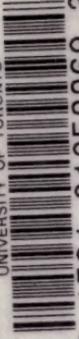
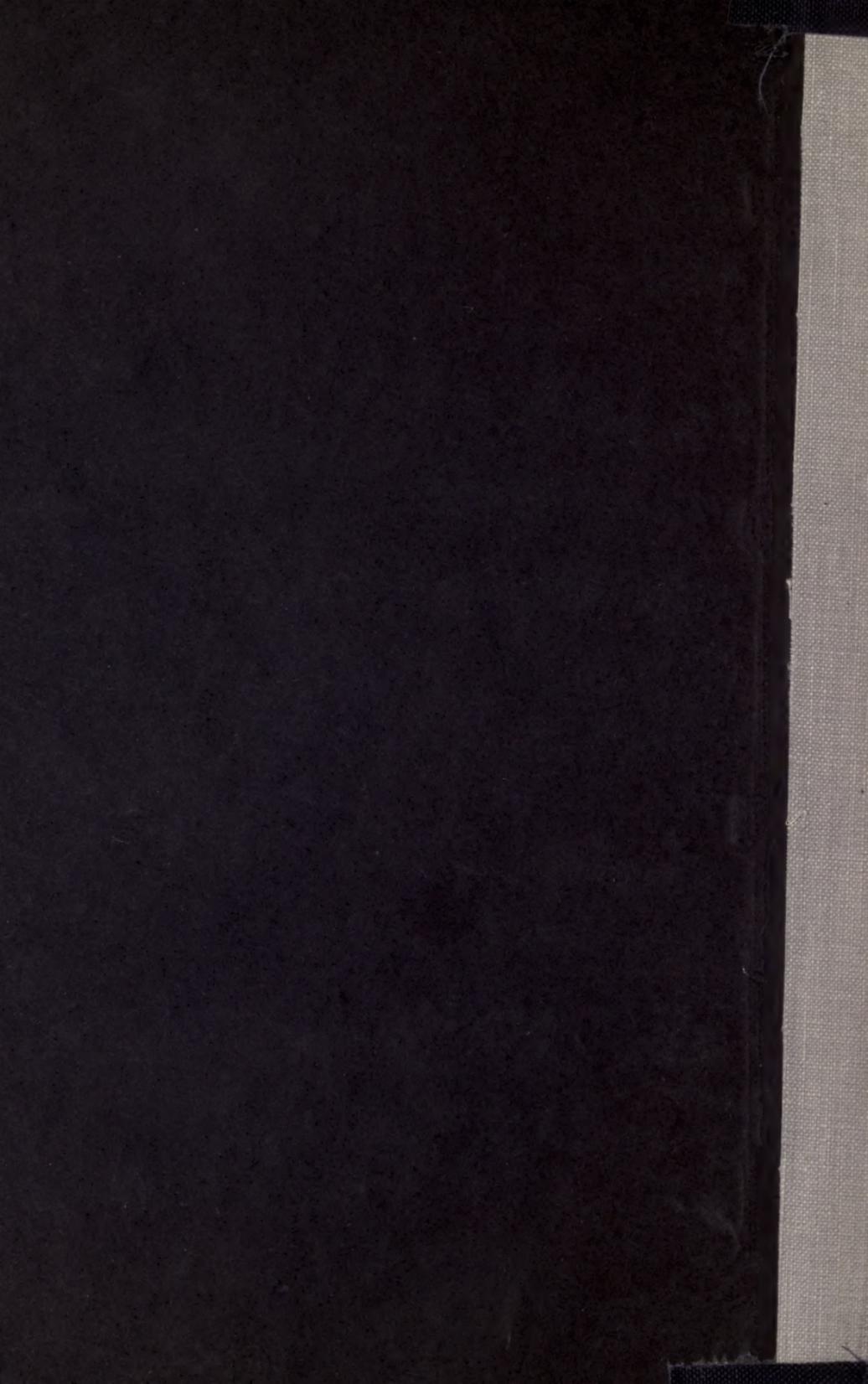


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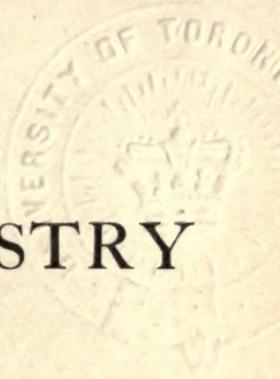
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# TEXT-BOOK OF ELECTROCHEMISTRY

BY  
*August*  
SVANTE ARRHENIUS

PROFESSOR AT THE UNIVERSITY OF STOCKHOLM

TRANSLATED BY JOHN McCRAE, Ph.D.



WITH NUMEROUS DIAGRAMMS

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## PREFACE

THE basis of this book is a series of lectures delivered by me at the University of Stockholm in the autumn of 1897.

The English translation has been made from the German edition.

In the German translation, made by Dr. H. Euler, many improvements and additions to the original Swedish edition were introduced with reference to the literature up till 1901. Only few alterations have been made in the present edition, and these refer mainly to typographical errors. By the list of literature-references collected by Dr. McCrae considerable value has been added to the book.

THE AUTHOR.

STOCKHOLM,  
*June, 1902.*



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# ELECTROCHEMISTRY

## CHAPTER I.

### INTRODUCTION.

#### Fundamental Physical and Chemical Conceptions.

**Polarisation.**—Suppose two plates of platinum, one ( $P_1$ ) connected with the positive and the other ( $P_2$ ) with the negative pole of a galvanic battery ( $B$ ), dipped into a solution ( $L$ ) of sodium sulphate (Fig. 1). Two phenomena may present themselves: (*a*) when the electromotive force of the battery is less than about 2·2 volts, no

bubbles of gas appear on the platinum plates, or (*b*) when the electromotive force of the battery is sufficiently great (over 2·2 volts), gas is evolved at each of the plates—oxygen at  $P_1$ , and hydrogen at  $P_2$ . In both cases, a current passes through the salt solution (in case (*a*) the current is very

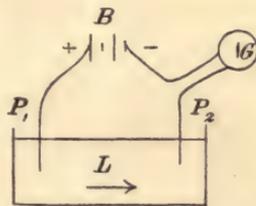


FIG. 1.

weak), and this can be recognised by the deflection of the needle of a galvanometer ( $G$ ) interposed in the circuit indicating that the current is passing in the direction from  $P_1$  to  $P_2$ . Suppose, now, that  $B$  be eliminated from the circuit by connecting  $P_1$  directly to the galvanometer by means of a wire; it will then be found that the needle of the galvanometer is deflected in the opposite direction, showing that a current is passing through the salt solution from  $P_2$  to  $P_1$ . This current is due to the so-called *polarisation*. If whilst  $B$

was in the circuit gas evolution had actually taken place, the polarisation current would be stronger, and would last longer than in the case where no bubbles of gas had been produced.

**Cause of Polarisation.**—Let us assume that gas had been evolved at the plates. After the battery has been in action for some time plate  $P_1$  has become covered with a film of oxygen and plate  $P_2$  has a similar envelope of hydrogen. The plates, originally quite similar, after the passage of the current behave like two different metals. In the same way that a current can be obtained between a copper plate and a zinc plate immersed in sodium sulphate solution, the current is now obtained when the platinum plate covered with oxygen is connected by means of a conducting-wire with the plate covered with hydrogen, both being immersed in the solution. The gases which cling to, or have penetrated into, the plates are used up in giving rise to the current which, consequently, soon stops.

Even in the case where no apparent evolution of gas has taken place when current has been drawn from the battery the plates behave in the same manner. It is, therefore, assumed that here too the gases are really separated, but in such small quantity as not to make themselves evident, and this assumption is supported by various considerations.

The polarisation of the plates presents itself, therefore, in the property which these have of behaving like two different metals which exert an opposing electromotive force against the electromotive force of the battery. Plate  $P_1$  is said to be "polarised" with oxygen, plate  $P_2$  with hydrogen.

**The Electrolytic Decomposition of Water.**—Other changes, besides the separation of gases, take place at the plates  $P_1$  and  $P_2$ , which also are of importance for the polarisation. If a few drops of litmus solution be added to the salt solution it is found that the liquid in the neighbourhood of plate  $P_1$  becomes red, whilst that near plate  $P_2$  remains (or becomes) blue, indicating that the salt solution, originally neutral, has altered near the electrodes, and has become acid at  $P_1$  and basic at  $P_2$ .

This process of passing a current through a salt solution is termed *electrolysis*. The result of the electrolysis here considered consists partly in the evolution of oxygen at  $P_1$  and hydrogen at  $P_2$ , and partly therein that the solution near  $P_1$  contains free acid, and that near  $P_2$  free alkali. These phenomena are typical for electrolysis in aqueous solution of oxygen salts of the alkali and alkaline earth metals.

**Electrolysis of Salts of the Heavy Metals.**—When the solution of a salt of a heavy metal, such as silver or copper, is electrolysed, the phenomenon is somewhat different. Let the plates  $P_1$  and  $P_2$  be of the same metal as that contained in the salt, *e.g.* silver electrodes in a solution of silver nitrate. In this case there is no evolution of gas, nor any change in the neutrality, and polarisation does not take place to an appreciable extent. The action of the current passing from  $P_1$  to  $P_2$  consists in the dissolving of some of the silver of the electrode  $P_1$  and deposition of the same amount of silver on  $P_2$ , and further, the solution near  $P_1$  becomes more concentrated, whilst that near  $P_2$  becomes more dilute. This concentration change gives rise to a weak electromotive force which corresponds, in a certain respect, to the above-mentioned polarisation electromotive force.

**Primary and Secondary Electrolysis.**—It may possibly appear strange that the salts of the heavy metals behave differently from the alkali salts on electrolysis. However, if these latter be electrolysed in the fused condition, the metal is separated at the negative electrode; and even from aqueous solution the alkali metal may be separated electrolytically if mercury be used as the negative pole. The formation of alkali at the negative pole in the previous example is not a direct consequence of the electrolysis, but is due to the chemical action of the water on the primarily separated metal. The alkali metal is deposited by “primary electrolysis,” and the secondary formation of alkali is termed “secondary electrolysis.” When a chloride, *e.g.* sodium chloride, is electrolysed between platinum plates, chlorine is primarily separated at the positive pole, and this

partially reacts "secondarily" with the water present to form oxygen and hydrochloric acid.

**Ions.**—During the course of the electrolysis certain substances, whose nature is determined by chemical analysis, are removed from the solution to each pole. Those substances which "migrate" to the positive electrode ( $P_1$ ), or anode, are called *anions*, those which migrate to the negative electrode ( $P_2$ ), or cathode, are called *cations* (see Chap. VIII.), this being the nomenclature introduced by Faraday.

**Coulomb.**—According to the law discovered by Faraday in 1834, the quantity of gas and the quantity of silver which separate at  $P_2$  in the examples given above are exactly proportional to the quantity of electricity which passes through the solution during the electrolysis. The mass of the deposited material, therefore, is a convenient measure of the quantity of electricity which passed through the electrolyte. The *coulomb*, our unit for the quantity of electricity, is that quantity required for the separation of 1.118 milligrams of silver (the equivalent quantity of copper, 0.3284 mgms., or of hydrogen, 0.0104 mgms., according to Faraday's law).

**Ampere.**—The current strength is determined by the quantity of electricity which passes through a circuit in a specified time. As unit, we use the *ampere* (amp.), which is obtained when 1 coulomb passes through the circuit in one second.

**Ohm.**—The unit of electrical resistance is that resistance offered at  $0^\circ$  by a column of pure mercury 106.30 cm. long with a section of one square millimetre. This is the international ohm, and is equal to 1.063 Siemens' units.

**Unit for Conductivity.**—The electrical conductivity of a substance is the reciprocal of the value of its resistance. As unit, the conductivity of a substance is used, a column of which 1 cm. long and of 1 sq. cm. section possesses the resistance of 1 ohm. The best conducting solutions of acids have nearly this conductivity at about  $40^\circ$ .

**The Absolute Systems.**—In scientific work it is frequently necessary to calculate the above "practical"

units into those of the "absolute system of measurement," and the electrical units have to be measured either in electrostatic or electro-dynamic units. The following table shows the relationship between the values referred to:—

Practical.	Electrostatic (C.G.S.).	Electromagnetic.
1 coulomb	$300 \times 10^7$	$10^{-1}$
1 ampere	$300 \times 10^7$	$10^{-1}$
1 ohm	$\frac{1}{900} \times 10^{-9}$	$10^9$
1 volt	$\frac{1}{3} \times 10^{-2}$	$10^8$

**Ohm's Law. Volt.**—If the terminals of a galvanic battery of electromotive force  $E$  be connected by means of a conducting-wire so that a current passes, then the electromotive force, the current strength ( $I$ ), and the resistance ( $R$ ) are connected by the following relationship:—

$$E = IR.$$

This is termed *Ohm's law*, after its discoverer. That electromotive force which in a circuit of resistance 1 ohm produces a current strength of 1 ampere is taken as unit, and is called a *volt*. Formerly, electromotive forces were referred to the tension (potential difference) between the poles of a Daniell element (zinc pole in 10 per cent. sulphuric acid, copper pole in saturated copper sulphate solution) at the ordinary temperature. This electromotive force, called a "daniell," is equal to about 1.10 volts (compare Chap. XI.). The electromotive force of a Clark element functioning at 15° is now generally used as standard (1.433 volts).

**Potential.**—The term "potential difference" is frequently used in place of electromotive force. Positive electricity tends always to pass from places of higher potential to those of lower potential; and this is an essential property or characteristic of the potential. In the subject of electricity the potential plays nearly the same part that the temperature does in the subject of heat, for heat always tends to pass from places of higher to those of lower temperature. In the subjects of electricity and heat, however, there is this difference, that

we differentiate between two kinds of electricity, whilst we recognise only one kind of heat (although formerly cold was often regarded as negative heat). For negative electricity the opposite to that which holds good for positive electricity obtains, *i.e.* negative electricity tends to pass from places at lower to those at higher potentials.

The cause of that displacement of the position of electricity which takes place without the expenditure of external work is therefore the inequality of the electric potentials at the different places. The difference of the potentials at two points is called the potential difference or electromotive force, and is that force which tends to make the electricity pass from one point to the other. In the example mentioned on p. 1 the positive electricity passes from electrode  $P_1$  to electrode  $P_2$  because the positive pole  $P_1$  has a higher potential than the negative pole  $P_2$ .

**Fall of Potential.**—In the example quoted it is customary to speak of a fall of potential<sup>1</sup> between the poles  $P_1$  and  $P_2$  in the solution.

If the potential difference between  $P_1$  and  $P_2$  amounts to  $V$  volts, and the distance between the plates is  $a$  cm., then the fall of potential is  $\frac{V}{a}$  volts (mean value) per cm.

If, however, the cross-section of the solution is not the same throughout, then the fall of potential per centimetre will be greater where the section is smaller. In any case, the fall of potential per centimetre has a definite value at each point, and this is the force (where  $10^7$  dynes =  $10 \cdot 2$  kilograms is the unit) with which, at this point, 1 coulomb of positive electricity is driven from the higher to the lower potential.

The potential corresponds, in a certain sense, to work. Thus if the potential difference between two points,  $P_1$  and

<sup>1</sup> In an analogous manner we speak of a fall of temperature. If the temperature at a point  $P_1$  is  $t_1$ , and at a point  $P_2$   $a$  cm. distant it is  $t_2$  ( $< t_1$ ), then between the two points there is a fall of temperature of  $\frac{(t_1 - t_2)}{a}$  degrees per cm.

$P_2$ , which are  $a$  cm. apart, is  $V$  volts, then at each point a force  $\frac{V}{a}$  is acting against the displacement of 1 coulomb of positive electricity from the lower to the higher potential. The total work which is done in moving 1 positive coulomb from  $P_2$  to  $P_1$  is, therefore,  $\frac{V}{a} \times a = V$ , expressed in 10.2 kilogram-centimetres as unit. Usage has led to the adoption of electromotive force as synonymous with potential difference, although the former expression is not quite exact.

**Current Density.**—The processes which take place at the poles  $P_1$  and  $P_2$  depend to a great extent on how much gas, or substance in general, is deposited on each square centimetre of the plates per second. If the current strength is  $A$  amperes, and if plate  $P_1$  has an area of  $y$  sq. cms., then the quantity deposited on 1 sq. cm. per second is given by  $\frac{A}{y}$ . The value of this expression is termed the “current density,” which obviously is measured in amperes per square centimetre. In the above example,  $\frac{A}{y}$  must only be regarded as an average value of the current density; but in those cases where the fall of potential in the solution is the same throughout, the current density has the same value at all parts of the plate.

**Electrochemical Equivalents.**—It has already been mentioned that 1 coulomb can bring about the deposition of 1.118 mgram. of silver, 0.3284 mgram. of copper, or 0.0104 mgram. of hydrogen. On this account, therefore, we say that 1.118 mgram. of silver, 0.3284 mgram. of copper, and 0.0104 mgram. of hydrogen are electrochemically equivalent.

The electrochemical equivalents correspond exactly with the chemical equivalents, which represent the weights of two substances capable of replacing each other in chemical compounds (Faraday's law). Thus, for instance, 31.8 grams of copper can replace 1 gram of hydrogen from 49 grams of sulphuric acid, and produce 79.8 grams of copper sulphate.

Setting the equivalent of oxygen equal to 8, the following numbers are obtained for other elements:—

Aluminium, Al, $\frac{27.1}{3}$ . . . 9.03	Lead, Pb, $\frac{206.9}{2}$ . . . 103.45
Barium, Ba, $\frac{137.4}{2}$ . . . 68.7	Lithium, Li, 7.03 . . . 7.03
Bromine, Br, 79.96 . . . 79.96	Magnesium, Mg, $\frac{24.36}{2}$ . . . 12.18
Cadmium, Cd, $\frac{112.4}{2}$ . . . 56.2	Manganese, Mn, $\frac{55}{2}$ . . . 27.5
Calcium, Ca, $\frac{40.1}{2}$ . . . 20.05	Mercury, Hg, $\frac{200.3}{1}$ . . . 200.3
Chlorine, Cl, 35.45 . . . 35.45	Mercury, Hg, $\frac{200.3}{2}$ . . . 100.15
Chromium, Cr, $\frac{52.1}{2}$ . . . 26.05	Nickel, Ni, $\frac{58.7}{2}$ . . . 29.35
Copper, Cu, $\frac{63.6}{1}$ . . . 63.6	Oxygen, O, $\frac{16}{2}$ . . . 8.00
Copper, Cu, $\frac{63.6}{2}$ . . . 31.8	Potassium, K, 39.15 . . . 39.15
Fluorine, F, 19.0 . . . 19.0	Silver, Ag, 107.93 . . . 107.93
Gold, Au, $\frac{197.2}{3}$ . . . 65.73	Sodium, Na, 23.05 . . . 23.05
Hydrogen, H, 1.008 . . . 1.008	Strontium, Sr, $\frac{87.6}{2}$ . . . 43.8
Iodine, I, 126.85 . . . 126.85	Zinc, Zn, $\frac{65.4}{2}$ . . . 32.7
Iron, Fe, $\frac{55.9}{2}$ . . . 27.95	
Iron, Fe, $\frac{55.9}{3}$ . . . 18.63	

**Atomic Weight.**—The atomic weights of the elements are whole multiples of the equivalent weights. The simplest relationship exists in the case of the so-called monovalent elements, like hydrogen, potassium, chlorine, etc., for which the atomic and equivalent weights are the same. The atomic weight of divalent elements, such as zinc, magnesium, calcium, iron (in ferrous compounds), mercury (in mercuric compounds), is double the equivalent weight; whilst in the case of trivalent elements like aluminium and iron (in ferric compounds), the atomic weight is three times the equivalent weight. In the above table the equivalent weights are given as fractions of the corresponding atomic weights.

