot}{}_2 + 2Cl' \rightleftharpoons Hg + HgCl_2.$$

Oxides

All these elements form oxides of the formula XO, and with the exception of beryllium and mercury all of them form peroxides either anhydrous or in the hydrated form.

The oxides of barium, strontium, calcium, and magnesium are all basic, and they are all slightly soluble in water to form alkaline solutions. Their heats of formation are very high, with the result that they are difficult to reduce, and that is why these metals are usually produced by the electrolysis of the fused chlorides.

The oxides of beryllium, zinc, and cadmium are all amphoteric. Zinc oxide and hydroxide dissolve quite readily in alkali, though it is very doubtful what happens during this reaction; it is uncertain whether zincate is

formed in the excess alkali, or whether the zinc hydroxide passes into colloidal solution. If it is the former the reaction can be represented by:

$$Zn(OH)_2 + 2OH' \rightleftharpoons ZnO_2'' + 2H_2O.$$

There is similar doubt over the reaction of beryllium oxide and hydroxide with excess alkali.

Cadmium oxide and hydroxide will not react in this way in solutions of alkali, but cadmiates are formed by fusion of cadmium oxide and the alkali concerned. Zincates are formed in the same way.

The oxides of cadmium and zinc are more easily reduced than those of the other metals; both these metals can be formed from their oxides by reduction with carbon. On the other hand the metals reduce carbon dioxide, so that their oxides cannot be reduced by carbon monoxide.

The oxides of mercury, both of which are basic, are very easily reduced: in fact they are decomposed by heat alone.

Carbonates

Barium, strontium, calcium, and magnesium will all form neutral carbonates of the general formula XCO_3. On the other hand beryllium, zinc, cadmium, and mercury also form basic carbonates; and so will magnesium if the solution from which it is precipitated is slightly alkaline.

Sulphides

The sulphides of barium, strontium, calcium, magnesium, and beryllium are all decomposed by water, forming the metallic hydroxide and hydrogen sulphide. The sulphides of the rest of the metals in this group are all insoluble in water, and they do not react with either alkali or ammonium polysulphide to form thio-salts.

Complexes

Beryllium, zinc, cadmium, and mercury form innumerable complexes of various kinds. In the cases of barium, strontium, calcium, and magnesium, the complexes are very much less common, but the ions of all these metals form hydrates with water and ammines with ammonia. Beryllium, zinc, and cadmium form complexes very readily of the general formula XCl_3', and there is evidence for the formation of similar complexes, in solution only, with calcium, strontium, and barium.

Beryllium, zinc, and cadmium form with cyanide complexes of general formula $X(CN)_4''$. The other metals in this group do not do this.

Covalent Substances

Barium, strontium, and calcium do not form any covalent compounds, but on the other hand magnesium, beryllium, zinc, cadmium, and mercury all form covalent alkyl compounds, and mercury forms many other covalent compounds with organic substances.

Uses

From a practical point of view the metals in this group are exceedingly important. In the case of barium, strontium, and calcium the metals themselves are not of great value, but their salts are. Barium sulphate is a constituent of lithopone, which is used for many purposes besides paint. Strontium oxide is used in the purification of cane sugar, for which considerable quantities are used. Calcium oxide is the most used cheap alkali, and it is used in many chemical processes. In particular, it is used, frequently in conjunction with magnesium oxide, as the lining for steel furnaces and other metallurgical furnaces; its high melting-point and resistance to oxidation are of considerable value. In some cases it acts as a

basic lining, for instance in the basic steel process, where it reacts with the oxide of phosphorus to form calcium phosphate. Calcium oxide is also used in making mortar and cement. Another large and most important use is in agriculture. Anhydrous calcium sulphate, which is called anhydrite, is now used in considerable quantities for producing sulphuric acid: the anhydrite is mixed with coke and clay and heated strongly in a furnace, giving as final products sulphur dioxide, which is converted to sulphuric acid, and cement.

A great deal of anhydrite is also used for manufacturing ammonium sulphate. When a suspension of anhydrite is stirred up with a solution of ammonia in water and carbon dioxide passed in there is formed a solution of ammonium sulphate and a precipitate of calcium carbonate. The reaction is really rather complex, but it can be summarized by the equation:

$$2NH_3 + H_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3.$$

Gypsum, calcium sulphate with two molecules of water of crystallization, is a very valuable natural product used for making plaster of many kinds for building purposes.

The salts of barium, strontium, and calcium are used for making coloured flares, and small quantities of impure calcium sulphide are used for making fluorescent paints.

In the case of magnesium, the metal itself is exceedingly important for making light alloys of many kinds. Small quantities of magnesium powder are also used in flash-powder and military flares. In addition to being used as furnace linings, as was mentioned above, magnesium oxide is used for insulating heater elements for use on electrical cooking stoves. It is a good electrical insulator, and it conducts heat quite well, so it is used for filling in the space between the hot wire in the centre of a steel tube and the steel tube itself. Magnesium hydroxide, com-

monly known as milk of magnesia, is used for medicine and for tooth-paste. Epsom salts are magnesium sulphate with seven molecules of water of crystallization.

Beryllium is another light metal which is now being used considerably for light alloys. Small quantities of the oxide are used for making crucibles, but care has to be used in the use of beryllium compounds because they are poisonous.

Important uses for zinc are for making brasses, and for galvanizing steel. Very pure forms of it are used for die-castings, particularly for small parts of motor-cars. However, there are innumerable smaller uses which cannot be mentioned here. Zinc oxide is used considerably in ointment and in paints. Zinc sulphide, cadmium sulphide, zinc phosphate, zinc silicate, cadmium tungstate, and calcium tungstate are all used in making fluorescent powders for illumination purposes.

Metallic cadmium is used mainly for plating and for alloying with nickel for making bearings for aero-engines: it also occurs in certain decorative bronzes, and small quantities are used in making alkaline batteries. Metallic mercury has many well-known uses in laboratories, but its greatest use is in mercury-arc rectifiers, and switch-gear for breaking small currents.

CHAPTER XI

ALUMINIUM

As was implied earlier on, there is very little similarity between aluminium and boron, though they are both members of Group 3 of the Periodic Table. Aluminium resembles beryllium far more closely than it does boron, an example of the oblique relationship mentioned under the Periodic Table.

As distinct from boron, aluminium has many metallic properties, and in these it resembles zinc quite closely, except, of course, that it is trivalent whereas zinc is divalent. The physical properties of aluminium are all those characteristic of quite a good metal; it is ductile and malleable, and conducts heat and electricity well, besides having a good metallic sheen. Furthermore, aluminium has a high electrode potential (+1·66 volts), a surprising thing in view of the fact that its hydroxide is amphoteric, forming aluminates with alkali. This peculiarity is probably due to the abnormal stability of the hydrated aluminium ion, the energy of the hydration being a major cause of the high electrode potential. On the other hand aluminium chloride is covalent, and the hydrated chloride on strong heating gives off hydrogen chloride and leaves aluminium oxide behind. This, of course, is characteristic of the hydrated chloride of a fairly weak metal, such as one of the transition elements, or Group 2B.

Metal

Metallic aluminium reacts with all the halogen acids to give hydrated aluminium ions, $Al6H_2O^{\cdots}$, but on the other hand oxidizing acids, such as nitric acid, do not react

at all owing to the formation of an oxide film on the metal, which renders it passive. When considering the properties of metallic aluminium it is very important indeed to remember the presence of this oxide film: if a reagent is unable to break the film down, it will not react with the aluminium. On the other hand a reagent which will break the film down frequently reacts with extreme vigour. This is illustrated in two simple ways. First of all a piece of aluminium which is amalgamated with mercury reacts violently with water, and also with the air. In the case of the water the aluminium displaces hydrogen ions and produces aluminium hydroxide. The action with the air gives a plentiful supply of aluminium oxide, which grows as a fine powder on the surface of the amalgam. The second interesting example is the reaction between metallic aluminium and solutions of alkalis, such as caustic soda. In this case the alkali first of all dissolves off the oxide film as an aluminate, and this cleans up the surface of the metal and enables it to react with the water, displacing hydrogen ions in spite of the concentration of hydroxyl ions to give aluminium ions and gaseous hydrogen. Likewise chlorides tend to break down the oxide film on aluminium and thereby enable it to react with water. This gives much trouble by causing corrosion in saline atmospheres.

Metallic aluminium reacts violently with the halogens, sulphur, oxygen, and nitrogen. It is a very strong reducing agent readily removing oxygen from many metallic oxides, such as those of iron, chromium, and manganese. This property is used in the thermite process for reducing the oxides of these metals: for instance, it reacts with chromic oxide and ferric oxide as follows:

$$Cr_2O_3+2Al \rightarrow Al_2O_3+2Cr$$
$$Fe_2O_3+2Al \rightarrow Al_2O_3+2Fe.$$

In both these cases a large amount of heat is given off during the reaction, and in fact the reaction is brought about owing to the extremely high heat of formation of aluminium oxide (400·3 kilo.cal. per gram molecule).