**Gram-equivalent.**—In electrochemistry the equivalent weights of the various substances play an important part; and on this account we find the term “gram-equivalent” very often applied. By a gram-equivalent of zinc we mean 32·7 grams of this metal; a gram-equivalent of a substance whose equivalent weight is  $E$ , is  $E$  grams. The idea of an equivalent (and consequently also equivalent weight) can be applied not only to chemical elements and those substances which occur as ions, *i.e.* can be separated at the electrodes, but also to all compounds which can react chemically with these. By a gram-equivalent of carbon dioxide is meant that quantity which unites with a gram-equivalent of lime to form a gram-equivalent of calcium carbonate.

**Gram-molecule.**—Even more important in chemistry than the equivalent weight is the molecular weight. The methods for the determination of the molecular weight of dissolved substances, which plays a most important part in all branches of chemistry, will be described later; molecular weights are only relative values being referred to that of hydrogen as equal to 2 (or, more exactly, 2·016), or to that of oxygen as 32. Here we make use of the term “molecular weight” in the sense in which it is always applied in chemistry. Thus, for example, the molecular weight of hydrochloric acid is 36·46, and consequently 1 gram-molecule of this (HCl) is 36·46 grams, that is, the equivalent weight in grams; a gram-molecule of sulphuric acid is 98 grams, *i.e.* twice the gram-equivalent.

A gram-molecule of aluminium chloride ( $\text{AlCl}_3$ ) is 133·5 grams, and one of ferric chloride ( $\text{FeCl}_3$ ) is 162·3 grams; these, therefore, are three times the corresponding equivalent weights. Recently the term “mol” has been introduced for gram-molecule.

Just as we speak of a gram-molecule, so may we also speak of a gram-ion. One gram-ion of chlorine signifies 35·45 grams of chlorine in the ionic condition ( $\overline{\text{Cl}}$ ); a gram-ion of  $\overline{\text{SO}}_4$  weighs 96 grams (96 being the sum of the atomic weights). In the same way a gram-atom of an element is

its atomic weight expressed in grams (1 gram-atom of chlorine (Cl) is 35.45 grams).

**Concentration.**—In theoretical chemistry it is convenient to express the composition of a solution, not by the absolute weight of the dissolved substance, but by the number of dissolved gram-molecules. The concentration is then expressed by the number of gram-molecules per unit of volume (the litre), and a solution which contains 1 gram-molecule in the litre is said to be "1 normal" ( $1n$ ) or simply "normal." A 0.1 normal solution of, for instance, hydrochloric acid, contains only 0.1 gram molecule, or 3.645 grams per litre: in a litre of normal sulphuric acid there are 98 grams of  $H_2SO_4$ . Use is frequently made of equivalent-normal solutions, that is solutions containing 1 gram-equivalent per litre. Thus an equivalent-normal solution of sulphuric acid contains 49 grams of sulphuric acid in the litre. In order to avoid confusion, this latter solution is denoted as  $n \frac{1}{2}H_2SO_4$ .

By "normal" is generally meant molecular-normal.<sup>1</sup>

Such a method of expressing the concentration has the disadvantage that it is not the same for one particular solution at all temperatures and pressures, since the volume of the solution changes slightly with variation of these factors. On this account the expression of concentration in percentage by weight may be preferable. However, the volume changes caused by variation of temperature and pressure, especially of aqueous solutions, are very inconsiderable. In practice the normality is determined at the ordinary temperature (+ 18° C.) and pressure (1 atmo.), and the value so obtained is used also for other temperatures and pressures. In more accurate work it is necessary to correct for the change of volume.

**Temperature.**—In scientific work all temperatures are registered in Celsius (or centigrade) degrees. In many calculations, particularly those used in the mechanical theory of heat and its applications, it is advisable to take as zero-

<sup>1</sup> In analytical practice equivalent-normal solutions are used.

point of the scale, not the melting point of ice, but the "absolute zero," which lies  $273^{\circ}$  lower. If the temperature of a body is  $t^{\circ}$  on the ordinary scale, then it is  $T^{\circ} = 273^{\circ} + t^{\circ}$  on the absolute scale.  $T$  is called the "absolute temperature" of the body.

**Mechanical Work.**—The work which is done in raising a kilogram through 1 metre is a "kilogram-metre." In scientific measurements the unit of force is the "dyne," and is that force which the earth by its attraction exerts on  $\frac{1}{981}$  gram. Since the unit of length chosen is the centimetre  $= 0.01$  metre, the kilogram-metre (kg.m.)  $= 9.81 \times 10^7$  cm. dynes  $= 9.81 \times 10^7$  ergs; 1 erg  $= 1$  cm. dyne, is the unit of work in the C.G.S. (centimetre, gram, second) system. Experimentally it has been determined that mechanical work of 426 gram-metres, or 0.426 kg.m. is required to produce one (small) calorie of heat. Consequently—

$$1 \text{ cal.} = 9.81 \times 0.426 \times 10^7 = 0.418 \times 10^8 \text{ ergs.}$$

In electricity the unity of work is the volt-coulomb, *i.e.* the work, which 1 coulomb balances over a fall of potential of 1 volt. For the value of this we have—

$$1 \text{ volt-coulomb} = \frac{1}{9.81} \text{ kg.m.} = 0.24 \text{ cal.}$$

**Work done : Effect.**—In the working of a machine we are concerned chiefly with the absolute value of the work done per second.

As a practical unit the *horse-power* has been chosen, which corresponds to a work of 75 kilog.met. per second. The electrical unit of work is the volt-ampere, or *watt*, which is equal to 1 volt-coulomb per second (since 1 amp.  $=$  1 coulomb per second). As the watt is much too small a unit for measuring the work done in a dynamo, use is made of a unit 1000 times larger—the "kilowatt." It is quite evident that—

$$1 \text{ kilowatt} = \frac{1000}{75 \times 9.81} = 1.36 \text{ horse-power.}$$

**Work done by Change of Volume.**—If we have  $v$  c.c. of a substance in the liquid condition contained in a vessel of 1 sq. cm. section, then its height in the vessel will be  $v$  cm. (Fig. 2). On the surface of the liquid let there rest a weighted piston, so that there is a pressure of  $P$  dynes opposing the expansion of the liquid.

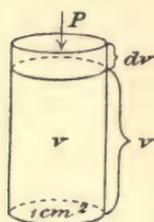


FIG. 2.

If the liquid be now warmed, or if a chemical reaction take place in it, then the volume changes; let the change be represented by an expansion of  $dv$  c.c.

In order that this expansion may take place, the weighted piston resting on the surface must be raised through  $dv$  cm., whereby the work  $Pdv$  will be done.

From this it is clear that when any substance whatever expands by  $dv$  c.c. the work done is  $Pdv$  ergs if the pressure  $P$  is expressed in dynes per square centimetre.

In Fig. 3 the shaded portion  $K$  represents the original volume of a substance, whilst the outer contour represents the volume after expansion. Let us consider the small element of surface  $dA$  sq. cm. This has been displaced through  $h$  cm., and the work done by it is  $P \cdot dA \cdot h$  ergs, since there is a pressure  $P \cdot dA$  on  $dA$ . If we denote the volume  $h \cdot dA$  by  $dw$ , then the work is  $P \cdot dw$  ergs; and if we

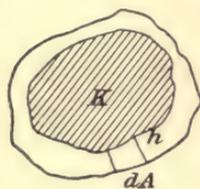


FIG. 3.

calculate for the whole substance we must take the sum of all the products,  $P \cdot dw$ . Since now  $P$  possesses the same value for all parts of the surface, and as the sum of all the volumes  $dw$  is evidently equal to the total change of volume  $dv$ , the total work done will be  $P \cdot dv$  ergs (as given above).

**Work done by Evolution of a Gas under Constant Pressure.**—We can now calculate the work done when a gas is formed at constant pressure; for instance, by the boiling of water. For the sake of simplicity, let us take a gram-molecule (18 grams) of water vaporising at a pressure of

760 mm. (1 atmo.). Since this pressure is that of a column of mercury 76 cm. high and of 1 sq. cm. section =  $76 \times 13.6$  grams, then in absolute measurement:

$$1 \text{ atmo.} = 76 \times 13.6 \times 981 = 1.014 \times 10^6 \text{ dynes per sq. cm.}$$

According to Avogadro's hypothesis (see below), a gram-molecule of a gas at  $0^\circ$  and 1 atmo. pressure occupies the volume 22,400 c.c.; and since, according to Gay-Lussac's (Charles's) law, the volume of a gas (at constant pressure) is proportional to its absolute temperature, the volume of a gram-molecule of water vapour (or any other gas) at  $100^\circ$  is—

$$v = \frac{22,400}{273} \times 373 = 82 \times 373 \text{ c.c.}$$

and at any other temperature  $T$  (in absolute degrees)

$$v_T = 82 T \text{ c.c.}$$

The work, therefore, which has to be done to bring a gram-molecule into the gaseous state is—

$$Pdv = 1.014 \times 82 \times 10^6 \times T \text{ ergs} = 83.2 \text{ megergs.}^1$$

We have already seen that 1 cal. = 41.8 megergs, consequently the work done on vaporising a gram-molecule, expressed in calories, is given by—

$$A = \frac{83.2}{41.8} T \text{ cal.} = 2T \text{ cal. (or more exactly } 1.99T \text{ cal.)}$$

The external work, therefore, which is done on evolving a gram-molecule of a gas is, when expressed in calories, twice the absolute temperature. The work done on forming a gram-molecule of steam at  $100^\circ$  is equivalent to  $2 \times 373 = 746$  calories.

This work is independent of the value of the external pressure. For if the pressure in the preceding example be 2 atmos. instead of one, then, according to Boyle's law, the

<sup>1</sup> The syllable meg- before a unit of measurement signifies a million. Thus 1 megerg = 1 million ergs, 1 megohm = 1 million ohms. The prefix micro- denotes a millionth; thus, 1 microvolt =  $10^{-6}$  volt.

volume will only be equal to half its former value. That is to say, in the expression

$$P \cdot dv = A$$

the value of  $P$  has been doubled, whilst the value of  $dv$  has been halved; consequently the product remains the same. It is evident that the law is valid for any variation of pressure whatsoever.

#### Expansion of Gases by Heat at Constant Pressure.—

In an analogous manner it can be seen that for a gas which is heated from the absolute temperature  $T$  to  $T + 1$  the volume changes from  $v_T = 82T$  c.c. to  $v_{T+1} = 82(T + 1)$  c.c., and the work done on so raising the temperature of a gram-molecule of a gas is—

$$A = \frac{83 \cdot 2}{41 \cdot 8} = 1 \cdot 99 \text{ cal.}$$

#### Expansion of Gases at Constant Temperature.—

Let us consider a gram-molecule at the temperature  $T$  and under a pressure of  $p$  atmos.; on expansion the pressure  $p$  changes, and the change is inversely proportional to the change of volume  $v$ . The work done on expanding from  $v_0$  to  $v_1$  is obtained by integrating  $p dv$ ; that is,

$$A = \int_{v_0}^{v_1} p dv.$$

From Boyle's law,  $p v = p_0 v_0$ , it follows for a gram-molecule of gas that if  $p_0 = 1$  atmo. = 1.014 megadynes per square centimetre, and if  $v_0 = 82T$  c.c.,

$$p_0 v_0 = p v = 1 \cdot 99 T \text{ cal.}$$

If we introduce this result into the above expression for  $A$  we obtain—

$$A = 1 \cdot 99 T \int_{v_0}^{v_1} \frac{dv}{v} \text{ cal.} = 1 \cdot 99 T \ln \frac{v_1}{v_0} \text{ cal.} = 1 \cdot 99 T \ln \frac{p_0}{p_1} \text{ cal.}$$

Since the final expression contains only the *ratio* between the initial and final volumes or pressures, it is immaterial in which system of units these values are measured. By replacing the natural logarithms by the ordinary (Brigg's) logarithms we obtain—

$$A = 4.58T \log \frac{v_1}{v_0} \text{ cal.} = 191.6T \log \frac{v_1}{v_0} \text{ megergs.}$$

In order, therefore, to expand a gram-molecule of a gas at  $0^\circ$  so far that its pressure sinks from 760 mm. to 76 mm., a work of  $191.6 \times 273 = 52,300$  megergs = 1251 cal. must be done. This work (or quantity of heat) is taken from the expanding gas, and since the temperature is kept constant at  $0^\circ$  during the process, heat must be introduced from outside in order that no cooling may take place. Expansion at constant temperature is called *isothermal*.

If we use  $n$  gram-molecules instead of 1, then the work done is  $n$  times that indicated by the preceding formulæ, but there is no other change in the result.

## CHAPTER II.

### Older Electrochemical Views.

**The First Electrochemical Investigations.**—The striking effects brought about by electricity formed the subject of much study about the middle of the eighteenth century. At that time friction electrical machines were in use, and in order to intensify the effects produced, very large machines were constructed. The most famous of these is still to be seen in the Teyler Museum in Haarlem. Pater Beccaria, some one hundred and thirty years ago, by using such machines found that metals could be “revivified” (*i.e.* reduced) from their calces (oxides) when the electric spark was passed between two pieces. In this way he obtained zinc and mercury. Some time later, Priestley investigated the action of the electric spark on air and observed that an acid was produced; he mistook this for carbonic acid, until Cavendish recognised it as nitric acid. Van Marum studied the behaviour of several other gases in the path of the electric spark [which led him to notice the formation of ozone], and made experiments also by passing the spark through liquids. Before him, Priestley had discovered that in oil and ether the electric spark produces gas, and proved that this gas contained hydrogen.

The first actual electrolysis was made by Deimann and Paets van Troostwyk in Haarlem in 1789, in which they successfully decomposed water into hydrogen and oxygen. In their experiments the water was contained in a cylindrical tube closed at the top, and having a metal wire sealed into its upper end. Another metal wire was introduced into the

lower end of the tube, which dipped into a basin of water. When the sparks struck through the water, bubbles of gas were disengaged from the metal wires, and, rising in the tube, gradually displaced the water. As soon as the column of water sank below the upper electrode, the gas, which was a mixture of hydrogen and oxygen, exploded. This experiment was later repeated by Ritter, using silver wires and a solution of a silver salt, and he observed that the negative pole became coated with precipitated silver. On changing the poles, silver was dissolved from one and deposited on the other (now the negative pole). In Deimann's experiment, oxygen and hydrogen were simultaneously formed, both at the positive and at the negative poles, so that the process was not a true electrolytic one like that of Ritter.

**Galvani and Volta.**—The whole state of the science was changed in a great degree by the discoveries of Galvani, and particularly by those of Volta. In 1795 Volta arranged the metals in a series according to their behaviour in galvanic experiments, and in 1798 Ritter showed that the same series is obtained when the properties of the metals to separate other metals from their salt solutions are compared.

After the introduction of Volta's pile (in 1800) the physiological and optical phenomena were less studied, and more attention was paid to the chemical actions. As opposed to the electrical machines, these piles gave large quantities of electricity at a comparatively low potential. Nicholson and Carlisle, in 1800, studied the evolution of oxygen and hydrogen in salt solutions at immersed gold electrodes which were connected with the poles of a Voltaic pile, and observed that litmus in the neighbourhood of the positive pole was turned red by the acid produced there.

Some years later Davy made his brilliant electrochemical discoveries. He succeeded in decomposing the oxides of the alkali and alkaline earth metals, which had previously been regarded as elementary substances, and in preparing the pure metals. Further progress in obtaining the more difficultly

reducible metals in this way was later made by Bunsen and his pupils.

**Berzelius's Investigations.**—In 1807, J. J. Berzelius, in conjunction with Baron Hisinger, published his first paper, which formed the foundation of his subsequent electrochemical theory. These investigators came to the following conclusions:—

Neutral salts are decomposed by the electric current. In general, chemical compounds are decomposed by the current, and the constituents collect at the poles.

Combustible substances, the alkalis, and earths migrate to the negative pole; oxygen, the acids, and oxidised compounds migrate to the positive pole. Thus, for example, nitrogen in ammonia goes to the negative pole, whilst in nitric acid the nitrogen goes with the oxygen to the positive pole.

The quantities of the products of decomposition are proportional to the quantities of electricity, and these are dependent upon the area of contact of the metals in the pile and on the moist conductor. Further, the quantities of substance decomposed are proportional to the electrical conductivities of the solutions.

The chemical processes taking place during an electrolysis are determined: firstly, by the affinities of the constituents to the metals of which the poles are constructed; secondly, by the reciprocal affinities of the constituents; and thirdly, by the cohesion (solubility) of the new compounds.

It was on these and similar conclusions drawn from experiment that Berzelius, as well as his precursor, Davy, founded their electrochemical theories.

**Davy's Electrochemical Theory.**—Davy proved that acid and base could not be formed from pure (free from salt) water, as had been erroneously believed. He found that by using pure water in a gold vessel no acid or base was produced, but where the vessel was one of gypsum, fluorspar, heavy spar, basalt, lava, or glass, partial solution of the material of which this was made took place, and the results formerly found could be explained.

Chemical affinity depends upon the electric properties of the atoms, and their attraction is due to their electric charges. According to Davy, the cause of the charge is to be found in the contact of the atoms, since Volta believed that he had proved that when two bodies are brought into contact, they become oppositely charged with electricity. Electrolysis consists in bringing back the atoms into the condition in which they were before union. The sign of the pole at which the atoms separate defines the nature of their charge, which is opposite to that of the pole.

Contrary to the prevailing view, Davy was of the opinion that electrolysis is principally a primary action, that is, the current decomposes electrolytes directly.

**Berzelius's Theory** differed essentially in one point from Davy's. Berzelius assumed that the atoms do not first become electrified by touching each other, but that they are already charged before coming into contact—a conclusion at which Schweigger had previously arrived, without, however, following it up further. The different kinds of electricity concentrated at the various points of the atoms do not act outwardly with the same force, but with different strengths.

The two quantities of electricity do not require, therefore, to be unequal; for the action might be compared with that which a magnet with two equally strong poles exerts on an object placed near one of these; in this case the action of the nearer pole preponderates.

The atoms behave similarly, they also have two (electric) poles, so that the most highly charged atoms do not necessarily show the strongest affinity. According as the action of the positive or negative pole preponderates, the body shows positive or negative properties, that is, is attracted by the negative or positive pole of a voltaic pile.

Since in all compounds the oxygen migrates to the positive pole, oxygen was regarded as the most negative of all substances. For a similar reason potassium (and afterwards cæsium) was held to be the most positive element.