Oxide

Aluminium oxide, which is the normal ore for the metal, occurs naturally as bauxite. This is an amphoteric oxide, giving rise to aluminium ions with six molecules of water of hydration with acids, and to aluminate when fused with alkalis:

$$Al_2O_3 + 2NaOH \rightarrow 2NaAlO_2 + H_2O.$$

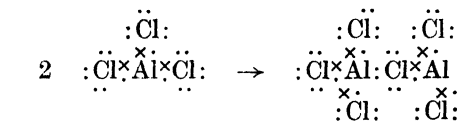
Aluminates are readily hydrolysed by water, giving aluminium hydroxide and the metallic hydroxide as products, and yet aluminium hydroxide, or aluminium oxide provided it is not completely anhydrous, dissolves readily in excess alkali to form a clear solution. For some time this was assumed to be due to the formation of aluminates, but it is not clear what really happens. These solutions in excess alkali have approximately the same electrical conductivity as has the pure alkali at the same concentration: a fact which suggests that the solutions do not contain any aluminate ions, because it is exceedingly unlikely that aluminate ions would have anything like the same mobility as hydroxyl ions, even though they do carry twice the charge. This fact suggests, therefore, that the solutions of aluminium hydroxide in excess alkali may well merely be peptized colloidal solutions of aluminium hydroxide. On the other hand such solutions, when treated with alcohol, give solid aluminates. It is therefore impossible to say dogmatically what happens when aluminium hydroxide dissolves in excess alkali to form a solution.

Aluminium hydroxide is very heavily hydrated, and it adsorbs many dyes and other substances on its surface.

For this reason it is very much used in the purification of water, and as a mordant in dyeing. The aluminium hydroxide is precipitated on to the fibre to be dyed by the hydrolysis of an aluminium salt, and then subsequently the dye is adsorbed on the surface of the aluminium hydroxide, thus dyeing the fibre.

CHLORIDE

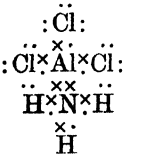
The chloride of aluminium, $AlCl_3$, is covalent. Owing to the fact that the covalency maximum of aluminium is six, the molecules of aluminium chloride polymerize to a solid owing to the formation of co-ordinate links in three dimensions:



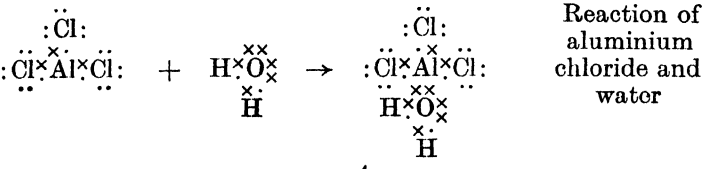
This process can continue in three dimensions, thereby building up a solid. When this solid is heated it readily passes into a vapour state, and when the vapour density of this is determined it is found to consist of Al_2Cl_6 molecules: thus the last co-ordinate link is a very strong one. This tendency for aluminium chloride to act as an acceptor of electrons explains its considerable catalytic activity for bringing about many reactions between organic compounds. It also probably explains its reaction with ammonia to give an addition product, and its reaction with water, which ultimately gives rise to a complete hydrolysis of the aluminium chloride.

The figure on p. 140 shows only one ammonia molecule forming a co-ordinate link with the aluminium chloride. In fact each molecule of aluminium chloride is combined with six molecules of ammonia, but it seems more than likely that a number of these molecules of ammonia are attached

to the other molecules by hydrogen bonds. On heating this compound it decomposes, giving off ammonia, and then finally there distils unchanged a compound containing one molecule of aluminium chloride attached to one molecule of ammonia, because this co-ordinate link is exceedingly stable.



Addition compound of ammonia and aluminium chloride



Reaction of aluminium chloride and water

A.

Though the mode of reaction of water on anhydrous aluminium chloride has not yet been fully investigated, its reaction with anhydrous aluminium bromide has been investigated experimentally,[1] and it seems probable that aluminium chloride reacts in the same way. The probable mechanism of the reaction is illustrated in the figure above. A molecule of water probably forms a co-ordinate link with a molecule of aluminium chloride, as shown at *A*. Since the covalency maximum for aluminium is six, two more molecules of water will also form co-ordinate links with the aluminium atom to form the compound $AlCl_3.3H_2O$. The corresponding compound of aluminium bromide is stable at low temperatures, but decomposes on heating, so it is very likely that the chloride compound behaves similarly. Chloride ions probably break away, thereby enabling more molecules of water to co-ordinate

[1] **Fairbrother and Frith,** *J. Chem. Soc.* **(1953), p. 2975.**

with the aluminium ion to form finally an aluminium ion with six molecules of water round it. If the temperature is too high this hydrated chloride decomposes to hydrogen chloride and aluminium hydroxide.

The fact that this reaction is exceedingly violent, and gives rise to a great deal of heat, is another example illustrating the extreme stability of aluminium-oxygen bonds. This property links aluminium more closely with boron and silicon than it does with elements in other groups.

Other Aluminium Salts

Aluminium sulphide, which can be formed directly from the elements, is completely hydrolysed to hydrogen sulphide and aluminium hydroxide. The halides and sulphate of aluminium are all soluble in water, and the carbonate is unknown: when solutions of aluminium salts are mixed with alkali carbonates aluminium hydroxide is precipitated.

The other important aluminium salts are the alumino silicates. Some of the silicon ions in the silicon-oxygen structures occurring in silicates can be replaced by aluminium ions. For every silicon ion thus replaced by an aluminium ion, there is a change in charge of one unit. This is because the silicon ion has on it four positive charges, whereas the aluminium ion has on it only three. Thus when the aluminium ion replaces the silicon ion, a net negative charge of one is left on the resulting structure, and it can then take up into its system a positively charged metallic ion. This interesting property is very important in a number of silicates, the commonest and perhaps the most important examples being the felspars, which are alumino silicates of sodium, potassium, and calcium:

Orthoclase: $K^{\cdot}(AlSi_3)O_8'$
Albite: $Na^{\cdot}(AlSi_3)O_8'$
Anorthite: $Ca^{\cdot\cdot}(Al_2Si_2)O_8''$.

These silicates are all massive in structure and consist essentially of the silicon–oxygen structure of quartz with one silicon ion in four replaced by an aluminium ion. For each silicon ion thus replaced by an aluminium ion one potassium or sodium ion can be taken up into the system, giving rise to the formulæ shown above for orthoclase and albite. In the case of anorthite, the calcium felspar, two silicon ions out of four have been replaced by aluminium ions, thereby giving double the charge to the silicon–oxygen system, and enabling it to take up a divalent calcium ion.

Complexes

Aluminium does not form complexes with cyanide ions, but the three common complexes already mentioned are:

$Al^{\cdots}6H_2O$, AlO_2', and in addition there is AlF_6'''.

The complex with fluorine is particularly important, because its sodium salt, cryolite, is used in the extraction of aluminium by the electrolysis of aluminium oxide dissolved in fused cryolite. Without this substance the commercial extraction of aluminium on any scale would be virtually impossible so far as is known at present.

Uses

Aluminium alloys are exceedingly important, particularly those with magnesium and copper. There are many of them, and they can be used for extrusion, spinning, casting, etc., and have a very large number of uses in modern engineering. Most of these alloys, particularly those with a high magnesium content, are protected by building up an artificial oxide film by anodizing them. Owing to the adsorptive properties of aluminium oxide, these films can quite easily be dyed, thereby giving a decorative finish. Small amounts of pure aluminium are

used for making foil for wrapping up chocolate and other sweets, and a considerable amount is used for electrical conductors, where its light weight and high conductivity are valuable. Considerable quantities are used in steel-making for removing the last traces of oxygen before teeming, and some is used for the reduction of oxides of chromium, manganese, etc., by the thermite process.

Aluminium sulphate is used to a considerable extent for water treatment. Dilute solutions of the sulphate are mixed with dilute solutions of sodium carbonate, giving rise to a fine gelatinous precipitate of aluminium hydroxide. This settles out on the sand filter beds and adsorbs many impurities from the water. Aluminium sulphate is also used as a mordant in dyeing, as was explained earlier on.

Bauxite, the naturally occurring oxide of aluminium, is used for the purification of many compounds in industrial chemistry, in particular for the purification of crude oil. On these occasions the adsorptive properties of the hydrated oxide are what are being used. Anhydrous aluminium oxide, commonly known as corundum, is used for making grinding wheels, and provides a very important contribution to precision engineering. Some of these wheels are made from natural aluminium oxide, commonly known as emery, and others are made from artificially fused bauxite or purified aluminium oxide.

Aluminium chloride is used a great deal as a catalyst in organic chemistry, and in oil technology, though to a great extent it is now being replaced by boron trifluoride.

Aluminium silicate, in the form of clay or china clay, is extremely important in the manufacture of earthenware and china.

CHAPTER XII

GROUP 4: CARBON, SILICON, TIN, AND LEAD

This group is particularly interesting for several reasons. First of all it is the first group in the Periodic Table which has in it non-metals and metals. With the exception of boron, all elements to the left of this group in the Periodic Table are metals. All elements to the right of Group 5 are non-metals, so that Groups 4 and 5 form a transition between these two extremes, and it is partly for this reason that these two groups are of particular interest. In Group 4 the only metals are tin and lead, which are weak, though they have positive electrode potentials. Carbon and silicon alloy with many metals, and have allotropes which possess several metallic properties.

In this group we meet for the first time allotropy. The two allotropic forms of carbon, namely diamond and graphite, are not only of extreme importance commercially, but they are of particular interest in that the carbon–carbon linkage in diamond is the same as that in all aliphatic organic compounds, and the type of linkage in graphite is found in aromatic compounds. Another outstanding feature of carbon is its ability to form carbon–carbon bonds to an apparently infinite extent, and furthermore the bonds between the carbon atoms can be single, double, or treble, thus giving rise to a very vast variety of compounds.

Silicon also forms silicon–silicon bonds, but not to anything like the same extent that carbon does. On the other hand, silicon–oxygen bonds are formed to an infinite extent in crystals of silica, and they occur in all silicates, where they frequently form very long chains or sheets.

An important point to note is that carbon has a co-

valency maximum of four, whereas silicon, tin, and lead have respectively six, six, and eight. As a result of this, carbon compounds, such as hydrides and chlorides, are very inert towards chemical reagents; whereas the corresponding ones of silicon and tin are very reactive. For instance, the halides of carbon react only with very great difficulty with water and they do not react with ammonia, whereas the corresponding halides of silicon and tin react very readily indeed with water and also very readily with ammonia.

Allotropy

Carbon and silicon both have metallic and non-metallic allotropic forms. The metallic forms have sheen and conduct electricity and heat very well, whereas the non-metallic forms are non-conductors of electricity and have no metallic sheen.

Tin exhibits enantiotropic allotropy, but lead has no allotropes.

In the diamond the carbon atoms are joined tetrahedrally by covalent bonds, thus forming what is in effect a macro-molecule. Diamond is a bad conductor of heat and a non-conductor of electricity, besides being the hardest substance known. As a result of its extreme hardness it has great commercial value for making dies for finishing wire drawing, and also for diamond-tipped tools, which give a particularly smooth finish when used in lathes. Another very important use is for truing carborundum and corundum wheels which are used in precision grinding. Without the diamonds for truing these wheels the accuracy of grinding would not be obtained. Diamond-impregnated wheels are also used for sharpening carbide-tipped tools, which are now used a very great deal in engineering.

Silicon carbide, which has the same structure as that

TABLE IV

	Atomic Volume	*Electrode Potential in Volts*[1]	*Heat of Formation of Oxide per gm.-atom of O_2 (k.cals.)*[2]	*Stability of Bond with Oxygen*	*Nature of Oxide XO_2*	*Strength of X—H Bond*	*Melting-point of XCl_4 (°C.)*	*Conductivity of Chloride XCl_4*	*Result of Hydrolysis of Chloride*	*Formation of X—X Chains*	*Formation of X—O—X Chains*	*Allotropy*
C	3·4	Form no ions in solution	−47·0		Acidic		−22·9	0	Does not react.	No known limit Single, double, and triple bonds.	Present in ethers and anhydrides.	Diamond Graphite
Si	11·3		−105·1		Acidic		−68	0	$Si(OH)_4$ 4HCl	Forms chains but bonds easily broken	No limits	Metallic Amorphous
Sn	16·3	+0·14	−69·4		Amphoteric		−33·3	0 $SnCl_2$ is ionic	$Sn(OH)_4$ +4HCl, and $Sn^{\cdots\cdots}6H_2O$ +4Cl′.	Do not form chains.	Limited e.g. $H_2Sn_5O_{11}$	White Grey
Pb	18·2	+0·126	−33 ·06		Acidic		−15	8×10^{-7} $PbCl_2$ is ionic	PbO_2 +4HCl		Probably formed in glasses.	None

[1] Bockris *et al.*, *Discussions of The Faraday Society*, 1947.
[2] National Bureau of Standards, Circular 500, Washington.

of diamond with alternate carbon atoms replaced by silicon atoms, is also an extremely hard substance, and it is used for grinding wheels under the name of carborundum. Other carbides, in particular those of tungsten and tantalum, are used for making hard tips for lathe tools. For this purpose the very brittle carbides, ground to a very fine powder, are embedded in a very tough metal, usually cobalt, the mixed compressed powders being first of all shaped and then sintered. The resulting tip, after being ground by a diamond wheel, is welded on to a shaft of steel for use as a lathe tool, and for tipping rock drills and similar tools. Such tools play an extremely important part in modern engineering.

Graphite, in contrast to diamond, is exceedingly soft and acts as an excellent lubricant. This is because it consists of planes of hexagonal rings of carbon atoms, these planes being held together merely by van der Waals forces, so that they slip over each other with great readiness. The structure of the planes in graphite is essentially the same as that found in aromatic compounds, in which alternate single and double bonds are expected between the carbon atoms. In fact the structure is nothing like as simple as this, and reference should be made to more advanced works on Organic Chemistry. Graphite is particularly valuable for crucibles and for lubrication, particularly under high temperature conditions, where a hydrocarbon lubricant would be decomposed.

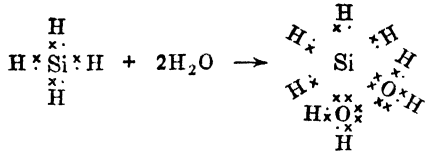
Hydrides

The hydrides of all the elements in this group are covalent, and their stabilities to heat decrease steadily from carbon to lead. The hydrides of carbon are not hydrolysed, and they react with few substances besides oxygen and the halogens fluorine, chlorine and bromine.

The hydrides of silicon are hydrolysed by water; for example:

$$SiH_4 + 4H_2O \rightarrow Si(OH)_4 + 4H_2.$$

It seems likely that the first stage of this reaction consists in the addition of two molecules of water by means of co-ordinate links:



The resulting compound presumably then reacts to give hydrated silica and hydrogen. This would explain why methane is completely inert to water, because carbon has a covalency maximum of 4, and therefore it is not possible for any water molecule to form a co-ordinate link with the carbon atom.

All the hydrides of silicon are spontaneously inflammable in the air to give silica and water.

The hydride of tin is very unstable to heat, and is of no particular interest. The hydride of lead is even more unstable.

Chlorides

All these elements form chlorides of the general formula XCl_4, and tin and lead have in addition chlorides of the general formula XCl_2. All the tetrachlorides in the anhydrous state are covalent, whereas the dichlorides of tin and lead are ionic.

Carbon tetrachloride and all the other chlorides of carbon corresponding to the hydrides are exceedingly inert: in the ordinary way they are not hydrolysed by acids, alkali, or water, and they do not react with ammonia.

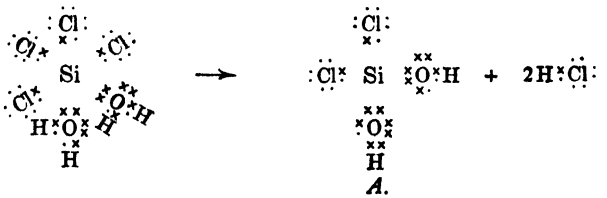
Silicon tetrachloride, on the other hand, is exceedingly reactive to water and to ammonia. With ammonia silicon tetrachloride forms an addition compound according to the following equation:

$$SiCl_4 + 6NH_3 \rightarrow SiCl_4.6NH_3.$$

This addition compound is rather unreactive towards water. The reactivity of silicon tetrachloride contrasts with the extreme inertness of carbon tetrachloride, and, as in the case of the hydrides, it seems very probable that the explanation is that silicon tetrachloride can take on two molecules of ammonia by means of co-ordinate links, whereas, having a covalency maximum of 4, carbon tetrachloride is unable to do this. Probably for the same reason, whereas carbon tetrachloride is inert to water, silicon tetrachloride reacts with it extremely vigorously to give hydrogen chloride and hydrated silica, according to the following equation:

$$SiCl_4 + 4H_2O \rightarrow Si(OH)_4 + 4HCl.$$

Here again it seems likely that the initiation of this reaction arises from the water forming a co-ordinate link with the silicon tetrachloride, the resulting compound presumably decomposing afterwards to give hydrated silica and hydrogen chloride:



A.

The compound *A* in the above equation has room for two more co-ordinate links to be formed with further water molecules. The resulting compound would then

decompose to two more molecules of hydrogen chloride and one of silicic acid.

Stannic chloride, $SnCl_4$, behaves very similarly to silicon tetrachloride in that it hydrolyses to stannic hydroxide with water, and it reacts with ammonia to give an addition compound similar to that formed with silicon tetrachloride.