After oxygen followed sulphur, chlorine, bromine, iodine, etc., which are all separated from their compounds at the positive pole. With oxygen, these negative substances form strong acids, which likewise separate at the positive pole. Close to the negative substances Berzelius set in the series those elements (all positive bodies) which could form acids with oxygen, and the stronger the acid which was formed, the nearer did these elements stand to the negative substances. Further, he placed those bodies which give difficultly reducible compounds with oxygen at the positive end of the series, on the assumption that compounds are the more stable the greater the charge possessed by the positive component.

Metals capable of separating others from their compounds were regarded as more positive, and substances with similar chemical properties were placed together. If an element lay between two others as far as chemical properties were concerned, it was placed between them also in the series—for example, bromine between chlorine and iodine.

In this way Berzelius, after many alterations, set up the following so-called *electrochemical series*, beginning with the negative elements :—

Oxygen	Boron	Palladium	Thorium
Sulphur	Carbon	Silver	Zirconium
Selenium	Antimony	Copper	Aluminium
Nitrogen	Tellurium	Uranium	Yttrium
Fluorine	Tantalum	Bismuth	Beryllium
Chlorine	Titanium	Tin	Magnesium
Bromine	Silicon	Lead	Calcium
Iodine	Hydrogen	Cadmium	Strontium
Phosphorus	Gold	Cobalt	Barium
Arsenic	Osmium	Nickel	Lithium
Chromium	Iridium	Iron	Sodium
Vanadium	Platinum	Zinc	Potassium
Molybdenum	Mercury	Manganese	
Tungsten	Rhodium	Cerium	

From what has been said, it is evident that this series was really only a chemical scheme, and that it is incomplete and arbitrary, may be gathered from the number of alterations



Ampère (in 1821) had already assumed that the atoms carry with them a certain invariable quantity of electricity, some carrying a positive charge, others a negative. The charge on the atoms binds an equal quantity of the opposite kind of electricity in the surrounding medium. If a positive and a negative atom collide, the bound electricity in the neighbourhood becomes free, the charges on the two atoms bind each other, and a union of the atoms takes place with formation of a neutral compound.

On the other hand, according to Berzelius the atoms are charged polarly, as in the scheme:  $\overset{\text{K}}{\text{--}+}$   $\overset{\text{Cl}}{\text{--}+}$ . When they combine, negative electricity from potassium and positive from chlorine become free, and there is formed  $\overset{\text{K}}{+}$   $\overset{\text{Cl}}{-}$ .

By this process heat and light phenomena were supposed to arise during a reaction. These and similar speculations on the part of Fechner, De la Rive, Schönbein, and Magnus, were too speculative to command attention for any length of time.

**Faraday's Law.**—Faraday (1),<sup>1</sup> in 1834, discovered that every equivalent binds the same quantity of electricity, so that a zinc atom takes up twice as much, and an aluminium atom three times as much, as a hydrogen atom (see p. 7). Berzelius strongly questioned this law, as it was not in agreement with the views which he had previously expressed.

**Hittorf's Investigation.**—In the course of the sixth decade of last century, Hittorf (2) performed his work on the migration of the ions, a piece of work of fundamental importance, to which, nevertheless, little attention was paid at the time. We return later to this subject.

**Helmholtz's Faraday Lecture (3).**—Helmholtz, one of the most brilliant devotees of the exact sciences, in 1881 delivered the Faraday lecture, in which he discussed the then modern development of Faraday's ideas on electricity. The

<sup>1</sup> The italic numbers enclosed in brackets refer to the literature references at the end of the book.

following abstract of the address may serve to indicate what were the best-founded electrochemical views of that period:—

Since the quantity of electricity on any atom is equal to, or is a whole multiple of, that on a hydrogen atom, Helmholtz proposed a unit for this—the *atomic charge*. Electricity is assumed to exist in matter in distinct homogeneous particles which correspond to the atoms. An atom can occur charged either positively or negatively—for example, in hydrogen sulphide the sulphur is negative, in sulphuric anhydride ( $\text{SO}_3$ ) it is positive.

According to Helmholtz, all substances are electrolytes, and better or worse conductors of electricity. After electrolysing the “non-conductor” turpentine for twenty-four hours, it was found that an electrometer placed between the two electrodes indicated a potential difference—that is, polarisation had taken place, proving that there had been some electrolysis (8 dll. caused a polarisation of 0.3 dll. in ether, oil, and turpentine, and of 0.8 dll. in benzene). Similarly, Helmholtz found a potential difference between metals, such as copper and zinc, which were separated by the best known insulators—glass, resin, shellac, paraffin, or sulphur—and proved that this result was not due to hygroscopic moisture. He called attention to the extraordinarily high values of the electric forces binding hydrogen and oxygen in water, which forces are able to completely change the properties of these elements on combination.

Helmholtz explained the capability of one element of separating another from its compound as due to the greater affinity for positive electricity. The Berzelius series is to be understood in this sense. This, too, is the cause of the Volta effect.

Each valence corresponds with a single charge, consequently the atoms combine in multiple proportions. In the case of unsaturated compounds with two free valencies, it is to be assumed that one of these corresponds with a positive, the other with a negative charge. Unsaturated compounds with an odd number of free valencies were assumed to exist

only at high temperatures, and possessed an excess (one atomic charge) of one kind of electricity. Nitric oxide (NO), which has one free valence, offered a great difficulty in this connection, for it is stable at the ordinary temperature, and does not conduct the current.

In concluding, Helmholtz remarked on the great importance of electrochemistry.

## CHAPTER III.

### The Laws of Avogadro and van't Hoff.

**Boyle's Law.**—When a gas is contained in a vessel the volume of which can vary, as, for instance, in a cylinder with a movable piston, then, if the volume  $v$  be changed by moving the piston, the pressure  $p$  changes in inverse proportion; if the volume be changed to half what it originally was, the pressure is doubled. This law is expressed by the general formula:—

$$pv = \text{constant.}$$

Boyle proved this for pressures greater than 1 atmo., and Mariotte afterwards proved it for lower pressures.

**Gay-Lussac's (Charles's) Law.**—The above law is only applicable when the temperature of the gas remains constant. If the temperature rises, the product  $pv$  increases, as Gay-Lussac found, by  $\frac{1}{273}$  of its value at  $0^\circ$  for each Celsius degree. In other words, the product  $pv$  is proportional to the absolute temperature  $T$ —

$$pv = \text{constant} \times T.$$

**Avogadro's Law.**—Avogadro showed that the constant in this formula was the same for all gases if a gram-molecule of the gas be taken. In the usual form of the equation—

$$pv = RT$$

$R = 84688$  when  $p$  is measured in grams per square centimetre and  $v$  in cubic centimetres.

This is found by considering 1 gram-molecule of oxygen,

the density of which was found by Regnault to be 0·00143011 at 0° and 760 mm. pressure; under these conditions ( $T = 273$ ,  $p = 1033\cdot6$  grams per square centimetre) the volume of 1 gram is  $\frac{1}{0\cdot00143011} = 699\cdot3$  c.c. and that of 32 grams is  $32 \times 699\cdot3$  c.c.; consequently—

$$1,033\cdot6 \times 32 \times 699\cdot3 = 273R$$

$$R = 84,688.$$

If the pressure is measured not in grams per square centimetre, but in millimetres of mercury, the value of  $R$  is 1·36 times smaller, *i.e.*  $R = 62,265$ .

We have already obtained (see p. 13) another expression of Avogadro's rule, extremely useful for calculations, namely—

$$pv = 2T \text{ cal.}$$

in which the value of  $R$  is 2 (or, more exactly, 1·99).

By means of this equation we can ascertain the pressure, volume, or temperature of a given mass of gas provided we know two of these factors.

It might be required to find, for example, how many litres of saturated water vapour are evolved from 1 litre of water at 0°. The vapour tension of water at this temperature is 4·60 mm. In our formula,  $pv = RT$ , we have to set  $p = 4\cdot6$ ,  $R = 62,265$ , and  $T = 273$ , and we find  $v = 3,612,000$  c.c., a value which applies to 1 gram-molecule, *i.e.* 18 grams, of water. A litre of water at 0° weighs 999·9 grams, and contains, therefore, 55·55 gram-molecules; consequently, in the state of gas it occupies a volume 55·55 times as great as that which we have calculated for 1 gram-molecule,  $55\cdot55 \times 3,612,000$  c.c. = 205,600 litres.

**Law of van der Waals.**—The relationship  $pv = RT$  represents a limit law—that is to say, it only becomes strictly correct at very great dilution. At moderate and high pressures the forces acting between the molecules, and the volume actually occupied by the molecules, become

appreciable. Van der Waals, correcting the pressure and volume for these circumstances, arrived at the formula—

$$\left( p + \frac{a}{v^2} \right) (v - b) = RT,$$

containing two new constants,  $a$  and  $b$ , which are functions of the “internal pressure” and of the molecular volume. Experimental results show a high degree of agreement with this formula.

**Isotonic Solutions.**—Certain parts of plants, when in a more or less dehydrated condition, are able when placed in water to absorb some of it without losing any of the cell-content—a fact which has long been known to physiologists. Further experiments with salt solutions and plant cells showed that at a certain concentration of the solution an equilibrium is established between it and the cell-contents. If the solution is too dilute, water passes into the cell; if too concentrated, water passes out from the cell. Those salt solutions which are in equilibrium with the cell-sap are said to be isotonic or isosmotic with it.

By using the same or quite similar cells—cells are used which lie close together in a homogeneously developed part of a plant—these could be compared with solutions of different substances, and the concentrations of the various dissolved substances in solutions which are isotonic with the cells could be determined. These solutions are, of course, isotonic with respect to each other.

De Vries (*1*) found, in a series of experiments with *Tradescantia discolor* and *Begonia manicata*, that solutions which contained in a litre equivalent quantities of potassium nitrate, sodium nitrate, and potassium chloride were isotonic with each other. But a solution containing 1 gram-molecule of potassium chloride had the same effect as a solution containing 1.7 gram-molecules of cane sugar or glycerol.

The cell preparations in the salt solution to be investigated are examined under the microscope. Each cell (Fig. 5 *a*) is surrounded by a solid cell-membrane, which allows both

water and dissolved substance to pass through its pores. Inside this cell-wall there is the real cell-content, the protoplasm. If the cell-content parts with water to the surrounding medium, it contracts and separates from the

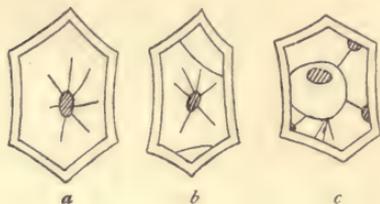


FIG. 5.

wall (plasmolysis), at first at the corners as represented in Fig. 5*b*. If much water is lost by the cell, the protoplasm aggregates to a mass which remains connected with the cell-wall only by a few fine threads

(Fig. 5*c*). The cell-content can easily be distinguished from the cell-wall by staining (methyl-violet, etc.).

**Semi-permeable Membranes.**—Living cells have the peculiar property of allowing water but not dissolved material to pass to or from the protoplasm.

After death or by the action of some poisons, the cell loses this property. An artificial cell possessed of this property is naturally of great value. The physiologist Traube (2) succeeded in preparing such a cell by precipitating a thin colloidal film of copper ferrocyanide within the walls of a porous cylinder. With so-called *semi-permeable membranes* of this nature, Pfeffer (3) carried out a series of striking experiments.

**Osmotic Pressure.**—Pfeffer filled a porous cylinder, *A*

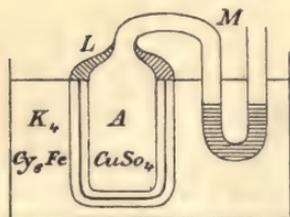


FIG. 6.

(Fig. 6), with copper sulphate solution, and immersed it in a solution of potassium ferrocyanide. Somewhere about the middle of the cell-wall the two solutions met, and there a fine membrane of copper ferrocyanide was formed, which gradually grew stronger. The cell

*A*, whose wall only served as a mechanical support, was washed out, and filled quite full with a solution of cane sugar. A cover, *L*, fitted with a manometer, *M*, was luted

on to the cylinder, and the whole apparatus was placed in a water-bath kept at a constant temperature. The water forced itself into the sugar solution, and the pressure in the cell rose to a maximum value, at which evidently water neither diffused into nor out of the cell. The equilibrium was established more quickly when mercury was poured into the open end of the manometer. If the pressure was increased beyond this maximum value, which is the *osmotic pressure* of the sugar solution in question, water was forced out of the cell into the outer bath.

Pfeffer first investigated the behaviour of solutions of cane sugar of different concentrations, and found the following values:—

Percentage of sugar	1	2	2.74	4	6
Osmotic pressure	535	1016	1513	2082	3075 mm. Hg.
$\frac{\text{Osmotic pressure}}{\text{Percentage of sugar}}$	535	508	554	521	513

The numbers in the last line are very nearly equal, and the differences are easily attributable to the errors of experiment, which are fairly appreciable. *The osmotic pressure is, therefore, proportional to the quantity of substance or the number of molecules in unit volume.* This corresponds exactly with gas pressure, which, according to the law of Boyle, is inversely proportional to the volume taken up by the gas—that is, directly proportional to the concentration of the gas.

Pfeffer also carried out experiments with other solutions of such substances as gum, dextrin, potassium sulphate, potassium nitrate, etc. With potassium nitrate he obtained the following results:—

Percentage of potassium nitrate	0.80	1.43	3.3
Osmotic pressure	1304	2185	4368 mm. Hg.
$\frac{\text{Osmotic pressure}}{\text{Percentage of KNO}_3}$	1630	1530	1330

In this case the osmotic pressure is not exactly proportional to the quantity of salt, but increases more slowly than the concentration. The cause of this deviation lies chiefly in the fact, which Pfeffer proved, that the membrane,

particularly at high pressures, is not quite impermeable for the salt.

Pfeffer further proved that the osmotic pressure increases slowly with rise of temperature as the following table shows:—

Temperature.	Osmotic pressure in cm. Hg.	
	Observed.	Calculated.
6.8°	50.5	50.5
13.5°	52.1	51.7
14.2°	53.1	51.8
22.0°	54.8	53.2

The numbers in the last column have been calculated on the assumption that the osmotic pressure, just as the gas pressure according to the law of Gay-Lussac, increases proportionally to the absolute temperature, and it will be shown later that this must be the case. Pfeffer's numbers do not justify this conclusion, but they at least show that the direction of the influence of temperature is in agreement with the assumption.

Lastly, we may try to find if Avogadro's law also obtains for the osmotic pressure—that is, whether for dissolved substances the constant  $R$  in the equation  $pV = RT$  has the same value as for gases.

At the absolute temperature 279.8° cane sugar in a 1 per cent. solution has a pressure of 505 mm. Hg. As the molecular weight of sugar is 342, if 1 gram is contained in 100 c.c. of solution, 1 gram-molecule is contained in 34,200 c.c.

From the equation—

$$505 \times 34,200 = R \times 279.8$$

$$R = 61,720,$$

instead of the value 62,265 found for gases (see p. 26).

This calculation was first made by van't Hoff (4), who

called attention to the great similarity which exists between the gas pressure and the osmotic pressure of dissolved substances. He expressed this by saying that the gas laws are also applicable to dilute solutions if the gas pressure be replaced by osmotic pressure. The law of Boyle, applicable to all gases at constant temperature, followed by Gay-Lussac's law for the single gases at all temperatures, then by Avogadro's law for all gases at all temperatures, and finally, by van't Hoff's generalisation for all finely dispersed material at every temperature, together form one of the most beautiful series of development in science.

Of all the laws of matter known to us, that of van't Hoff is one of the most general.

**Osmotic Pressure of Gases.**—Experiments with semi-permeable membranes offer as a rule considerable difficulties, since the pressure equilibrium is only slowly established. The best results are obtained by working with gases. Ramsay (5) carried out the following experiment, first suggested by me:—

Two vessels, *A* and *B* (Fig. 7), each provided with a manometer,  $m_1$  and  $m_2$ , are separated by a palladium wall, *P*. *A* is filled with hydrogen and *B* with nitrogen, both at atmospheric pressure and ordinary temperature; the manometers then indicate the same pressure in each vessel. The apparatus, but not the manometers, is then heated to 600°. Hot palladium has the peculiar property of taking up hydrogen and allowing it, but not nitrogen, to pass through. Hydrogen, therefore, can pass from *A* to *B* until the hydrogen pressure is the same on both sides of the palladium wall— $\frac{1}{2}$  atmo., if *A* and *B* are of equal volume. When the apparatus is now brought back to the ordinary temperature, there will be found in *B* nitrogen at 1 atmo. pressure and hydrogen at  $\frac{1}{2}$  atmo.,

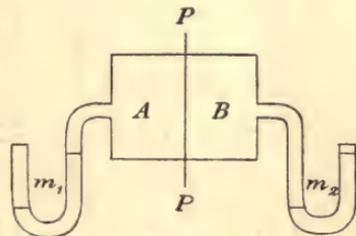


FIG. 7.

whilst in *A* there is only hydrogen at  $\frac{1}{2}$  atmo. pressure. The excess of pressure in *B* may be termed the osmotic pressure of nitrogen. In this case it is quite clear that the osmotic pressure of nitrogen in *B* (according to Dalton's law) is equal to the pressure which obtains if it alone occupied the volume *B* in the state of gas.

A similar experiment may be carried out at the ordinary temperature with carbon dioxide and hydrogen, if the palladium be replaced by a caoutchouc membrane. Carbon dioxide is much more soluble—about 60 times—than hydrogen in caoutchouc, and consequently the carbon dioxide passes from *A* to *B* comparatively quickly, whilst the hydrogen almost all remains in *B*. Complete equilibrium is established in this case when the carbon dioxide and hydrogen have distributed themselves equally between *A* and *B*. But at the beginning a rapid rise is noticed at the manometer *m*<sub>2</sub>, which then sinks slowly after some time. With respect to

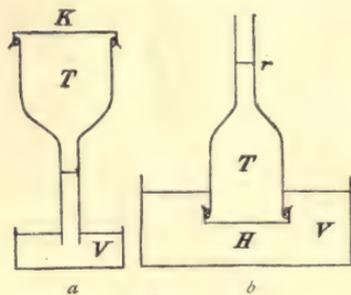


FIG. 8.

hydrogen and carbon dioxide, caoutchouc is, therefore, not a perfect semi-permeable membrane; and a similar imperfection is to be found in all semi-permeable membranes.

The above experiment can also be carried out in the following way: The wide end of a funnel, *T* (Fig. 8*a*), is covered with a sheet of rubber. The funnel is then filled with carbon dioxide, and the narrow end dipped into water or other liquid, *V*. The liquid rises against the external pressure, because the carbon dioxide diffuses more quickly outwards through *K* than air diffuses inwards.

**Osmotic Experiments with Liquids.**—Dutrochet in 1826 carried out a similar experiment with a liquid. He closed a funnel with an animal membrane, *H*, and after filling the funnel with copper sulphate solution, dipped it into water. As water passes through the membrane more quickly than

the copper sulphate solution, the liquid rises in the tube *r* against the external pressure (Fig. 8*b*). After some time, however, the level of the liquid in the tube sinks to that of the liquid outside, because the membrane *H* does not completely prevent the diffusion of the copper sulphate.

The Abbé de Nollet in 1750 had performed the same experiment, using alcohol instead of copper sulphate.

The so-called "chemical garden" is an osmotic phenomenon from which much may be learned. If a crystal of ferric chloride be thrown into a dilute solution of potassium ferrocyanide, it sinks and becomes enveloped in a film of Prussian blue, which is permeable by water but not by ferric chloride or potassium ferrocyanide. Consequently water

forces its way into this semi-permeable cell of Prussian blue and expands it. Further quantities of the ferric chloride will be dissolved by the water which has entered, so that the osmotic pressure is always kept high. If the inflowing water bursts the membrane, a new precipitation takes place at the same spot, and so the cell at once closes. The small air-bubbles originally attached to the ferric chloride crystal exert an upward pull on the cell, and a more or less tree-like formation is noticed; at the higher extremities the small air-bubbles are frequently visible (Fig. 9).

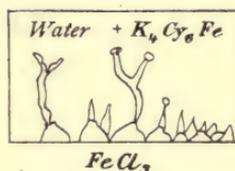


FIG. 9.

**Nature of Osmotic Pressure.**—Ramsay's application of palladium as a semi-permeable membrane teaches us much. If we imagine the hydrogen replaced by water, the nitrogen by sugar, and the sheet of palladium by a film of copper ferrocyanide, then we have Pfeffer's experiment.

The water forces its way into *B* (Fig. 7), dissolves the sugar there, and fills *B* with the solution until the manometer indicates an excess of pressure, which corresponds with the osmotic pressure of the sugar. In Ramsay's experiment the pressure of the hydrogen was the same on both sides of

the palladium, so also in Pfeffer's experiment the pressure of the water is the same in *A* and *B*. The excess of pressure in *B* is in this case due to sugar, just as in the former case it is due to nitrogen. We generally conceive gas pressure as due to the impact of the molecules against the walls of the containing vessel; in the same way the osmotic pressure of the sugar may be imagined to be due to impacts of the sugar molecules against the membrane. The impacts of the molecules of a substance exert the same action whether the substance be in the gaseous or dissolved (liquid) state.

It is, however, quite unnecessary to rely on the kinetic view. It is well known that a gas tends to expand so as to fill the volume placed at its disposal, and this tendency evidences itself in the pressure.

The dissolved sugar has a similar tendency to become evenly distributed over the solvent, water, and the measure of this is the osmotic pressure. This expansion tendency of gaseous and dissolved substances at the same temperature, and with the same number of molecules in unit volume, is the same for all substances; it increases directly with the absolute temperature and with the concentration.

From the preceding examples it will be seen what is meant by a semi-permeable membrane. It is a medium which is capable of taking up one component of a (gaseous or liquid) mixture and holding the other back. As a rule one of the components is water, the other a dissolved substance. The envelopes of protoplasm, copper ferrocyanide, Prussian blue, etc., take up water, but not substances dissolved therein; palladium dissolves hydrogen, but not nitrogen; caoutchouc dissolves carbon dioxide, but not (in appreciable amount) hydrogen.

The above definition of a semi-permeable wall corresponds with two cases, the meaning of which we now come to. One case is the vacuum or a gas: the water may be taken out of a sugar solution in the form of vapour, but the sugar remains, being practically non-volatile. The other case is ice. If water

be allowed to freeze out of a sugar solution, it is found that only ice (*i.e.* water) separates, and the sugar remains entirely dissolved.

If a vessel, *A*, containing water, and another, *B*, containing an aqueous solution, be placed under a glass globe (Fig. 10), water will pass from *A* to *B*, the air acting as semi-permeable wall.

If in a vessel, *KK* (Fig. 11), one half, *A*, be filled with

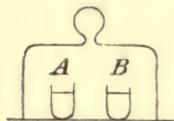


FIG. 10.

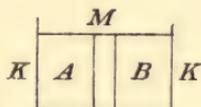


FIG. 11.

water and the other half, *B*, with a sugar solution, and if these be separated by a sheet of ice, water can pass from *A* to *B* by the thawing of the ice on the side next to the sugar solution and the freezing of the same quantity of water on the other side.

**Physiological Measurement of the Relative Osmotic Pressures in Different Solutions.**—Physiological experiments have been made with isotonic solutions, and these will be discussed in this section. Donders and Hamburger (6) found that two solutions which were isotonic at  $0^{\circ}$  were isotonic also at  $34^{\circ}$ . This corresponds with the fact that the pressure varies with the temperature in the same way for all gases (at constant volume), so that they will have nearly the same pressure at any temperature whatever, if at one particular temperature their pressures are equal.

De Vries (*1*) showed by means of plant cells that equimolecular solutions of non-electrolytes—that is, solutions containing the same number of molecules in the litre—are isotonic, as exhibited in the following table. For salts this same relationship does not hold good. The table gives the so-called isotonic coefficients, that of potassium nitrate being taken as 3. 1.78 for glycerol indicates, therefore, that

a solution which contains 3 gram-molecules of glycerol in the litre is isotonic with a solution of potassium nitrate containing 1.78 gram-molecules in the litre.

Glycerol . . . . .	1.78	Potassium iodide . . . . .	3.04
Glucose . . . . .	1.88	Sodium nitrate . . . . .	3
Cane sugar . . . . .	1.81	Sodium iodide . . . . .	2.90
Malic acid . . . . .	1.98	Sodium bromide . . . . .	3.05
Tartaric acid . . . . .	2.02	Potassium acetate . . . . .	2.85
Citric acid . . . . .	2.02	Potassium bromide . . . . .	3.05
Magnesium sulphate . . . . .	1.96	Potassium sulphate . . . . .	3.9
Potassium nitrate . . . . .	3	Calcium chloride . . . . .	4.05
Potassium chloride . . . . .	3	Potassium citrate . . . . .	4.74
Sodium chloride . . . . .	3		

Donders, Hamburger, and Hedin (?) have obtained analogous results using blood corpuscles. When the red corpuscles are introduced into a solution, which is so concentrated that it abstracts water from them, the corpuscles sink. If, on the other hand, the corpuscles absorb water from the solution, they at the same time lose part of their colouring matter, and the solution becomes red. In this way it is easy to determine the concentration of a solution which is isotonic with the corpuscles.

Donders and Hamburger investigated blood corpuscles from the various vertebrates, from the frog to the ox, and always obtained the same results, which, moreover, agreed with those arrived at by De Vries.

Experiments in which living cells are used have the disadvantage that isotonic can only be proved between such solutions as have the same osmotic pressure as the cell. The osmotic pressure of the cells, however, does not vary very much, for most of the cells available for investigation show a pressure of about 4 atmos. Young cells have a higher pressure than older ones, on which fact their power of development depends.

In certain species of bacteria the osmotic pressure rises to as much as 10 atmos., which high pressure is closely connected with their power of destroying other organisms of

lower osmotic pressure. Sea-weed has, as a rule, an osmotic pressure greater by about 4 atmos. than the water surrounding it.

**Tammann's Measurements.**—The method devised by Tammann ( $\delta$ ) is capable of more general application. The method consists in observing the diffusion currents in Töpler's apparatus. If in a liquid the density is greater or less at any one point than in the neighbourhood, then at this point the liquid either falls or rises, and this is easily seen on account of the different refractive indices of the solutions of different densities. Thereby the well-known phenomenon of streaking is produced, a phenomenon which is often to be noticed when the sun shines on a wall, producing a slow upward current of air.

Tammann uses as bath a solution of potassium ferrocyanide. Into this is introduced a drop of a solution of a copper or zinc salt hanging from the end of a glass point; the drop at once becomes covered with a semi-permeable membrane of copper or zinc ferrocyanide. If the drop is isotonic with the solution in the bath, no change of concentration takes place in its neighbourhood, and no streaking is formed. If the drop is more concentrated than the ferrocyanide solution, it absorbs water from the solution in immediate contact with it, thus making part of the solution specifically heavier than the mass of liquid in the bath, and it sinks, producing a streakiness along its course. The opposite action takes place when the solution within the membrane is too dilute.

In Tammann's experiments, the drops contained in some cases other substances, such as ethyl alcohol, cane sugar, etc., besides the copper salt. The osmotic pressure of the substances was calculated on the assumption that the total osmotic pressure is the sum of the osmotic pressure of the copper salt and that of the substance added.

The following table, which contains the chief results obtained by Tammann, gives the isotonic coefficients of those solutions which correspond with  $0.1 n$  and  $0.3 n$  solutions of

potassium ferrocyanide, the coefficients of these latter solutions being set equal to 1:—

	$n = 0.1$	$n = 0.3$		$n = 0.1$	$n = 0.3$
Potassium ferrocyanide	1	1	Cane sugar . . . . .	0.40	0.40
Ammonium sulphate . . . . .	0.75	0.80	Salicin . . . . .	0.42	—
Cupric nitrate . . . . .	0.82	0.93	Chloral hydrate . . . . .	0.46	0.45
Copper acetate . . . . .	0.69	0.66	Ether . . . . .	0.45	—
Copper chloride . . . . .	0.90	1.00	Urea . . . . .	0.50	—
Magnesium sulphate . . . . .	0.33	0.37	Propyl alcohol . . . . .	0.45	—
Zinc sulphate . . . . .	0.40	0.34	Isobutyl alcohol . . . . .	0.45	—
Copper sulphate . . . . .	0.41	0.36	Ethyl acetate . . . . .	0.45	—
Ethyl alcohol . . . . .	0.45	0.45			

**Further Experiments on Osmotic Pressure.**—Adie (9) has in a large measure overcome the technical difficulties in connection with osmotic experiments; he has determined the osmotic pressure of salt solutions, and obtained results which agree remarkably well with the requirements of the theory, so long as dilute solutions are used. For concentrated solutions, however, it has not yet been possible to prepare perfect semi-permeable membranes.

In this respect the experiments of G. Hedin (7) and Köppe (10) are interesting. A certain quantity of blood was added to equal quantities of various salt solutions placed in tubes in a centrifugal machine. The blood corpuscles collected together in the end of the tube in a cylindrical mass from the height of which the total volume of corpuscles added to the salt solution could be estimated. This volume was found to be the smaller the higher the osmotic pressure of the salt solution. Hedin and Köppe obtained results for the osmotic pressure of different solutions which were in close agreement with theory.

## CHAPTER IV.

### Vapour Pressure of Solutions.

**The Vapour Pressure of a Solution is lower than that of the Pure Solvent.**—It has been well known for a long time that a solution in water of a substance which has no appreciable vapour pressure has a lower vapour tension than water. Thus, for instance, the vapour tension of water can be reduced by the addition of sulphuric acid, and such solutions are, therefore, used to extract the moisture from the air. If the vapour tension is lowered, the boiling point must be raised, because when a liquid boils, its vapour pressure amounts to 1 atmo., and consequently, when the vapour pressure is diminished by the addition of some foreign substance, the temperature must be raised in order that the pressure may reach the value of 1 atmo.

This corollary has also been known for a long time; for instance, if a salt be dissolved in water, the boiling point of the solution (at 760 mm. Hg) is higher than  $100^{\circ}$ , and the more salt is added the higher is the boiling point. (Faraday, 1822; Legrand, 1833.)

**Connection between Vapour Pressure and Osmotic Pressure of a Solution.**—In the very first investigation made on osmotic pressure, it was found that the depression of the vapour pressure of a solution was almost exactly proportional to the osmotic pressure. A conclusive proof of this proportionality, based on the mechanical theory of heat, was first deduced by van't Hoff (1) in a paper to the Swedish Academy (1886). I (2) have later deduced the same

thing in a simpler way, and this development may fitly be introduced here.

A basin,  $S$ , containing a liquid, is placed under a glass globe,  $A$ , from which the air can be pumped out (Fig. 12). The wide end of a funnel which is closed by a semi-permeable membrane,  $M$ , dips into the liquid in the basin; the funnel is provided with a long stem,  $r$ . The funnel contains a solution, the solvent being the same as the liquid in  $S$ , and the dissolved substance being non-volatile.

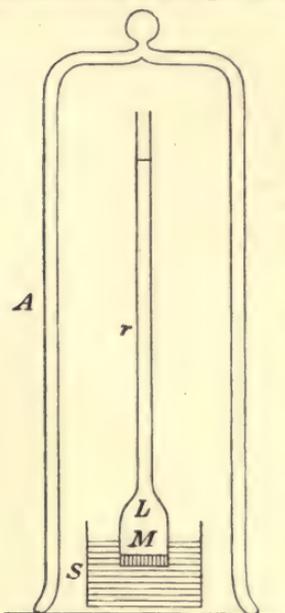


FIG. 12.

The liquid in  $S$  passes through the semi-permeable membrane and rises in  $r$ , until there is a hydrostatic pressure on  $M$ , equal to the osmotic pressure of the solution  $L$ .

In this case we have two semi-permeable media, namely, the membrane  $M$  and the vacuous space between the surfaces of the liquids in  $r$  and  $S$ . Suppose that the solution  $L$  contains  $N$  molecules of solvent of molecular weight  $M$  for 1 molecule of dissolved substance,  $N$

being large—that is, the solution a dilute one.

The osmotic pressure, and from this the height of the column of liquid in the tube  $r$ , can be calculated. The equation  $pv = RT$  gives us  $p$ , when  $v$  and  $T$  are known.  $v$  is the volume which contains 1 gram-molecule of dissolved substance. In this volume there are, according to the above assumption,  $N$  gram-molecules of solvent of molecular weight  $M$ —that is,  $NM$  grams of solvent, the specific gravity of which may be  $s$ . Therefore—

$$v = \frac{MN}{s},$$

and consequently—

$$p = \frac{RT \times s}{MN}.$$

The height  $h$  of the column in  $r$ , since the pressure per square centimetre must be  $p$  grams, is given by—

$$h = \frac{p}{s} = \frac{RT}{MN}.$$

The vapour pressure over the solution in  $r$  has now to be found. The decrease of pressure from the surface of the liquid in  $S$  to that in  $r$  is equal to the weight of a column of vapour  $h$  cm. high and of 1 sq. cm. cross-section. If  $p$  be the vapour pressure at the lower and  $p'$  that at the higher surface, this weight is equal to  $p - p'$ .

Now we know that the weight  $M$  of a gram-molecule of a gas at pressure  $p$  is contained in the volume  $v = \frac{RT}{p}$ .  $M$  grams occupy  $v$  c.c., and consequently 1 c.c. weighs  $\frac{1}{v}M$  grams, and  $h$  c.c. weigh  $\frac{h}{v}M$  grams. The weight of a column of vapour of 1 sq. cm. section between the two liquid surfaces is, therefore, equal to  $p - p'$  and to  $\frac{h}{v}M$ .

If we now substitute the values found above for  $h$  and  $v$ , we obtain—

$$p - p' = \frac{h}{v}M = M \frac{RT}{MN} \div \frac{RT}{p} = \frac{p}{N}$$

or—

$$\frac{p - p'}{p} = \frac{1}{N}.$$

**The Relative Lowering of Vapour Pressure.**—The relationship just deduced may be brought into a very simple form.  $\frac{p - p'}{p}$  is called the relative lowering of vapour pressure, and it obviously gives the difference between the vapour pressure of solvent and that of the solution referred to the vapour pressure of the solvent. It is independent of the temperature, of the nature of the solvent, and of the nature

of the dissolved substance, and is conditioned solely by the number of dissolved and solvent molecules.

This law was first established by Raoult (3) from purely experimental results; the connection with osmotic pressure was later shown by van't Hoff (4).

If one gram-molecule of a substance be dissolved in 100 gram-molecules of a solvent, the relative lowering of the vapour pressure should amount to  $\frac{1}{100}$ . Raoult carried out a large number of experiments on this subject.

The following table gives the mean values for a series of solvents from results obtained with various dissolved substances :—

Water . . . . .	0·0102	Methyl iodide . . . . .	0·0105
Phosphorus trichloride . . . . .	0·0108	Methyl bromide . . . . .	0·0109
Carbon disulphide . . . . .	0·0105	Ether . . . . .	0·0096
Carbon tetrachloride . . . . .	0·0105	Acetone . . . . .	0·0101
Chloroform . . . . .	0·0109	Methyl alcohol . . . . .	0·0103
Amylene . . . . .	0·0106	Ethyl alcohol . . . . .	0·0101
Benzene . . . . .	0·0106	Acetic acid . . . . .	0·0163

It has occasionally been assumed that by means of the above formula the molecular weight of the solvent could be calculated as that of the dissolved substance can be, since the relationship between the number of molecules of dissolved substance and of the solvent apparently occurs in the equation. If we regard the deduction more closely, however, we see that we have assumed the same molecular weight for the solvent in the liquid and in the vapour state. The molecular weight for the solvent in the vapour state must be that deduced from the vapour density, for otherwise Avogadro's law, which is used in developing the formula, would not be applicable. When Raoult experimented with acetic acid, the molecular weight of which, according to the chemical formula, is 60, but from the vapour density is 97·2 ( $= 1·62 \times 60$ ), he obtained for the relative lowering of the vapour pressure a number which was nearly 1·62 (exactly 1·63) times greater than that calculated, assuming 60 for the molecular weight. This apparent deviation is, therefore, in complete accord with the law.

It should be mentioned that here also salts seem to behave anomalously. Raoult only investigated few of these. We return later to a consideration of their behaviour.

**Vapour Pressure of Solutions in Ether.**—Raoult proved that for solutions in ethyl ether the relative lowering of vapour pressure is independent of the temperature. He used the ordinary method for determining the vapour pressure, namely allowing the liquid to evaporate in a barometer vacuum. The barometric height  $h$  was read off on the barometer *A* (Fig. 13); into another barometer, *B*, ether was introduced, and the mercury meniscus sank to  $h_1$ . The vapour pressure  $p$  of the ether is given by  $h - h_1$ . Into a third barometer, *C*, was introduced a solution, *e.g.* of 1 gram-molecule (136 grams) of turpentine in 1000 grams, that is,  $\frac{1000}{74}$  gram-molecules, of ether.

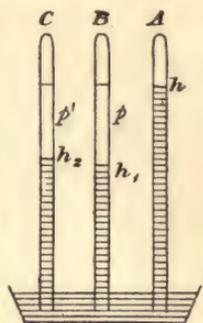


FIG. 13.

For this solution Raoult found the vapour pressure  $p'$ . The calculation leads to—

$$\frac{p - p'}{p} = \frac{1}{\frac{1000}{74}} = 0.074.$$

whilst the experiment gave 0.071.

The experiments were carried out in a room in which the temperature varied between  $0^\circ$  and  $20^\circ$ , but the same lowering,  $\frac{p - p'}{p} = P$ , was always obtained, although  $p$  varied over a tolerably wide range (from 185 to 442 mm.).

Other substances besides turpentine were examined, in all cases 1 gram-molecule in 1000 grams of ether being taken. The values obtained, which are given in the following table, all agree, within the limits of experimental error, with the result found for turpentine 0.071 and the theoretical value 0.074.