With excess water stannic chloride hydrolyses to give hydrated stannic ions and chloride ions, as shown by the following equation:

$$SnCl_4 + 6H_2O \rightarrow Sn^{\cdots\cdot}6H_2O + 4Cl'.$$

Solutions of this compound are acidic due to the fact that the hydrated stannic ion is itself acidic, giving rise to hydrogen ions according to the equation:

$$Sn^{\cdots\cdot}6H_2O + H_2O \rightleftharpoons [Sn(OH)5H_2O]^{\cdots\cdot} + H_3O^{\cdot}.$$

Lead tetrachloride, $PbCl_4$, is also a covalent chloride, though it is very readily decomposed even at room temperature to plumbous chloride, $PbCl_2$, and chlorine. With water it hydrolyses as follows:

(a) $$PbCl_4 + 2H_2O \rightarrow PbO_2 + 4HCl$$

(b) $$PbCl_4 \rightarrow PbCl_2 + Cl_2.$$

While most of the lead tetrachloride is converted to lead dioxide and hydrochloric acid, a small proportion is decomposed to plumbous chloride and chlorine, presumably due to the heat liberated by the reaction shown above under (a).

Stannous chloride, $SnCl_2$, is ionic, and it is soluble in water to give hydrated stannous ions and chloride ions. Since the hydrated stannous ion is itself acidic the solutions are acid.

Plumbous chloride, $PbCl_2$, is ionic and slightly soluble in water, giving a solution which is acidic due to the hydrated plumbous ions. This chloride differs from stannic chloride and stannous chloride in that if the solution is diluted very heavily with water it is not hydrolysed through to the oxide or hydroxide, whereas both stannic chloride and stannous chloride are hydrolysed to their hydroxides.

Plumbous chloride dissolves in concentrated hydrochloric acid to give chloroplumbic acid, H_2PbCl_4, which with excess chlorine passes to chloroplumbic acid, H_2PbCl_6. Stannic chloride and stannous chloride form the corresponding complex acids H_2SnCl_6 and H_2SnCl_4. The salts of these acids can be obtained in the solid state. Neither silicon tetrachloride nor carbon tetrachloride forms the corresponding acid, though in the case of silicon the acid H_2SiF_6 is quite stable, and so are its salts. The acid is formed when silicon tetrafluoride reacts with water.

Oxides

The oxides of carbon, carbon monoxide and carbon dioxide, are both covalent and gases, whereas the oxides of all the other elements in this group are solids, and have structures intermediate between covalent and ionic.

Carbon dioxide is acidic, forming in solution the acid H_2CO_3. SiO_2 is also acidic, but the silicates consist of a whole range of salts from those of H_2SiO_3 to salts of very highly complex acids formed by a series of silicon oxygen linkages, which can take place to an unlimited extent in either massive form, chains, or sheets: hence the silicates are extremely complex. This property of forming X—O—X bonds is confined almost entirely to silicon, and does not apply to tin and lead, except perhaps in glasses and in the case of metastannic acid $H_2Sn_5O_{11}$. Stannous

oxide, SnO, and plumbous oxide, PbO, are both amphoteric. They dissolve in acids to form stannous and plumbous salts respectively, and when fused with alkali they react to form stannites and plumbites. They also dissolve in aqueous alkali, but it is not certain what is formed in solution.

Carbon monoxide is usually regarded as a neutral oxide, but, since under pressure it reacts with alkalis to form formates, it can be regarded as having acidic tendencies. It is a fairly strong reducing agent.

Stannic oxide, SnO_2, is amphoteric in that it dissolves in acid to form stannic salts, and reacts with alkalis when fused to form stannates.

Lead dioxide, PbO_2, is acidic, giving rise to plumbates on fusion with alkali. It differs from all the other oxides in this group in that it is a strong oxidizing agent. Red lead, Pb_3O_4, is probably best regarded as a salt, plumbous orthoplumbate, namely $(PbO)_2PbO_2$.

Industrial Importance

All the elements in this group have very considerable industrial importance, with the exception of germanium, which until recently was regarded as a very rare element. However, a number of deposits of this metal's ores have been discovered recently and it seems likely that, owing to its importance in radio work, it will be developed very considerably in the near future.

The importance of carbon in organic compounds is very obvious, and of course covers an extremely great field which cannot be mentioned here. The applications of the two allotropic forms of carbon and graphite have already been mentioned under the heading of the element.

Carbon monoxide is extremely valuable as a fuel, and also as a reducing agent in metallurgical operations, be-

sides being of value in organic syntheses. Carbon dioxide is of very much less use directly, though a large quantity of it is converted to solid carbon dioxide for preserving ice-creams, to liquid dioxide for fire-extinguishing purposes, and to urea by reaction with ammonia.

Though the element silicon is not of great importance industrially, it is used a great deal in alloy steels for heat resisting steels, transformer cores, and springs. For this purpose it is customary to make ferro-silicon in an electric furnace. Silicon carbide has already been mentioned as important for grinding wheels.

The oxide silica has considerable use for furnace linings in the steel industry, where it provides a suitable high-melting-point acidic lining. Another very large use is, of course, in the manufacture of glass, most of which is made by fusing mixtures of silica, sodium carbonate, and calcium carbonate.

Of the many silicates which are used industrially the best known are asbestos and mica. Sillimanite, an aluminium silicate, is used for making the elements of gas fires and the mountings for the elements of electric fires, because it has a very high melting-point and is resistant to heat and oxidation. Clay, an impure silicate of aluminium, is used in huge quantities for making bricks, earthenware, and china.

Natural crystals of silica are extremely valuable for the control of frequency of radio transmitters, and also for the new standard clock. Thin sheets of these crystals form the dielectric in condensers which are held at a constant temperature in thermostatically controlled ovens, and these condensers control the frequency of the electrical oscillations in the oscillatory circuits.

Recently there has been developed a new class of compounds called silicones. These are made by reacting silicon tetrachloride with Grignard reagents, such as methyl

magnesium iodide, giving a product dimethyl silicon tetrachloride, as shown in the equation below:

$$SiCl_4 + 2MgI{\cdot}CH_3 \rightarrow Cl{-}Si(CH_3)_2{-}Cl + MgI_2 + MgCl_2.$$

When this last compound is hydrolysed with water, it gives rise to an intermediate product which polymerizes.

$$Cl{-}Si(CH_3)_2{-}Cl + H_2O \rightarrow {-}Si(CH_3)_2{-}O{-}$$

Dimethyl siloxane

The resulting dimethyl siloxane can be polymerized into chains varying in length from those containing two silicon atoms to those containing about 2,000 atoms.

$$CH_3{-}Si(CH_3)_2{-}O{-}[Si(CH_3)_2{-}O]_n{-}Si(CH_3)_2{-}CH_3$$

The silicon–oxygen link giving rise to straight chains in this way is very stable, and the liquids thereby produced are used for lubrication purposes: some of the silicones of high molecular weight are greases. Cyclical compounds also can be formed.

By controlling the way in which these elementary chains polymerize, it is possible to make a whole range of rubbery substances, all of which are resistant to heat. These products are used for the insulation of electrical conductors and for many purposes where the temperature is sufficiently high to decompose ordinary rubber. Being ex-

pensive, these silicones are not used where their properties are not essential; that is to say they only replace rubber and other insulating materials when the temperature conditions under which the apparatus is to work are very high. An additional valuable property is that many of the silicones are very water resistant.

Tin

The principal uses for tin are the tinning of steel for manufacturing food containers, alloying with copper to produce bronze, and alloying with antimony and other metals to produce bearing metals, solder, etc. Hydrated stannic chloride is used as a mordant in dyeing.

Stannic oxide is used to a considerable extent in making opal glass and glazed bricks.

Lead

The main use for metallic lead is in making tanks and pipes, not only for domestic use but also for chemical purposes, where its resistance to such substances as sulphuric acid is considerable and therefore of value. A certain amount of lead is used in making basic carbonate for use in paint, and the other major use is for accumulators, in which the framework for both positive and negative plates is made of an alloyed lead, and the negative plate itself is made up of spongy lead.

Lead dioxide, PbO_2, is used for filling the positive plates of lead accumulators, and red lead, Pb_3O_4, is used to a considerable extent as a cement when mixed with linseed oil, and for making glass with a high refractive index for optical purposes.

Complexes

The complexes with oxygen found in silicates, stannites, stannates, plumbites, and plumbates, link these elements

on the one hand with Group 2B, and on the other hand with Groups 5, 6, and 7.

The complex chlorides mentioned under the heading of halides link these elements with the transition elements, such as copper, platinum, etc.

Boron

Apart from the fact that the valency of boron is 3, many of its compounds resemble very closely the corresponding compounds of silicon. For instance, the hydrides are all covalent, and they are hydrolysed very readily by water to give hydrogen chloride and boric acid. The hydrides of boron all have peculiar valency arrangements. For instance the lowest hydride has the formula B_2H_6, in a molecule in which there are insufficient valency electrons to provide two electrons for each bond.

Boric acid, $B(OH)_3$, is an exceedingly weak acid in solution, and it is volatile in steam. Like silicates, the borates can be very complicated owing to the fact that we have boron–oxygen linkages involved in their structure.

Boron trichloride closely resembles silicon tetrachloride in its properties. It is readily hydrolysed by water, and it forms addition compounds with ammonia. Owing to its tendency to form co-ordinate links, it has considerable value as a catalyst for use in organic chemical reactions.

The property of forming boron–oxygen linkages to a considerable extent is used in the boron glasses, in which sodium pyro-borate is mixed in with silica and the other ingredients of glasses. These glasses are valuable because they have a low coefficient of expansion, and so are less liable to crack with changes in temperature. They are used for chemical glassware and for ovenware.

*

CHAPTER XIII

GROUP 5: NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH

General

In this group, as in the last one, allotropy is found. Every element in the group, except bismuth and nitrogen, has two allotropic forms: one of which is metallic in nature, and the other non-metallic. Strictly speaking, nitrogen really has no allotrope, in that active nitrogen, if it can be described as such, is merely an activated form of ordinary gaseous nitrogen, and is therefore better not regarded as an allotropic form. Phosphorus probably has at least three allotropic forms, but it is uncertain what these really are. The yellow form is quite definitely a non-metallic allotrope, and another form, called black phosphorus, is a poor conductor of heat and electricity, but may possibly be regarded as a metallic form. In the cases of arsenic and antimony one form is definitely non-metallic and the other metallic, with poor properties for conducting heat and electricity. Bismuth is a metal with no allotropic forms.

Throughout this group the elements become increasingly metallic as the group is descended towards bismuth. Nitrogen, phosphorus, and arsenic do not form positive ions, though the metallic form of arsenic has a slight sheen and is a reasonable conductor of electricity and heat. On the other hand antimony and bismuth are weak metals in that they have positive electrode potentials and amphoteric oxides. However, all these elements alloy with several metals, and this can be regarded as a weak metallic property.

Nitrogen is particularly inert owing to the extreme stability of the bond joining the two atoms together to form the molecule. Phosphorus on the other hand is exceedingly reactive, and combines vigorously with oxygen, the halogens, sulphur, and most of the metals to form phosphides. The other elements in this group combine with considerable vigour with the halogens, sulphur, and oxygen, and alloy with many metals.

Hydrides

All the hydrides of formula XH_3 of the elements in this group are covalent, and they are all gaseous at room temperature. Their stabilities decrease progressively from nitrogen to bismuth, bismuth hydride being exceedingly unstable.

Ammonia is a very strong base, so much so that liquid ammonia is a conductor of electricity due to the fact that it forms ammonium ions and NH_2' ions as follows:

$$NH_3 + NH_3 \rightleftharpoons NH_4^{\cdot} + NH_2'.$$

Another illustration of the strength of ammonia as a base is the stability of ammonium salts in solution and in the solid state.

Phosphine is a very weak base, for instance forming phosphonium iodide with gaseous hydrogen iodide, but all phosphonium salts are hydrolysed by water. The hydrides of arsenic and antimony are not basic at all, forming no salts.

It is interesting to note that since the hydrides of nitrogen, phosphorus, arsenic, and antimony are obtainable by the hydrolysis of respectively nitrides, phosphides, arsenides, and stibides, these hydrides must in a way have acidic properties, being given off when their salts are hydrolysed. However, there is no sign of acidity when these hydrides come into contact with water. With the

TABLE V

	Atomic Volume	*Electrode Potential in volts*[1]	*Allotropy*	*Heat of Formation of Hydride: in k.cals.*[2]	*Nature of XH_3*	*Stability of Bond with Oxygen*	*Nature of X_2O_3*	*Nature of X_2O_5*	*Chloride XCl_3*	*Sulphides*	*Nitrates*
N	13·6	↑ Do not form positive ions ↓	None	−11·04 (gas)	Strongly basic. NH^+_4 stable in water.					Neutral.	None.
P	Metallic 13·2 Yellow 16·9		Metallic, and non-metallic in several forms.	+2·21 (gas)	Weakly basic. PH^+_4 not stable in water.		Acidic		Covalent — Hydrolysed to oxyacids.	Neutral.	None.
As	Metallic 13·1 Yellow 19·8		Metallic and non-metallic (yellow).	+41·0 (gas)	↑ Neither basic nor acidic ↓		Give the -ous acids.	Acidic		Acidic. Form thio-salts.	None.
Sb	Metallic 18·7 Amorphous 19·6	−0·10	Metallic and non-metallic.	+34·82 (gas)			Amphoteric	Give the -ic acids.	Probably a weak electrolyte. Hydrolysed to SbOCl.	Acidic. Form thio-salts.	Gives basic nitrates with water.
Bi	21·4	−0·23	None.	?					Similar to $SbCl_3$.	Not acidic.	Gives basic nitrates with water.

[1] *Handbook of Chemistry and Physics*, 29th edition.
[2] National Bureau of Standards, Circular 500, Washington.

exception of ammonia, which is exceedingly soluble, and phosphine which is only slightly soluble, all these hydrides are insoluble in water.

Chlorides

All these elements form chlorides of the general formula XCl_3, all of which, with the exception of nitrogen trichloride, are hydrolysed by water to give hydrogen chloride, according to the following equations:

$$2AsCl_3 + 3H_2O \rightarrow As_2O_3 + 6HCl$$

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl$$

$$BiCl_3 + H_2O \rightarrow BiOCl + 2HCl.$$

On the other hand, nitrogen trichloride is a donor of electrons and not an acceptor, and so is hydrolysed in an entirely different way according to the following equation:

$$NCl_3 + 3H{\cdot}OH \rightarrow NH_3 + 3HClO.$$

Of course, in practice a solution of ammonium hypochlorite is formed. It is interesting to note that the reason that nitrogen trichloride behaves in quite a different way from the chlorides of the rest of the elements in this group, is that whereas nitrogen has a covalency maximum of 4, the other elements have one of 6 or more. As a result of this nitrogen can act only as a donor. The other elements usually act as acceptors, though phosphorus acts as a donor in the phosphonium salts. Thus the first element in this group is distinguished from the rest of the elements in the group in the same way that carbon is distinguished from the remaining elements in Group 4.

Phosphorus and antimony form pentachlorides of the general formula XCl_5, but arsenic and bismuth do not do this. The pentachlorides hydrolyse to the acids according to the following equations:

$$PCl_5 + 3H_2O \rightarrow HPO_3 + 5HCl$$

$$SbCl_5 + 4H_2O \rightarrow H_3SbO_4 + 5HCl.$$

The trichlorides of all these elements except bismuth are covalent.

Oxides

The oxides of nitrogen are more numerous than those of the other elements of this group. They are as follows:

Nitrous Oxide, N_2O
Nitric Oxide, NO } Neutral oxides.

Nitrogen trioxide, N_2O_3: Acidic, the anhydride of nitrous acid.

Nitrogen dioxide, NO_2: Acidic, giving nitrous and nitric acids with water.

Nitrogen pentoxide, N_2O_5: Acidic, giving nitric acid with water.

All these oxides are fairly strong oxidizing agents, and are reduced to nitrogen by metals. Whereas nitrous and nitric oxides are both neutral, the other three are acidic. Phosphorus trioxide, which is very readily oxidized to phosphorus pentoxide, on hydrolysis gives phosphorous acid. Phosphorous pentoxide on hydrolysis gives meta-phosphoric acid in the first instance, and on boiling this is converted to ortho-phosphoric acid, H_3PO_4.

$$P_2O_3 + 3H_2O \rightarrow 2H_3PO_3$$

$$P_2O_5 + H_2O \rightarrow 2HPO_3$$

$$HPO_3 + H_2O \rightarrow H_3PO_4.$$

Both of these oxides are covalent.

The trioxide and pentoxide of arsenic behave very

similarly to the corresponding oxides of phosphorus, and on hydrolysis give rise respectively to arsenious acid and arsenic acid. Arsenious oxide is not particularly soluble in water, though with alkali it dissolves readily to give sodium arsenite. Provided they are kept very slightly alkaline, arsenite solutions are readily oxidized quantitatively by means of iodine to arsenates, according to the following equation:

$$AsO_3''' + I_2 + H_2O \rightarrow AsO_4''' + 2I' + 2H^{\cdot}.$$

The reverse reaction occurs under acid conditions.

Arsenites are readily converted to arsenic sulphide by means of hydrogen sulphide, but arsenates are not. However, arsenates are reduced to arsenites by sulphur dioxide in solution.

The tri- and pent-oxides of antimony are very similar in their behaviour to those of arsenic, except that the antimonites are readily hydrolysed by water, to which they are not stable. They can be made, however, by fusing antimony trioxide with an alkali. Bismuth trioxide is amphoteric, forming salts with acids, and bismuthites when fused with an alkali. Bismuth pentoxide is entirely acidic, giving a bismuthate on fusing with alkali.

Oxy-acids

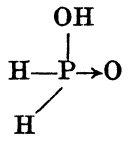
Nitrogen has many oxy-acids, but the only important ones are nitrous and nitric acids. As the main properties of these have been thoroughly covered at the School Certificate stage, it is not necessary to repeat them here. Important things to note are that nitrous acid is a very weak acid, whereas nitric acid is a strong one. Both are oxidizing agents, and under certain circumstances nitrous acid can act as a reducing agent. This fits in with the corresponding acids of arsenic, antimony and

bismuth, though the acids of phosphorus are not oxidizing agents.