	$M$	$P$		$M$	$P$
Perchloro-ethylene . . .	237	0.071	Benzaldehyde . . .	106	0.072
Methyl salicylate . . .	152	0.071	Capryl alcohol . . .	130	0.073
Methyl azocuminate . . .	382	0.068	Cyanamide . . . . .	42	0.074
Cyanic acid . . . . .	43	0.070	Aniline . . . . .	93	0.071
Benzoic acid . . . . .	122	0.071	Mercury diethyl . . .	258	0.069
Trichloroacetic acid . . .	163.5	0.071	Antimony trichloride	228.5	0.067

**Higher Concentrations.**—The formula no longer applies when the solution is concentrated, for when  $N = 1$ —that is, when the number of molecules of solvent is the same as the number of molecules of dissolved substance, then  $\frac{p - p'}{p}$  should be equal to 1, or, in other words,  $p' = 0$ , which would indicate that the solution has no vapour pressure. Experience teaches that this is incorrect, and, as Raoult has shown, the results are in agreement with the formula—

$$\frac{p - p'}{p} = \frac{1}{1 + N}.$$

which coincides with the former one when  $N$  becomes great in comparison with 1.

Good results can also be obtained for concentrated solutions if we assume that the relative lowering of the vapour pressure increases proportionally with the concentration of the solution, provided this is measured in gram-molecules per litre. If  $d$  is the specific gravity of the solvent, then the weight of a litre is  $1000d$  grams, or  $\frac{1000d}{M}$  gram-molecules are contained in a litre. The vapour tension of a solution which contains 1 gram-molecule of a dissolved substance in 100 litres can, therefore, be found from—

$$\frac{p - p'}{p} = \frac{M}{100,000d},$$

because at such great dilution we may set the volume of the

solvent equal to that of the solution. If the solution contains  $n_1$  gram-molecules of dissolved substance per litre, then—

$$\frac{p - p'}{p} = \frac{n_1 M}{1000d}.$$

This formula has been tested with the data accumulated by Raoult for concentrated solutions, and a very perfect agreement has been found.

**Aqueous Solutions.**—In one investigation Tammann (5) measured the external pressure under which aqueous solutions boil at  $100^\circ$ , and in this way found the vapour pressures of the solutions at this particular temperature. From the last formula of the preceding section we find for a normal solution in water (since  $p = 760$  mm.,  $n = 1$ ,  $M = 18$ , and  $d = 0.959$ )

$$p - p' = 760 \frac{n_1 18}{1000 \times 0.959} = 14.3 \text{ mm. Hg.}$$

One hundred and eighty substances were examined at various dilutions. In the following table, which contains some of Tammann's results, the concentration is expressed in gram-molecules dissolved in 1000 grams of water. A dilute solution containing  $n$  mols dissolved in 1000 grams of water corresponds at  $4^\circ$  almost exactly with an  $n$ -normal solution; at  $100^\circ$  it corresponds with a  $0.959 n$ -normal solution.

$n_1 =$	0.5	1	2	3	4	5	6
Calculated value . . . .	6.8	13.7	27.4	41.0	54.7	68.4	75.2
Potassium chloride, KCl . .	12.2	24.4	48.8	74.1	100.9	128.5	152.2
Sodium chloride, NaCl . . .	12.3	25.2	52.1	80.0	111.0	143.0	176.5
Potassium hydroxide, KOH .	15.0	29.5	64.0	99.2	140.0	181.8	223.0
Aluminium chloride, AlCl <sub>3</sub> .	22.5	61.0	179.0	318.0	—	—	—
Calcium chloride, CaCl <sub>2</sub> . .	17.0	39.8	95.3	166.6	241.5	319.5	—
Sodium sulphate, Na <sub>2</sub> SO <sub>4</sub> . .	12.6	25.0	48.9	74.2	—	—	—
Succinic acid, C <sub>4</sub> H <sub>6</sub> O <sub>4</sub> . . .	6.2	12.4	24.8	36.7	48.5	59.7	71.2
Citric acid, C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> . . . .	7.9	15.0	31.8	50.0	71.1	92.8	—
Lactic acid, C <sub>3</sub> H <sub>6</sub> O <sub>3</sub> . . . .	6.5	12.4	24.0	34.3	44.7	55.8	65.6
Boric acid, B(OH) <sub>3</sub> . . . . .	6.0	12.3	25.1	38.0	51.0	—	—
Sulphuric acid, H <sub>2</sub> SO <sub>4</sub> . . .	12.9	26.5	62.8	104.0	148.0	198.4	247.0

It is clear that in the case of the not too concentrated solutions of the four weak acids—succinic, citric, lactic, and boric—the agreement between the calculated and the experimental values is satisfactory, and would be better if a correction were introduced for the increase of volume which takes place on dissolving the substance. On the other hand, the strong acids and bases ( $\text{H}_2\text{SO}_4$  and  $\text{KOH}$ ) and all the salts give results which are not at all in agreement with the values calculated. The solutions giving apparently anomalous results are all good conductors of electricity, and it may be noticed that the deviation between calculated and experimental value is greater the more radicles (ions) the dissolved substance contains, just as was found to be the case with the osmotic pressure.

We return later to this behaviour of strong electrolytes.

For very concentrated solutions enormous differences are found between the theoretical and the experimental results. Particularly is this the case with very hygroscopic substances such as caustic potash, calcium chloride, and sulphuric acid, and the application of these as drying agents depends on the fact that the vapour pressure of their solutions is small, and consequently water passes to them from places of higher pressure.

## CHAPTER V.

### Boiling Point and Freezing Point of Solutions.

**Calculation of the Boiling Point of a Solution.**—The curve  $pp$  (Fig. 14) represents the change of vapour pressure of water (or other solvent) with temperature near the boiling point (at 760 mm.); the curve  $p'p'$  represents in the same way the vapour pressure of a solution in the same solvent, which, according to what has

been stated above, must be lower than that of the pure solvent. The boiling point of the solution (at 760 mm.) is found by drawing through  $A$ , which lies on  $pp$  directly above  $T$ , a line parallel to the abscissa-axis. This horizontal line corresponds with a pressure of 760 mm., and cuts the curve  $p'p'$  at  $B$ . A line is then dropped perpendicularly from  $B$ , cutting the abscissa-axis at  $E$ , or  $T + dT$ . The perpendicular cuts  $pp$

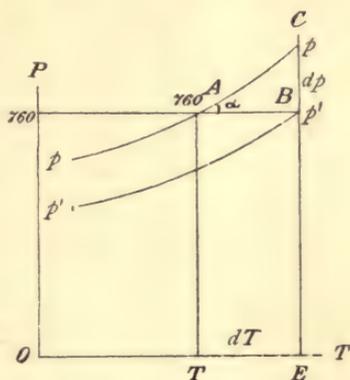


FIG. 14.

at  $C$ , which corresponds with a pressure of 760 mm. +  $dp$ . If the inclination  $\alpha$  of the curve at  $A$  is known, we can find

$$\tan \alpha = \frac{dp}{dT}$$

The part  $AC$  of the curve may be regarded as a straight line, and we then have—

$$CB = p - p' = \left(\frac{dp}{dT}\right)dT = dT \tan \alpha.$$

If, then, by experiment the vapour pressure of the solvent has been determined for all temperatures, and thereby  $\tan a$  has been found, we can calculate the rise of boiling point  $dT$ , knowing the value of  $p - p'$ , which is the relative lowering of the vapour pressure referred to in the preceding chapter.

The mechanical theory of heat gives us the following formula (Clapeyron's equation) for  $\frac{dp}{dT}$  or for  $\tan a$ —

$$\frac{dp}{dT} = \frac{\lambda}{(v - v_1)T}$$

where  $T$  is the absolute temperature at which the vapour pressure is  $p$ ,  $\lambda$  is the heat of vaporisation of 1 gram-molecule of the solvent, and  $v$  and  $v_1$  are the volumes of the gram-molecule in the gaseous and liquid states. Compared with  $v$ ,  $v_1$  is so small that without introducing an appreciable error it may be entirely omitted.

Further, we have the relationship—

$$pv = RT$$

(where  $p$  and  $v$  denote the pressure and volume of the gaseous solvent); and if this be introduced into the above equation, we obtain—

$$\frac{dp}{dT} = \frac{\lambda p}{RT^2} \text{ and } p - p' = \frac{\lambda}{RT^2} p dT.$$

or—

$$dT = \frac{p - p'}{p} \cdot \frac{RT^2}{\lambda}.$$

Since  $\lambda$  is not measured in mechanical units but in calories,  $R$  also must be expressed in calories. The value of  $R$  in calories has already been shown (see pp. 13 and 26) to be equal to 1.99, for which, with a sufficiently close approximation, we may set 2. For a solution which contains  $n$  dissolved molecules per 100 molecules of solvent, we know that  $\frac{p - p'}{p} = \frac{n}{100}$ , and for a solution which contains  $n_1$  gram-molecules of dissolved substance per litre, we have

$\frac{p - p'}{p} = \frac{n_1 M}{1000d}$  (see p. 45). From this it follows that for the rise of boiling point  $dT$ —

$$dT = \frac{n}{100} \cdot \frac{2T^2}{\lambda} \text{ and } dT = \frac{2n_1 M T^2}{1000d\lambda}.$$

It should be carefully noticed that  $T$  denotes the absolute temperature of the boiling point of the solvent, and  $\lambda$  is the heat of vaporisation of a gram-molecule of it at the same temperature (compare p. 56).

**Freezing Point of Solutions.**—In the same way we can calculate the freezing point of a solution, as has been shown by Guldberg (1) and van't Hoff (2). Let us consider a solvent—water, for example—which freezes at the temperature  $A$  (Fig. 15). The vapour pressure of the liquid solvent is represented by  $pp$ , the temperature being marked off as abscissa and the pressure as ordinate. At  $0^\circ$  (temperature  $A$ ) the tension

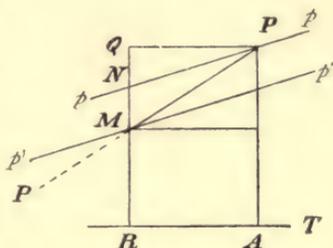


FIG. 15.

of water vapour, represented by the point  $P$ , is 4.61 mm.; at lower temperatures the tension is smaller, and exact measurements of this have been made by Juhlin (3). Water in the solid form, ice, also has a vapour pressure represented by  $PP$ , which at the same temperature is lower than that for liquid water; at the freezing point, water and ice must have the same vapour pressure. In order to prove this, suppose that we have a closed vessel containing ice, water, and water vapour at  $0^\circ$  (Fig. 16). If the vapour tension over the ice were smaller than that over the liquid, the water would distil over to the ice until it was all converted into ice. And, on the other hand, if the tension over the water were lower than that over the ice, then this latter would by distillation be

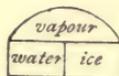


FIG. 16.

transformed into water. But since the freezing point is the point at which there is an equilibrium between ice and water, it necessarily follows that at this temperature they must have the same vapour pressure. Similarly, the solution whose vapour pressure is represented by  $p'p'$  must at its freezing point have the same vapour pressure as the pure ice which freezes out. This point falls, therefore, exactly where the curves  $PP$  and  $p'p'$  cut each other.

(It follows from the above that neither water nor solution can exist below the freezing point in presence of ice; the introduction of a crystal of ice causes the solidification of the supercooled liquid.)

If now a line parallel to the abscissa-axis be drawn through  $P$ , and through  $M$  a line perpendicular to this, the two cut at  $Q$ , and the perpendicular meets  $pp$  at  $N$  and the abscissa-axis at  $R$ .  $RA$ , which is equal to  $PQ$ , is denoted by  $dT$ , and represents the depression of the freezing point—that is, the difference between the freezing point of the solvent and that of the solution. We then obtain—

$$QM = PQ \tan MPQ,$$

$$\text{and } QN = PQ \tan NPQ.$$

Further, according to the modified formula of Claperyon (see p. 48)—

$$\tan MPQ = \frac{dP}{dT} = \frac{(\lambda + u)P}{RT^2},$$

$$\tan NPQ = \frac{dp}{dT} = \frac{\lambda p}{RT^2}.$$

In this formula,  $(\lambda + u)$  is the heat of vaporisation of ice, *i.e.* the sum of the heat of vaporisation  $\lambda$  of the water at  $0^\circ$ , and the heat of fusion  $u$  of the ice at the same temperature.

If we denote the vapour pressure of ice at the freezing point  $R$  of the solution by  $p'_r$  and the corresponding value of water by  $p_r$ , then—

$$MN = p_r - p'_r = dT \left( \frac{(\lambda + u)P}{RT^2} - \frac{\lambda p}{RT^2} \right) = dT \frac{up}{RT^2}$$

since at the freezing point of the solvent the vapour pressure  $P$  of ice and that  $p$  of the liquid must be the same, and for this we may, without appreciable error, use  $p_R$ .

If we introduce the values—

$$\frac{p_R - p'_R}{p_R} = \frac{n}{100}, \quad \frac{p_R - p'_R}{p_R} = \frac{n_1 M}{1000d},$$

and  $R = 2$ , we find for  $dT$ —

$$dT = \frac{n}{100} \cdot \frac{2T^2}{u},$$

$$dT = \frac{2n_1 M T^2}{1000du}$$

that is, the same formulæ as were found for the rise of boiling point with the heat of vaporisation  $\lambda$  replaced by the heat of fusion  $u$ .

#### Experimental Determination of the Freezing Point.

—The depression of the freezing point and the rise of the boiling point can now be determined with a very high degree of accuracy by the methods worked out by E. Beckmann (*4*). The apparatus devised by him for the determination of freezing points is shown in Fig. 17. A known weight of the solvent whose freezing point is to be determined is introduced into the tube  $A$ , which is about the size of an ordinary test-tube, and is provided with a side tube  $B$ . Through a rubber stopper in  $A$  there passes a platinum wire,  $G$ , which serves as a stirrer, and a thermometer,  $C$ , graduated into hundredths of a degree. The tube  $A$  is surrounded by an air-mantle by inserting it into a wider tube,  $D$ . The whole apparatus is placed in a freezing mixture contained in the vessel  $E$ , which is provided

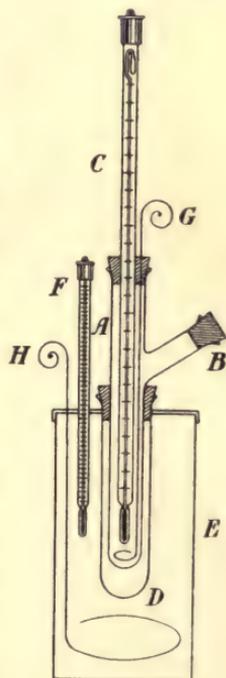


FIG. 17.

with a cover of sheet metal and the stirrer *H*. The thermometer scale extends only over five or six degrees, in order not to require to be of inconvenient length. In order, however, to make this thermometer available for the registration of temperature over a large interval, the capillary is bent at the top, and enters a reservoir, as shown in Fig. 18 (see

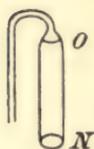


FIG. 18.

also Fig. 19). When the bulb of the thermometer is warmed, the mercury rises in the capillary stem, and overflows into the top of the reservoir. By adhesion to the glass, however, the mercury is prevented from falling off into the bottom of the reservoir. By gently tapping, the thread can be broken, and the excess of mercury drops into the reservoir. In this way the quantity of mercury in the thermometer can be varied at pleasure, and the quantity is so arranged that at the freezing point of the solvent the meniscus will stand near the top of the scale. The temperature of the freezing mixture should be only very little lower than the freezing point to be determined, and all disturbances due to radiation should be avoided.

After the freezing point of the solvent has been determined, a weighed quantity of substance is introduced through *B*, and dissolved by stirring with the wire *G*. The temperature is now allowed to sink a little below the freezing point, and a small crystal of the solidified solvent is dropped in. This causes deposition of solid from the super-cooled solution, and the mixture is now vigorously stirred when the temperature rises to a maximum (the freezing point) and remains constant for a considerable time, then falls slowly on account of the solution becoming more concentrated because of the separation of ice, whereby the freezing point is continually decreasing.

**Experimental Determination of the Boiling Point.**—The boiling point apparatus devised by Beckmann (5) is very similar to that used for the determination of the freezing point. The inner tube *A* (Fig. 19) is the same as that described above, but a short platinum wire, *a*, is sealed into the bottom of it.

The tube contains, besides the liquid to be examined, the thermometer *G* and a column of glass beads, 2 to 3 cm. high, which causes the boiling to be more even. This vessel is surrounded by a vapour-mantle, *D*, made of glass, porcelain, or metal, which is half filled with the same solvent (or solution) as is contained in *A*. The tube and the mantle are separated below by a ring of asbestos, and both are provided with air-condensers, or, if the solvent be very volatile, with small Liebig condensers, *C* and *F*. The apparatus rests on an asbestos stand, fitted with funnels, so that the heat can be easily regulated. With this arrangement Beckmann has succeeded in maintaining the boiling point constant within a few thousandths of a degree, a result which had previously never been expected.

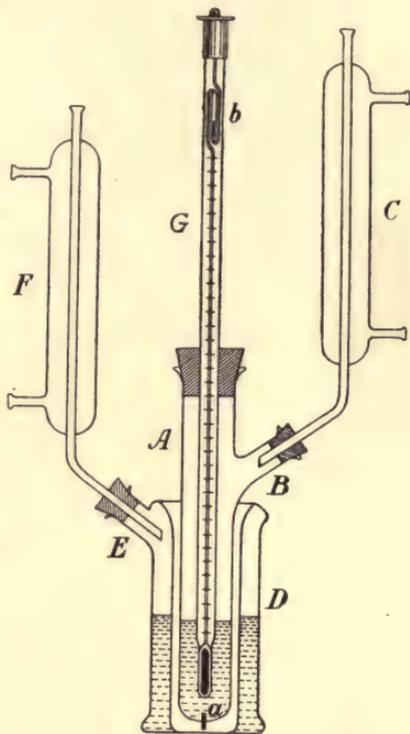


FIG. 19.

[Another method has been devised by Landsberger (*Ber.*, 1898, **31**, 458), and modified by Walker and Lumsden (*J. Chem. Soc.*, 1898, **73**, 502).]

**Advantages of the Freezing Point Method.**—The determination of the boiling point or the vapour pressure does not permit of the calculation of the molecular weight of such dissolved substances as have themselves an appreciable vapour tension. The method of the freezing point is free from this disadvantage, for it is only the vapour pressure of the solvent which plays any part in it; thus, for instance,

it gives correct values for a solution of alcohol in water, although the alcohol has a much higher vapour tension than the water. Furthermore, the freezing point method gives much more exact values than the boiling point method. This latter is consequently chiefly used for the determination of the molecular weight in cases where the freezing point of the solvent, *e.g.* alcohol, ether, carbon disulphide, can only be reached with difficulty.

**Connection between Depression of Vapour Pressure and Depression of Freezing Point.**—In 1870, Guldberg (1) proved theoretically that the vapour pressure and the freezing point stand in close relationship, so that the two corresponding depressions run parallel; and he further showed that this was confirmed by experiment. On the basis of purely experimental data, Raoult, in 1878, again brought forward this same statement, and showed that it applied to one per cent. salt solutions. As the numbers obtained by Raoult possess a certain historical interest, they are reproduced in the following table:—

Salt.	Lowering of the	
	Freezing point.	Vapour pressure in mm. Hg at 100°.
	Degree.	
Mercuric chloride . . . . .	0·048	0·058 × 7·6
Mercuric cyanide . . . . .	0·059	0·087 "
Lead nitrate . . . . .	0·104	0·110 "
Barium nitrate . . . . .	0·145	0·137 "
Silver nitrate . . . . .	0·146	0·160 "
Potassium ferricyanide . . . . .	0·146	0·165 "
Potassium chromate . . . . .	0·200	0·213 "
Potassium sulphate . . . . .	0·210	0·201 "
Potassium iodide . . . . .	0·215	0·225 "
Potassium chlorate . . . . .	0·215	0·240 "
Potassium nitrate . . . . .	0·245	0·280 "
Ammonium sulphate . . . . .	0·273	0·230 "
Potassium bromide . . . . .	0·295	0·310 "
Sodium nitrate . . . . .	0·347	0·380 "
Ammonium nitrate . . . . .	0·378	0·361 "
Potassium chloride . . . . .	0·446	0·450 "
Sodium chloride . . . . .	0·660	0·604 "
Ammonium chloride . . . . .	0·639	0·565 "

The proportionality is not so good as perhaps might be

desired. The agreement is much better if Tammann's results be compared with the older determinations of the freezing point by Rüdorff and de Coppet, and there is no doubt that fresh and more accurate determinations would lead to a much better result.

### Connection between the Osmotic Pressure of a Solution and its Freezing Point and Vapour Pressure.

—This connection was first shown empirically by De Vries in 1884. Soon after, van't Hoff deduced from the laws of the osmotic pressure both Raoult's law of the depression of the vapour pressure and his own law of the depression of the freezing point; and in the manner given by van't Hoff I developed the formula for the rise of boiling point.

It may be here noticed that Raoult, after collecting a very large number of data on the freezing points of solutions, empirically found a connection which he expressed in the following formula:—

$$dT = 0.63 \times n.$$

According to this formula,  $0.63 \times n$  is the depression of the freezing point of a solution which contains  $n$  molecules in 100 molecules of solvent. This formula only agrees with the law of van't Hoff when applied to formic acid, acetic acid, and benzene, for which the law requires the values 0.62, 0.65, and 0.68. On the other hand, the value for water is 1.05, and Raoult takes this to indicate that some of the water molecules have condensed to complexes  $2\text{H}_2\text{O}$  and  $3\text{H}_2\text{O}$ . In this connection Eykman (6) carried out an investigation, in which he obtained the following results:—

Solvent.	$dT$ (observed).	$dT$ (calculated). van't Hoff.	$dT$ (calculated). Raoult.
Phenol . . . . .	74	77	58.3
Naphthalene . . . . .	69	69.4	79.4
<i>p</i> -Toluidine . . . . .	51	49	66.3
Diphenylamine . . . . .	88	98.6	104.8
Naphthylamine . . . . .	78	102.5 (?)	88.7
Lauric acid . . . . .	44	45.2	124
Palmitic acid . . . . .	44	44.3	158.7

In this table  $dT$  represents the so-called molecular lowering of the freezing point, *i.e.* that lowering produced by dissolving a gram-molecule in 100 grams of solvent.

The formula—

$$dT = \frac{2}{100} \cdot \frac{T^2}{u}$$

based on theory and confirmed by Eykman's results, gives the lowering of the freezing point caused by the solution of a gram-molecule in 100 gram-molecules of solvent. As above,  $u$  denotes the heat of fusion of a gram-molecule of the solvent. If the gram-molecule be dissolved in 100 grams of the solvent (and not in  $M100$  grams), the concentration will be  $M$  times as great, and the lowering of the freezing point will be correspondingly increased. This can also be expressed by the above formula, if we understand by  $u$  the latent heat of fusion of a gram (not, as formerly, a gram-molecule) of the solvent; for since the value of the denominator becomes  $M$  times smaller, that of  $dT$  must become just as much greater. And the same applies to the rise of boiling point.

From what has been said, it is evident that the value of  $n$  can be ascertained either from the depression of the vapour pressure, the rise of the boiling point, or the depression of the freezing point,  $n$  being the number of dissolved molecules in the liquid. Since the quantity of dissolved substance is known, if we know  $n$  we can calculate the weight of a gram-molecule of the dissolved substance. These three methods of determining the molecular weight, particularly the method of the freezing point, on account of their simplicity and their general applicability, are fast displacing the older methods in which the gas density is determined.

**Molecular Lowering of the Freezing Point.**—The following tables contain some data on the molecular lowering of the freezing point, taken from Raoult's (7) results with aqueous solutions, and Beckmann's (8) extremely exact determinations with solutions in benzene. The value at the top of each table is that calculated by means of van't Hoff's formula.

## SOLUTIONS IN WATER.

(Calculated Molecular Lowering, 18.6.)

Methyl alcohol . . . . .	17.3	Hydrochloric acid . . . . .	39.1
Ethyl alcohol . . . . .	17.3	Nitric acid . . . . .	35.8
Glycerol . . . . .	17.1	Sulphuric acid . . . . .	38.2
Cane sugar . . . . .	18.5	Potassium hydroxide . . . . .	35.3
Formic acid . . . . .	19.3	Sodium hydroxide . . . . .	36.2
Phenol . . . . .	15.5	Potassium chloride . . . . .	33.6
Acetic acid . . . . .	19.0	Sodium chloride . . . . .	35.1
Butyric acid . . . . .	18.7	Calcium chloride . . . . .	49.9
Ether . . . . .	16.6	Barium chloride . . . . .	48.6
Ammonia . . . . .	19.9	Potassium nitrate . . . . .	30.8
Aniline . . . . .	15.3	Magnesium sulphate . . . . .	19.2
Oxalic acid . . . . .	22.9	Copper sulphate . . . . .	18.0

## SOLUTIONS IN BENZENE.

(Calculated Molecular Lowering, 53.)

Methyl iodide . . . . .	50.4	Aniline . . . . .	46.3
Chloroform . . . . .	51.1	Formic acid . . . . .	23.2
Carbon disulphide . . . . .	49.7	Acetic acid . . . . .	25.3
Ethylene chloride . . . . .	48.6	Benzoic acid . . . . .	25.4
Nitro-benzene . . . . .	48.0	Methyl alcohol . . . . .	25.3
Ether . . . . .	49.7	Ethyl alcohol . . . . .	28.2
Chloral . . . . .	50.3	Amyl alcohol . . . . .	39.7
Nitro-glycerol . . . . .	49.9	Phenol . . . . .	32.4

From the results given, it is evident that in the majority of cases the experimental result agrees with the theoretical. There are, however, a number of exceptions. In benzene solution many substances (alcohols, phenol, and organic acids) give smaller values for the molecular lowering than would be expected; thus, *e.g.*, a gram-molecule of methyl alcohol ( $\text{CH}_3\text{OH} = 32$ ) only exerts about half its normal action.

This deviation is easily explained by assuming that a gram-molecule of methyl alcohol in benzene solution weighs 64 grams, or, in other words, the chemical formula for this alcohol in benzene solution is  $(\text{CH}_3\text{OH})_2$ ; the molecular lowering is then calculated to be 50.6. Other deviations between experimental and theoretical results can in most

cases be accounted for in a similar manner, leaving for the moment aqueous solutions out of account.

The existence of such double molecules, which, of course, are mixed with simple molecules and higher complexes, is by no means improbable. On the contrary, such relationships were formerly considered as the normal, and the difference between the liquid and gaseous conditions were attributed to them. More recent researches have, however, shown that at moderate dilutions it is only in exceptional cases that double molecules are formed. The substances which most easily form these double molecules belong to the classes already mentioned, namely, alcohols, phenols, and organic acids (particularly the fatty acids).

**Molecule Complexes.**—The formation of double, triple, etc., molecules of dissolved substances depends to a great extent on the nature of the solvent. It appears to take place very seldom in aqueous solution, although it does so in the case of some salts of cadmium and mercury, and with the sulphates of magnesium, zinc, and copper. (This matter is discussed in more detail below.) The formation of these double molecules takes place more frequently when the solvent is acetic acid or formic acid, and still more so with benzene or other hydrocarbon.

The dielectric constant of the solvent has a great influence on the complex formation taking place in the solution. Liquids with a high dielectric constant have the power of decomposing the dissolved substance into simple molecules, and this power increases with the dielectric constant. These constants vary greatly with the chemical nature of the media; of the solvents in common use water has the highest dielectric constant ( $DE$ ), namely, 80; for formic acid  $DE = 57$ , for acetic acid  $DE = 6.5$ , for ethyl alcohol  $DE = 21.7$ , and for benzene  $DE = 2.2$ .

As we shall see later, the same holds good for the power of a solvent to dissociate an electrolyte into ions (9).

As the dilution increases the complex molecules become broken up into simpler ones, as the following results of

Beckmann (10) show.<sup>1</sup> Thus, for instance, if the concentration of ethyl alcohol be increased from 0·2 per cent. to 6 per cent., its molecular weight in benzene increases from 46 to 128, and in acetic acid from 47 to 54, whilst in water it remains almost constant.

Ethyl alcohol ( $C_2H_5O = 46$ ) in benzene.		Acetic acid ( $CH_3COOH = 60$ ) in benzene.		Phenol ( $C_6H_5OH = 94$ ) in benzene.		Ethyl alcohol ( $C_2H_5O = 46$ ) in acetic acid.		Ethyl alcohol ( $C_2H_5O = 46$ ) in water.	
Conc. %	Mol. weight.	Conc. %	Mol. weight.	Conc. %	Mol. weight.	Conc. %	Mol. weight.	Conc. %	Mol. weight.
0·164	46	0·465	110	0·34	144	0·25	47	0·6	47
0·494	50	1·2	115	1·2	153	1·08	50	1·4	46
1·09	61	2·3	117	2·5	161	2·81	52	2·9	46
2·29	82	4·5	122	4·0	168	6·2	54	5·7	44
3·48	100	8·2	129	8·0	188	9·7	56		
5·81	128	15·2	141	17·3	223	14·2	58		
8·84	159	22·8	153	26·8	252				
14·63	208								
22·6	265								
32·5	318								

**Dissociation of Electrolytes.**—The deviations which have been found for electrolytes in aqueous solution must be explained otherwise than by the assumption that complex formation takes place. Van't Hoff limited himself to showing that most salts, as well as the strong acids and bases, or, generally, strong electrolytes, give too large a molecular lowering of the freezing point, without discussing the cause. Since that time different explanations have been brought forward. It has been assumed that the molecules of the solvent can combine with those of the dissolved substance, or exert an attraction on them, but none of these hypotheses has been able to withstand full investigation, except that one

<sup>1</sup> In the gaseous condition, too, the fatty acids tend to form double molecules (see p. 42). In a less degree this applies also to alcohols. Also for the gaseous state theory predicts, and in this is confirmed by experiment, that fewer molecules combine to complexes the lower the concentration is. In a highly concentrated (or liquid) form the substances mentioned aggregate to a great extent to molecular complexes, as the results obtained in connection with the capillary forces and at the critical point prove.

which appears to be the most evident. If the deviation in benzene solutions, in which the molecular lowering of the freezing point is too small, is to be explained by assuming that the dissolved molecules are greater than is expressed by the chemical formula, then the deviation in aqueous solutions, where the lowering of the freezing point is greater than that calculated, may be assumed to be due to the dissolved molecules being smaller than indicated by the chemical formula. In the first case we imagine that a combination of simple molecules to a molecular complex takes place, and in the second case we have to assume that the simple molecules split up into smaller parts. As we shall see later, this assumption is quite justified. In the case of certain salts, as, for instance, sodium chloride (NaCl), there can be no doubt what the parts are because only one kind of splitting seems possible, namely, into Na and Cl. In order to receive general credence, this assumption must be supported by other experimental evidence; for it does appear strange at first sight that in a solution of salt this substance has always the same constant composition, although the constituents Na and Cl in the solution are separated from each other.

**Range of Validity of van't Hoff's Law.**—The following values for the molecular lowering of the freezing point, obtained as mean values from experiments with a large number of dissolved substances, were used by van't Hoff in support of his theory:—

Solvent.	<i>T</i> .	<i>u</i> .	$0.02 \frac{T^2}{u}$	<i>dT</i> (calculated).
Water . . . . .	273	80	18.6	18.5
Acetic acid . . . . .	290	43.2	38.8	38.6
Formic acid . . . . .	281.5	55.6	28.4	27.7
Benzene . . . . .	277.9	29.1	53.0	50.0
Nitro-benzene . . . . .	278.3	22.3	69.5	70.7

The van't Hoff law is only valid for dilute solutions, for in more concentrated solutions forces come into play which

disturb its simplicity. This recalls the behaviour of gases which at high pressure deviate from Boyle's law.

It is well known that van der Waals has sought to explain these deviations by forces of attraction which act between the gas molecules. In the same way we may assume that in solution there is an attraction between the dissolved molecules, and also between these and the molecules of the solvent. The former attraction causes a diminution in the molecular lowering of the freezing point as the concentration increases, and the latter causes a rise. Both cases occur frequently, the latter particularly in aqueous solutions, and the former in most other solutions. Almost the greatest deviation which has been noticed at high concentration was with a solution of cane sugar in water. In this case the molecular depression rises (almost proportionally with the concentration) from the value 18.6 at high dilution to 27.0 for a normal solution. Consequently, when the molecular weight of a dissolved substance is to be determined, it should be investigated in very dilute solution, or it should be examined at several concentrations, and from the results the value at concentration 0 is ascertained by extrapolation. Raoult found this rule empirically.

**Alloys.**—W. Ramsay (11) investigated the vapour pressure of solutions of various metals in mercury in the following way. A U-tube, closed at one end, was filled with mercury, and a similar tube contained the amalgam to be investigated. These were immersed in a mercury bath at high temperature and the vapour pressures were measured. A lowering of the vapour pressure was always observed on dissolving foreign metals in the mercury, and Ramsay was thus able to determine the molecular weight of the dissolved metal; for most metals, namely, Li, Na, Mg, Zn, Cd, Ga, Tl, Sn, Pb, Mn, Ag, and Au, he obtained results which agreed with the atomic weights within the experimental error. For potassium, calcium, and barium he found numbers which are very appreciably lower (about half) than the atomic weights, a peculiar phenomenon which has not yet been explained. The

molecular weights found for aluminium, antimony, and bismuth are considerably greater than the atomic weights of these elements, indicating that their molecules consist of several, probably two, atoms. On the whole, the results agree remarkably well with what is known of the molecular weights of the metals in the gaseous state.

Ramsay's observations have been confirmed by the experiments on the freezing points of metal alloys made by Tammann. From his results, Tammann (*12*) calculated the molecular weights of some metals, and these, along with the corresponding atomic weights, are contained in the following table:—

SOLUTIONS IN MERCURY (TAMMANN).

$$dT \text{ (theoretical)} = 425.$$

Metal.	Mol. weight.	Atom. weight.
Potassium . . . . .	40.5	30.1
Sodium . . . . .	22.8	23.0
Thallium . . . . .	181	204
Zinc . . . . .	59	65.4

Heycock and Neville (*13*) made similar experiments, using sodium, and afterwards tin, bismuth, cadmium, lead, thallium, and zinc, as solvent. In the next table some of their results are reproduced; the numbers given are the depressions of the freezing point produced by the solution of a gram-atom of the metal in 1880 grams of tin. The theoretical value is 2.98.

Nickel . . . . .	2.94	Lead . . . . .	2.76
Silver . . . . .	2.93	Zinc . . . . .	2.64
Gold . . . . .	2.93	Cadmium . . . . .	2.43
Copper . . . . .	2.91	Mercury . . . . .	2.39
Thallium . . . . .	2.86	Bismuth . . . . .	2.40
Sodium . . . . .	2.84	Calcium . . . . .	2.40
Palladium . . . . .	2.78	Indium . . . . .	1.86
Magnesium . . . . .	2.76	Aluminium . . . . .	1.25

The experiments of Roberts-Austen (14) and of G. Meyer (15) on the diffusion of metals in mercury confirmed the above results.

**Solid Solutions.**—Van't Hoff's formula for the calculation of the molecular weight can only be applied provided that the solvent separates in the pure form when the solution freezes, or that when the boiling point method is used the dissolved substance does not volatilise. These conditions are not always fulfilled, and this is particularly the case when the dissolved substance chemically resembles the solvent. Thus when the dissolved substance is  $\beta$ -naphthol and the solvent is naphthalene, or the dissolved substance is antimony and the solvent tin, it is found that the two separate out in union, and abnormally low depressions of the freezing point are obtained (16). A similar behaviour is sometimes noticed, *e.g.* iodine in benzene, when the substances are in no way chemically related. As a general rule the concentrations of the dissolved substance in the liquid and in the solid (separated) solvent bear a constant ratio to each other (distribution ratio).

In these cases, and in many others, a solid substance acts as a solvent. Van't Hoff (17) has shown that substances dissolved by solids have an osmotic pressure, and so we may speak of "solid solutions." The chief result with respect to the determination of the molecular weight in solids is, as the recent investigations of Bruni (18) and others have proved, that apparently the solid state is in no way connected with a high degree of polymerisation.

Hydrogen, which possesses many metallic properties, is monatomic when dissolved in palladium; as Hoitsema found, the dissolved molecule has the formula H and not H<sub>2</sub>.

#### Experimental Results on the Rise of Boiling Point.

—The correctness of the theoretical formula  $dT = 0.02 \frac{T^2}{\lambda}$  may be gathered from the results obtained by Beckmann (19) contained in the following table in the column headed  $dT$  (observed):—

Solvent.	$dT$ (observed).	$dT$ (calculated).
Water . . . . .	4 - 5	5.2
Ethyl alcohol . . . . .	10 - 12	11.5
Acetone . . . . .	17 - 18	16.7
Ether . . . . .	21 - 22	21.1
Carbon disulphide . . . . .	22 - 24	23.7
Acetic acid . . . . .	25	25.3
Ethyl acetate . . . . .	25 - 26	26.0
Benzene . . . . .	25 - 27	26.7
Chloroform . . . . .	35 - 36	36.6

The following numbers show that in some cases (denoted in the table by an asterisk \*), exceptional results are obtained in the same manner as for the lowering of the freezing point:—

#### MOLECULAR RISE IN BOILING POINT IN BENZENE.

$$dT \text{ (calculated)} = 26.7.$$

Anthracene . . . . .	26.2	*Benzoic acid . . . . .	18.6
Naphthalene . . . . .	24.7	*Salicylic acid . . . . .	21.0
Benzil . . . . .	26.0	Phenyl salicylate . . . . .	24.4
Phenyl benzoate . . . . .	26.1	Borneol . . . . .	27.2
Ethyl benzoate . . . . .	25.0	Acetophenone oxime . . . . .	26.0
Benzoic anhydride . . . . .	26.9	Acetanilide . . . . .	25.0

#### MOLECULAR RISE IN BOILING POINT IN CHLOROFORM.

$$dT \text{ (calculated)} = 36.6.$$

Naphthalene . . . . .	36.2	*Benzoic acid . . . . .	24.5
Camphor . . . . .	36.0	*Salicylic acid . . . . .	26.5
Ethyl benzoate . . . . .	34.5		

#### MOLECULAR RISE IN BOILING POINT IN ETHYL ALCOHOL.

$$dT \text{ (calculated)} = 11.5.$$

Benzil . . . . .	11.1	Tartaric acid . . . . .	11.1
Phenyl benzoate . . . . .	11.1	Borneol . . . . .	11.4
Ethyl benzoate . . . . .	10.3	*Lithium chloride . . . . .	13.2
Benzoic acid . . . . .	11.3	Mercuric chloride . . . . .	11.8
Salicylic acid . . . . .	11.5	*Cadmium iodide . . . . .	12.9
*Potassium acetate . . . . .	14.5	*Sodium iodide . . . . .	16.8

#### MOLECULAR RISE IN BOILING POINT IN GLACIAL ACETIC ACID.

$$dT \text{ (calculated)} = 25.3.$$

Anthracene . . . . .	25.0	Benzoic acid . . . . .	25.0
Benzil . . . . .	24.7	*Sodium acetate . . . . .	30.8

## MOLECULAR RISE IN BOILING POINT IN WATER.

$$dT \text{ (calculated)} = 5.2.$$

Mannitol . . . . .	5.0	Mercuric chloride . . . . .	5.0
Cane sugar . . . . .	4.9	Cadmium iodide . . . . .	5.3
Boric acid . . . . .	4.8	*Sodium acetate . . . . .	9.4

Attention may here be called to the following results. The dissimilar colours of iodine in benzene, ether, and acetic acid (brown), and in carbon disulphide (violet), were previously attributed to different molecular magnitudes of the iodine. Beckmann's results (20), however, indicate that in all these solvents the molecular weight of the dissolved iodine corresponds with the formula  $I_2$  (254), and is the same as that of iodine vapour at low temperatures. Phosphorus has the same molecular weight ( $P_4 = 124$ ) when dissolved in carbon disulphide as in the gaseous state. For sulphur dissolved in carbon disulphide, Beckmann found the molecular weight, 256, corresponding with the formula  $S_8$ , which is the same as that obtained by Biltz and V. Meyer (21) for sulphur vapour.