The oxy-acids of phosphorus are also fairly numerous, and the structures of the most important ones are given below.

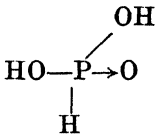
Phosphorous Acids

Hypophosphorous acid



Fairly strong; monobasic

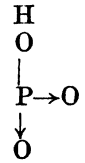
Phosphorous acid



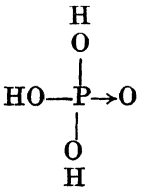
Weak; dibasic.

Phosphoric Acids

Metaphosphoric acid

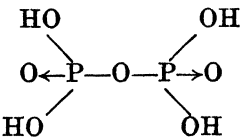


Orthophosphoric acid



Tribasic.

Pyrophosphoric acid



Tetrabasic

Hypophosphorous acid and phosphorous acid are both strong reducing agents, being oxidized in both cases to

orthophosphoric acid. On being heated both acids decompose to give phosphine and phosphoric acid.

$$2H_3PO_2 \rightarrow H_3PO_4 + PH_3$$
$$4P(OH)_3 \rightarrow 3H_3PO_4 + PH_3.$$

When the salts of these acids are heated they also yield a phosphate and phosphine.

Arsenic and antimony have acids corresponding to phosphorous and phosphoric acids, but of these only arsenic acid can be isolated in the pure state. When arsenious acid or either of the antimony acids is liberated it immediately becomes dehydrated and forms the oxide. As was mentioned under the heading of oxides, arsenious oxide and arsenites can be oxidized to arsenates. Bismuth trioxide is insoluble in water, and it is doubtful whether it forms a true bismuthite when fused with an alkali.

No bismuthates derived from the acid H_3BiO_4 have yet been identified, but ones derived from the acid $HBiO_3$ are known, and bismuth pentoxide, Bi_2O_5, has been prepared in an impure state. Bismuthates are strong oxidizing agents, a particularly interesting case being the oxidation of manganese salts to permanganate in acid solutions. This forms quite a good confirmatory test for a manganese salt in qualitative analysis.

The oxy-acids of phosphorus, arsenic and antimony all form condensed acids, of which pyrophosphoric acid is a typical example. The others are not important, though the sodium salts of condensed metaphosphoric acid are used to prevent scale formation in hot water systems. When condensed metaphosphates are present the crystals of calcium carbonate, which form from the bicarbonate when hard water is heated, are prevented from growing to any size, and form a fine suspension in the water. Thus

the precipitated calcium carbonate passes out of the pipes and boiler with the water, whereas if metaphosphates are not present the calcium carbonate crystals form a scale on the boiler and pipes.

Sulphides

The sulphides of nitrogen are of no importance: like those of phosphorus they are neutral. There are four sulphides of phosphorus, as shown below, three of which are readily decomposed by water, but the fourth, tetraphosphorustrisulphide, P_4S_3, is only very slowly decomposed by water. This last is of importance for its use in matches.

P_4S_3: Only slowly decomposed by water.

P_4S_5, P_4S_7, P_4S_{10}: Readily decomposed by water to give hydrogen sulphide and phosphoric acid.

The sulphides of arsenic are acidic in nature in that they react with alkalis to give mixtures of thio-salts and arsenite or arsenate. They also react with alkaline sulphides to give the thio-salts as shown below:

$$As_2S_3 + 3S'' \rightarrow 2AsS_3'''$$

or

$$As_2S_3 + 3S_2'' \rightarrow 2AsS_4''' + S$$

$$As_2S_5 + 3S'' \rightarrow 2AsS_4'''.$$

Antimony trisulphide and antimony pentasulphide behave in exactly the same way as the corresponding sulphides of arsenic. Bismuth trisulphide, which is the only certain sulphide of bismuth, does not react with alkalis or with water. These facts are used for separating arsenic and antimony sulphides from bismuth sulphide in analysis.

Nitrates

As would be expected, neither nitrogen, phosphorus, nor arsenic have any nitrates, but it is interesting to note that both antimony and bismuth form basic nitrates.

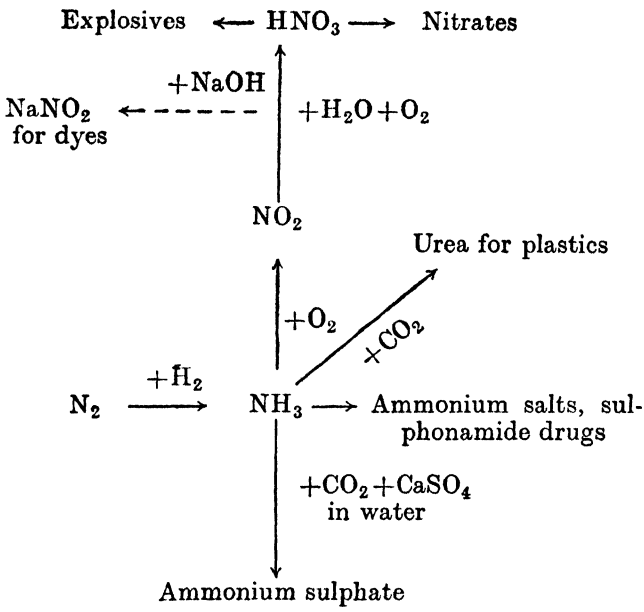
Uses of the Elements and their Compounds

Nitrogen

The importance of nitrogen is so very great that it is possible here to give only the merest outline of the most important compounds and their uses. Owing to the fact that nitrogen is an essential of proteins, it is clearly necessary for life of any kind on this earth, and it is for this reason that nitrogen compounds are extremely important in agriculture. In addition nitrogen is an essential in many dyes, drugs, and explosives.

Elemental nitrogen is used very extensively for producing an inert atmosphere for annealing steel or other metal. It is also used for sweeping out remaining oxygen from electric light lamps during their manufacture.

From the point of view of quantity, the greatest use for nitrogen is in the synthetic production of ammonia, from which most of the other compounds of nitrogen are derived. The plant involved in this process is so enormous that it constitutes a complete works on its own. This is partly due to the scale on which the operation is carried out, and partly due to the fact that during this operation there are a large number of by-products, all of which lead to further plant for their conversion into some useful product. The main processes involved in the fixation of nitrogen and the subsequent treatment of the ammonia, are summarized in the diagrammatic form shown below.



The ammonia formed by the catalytic action of nitrogen on hydrogen is first of all oxidized by atmospheric oxygen and a platinum catalyst to nitric oxide. After cooling, this is further oxidized direct to nitrogen dioxide. With excess air this is passed up a tower down which water is falling, and this reacts with the water to produce a mixture of nitrous and nitric acids.

$$2NO_2+H_2O \rightleftharpoons H^{\cdot}+NO_3{}'+HNO_2$$
$$2HNO_2 \rightleftharpoons H_2O+NO_2+NO.$$

Being weak and unstable, the nitrous acid very soon gets saturated and it then decomposes to water, nitrogen dioxide, and nitric oxide in equal proportions. In the air spaces in the tower the resulting nitric oxide is oxidized to nitrogen dioxide, which then meets a further supply of

water and reacts again according to the previous equation. When this process has continued for some time, there results a dilute solution of nitric acid, which can be concentrated by distillation with concentrated sulphuric acid, and an equi-molecular proportion of nitrogen dioxide and nitric oxide, which escapes from the top of the tower. This mixture is washed with dilute caustic soda solution to give a solution of sodium nitrite according to the following equation:

$$NO_2 + NO + 2NaOH \rightarrow 2NaNO_2 + H_2O.$$

On concentration, the sodium nitrite crystallizes out, and this is used in the dye industry for the production of nitrous acid.

Some of the nitric acid is used for the production of nitrates, of which ammonium nitrate and calcium nitrate are used for agricultural purposes. Most of the remainder of the nitric acid is used in the production of explosives as nitro-compounds or esters. Common examples are trinitrophenol, frequently known as picric acid, cellulose nitrate, and glyceryl trinitrate, which are known respectively as nitro-cellulose and nitro-glycerine.

A certain amount of ammonia is used as a mild alkali for cleaning and other purposes, and smaller amounts are compressed into steel cylinders as liquid. Some of this is subsequently used for nitriding steel in order to give a very hard surface, but the majority of it is converted into sulphonamide drugs.