**Comparison between the Various Methods for the Determination of Molecular Weights.**—It must now be clear that the several methods for determining the molecular weight, by measurement of the osmotic pressure, of the depression of vapour pressure and freezing point, and of the rise of boiling point, lead to the same result, provided that in all cases the temperature is the same. The results of Donders and Hamburger (22) show that temperature has only a small influence on the relative values of the osmotic pressure, and this is further proved by a comparison of the values obtained by Tammann for the lowering of the vapour pressure at  $100^\circ$  with those found by Dieterici (23) at  $0^\circ$ . This result is also required by theory, as we shall see later, in those cases where no heat change takes place on dilution of the solution, a condition which is very nearly fulfilled with dilute solutions. Consequently we may assume that when results are obtained which are at variance with the theory,

these are due either to accident or to the characteristic peculiarities possessed by every method; in this respect the large number of possible methods of determining the molecular weight is of great importance.

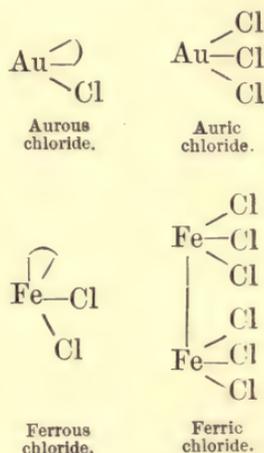
**Review of the Results obtained.**—These various methods opened up to the investigator a new world which was formerly regarded as quite unattainable. Up till the time of the discovery of these methods the molecular weight was only known for a limited number of substances, namely, those which could be gasified. On account of the great theoretical importance of the molecular weight, a scheme was drawn up from these few results which was supposed to cover the whole field of chemistry. The fundamental doctrine of this was that free valencies of the atoms cannot occur. This was believed to be a reason why two hydrogen atoms always combine to form a molecule; for if the molecule of hydrogen consisted of a single atom it would possess an unsaturated valency. It is true that the gas densities of mercury and cadmium show that the molecules of these elements consist of single atoms, but as they are divalent the difficulty was got over by assuming that the two valencies of an atom saturated each other. It was, however, later found that the molecule of certain monatomic metals also consisted of a single atom; and the same was found to be true for bromine and iodine at high temperature. It was then considered as satisfactory to say that at high temperature the doctrine of valency lost its validity, and little importance was attached to the so-called exceptions.

By the newer methods of determining the molecular weight it has been proved that also at low temperature—for instance, at the melting point of mercury—the molecules of the metals, monovalent as well as polyvalent, are as a rule monatomic. It has already been pointed out that the atoms of sulphur and phosphorus form molecules of the same magnitude, namely,  $S_8$  and  $P_4$ , both in the gaseous and in the dissolved state. It would, therefore, seem as if the

molecules of the elements were always formed by a certain number of atoms, quite independent of the state of aggregation in which they exist.

Compound molecules behave in the same way—that is to say, the molecular weight is the same in the gaseous and in the dissolved condition. In so far as the composition of the dissolved molecules is concerned, there frequently exists a slight difference between two solvents, as, for instance, between water and benzene, in the same way as there is a difference between these liquids and a vacuum, which may be conceived as a solvent for gases.

A further conclusion drawn from the doctrine that no free valencies could occur in molecules, was that the valency of an element could only change by an even number. Thus, gold could be monovalent or trivalent; but the assumption was made that gold is trivalent, and two of the valencies may saturate each other and so allow the gold atom to appear monovalent. Auric and aurous chlorides were assumed to have the constitutions shown. Nevertheless, several cases were known in which the number of valencies changes by an uneven number, as, for example, in ferrous chloride ( $\text{FeCl}_2$ ) and ferric chloride ( $\text{FeCl}_3$ ). In order to explain this anomaly it was assumed that iron is di- and tetra-valent in these compounds which are constituted as shown in the diagram given.



So long as the molecular weights of these substances could not be determined such assumptions appeared quite valid. But it is much more difficult to explain the exceptions formed by the series of nitrogen oxides. Nitrogen is pentavalent, and accordingly the only compounds which should be capable of existence are  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_3$ , and  $\text{N}_2\text{O}_5$ . Besides these, however, the oxides  $\text{NO}$  and  $\text{NO}_2$  are also known, and their gas densities

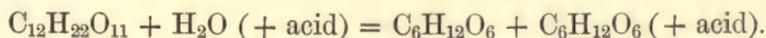
correspond with the simple formulæ given. In this case it is evident that the valency changes by an uneven number. The same was later found to be the case with the chlorides of indium (24). Quite the greatest difficulties have arisen from the results of recent investigation, whereby it has been proved that in a solution of sodium chloride the chlorine and the sodium atoms exist for the most part as molecules. In its old form the doctrine of valency is no longer tenable.

## CHAPTER VI.

### General Conditions of Equilibrium.

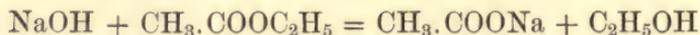
**Chemical Reactions.**—In many cases when two substances which react chemically upon each other are brought into contact, it may be observed that the reaction proceeds gradually. This is particularly evident when there is a visible surface of separation between the two reacting bodies, as, for instance, zinc and sulphuric acid; that is, when the system is *heterogeneous*. On the other hand, if there is no surface of separation between the two reacting substances—that is, if they be perfectly mixed or dissolved in each other, either in presence or absence of a third substance (solvent)—physical or chemical methods must be applied in order to detect any change of the properties of the solution which depends on the chemical composition.

The typical example of such a *homogeneous system* in which a physical property, easy to be examined, changes, is a solution of cane sugar in water to which some acid has been added. Such a solution possesses the power of rotating the plane of polarised light through a certain angle; this power gradually changes as the dextro-rotatory cane sugar is transformed into lævo-rotatory invert sugar (a mixture of equal parts of dextrose and levulose), according to the equation—



If the change in the rotatory power of the solution be followed we can estimate how far the reaction has proceeded at each moment.

As an example of a homogeneous system in which the change can be conveniently followed by chemical investigation, we may instance a solution containing sodium hydroxide and ethyl acetate which decompose according to the equation—



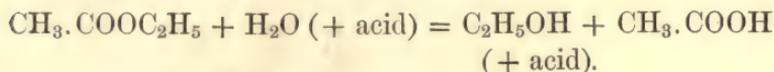
into sodium acetate and ethyl alcohol.

As the reaction proceeds, the quantity of sodium hydroxide in the solution decreases, and the amount present at any moment can be ascertained by titrating a portion with acid.

The amount of substance, expressed in gram-molecules per litre, which is transformed in unit of time, is termed the *velocity of reaction* of the system.

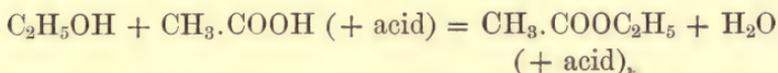
The velocity of reaction is frequently so great that by the methods known to us at present it is impossible to determine it. Nevertheless it can hardly be doubted that every chemical reaction requires a certain time in which to take place. In heterogeneous systems this time is considerable, for reaction can only take place at the surface of contact of the reacting substances, and consequently cannot go on suddenly. This is expressed in the old dictum: *corpora non agunt nisi soluta*. In a heterogeneous mixture, however, the velocity of reaction may be very high, as is shown by the explosive power of gunpowder, in which all the reacting substances are solid, and by that of flour-dust, where one of the substances is solid and the other (the oxygen of the air) gaseous. In all such cases the surface of contact is very great, either on account of the close incorporation or on account of the fine state of division of the reacting substances.

**Chemical Equilibrium.**—If ethyl acetate and water be mixed in molecular proportions and a little acid (*e.g.* hydrochloric acid) added, then at the ordinary temperature a slow change takes place, the ester being converted into ethyl alcohol and acetic acid by taking up water—



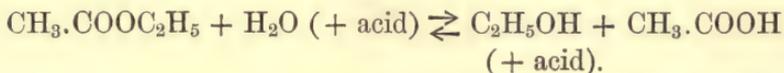
A chemical action of this sort in which one of the substances present, although essential for the speed of the reaction, does not suffer any change, is termed *catalysis* or a catalytic reaction. The decomposition of cane sugar into invert sugar is a similar process.

The catalysis of ethyl acetate does not proceed, as might be expected from the chemical equation, so that the whole quantity of ester is changed into alcohol and acetic acid, but the reaction approaches a limit, the so-called *limit of reaction*. In this case the limit is reached when two-thirds of the ethyl acetate has decomposed. On the other hand, if equimolecular quantities of alcohol and acetic acid be mixed, and a little hydrochloric acid added, ethyl acetate and water are gradually formed according to the equation—



that is to say, a reaction opposed to the above catalysis takes place. This reaction also approaches a limit which is the same as that already mentioned, and is reached when a third of the alcohol and acetic acid have formed ester.

In order to express that a measurable equilibrium is established, the reaction is written in the following way, according to the suggestion of van't Hoff—

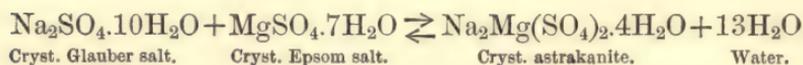


The double arrow sign ( $\rightleftharpoons$ ), used in place of the usual sign of equality (=), denotes that the reaction may proceed in one direction or the other, depending on the concentrations of the reacting substances, and that finally an equilibrium will be established when the two opposite reactions take place at the same speed.

Besides these "incomplete" reactions—*i.e.* those in which the extent of reaction is limited—there are other reactions in which practically the whole of the substance originally present is transformed; the inversion of cane sugar is an

example of a reaction of this type. In the chemical equations representing reactions belonging to this class the ordinary sign of equality is used. There are theoretical reasons for believing that reactions in a homogeneous system never take place absolutely completely. According to the theory an equilibrium is always established; but in many cases the reaction proceeds so nearly to completion that by the chemical or physical methods at present available it is impossible to detect the presence of the substances represented on one side of the equation.

Complete reactions occur during chemical change in a heterogeneous system. The simplest case of such a transformation is the change of the state of aggregation of a substance. Water under normal pressure (760 mm. Hg) passes completely into ice if the temperature be lower than  $0^{\circ}$ , and the opposite change takes place completely if the temperature be higher. If the pressure be 760 mm. ice and water can only be in equilibrium at  $0^{\circ}$ . That point at which an equilibrium may exist (temp. =  $0^{\circ}$ , press. = 760 mm.) is called the *transition point* of the system. In this special case, and in general when gases do not take part in the equilibrium, and when the pressure exerts but little influence, it is customary to state that the transition point of the system, ice  $\rightleftharpoons$  water: is  $0^{\circ}$ . According to Reicher's determination (1) the transition between monoclinic and rhombic sulphur takes place at  $95.6^{\circ}$ . The system—



has a transition point (determined by various methods) which lies at about  $21.5^{\circ}$ . If crystals of Glauber salt be mixed with crystals of Epsom salt below  $21.5^{\circ}$  no change takes place; but if this mixture be heated to above  $21.5^{\circ}$  it is transformed into astrakanite and water.

Systems in which no gases occur (and in which solutions play only an unimportant part) are termed *condensed systems* by van't Hoff, who, with his pupils, has studied the

transition points of many of these. Condensed systems are characterised by having a surface of separation between the substances on the two sides of the equilibrium sign ( $\rightleftharpoons$ ) in the equation, and are thus necessarily heterogeneous. Thus, in the example mentioned, the Glauber salt crystals and the Epsom salts crystals are separated from the astrakanite crystals and the water by well-defined surfaces. For the liquid part of the system formed by the water and the salts dissolved therein, the law of condensed systems "that the components are only stable in presence of each other at the transition point,  $21.5^\circ$ ," does not hold.

In so far as the quantitative respect is concerned, the case is somewhat different for those physical and chemical changes in which a gas is produced. As an example of this kind we may conveniently take the system: water  $\rightleftharpoons$  steam (or water vapour). At  $20^\circ$  and 17.4 mm. pressure this system possesses a transition point, for at this pressure water is only stable under  $20^\circ$  and steam only above  $20^\circ$ , but at  $20^\circ$  the two forms can "co-exist." Here it is evidently necessary, in distinction to condensed systems, to give the (vapour) pressure for the transition point, since this has now as much influence as the temperature.

Formerly it was supposed that all chemical reactions took place completely. It was conceived that the stronger affinity caused the reaction to be complete at the expense of the weaker affinity. This view of chemical reactions was first systematised by Torbern Bergman, and it prevailed until quite recent times. Thermochemists, more particularly Berthelot, have striven to uphold this conception, which has no strict scientific foundation.

**The Phase Rule of Gibbs.**—A state of equilibrium between substances in a homogeneous system is usually termed a *homogeneous equilibrium*. The corresponding name for equilibrium in a heterogeneous system is *heterogeneous equilibrium*. W. Gibbs (2) calls the homogeneous parts of a heterogeneous system the "phases" of the system. In the equilibrium between ice, water, and water vapour (at  $0^\circ$

and 4.6 mm. pressure) there are three phases—one solid (ice), one liquid (water), and one gaseous (water vapour). Gibbs has deduced a law for the number of these phases which is known as “Gibbs’s phase rule.” This law may be stated as follows:  $n$  bodies (different chemical substances, simple or compound) can form  $n + 2$  phases, and these co-exist only at a single point (*i.e.* all the external conditions of the system, pressure, temperature, and composition of each phase, are given). Let us consider the substance water; here  $n = 1$ , and therefore three phases of the substance, the solid, the liquid, and the gaseous, may co-exist, but only at one point, namely, at  $0^\circ$  and 4.6 mm. pressure. The composition must be the same throughout, since only one kind of molecule is present. If the system consists of two bodies, *e.g.* common salt and water, then  $n = 2$  and the number of phases is  $n + 2 = 4$ . These phases can co-exist at about  $-21^\circ$ , at which temperature by loss of heat a so-called cryohydrate (constant mixture of ice and salt crystals) separates from the saturated solution.

At this temperature ( $-21^\circ$ , the corresponding pressure being 0.73 mm.) there are present two solid phases (ice and salt), a liquid (saturated salt solution, which contains 36 grams of salt to 100 grams of water), and a gaseous phase (water vapour at 0.73 mm. pressure).

When the number of phases is only  $n + 1$ , one of the external conditions can (within certain limits) be fixed at pleasure; thereby, however, the other conditions are also fixed. Thus if we take water ( $n = 1$ ) in the liquid and gaseous states, the number of phases is  $n + 1 = 2$ . At any particular temperature we may happen to choose, the pressure at which the two phases can exist in presence of each other can only have one value. (Saturated water vapour at  $20^\circ$  has a pressure of 17.4 mm.)

Two bodies, such as salt and water ( $n = 2$ ), can co-exist at a temperature of, say,  $20^\circ$  in  $n + 1 = 3$  phases; these are (1) salt crystals; (2) saturated solution, containing 36 grams of salt to 100 grams of water; and (3) water vapour of pressure

about 13·4 mm. At any given temperature the pressure and composition of the phases are fixed. If the composition of the liquid phase were given, such a saturated solution could only be obtained at a single temperature and with a single pressure of water vapour.

If the number of co-existing phases is the same as the number of bodies present in the system, then two of the external conditions may be chosen (*e.g.* temperature and pressure), but the composition of the phases is then determined. If, therefore, we have two bodies, salt and water, in two phases, namely, solution and vapour, and the system is to have a particular temperature and pressure, the composition of the solution can only have one value. In other words, there is only one concentration of the solution which at a given temperature possesses a particular vapour pressure.

**Osmotic Work.**—In order to derive the various conditions of equilibria it is necessary to know how much work is done when a dissolved substance passes from one concentration to another by removal of the solvent. This removal may be carried out in different ways, as by evaporation, by freezing out, or by forcing solvent out from the solution by means of a semi-permeable piston which does not allow the dissolved substance to pass through. In our derivation we shall make use of this last method. We premise that a semi-permeable membrane can be found for every substance which will allow this but no other substance present in the solution to pass through. In reality this is not quite the case, but in general an arrangement can be made which closely approximates to the condition of semi-permeability.

The simplest case is offered by a solid substance which dissolves in a liquid, so that the solution in contact with the solid is always saturated. Suppose a piston, permeable by the solvent but not by the dissolved substance, resting on the surface of the solution, and suppose further that there is solvent above the piston. In order that there may be a condition of equilibrium so that the pure solvent does not pass into the solution, the piston, according to our previous

calculations (see p. 29), must be so weighted that it exerts on the solution a pressure ( $P$  per square centimetre) equal to the osmotic pressure. By raising the piston, in doing which work must be done, a volume  $dv$  of the solvent is caused to pass into the solution. Since solid substance is present in contact with the solution, the concentration, and consequently also the osmotic pressure, remain constant, and the work done during the solution process is, like that done by evaporation of a liquid—

$$dA = Pdv.$$

When a gram-molecule of a solid substance dissolves, the work done is, according to van't Hoff's law, the same as for a liquid which is vaporised—

$$A = PV = 1.99T \text{ cal.},$$

where  $V$  is the volume occupied by a gram-molecule, and  $T$  denotes the absolute temperature. This work, like that done during the evaporation of a liquid, is independent of the pressure under which the vaporisation takes place, but is proportional to the absolute temperature.