Phosphorus

Practically all phosphorus compounds are now made from the raw material calcium phosphate, which is found in certain parts of the earth as a deposit. This phosphate is reduced in electric arc furnaces to elemental phos-

phorus, which of course is recovered in the yellow form. Some of this is converted to the red variety for use in the match industry, and a further quantity is converted into tetraphosphorus trisulphide P_4S_3, which is used in making match heads. Of the remaining phosphorus, a small quantity is converted into phosphorus trichloride or bromide, and phosphorus pentachloride, for use in the organic chemical industry. The remaining phosphorus is oxidized by burning in air to phosphorus pentoxide,

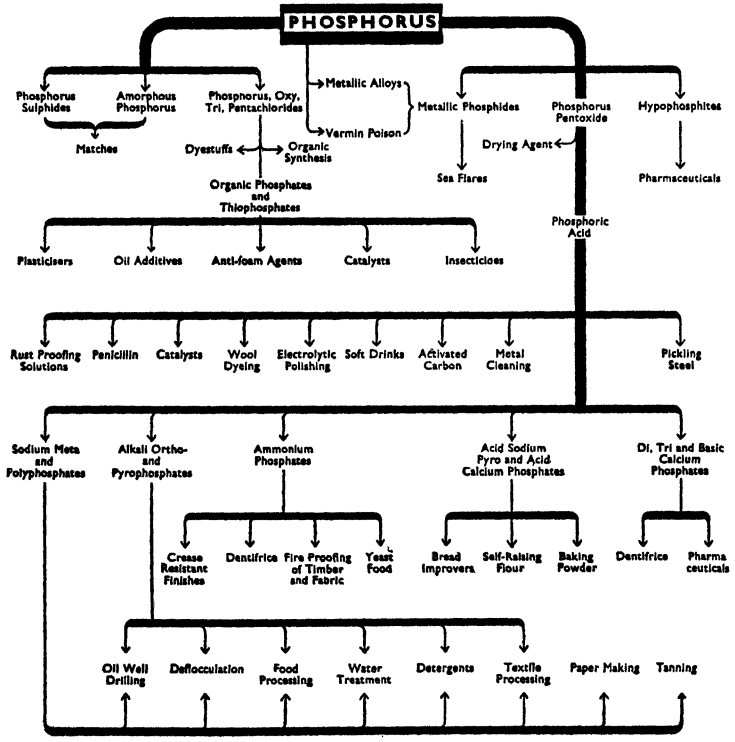


FIG. 1. Phosphorus derivatives

(By courtesy of Messrs. Albright & Wilson, Ltd.)

which is subsequently converted to orthophosphoric acid by solution in water and boiling. From this many products are produced, which are shown in the diagram.

Arsenic

There are relatively few uses for either arsenic or its compounds, but small quantities of the element are used for hardening lead for making lead shot. Arsenious oxide is frequently incorporated in mixes for making glass, and small quantities of it and of arsenites are used as weed-killers.

Antimony

Antimony is a constituent of many alloys, of which one of the important ones is an alloy of lead used in making the plates of accumulators. This alloy is more resistant to acids than is pure lead. Other important alloys are used in making type-metal, and their peculiar properties make possible modern high-speed type-casting machines for printing. Without these the setting up of type is a very laborious process.

Antimony trioxide, Sb_2O_3, is used for making enamels, but, owing to the fact that these enamels are poisonous, they cannot be used on cooking vessels.

Antimony trisulphide, Sb_2S_3, is used in considerable quantities in the manufacture of safety matches.

Bismuth

Bismuth metal is a constituent of several alloys, the most important of which have very low melting-points, which are below the boiling-point of water. These are essential for automatic sprinklers to protect large buildings from fire. Any fire developing melts the alloy and

automatically releases a shower of water into the room. Alternatively it may release a supply of carbon dioxide obtained from liquid carbon dioxide in a battery of steel cylinders.

Bismuth carbonate is used in small quantities medicinally, and the trioxide, Bi_2O_3, is used for glazing pottery.

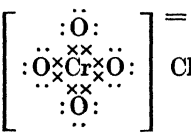
CHAPTER XIV

THE TRANSITION ELEMENTS: CHROMIUM, MANGANESE, AND IRON

General

In their electronic structures these elements have a common feature in that the *N* level in each case has two electrons in it. When these two electrons are used for valency purposes, the element is, in every case, divalent. However, in the case of each of these metals it is also possible for one or more of the electrons in the *M* shell to be used for valency purposes. This gives rise to one of the most characteristic properties of the transition elements, namely, variable valency. In the case of manganese the divalent manganous compounds are the more stable. In the case of chromium the trivalent chromic compounds are the more stable, and in the case of iron the ferrous and ferric are almost equally stable.

In the acid radicals of the oxy-acids, not only are the two electrons in the *N* level used for forming co-ordinate links, but so also are some of those in the *M* level, in addition to extra electrons obtained from outside to give the ion its negative charge. Examples are given in Table VI, opposite.



In the chromate ion, which has two electric charges, there are altogether eight electrons round the chromium atom which have formed co-ordinate links with oxygen

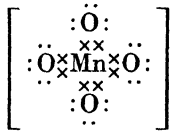
TABLE VI

	Electrode Potential Volts[1]	*Electronic Structure*	*Chloride* XCl_2	*Chloride* XCl_3	*Oxide* XO	*Oxide* X_2O_3	*Other Oxides*	*Sulphides*	*Stable salts*	*Complexes*
Cr	+0·71 ($Cr^{\cdot\cdot}$)	K2; L8; M8·4; N2	Ionic	Covalent ↓ $+H_2O$ $Cr^{\cdot\cdot\cdot\cdot}6H_2O$ $+3Cl^{-}$	Basic	Amphoteric	CrO_3 acidic	CrS insol. Cr_2S_3 hydrolysed.	Chromic	$Cr^{\cdot\cdot\cdot\cdot}6H_2O$ A large number of other complexes formed.
Mn	+1·06 ($Mn^{\cdot\cdot}$)	K2; L8; M8·5; N2	Ionic	Not isolated	Basic	Basic	Mn_3O_4 (salt) MnO_2 acidic Mn_2O_7 acidic	MnS insol. MnS_2 insol.	Manganous	$Mn6\ H_2O$ $MnCl_6^{''}$ $Mn(CN)_6^{''''}$ $Mn(CN)_6^{'''}$
Fe	+0·44 ($Fe^{\cdot\cdot}$)	K2; L8; M8·6; N2	Ionic	Covalent ↓ $+H_2O$ $Fe^{\cdot\cdot\cdot\cdot}6H_2O$ $+3Cl^{-}$	Basic	Amphoteric	Fe_3O_4 (salt)	FeS insol. Fe_2S_3 insol. FeS_2 insol.	Ferrous and ferric.	$Fe^{\cdot\cdot\cdot\cdot}6H_2O$ $Fe(CN_6)^{''''}$ $Fe(CN)_6^{'''}$

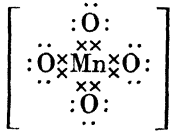
[1] Bockris, *et al.*, *Discussions of The Faraday Society*, 1947.

atoms. These eight consist of the two from the *N* level, the four from the *M* level, and the two extra electrons.

A similar arrangement is found in manganate and permanganate ions:



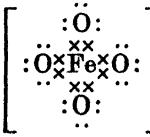
Manganate ion.



Permanganate ion.

As in the case of the chromate ion, in the manganate ion the manganese atom has round it eight electrons which have formed co-ordinate links with oxygen atoms. Of these eight electrons two are derived from outside, two from the *N* level, and four out of the five from the *M* level, giving rise to a doubly charged ion. In the case of the permanganate ion, since only one electron has been derived from the external sources, all five of the electrons from the *M* level have been utilized, giving rise to an ion essentially of the same structure as that of the manganate ion, but having only unit charge on it.

Likewise, in the ferrate ion two electrons derived from external sources, the two electrons from the *N* level, together with four from the *M* level, are utilized in forming co-ordinate links, giving rise to an ion with double charge:



Ferrate ion.

Metals

Chromium, manganese, and iron are all metals, having positive electrode potentials. Chromium and iron have little action on water, but they dissolve quite readily in dilute acids, giving off hydrogen, and forming respectively chromous and ferrous ions. The chromous ions are then usually oxidized by dissolved oxygen. Both these metals become passive in concentrated nitric acid, which forms an oxide film on them.

Manganese has such a high positive electrode potential that it not only displaces hydrogen from acid, but also from water, giving manganous ions.

All three metals react at fairly high temperatures with oxygen, sulphur, the halogens, and phosphorus. When exposed to the air chromium forms a tough oxide film which, though invisible, protects the metal from further oxidation; this makes chromium a very useful metal for plating other metals.

Hydrides

Iron very readily forms alloys with hydrogen, and chromium also forms compounds with hydrogen below 60°C. Manganese on the other hand forms no compounds with hydrogen.

Chlorides

The divalent chlorides of all three metals are ionic, and pass readily into solution, forming hydrated ions: their solutions are not acidic.

Manganese trichloride does not exist, except perhaps in ethereal solutions obtained by shaking up ether with a solution of manganese dioxide in concentrated hydrochloric acid. However, the trichlorides of chromium and

iron are quite stable, and are covalent in the anhydrous state. With water they both pass into solution, giving hydrated ions with six molecules of water per ion, and these solutions are acidic due to the fact that the hydrated ferric and chromic ions are both acidic.

Chromous chloride is a very strong reducing agent, and in solution rapidly becomes oxidized to chromic chloride.

When hydrated ferric chloride is strongly heated, it decomposes in two ways. The majority of it gives off hydrogen chloride, leaving ferric oxide behind, but a small proportion gives off water only, and leaves anhydrous ferric chloride, according to the following equations:

$$Fe^{\cdots}6H_2O + 3Cl' \rightarrow \underset{\text{(covalent)}}{FeCl_3} + 6H_2O$$

and

$$2Fe^{\cdots}6H_2O + 6Cl' \rightarrow Fe_2O_3 + 6HCl + 3H_2O.$$

If hydrated chromic chloride is strongly heated, similar reactions take place.

Oxides

All the oxides with formula XO are basic, and with acids give rise to divalent salts. Chromic oxide, Cr_2O_3, and ferric oxide, Fe_2O_3, are both amphoteric. With acids they give rise to respectively chromic and ferric salts in solution, and when fused with alkalis they give rise to chromites and ferrites:

$$Fe_2O_3 + CaO \rightarrow Ca^{\cdot\cdot}(FeO_2')_2 \text{ Calcium ferrite.}$$

$$Cr_2O_3 + Na_2O \rightarrow 2Na^{\cdot}CrO_2' \text{ Sodium chromite.}$$

Manganic oxide, Mn_2O_3, is entirely basic, and with acids presumably gives rise to unstable manganic salts, about which very little is known.

Chromium trioxide, CrO_3, is entirely acidic, giving rise to chromates according to the following equation:

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \text{ Chromic acid.}$$

Chromium trioxide is also a very strong oxidizing agent.

Manganese dioxide, MnO_2, is entirely acidic, giving rise to manganites, which are easily oxidized to manganates:

$$[O] + MnO_2 + Na_2O \rightarrow Na_2MnO_4 \text{ Sodium manganate.}$$

The oxygen shown in this equation comes from the air, and it is possible that a manganite is formed as an intermediate stage.

Manganese dioxide is a strong oxidizing agent, and when it is acted on by concentrated hydrochloric acid it liberates chlorine, and manganous chloride is formed: this is a well-known method of preparing chlorine in the laboratory.

Mangano-manganic oxide, Mn_3O_4, is probably best regarded as a salt, manganous-manganite:

$$2MnO \cdot MnO_2 \text{ Manganous manganite.}$$

Manganese heptoxide, Mn_2O_7, is entirely acidic, giving rise to permanganates:

$$Mn_2O_7 + H_2O \rightarrow 2HMnO_4 \text{ Permanganic acid.}$$

It is a covalent liquid giving rise to a purple gas, which is highly explosive, and for this reason it should not be prepared.

Triferric tetroxide, Fe_3O_4, behaves as a double compound of ferrous oxide and ferric oxide. For instance, with acids it gives rise to an equi-molecular mixture of ferrous and ferric salts. This may be regarded as ferrous-ferrite:

$$FeO + Fe_2O_3 \rightarrow Fe^{\cdot\cdot}(FeO_2')_2 \text{ Ferrous ferrite.}$$

Though no other oxides of iron have been found, it is interesting to note that the salts of higher oxy-acids are known, but they are of no importance.

Complexes

All three of these elements form hydrated ions containing six molecules of water per ion.

Although manganese compounds do not form ammines with ammonia, chromium and iron ones do, and when saturated both metallic ammines contain six molecules of ammonia, per molecule of metallic salt. The chromium ammines are stable in solution, but those of iron are decomposed by water. Chromium forms a very large number of other complex compounds.

Iron forms both ferro-cyanides and ferri-cyanides, and manganese forms the corresponding compounds.

Manganese also forms salts containing the complex ion $MnCl_6''$.

SULPHIDES AND SULPHATES

With the exception of chromic sulphide, Cr_2S_3, which is hydrolysed, all sulphides of these elements are insoluble in water. They are listed in the summary.

Iron pyrites, FeS_2, is a polysulphide in which the second sulphur atom is co-ordinately linked to the sulphide ion, as shown below:

$$Fe^{\cdot\cdot} + S'' \rightarrow S.$$

It is not surprising, therefore, that on strong heating iron pyrites give off sulphur, leaving behind ferrous sulphide.

None of these sulphides react with alkali, or ammonium sulphide solution.

All the sulphates of these elements are soluble in water.

USES OF THE ELEMENTS AND THEIR COMPOUNDS

Considerable quantities of chromium are used in making steels which are tough and hard. For example, chromium steel is used in armour plating. Considerable quantities of chromium are used nowadays in making the elements

of electric fires. These are made of an alloy called nichrome, which is mainly composed of nickel and chromium, in approximately equal proportions. For this purpose metallic chromium is used, and this is produced by reducing chromic oxide by means of aluminium powder. For use in steel the chromium is normally smelted from the ore as ferrochrome.

When hot solutions of dichromates are electrolysed with a fairly high current density, metallic chromium is liberated at the cathode. Since hydrogen is liberated at the same time, the chromium plating is invariably porous, but provided it has some resistant coating underneath, it gives an untarnishable finish to the object plated. This is because in the air chromium forms an oxide film, which protects it from further action. The same property is used in a certain range of rustless steels which contain a high percentage of chromium.

Chromic oxide is used to a considerable extent in the colouring of pottery. It is used also to a small extent for polishing.

Dichromate is used for tanning leather, and the chromates, particularly lead chromate, are used for pigments in paint, and also as rust inhibitors.

Manganese is an important constituent of many alloys, in which it frequently functions as a deoxidant as well as modifying their properties. Two particularly important types of alloy are the manganese brasses (frequently called the manganese bronzes), and the manganese steels. High tensile brasses, many of which contain manganese, are particularly important in marine engineering, where they are used for such objects as propeller shafts, propellers, and the posts of rudders.

In steel-making, manganese is almost always essential in that it is very important as a deoxidant. Steels containing a very large percentage of manganese are austenitic

even at room temperature, and as a result they are non-magnetic. Such steels are also exceedingly resistant to wear, because as soon as they are worked in any way they immediately harden owing to the formation of martensite. As a result of this, though they are expensive, they are used for heavily loaded railway crossings, and the tips of dredgers and diggers used in mining ores.

Another important alloy of manganese is the manganin used for standard resistances. This is an alloy containing approximately 85 per cent copper, about 4 per cent nickel, and some 4 per cent manganese. It is important because it has a very low temperature coefficient, and furthermore it does not change its properties appreciably with time: as a result it is the key to accurate standard resistances for use in resistance boxes and shunts.

Manganese dioxide is frequently used for decolorizing glass. This is brought about in two ways. Any ferrous ion is oxidized to ferric, thus removing green ferrous silicate and replacing it by very pale yellow ferric silicate. At the same time the manganic silicate formed by reaction between the oxide and silica has an amethyst colour which neutralizes the pale yellow of the ferric silicate, thus making the glass virtually colourless. Manganese dioxide is also a constituent of many colouring matters used for pottery, and it is used as a depolarizer in dry cells, and as a dryer in paints.

Iron is still by far the most valuable metal which we have, though it is never used in the pure state. Alloyed with other metals, such as manganese, chromium, tungsten, molybdenum, nickel, and vanadium, iron is the basis of the innumerable types of steel. Though steels have in common the property that they can be heat treated, they vary considerably in toughness, tensile strength, and brittleness. Some are resistant to heat, others are magnetic, while some are non-magnetic, thereby giving a very

large range of structural material. To give any idea of the extent of this range here is quite impossible.

Another form in which iron is still used is wrought iron. This material was originally developed when blast-furnaces began to produce cast iron instead of wrought iron, a change which was brought about in approximately the fifteenth century. Prior to that, iron was obtained from bloomeries, and the resulting material was somewhat similar to modern wrought iron. In these bloomeries the temperature was never high enough for the iron to alloy with carbon, and as a result it was never in a molten state. On the introduction of a power blast worked by water wheels higher temperatures were produced in the blast-furnaces, and this gave rise to cast iron. Since cast iron is much too brittle for most purposes, it then became necessary to develop the puddling process by which wrought iron is obtained from cast iron. One of these processes for puddling is still worked, and considerable quantities of wrought iron are made, chiefly in the Black Country near Birmingham.

With the very large range of steels now available, it is interesting to note why wrought iron is still required. Compared with steels wrought iron is more resistant to shock and corrosion. It is more able to recover from overstrain, a property which provides considerable safety in the case of chains and hooks for cranes. Instead of snapping without warning, as is usually the case with steel, wrought iron stretches ominously, and gives due warning that it is overstrained. Furthermore, wrought iron has a very high resistance to fatigue, and it does not become hard or suffer from temper brittleness when heated. An additional useful property is that at about 800° or 900°C. it is quite easy to weld wrought iron together by hammering it. As a result of these properties, wrought iron is still preferable for use for chain cables for ships, chains and

hooks for cranes, railway couplings, and to a certain extent for boiler stays in locomotive and marine boilers.

Of the compounds of iron, not very many are particularly important industrially, but ferrous sulphate is used in considerable quantities as a weed-killer, and also for making ink. Ferric oxide is used for polishing, and also as a cheap pigment in paint, and triferric tetroxide has a small use for tape-recording machines, where its magnetic properties are used.

INDEX

References to the majority of compounds have been omitted. The relevant chapters may be found by reference to the elements concerned.