This does not, of course, apply to the solution of those substances (salts, strong acids and bases) which exert an osmotic pressure greater than that which can be calculated by van't Hoff's law. In such cases a correction must be introduced, and this can easily be done. If it has been ascertained by experiment that the osmotic pressure of the solution in question is  $i$  times greater than it should be according to van't Hoff's law, we must multiply by this factor, and obtain—

$$A = 1.99iT \text{ cal.}$$

Let us now take the case of a solution containing a certain amount of a dissolved substance and no solid in contact with it. As before, let the solution be contained in a vessel with a piston above which there is pure solvent. By raising the piston we allow some of the solvent to enter the solution,

the osmotic pressure of which is variable, and follows van't Hoff's law—

$$PV = 1.99T,$$

where  $V$  is the (variable) volume in which a gram-molecule is dissolved. The pressure which the substance exerts on the piston is the same as that which would be exerted by the same number of gram-molecules in the gaseous state, instead of dissolved, contained in the same volume. If, therefore, by the introduction of solvent, the volume of the solution increases from  $v_0$  to  $v_1$  (whilst the osmotic pressure diminishes from  $p_0$  to  $p_1$ ) at constant temperature, the work done by the solution during this process will be the same as that done by a mass of gas containing the same number of molecules when it increases in volume by the same amount. At constant temperature  $T$  this work amounts for each gram-molecule of dissolved substance to—

$$A = 1.99T \ln \frac{v_1}{v_0} = 1.99T \ln \frac{p_0}{p_1}.$$

For substances which deviate from van't Hoff's law the value given must be multiplied by  $i$ , just as before.

As no known gas exactly follows the law of Avogadro (and also those of Boyle and Gay-Lussac), we often consider a so-called *ideal gas* which exactly obeys these laws; in the same way there is no solution which absolutely obeys van't Hoff's law, and so we often make use of the *ideal* (dilute) *solution* to which we assume the law rigidly applies.

**Henry's Law.**—In the following development of the laws of equilibria we start with the fundamental doctrine that, when a substance is transferred from one system to another, and then at the same temperature is brought back to its original condition, the sum of the works done is zero. Thus: if we have a gas, *e.g.* oxygen, at pressure  $p$ , in contact with a liquid, *e.g.* water, in a closed vessel,  $A$ , the gas dissolves to a certain extent; let the osmotic pressure which it exerts when equilibrium is established be  $\pi$ . In another closed vessel,  $B$ , let there be the same gas, but at a

higher pressure  $p_1$ , also in contact with the same liquid, and, when equilibrium has been established, let the osmotic pressure be  $\pi_1$ . We now cause a very small quantity of the gas,  $a$  gram-molecule, where  $a$  is a small number, to pass from vessel  $A$  to vessel  $B$  at constant temperature. The work done by the change of pressure is given by—

$$A_1 = 1.99aT \ln \frac{p}{p_1}.$$

The  $a$  gram-molecule of gas is now forced into the liquid in vessel  $B$ ; for this no work is necessary, because the gas and solution are in equilibrium, and  $a$  is so small that the concentration in the liquid is not appreciably altered. On the contrary, a (negative) work  $A_2$ , is done by the disappearance of the  $a$  gram-molecule of gas—

$$A_2 = -1.99aT.$$

The gas in  $B$  is now separated from the liquid, and by means of a semi-permeable membrane, which does not allow the gas to pass through, the liquid is allowed to take up so much solvent ( $v_1$  c.c.) as is necessary to dissolve the  $a$  gram-molecule, so that the concentration is the same as that originally in  $B$ . The corresponding work is—

$$A_3 = 1.99aT$$

(and it is evident that the two last processes can be carried out in several smaller portions, whereby the whole work required to force the gas into the liquid disappears).

A quantity of liquid containing  $a$  gram-molecule of gas is removed from vessel  $B$  (the contents of which evidently return to their original condition), and this is allowed to absorb so much solvent ( $v - v_1$  c.c.) that its osmotic pressure sinks from  $\pi_1$  to  $\pi$ , that which obtains in vessel  $A$ . The work done during this process is—

$$A_4 = 1.99aT \ln \frac{\pi_1}{\pi}.$$

The new quantity of liquid, which still contains  $a$  gram-molecule of dissolved gas, is united with the liquid in  $A$ —the gas and liquid in this vessel having previously been separated. A volume,  $v$ , of liquid is now forced out through a semi-permeable membrane, whilst the  $a$  gram-molecule remains in the vessel  $A$ . The work then done will be—

$$A_5 = -1.99aT = -A_3.$$

Finally, the dissolved  $a$  gram-molecule of gas is permitted to evolve from the liquid in  $A$  into the gas above at pressure  $p$ , and the work—

$$A_6 = 1.99aT = -A_2$$

is done, the same as when the gas was forced into the liquid, but with the sign changed. The condition in  $A$  is now the same as initially.

Summing up, we have

$$A_1 + A_4 = 1.99aT \left[ \ln \frac{p}{p_1} + \ln \frac{\pi_1}{\pi} \right] = 0$$

or—

$$\frac{p}{p_1} = \frac{\pi}{\pi_1} = \text{constant},$$

*i.e.* the osmotic pressure of the dissolved gas is proportional to the pressure of the gas above the solution.

Since the osmotic pressure is proportional on the one hand to the concentration, and on the other hand to the pressure of the gas, it is clear that the concentration of the gas in the solution must stand in a constant ratio to the concentration, or density, of the gas over the solution. This law is called, after its discoverer, Henry's law.

The same development would lead to a different result if the substance in the gaseous state and when dissolved had different molecular weights. If, for instance, the substance when dissolved had a molecular weight double that in the gaseous state, the work  $A_4$  would consist in changing the osmotic pressure of  $\frac{a}{2}$  gram-molecule from osmotic pressure  $\pi_1$  to osmotic pressure  $\pi$ , and we should obtain—

$$A_1 + A_4 = aT \left[ 2 \ln \frac{p}{p_1} + \ln \frac{\pi_1}{\pi} \right] = 0,$$

or—

$$\left[ \frac{p}{p_1} \right]^2 = \frac{\pi}{\pi_1} = \frac{c}{c_1}.$$

Van't Hoff (*B*) has shown that when Henry's law—that the quantity of gas dissolved per unit volume is proportional to the gas-pressure—obtains, the gas has the same molecular magnitude in the two conditions (gaseous and dissolved). We might have a solution of the gas in another solvent (*e.g.* ether) in contact with the liquid (water) instead of the gas itself. If in the first process of the foregoing series we make use of a semi-permeable membrane, which allows the ether but not the gas to pass through, it can be shown that—

$$\frac{\phi}{\phi_1} = \frac{\pi}{\pi_1} = \frac{p}{p_1};$$

$\phi$  and  $\phi_1$  denote the osmotic pressures of the dissolved gas in the ether in vessels *A* and *B*.

Provided that a substance—whether capable of existence in the gaseous state or not—possesses the same molecular weight in two solvents, the osmotic pressures, and consequently also the concentrations of the substance in the two liquids, must stand to each other in a constant ratio.

**Distribution Law.**—If an aqueous solution of succinic acid be shaken with ether, part of the dissolved substance passes into the ether. If this be carried out with aqueous solutions of different concentrations, the amount of succinic acid which passes into solution in unit volume of ether must increase with rising concentration of the aqueous solution. Experimentally it has been found that the following law of distribution holds good: when equilibrium is established the concentration of the ethereal solution is proportional to that of the aqueous solution. The following table contains the results obtained at 15° by Berthelot and Jungfleisch (*4*);  $c_1$  and  $c_2$  denote the weights in grams of succinic acid in 10 c.c. of water and ether respectively. At higher concentrations

deviations occur, which, however, do not attain a particularly high value. The influence of temperature on this distribution ratio is such that  $\frac{c_1}{c_2}$  increases with rising temperature.

$c_1$ .	$c_2$ .	$\frac{c_1}{c_2}$ .
0.024	0.0046	5.2
0.070	0.013	5.2
0.121	0.022	5.4
0.236	0.041	5.7
0.365	0.061	6.0
0.420	0.067	6.3
0.486	0.073	6.6

Other experiments were made on the distribution of bromine and iodine between carbon disulphide and water, and of benzoic acid, oxalic acid, malic acid, and tartaric acid between ether and water.

If an excess of solid succinic acid be shaken with water and ether, two saturated solutions are formed; and if the excess of solid be now removed, the equilibrium must nevertheless persist. The distribution coefficient of succinic acid between water and ether must, therefore, be the ratio of the solubilities of this substance in the two solvents. It must, however, be remembered that in this case the water is not free from dissolved ether, and the ether is not free from dissolved water, and consequently perfect agreement cannot be expected between the distribution result and that obtained when the solubilities in the pure solvents are used.

If a substance (or, more strictly, one kind of molecule) is present in two phases (*e.g.* in aqueous and ethereal solution), the concentration in one phase must stand to the concentration in the other phase in a constant ratio, provided that the temperature is kept constant (5). This general statement embraces Henry's law as a special case in which one of the phases is gaseous.

Other special cases of the law of distribution are the laws that a solid substance dissolves in a particular liquid until a certain degree of concentration is reached (until a saturated solution is formed), and that liquids and solid substances at a particular temperature give off vapour until a certain pressure is reached.

**Kinetic Considerations.**—The development made above is based on the mechanical theory of heat (thermodynamics), and is therefore strictly exact. However, it is usual also to regard these laws from a kinetic point of view, and as this has been of great service and is of assistance in visualising the matter, a short account may be given here.

Let us suppose that we have water at a certain temperature in a vacuum. Part of the water vaporises, and so fills the space above with water vapour. This evaporation takes place until the number of molecules which pass into the water per second is exactly equal to the number which leave it. The equilibrium which obtains is *mobile*. It is clear that this equilibrium depends only on the conditions in the immediate neighbourhood of the surface of separation of liquid and vapour. If the vapour-space be increased, the new volume must become filled with vapour at the same pressure as that in the original space, otherwise there would not be an equilibrium between this latter and the new portion. At the surface of separation no change whatever occurs. A liquid, therefore, at a given temperature must possess a certain definite vapour pressure which is independent of the quantity of vapour and liquid present.

In the same way it can be imagined that the solution of a solid substance in a liquid takes place until in unit time there are as many molecules leaving the solid as there are molecules separating from the solution. The same consideration as that used for the evaporation of a liquid leads to the conclusion that a solid substance in contact with a liquid forms a saturated solution, the concentration of which depends on the temperature, but is entirely independent of the quantity of solid and liquid present.

A further consequence of this view is that no solid substance is entirely free from gas pressure or entirely insoluble in a liquid, for it must be assumed that in a certain time some, even if few, molecules leave the solid and pass either into the gas-space or into the dissolving liquid. This conclusion, although impossible to prove experimentally in those cases where, by analytical methods, the presence of dissolved or gaseous substance cannot be recognised, is of extreme importance from a theoretical point of view.

Let us consider more closely a gas in contact with a liquid. A number of gas molecules pass into the liquid until the equilibrium between the gas and the saturated solution is reached. If now the number of gram-molecules in the gas-space be doubled, then in unit time twice as many molecules pass into the liquid as before, since the movements of the gas molecules are independent of each other. In order that equilibrium may exist, double as many gram-molecules must leave the solution in unit time as previously. This occurs when the concentration of the solution in gas molecules has been doubled. It is easy, therefore, to see that the concentration (partial pressure) of the gas must be proportional to the concentration of molecules dissolved in the liquid (Henry's law). The general law of distribution can be derived in a similar manner.

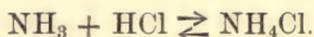
**Depression of Solubility.**—Nernst's method (6) of determining the molecular weight by the depression of the solubility shows the analogy between a solution and a gas. Ether dissolves in water at  $0^{\circ}$  to such an extent that a solution is obtained which freezes at  $-3.85^{\circ}$  (about 2-normal). If to this solution a substance be added, like camphor, which is soluble in ether and practically insoluble in water, the vapour tension of the ether and its solubility in water will both be diminished, and both in the same proportion. When 1 gram-molecule of the substance to be investigated is dissolved in  $N$  gram-molecules of ether, the relative lowering of the solubility of the ether is  $\frac{1}{N}$ , and the freezing

point of the ether-water solution rises by  $\frac{3.85 \times 1^\circ}{N}$ , which can easily be measured by a Beckmann thermometer.

To carry out the determination, the tube of a Beckmann apparatus is filled with water so that the level of this stands above the bulb of the thermometer, and on to it is poured a weighed quantity of ether. After the water has become saturated with ether, its freezing point is determined. A weighed amount of the substance is then introduced, and after it has dissolved in the ether, the freezing point is again determined.

As already mentioned, one condition of the experiment is that the substance must not be appreciably soluble in water. The principle of the method is a consequence of Henry's law applied to the solubility of ether vapour in water.

**Homogeneous Equilibria.**—Suppose we have two vessels containing ammonium chloride vapour at high temperature. The ammonium chloride is partially decomposed according to the equation—



The sign  $\rightleftharpoons$  denotes that there is an equilibrium—that in any specified time there is as much ammonium chloride decomposed as there is formed from the products of decomposition. Let the partial pressures of the three components be  $C_1$ ,  $C_2$ , and  $C_3$  in the first vessel, and  $C_4$ ,  $C_5$ , and  $C_6$  in the second. Suppose, further, that both vessels are very large. If now a gram-molecule of ammonia and a corresponding quantity of hydrochloric acid be introduced into the first vessel through a semi-permeable wall under the constant pressure  $C_1$  (or  $C_2$ ), the work done is  $pv = RT = 1.99T$  cal. for each sort of molecule.

Suppose that the two substances then combine to form ammonium chloride, which is simultaneously removed through a semi-permeable wall in such a way that the pressure remains constant. By the passing out of the gram-

molecule of ammonium chloride so formed work will be done which amounts to  $pv = RT = 1.99T$  cal.

Now allow the ammonium chloride to pass isothermally from concentration  $C_3$  to concentration  $C_6$ , and the work done will be—

$$-A = -RT \ln \frac{C_6}{C_3}.$$

The ammonium chloride is then forced at this pressure into the second vessel, where it decomposes into ammonia and hydrochloric acid at pressures  $C_4$  and  $C_5$  respectively, and no work has to be done to accomplish this (exactly as in the case of the evaporation of water where no work is done, but there is a loss of heat). The new quantities of ammonia and hydrochloric acid at the pressures  $C_4$  and  $C_5$  are now removed, each through a semi-permeable wall.

The work done for the gram-molecule of ammonium chloride is  $pv = RT$ , and that done by the gram-molecule of each of the gases, ammonia and hydrochloric acid, is  $pv = RT$ . Finally, if the gram-molecule of ammonia and that of hydrochloric acid are allowed to expand isothermally from pressure  $C_4$  to  $C_1$  or from  $C_5$  to  $C_2$  in the different cases, the original condition is established. During this last process the work done will be—

$$A_1 = RT \ln \frac{C_4}{C_1} \text{ and } A_2 = RT \ln \frac{C_5}{C_2}.$$

During the cycle certain amounts of work are done on the system, and equal quantities are regained at other points in the process, but there still remain  $-A, A_1, A_2$ . Since the cycle was carried out at constant temperature and completely reversibly the sum of these three quantities must be zero. We therefore obtain the equation—

$$-A + A_1 + A_2 = 0 = -RT \left( \ln \frac{C_6}{C_3} - \ln \frac{C_4}{C_1} - \ln \frac{C_5}{C_2} \right),$$

or— 
$$\frac{C_6}{C_3} = \frac{C_4 \times C_5}{C_1 \times C_2},$$

or— 
$$C_1 \times C_2 = kC_3 \text{ and } C_4 \times C_5 = kC_6$$

where  $k$  is a constant, the value of which depends on the temperature.

If we had an equation of the form—

$$mP + nQ + oR + \dots = fS + gT + hV + \dots$$

which denotes a reaction where  $m$  molecules of a substance  $P$ ,  $n$  molecules of substance  $Q$ , and  $o$  molecules of substance  $R$ , etc., react to produce  $f$  molecules of substance  $S$ ,  $g$  molecules of substance  $T$ , and  $h$  molecules of substance  $V$ , etc., the result would be—

$$m \ln C_p + n \ln C_q + o \ln C_r + \dots = f \ln C_s + g \ln C_t + h \ln C_v + \dots$$

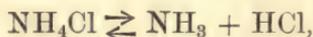
or—

$$C_p^m \times C_q^n \times C_r^o = k C_s^f \times C_t^g \times C_v^h,$$

where  $k$  is again a constant and  $C$  is the partial pressure of each of the substances indicated by the index.

Since at low pressures or in very dilute solution the partial pressure is almost proportional to the concentration,  $C$  in this case may be taken to mean simply the concentration. The "law of mass action" expressed in the above formula is called, after its two Norwegian discoverers, the Guldberg and Waage law ( $\gamma$ ). The law as originally stated referred to the concentrations of the reacting substances, but it was later shown to apply more strictly when  $C$  in the above formula indicates the partial pressure.

The law can be more simply derived by considering the action kinetically. Let us take the same example as before, that represented by the equation—



and let us consider the quantities in unit volume (1 c.c.), *i.e.* the concentrations  $C_3$ ,  $C_1$ , and  $C_2$  of the three substances present.

The number of decomposing molecules of ammonium chloride in unit volume is proportional to the total quantity of this substance ( $C_3$ ) present in the same volume, for each

molecule decomposes independently of the others. The number of molecules decomposing in unit time is therefore given by—

$$N = kC_3$$

where  $k$  is a constant depending on the temperature.

For the formation of a molecule of ammonium chloride from a molecule of ammonia and one of hydrochloric acid it is necessary for these to meet. The number of molecules formed must consequently be proportional to the number of such collisions. The possibility of a single molecule of ammonia coming into collision with a molecule of hydrochloric acid in unit volume is evidently proportional to the number of hydrochloric acid molecules present, *i.e.* to  $C_2$ . For  $C_1$  molecules of ammonia the number of collisions with  $C_2$  molecules of hydrochloric acid will be  $C_1$  times as great. The number of collisions  $N_1$  between ammonia and hydrochloric acid molecules is therefore proportional to  $C_1C_2$ , or

$$N_1 = k_1C_1C_2.$$

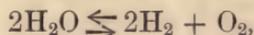
Now, it is required that—

$$N = N_1,$$

therefore  $kC_3$  must be equal to  $k_1C_1C_2$ , or

$$C_3 = KC_1C_2.$$

To take another example, if water vapour at high temperature decomposes into hydrogen and oxygen according to—

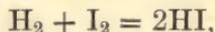


then, in order that a decomposition may take place, one water molecule must collide with another one; and on the other hand, in order that a molecule of water may be formed, two molecules of hydrogen and one molecule of oxygen must collide. If the concentrations of water, hydrogen and oxygen, are  $C_3$ ,  $C_1$ , and  $C_2$ , and  $K$  is a constant, then in the condition of equilibrium—

$$C_3^2 = KC_1^2C_2.$$

The coefficients of the chemical equation become exponents in the equation of equilibrium, whilst the signs of addition become signs of multiplication; in place of the molecular formulæ we have the concentrations of the substances, and the sign  $\rightleftharpoons$  is changed into  $=K$ .

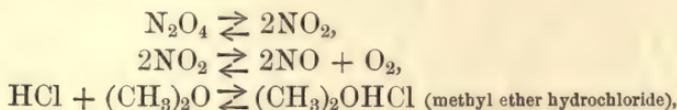
These equilibria have been studied both in gaseous and liquid systems. Lemoine (8) found for a mixture of iodine and hydrogen which combine partially to hydriodic acid according to the equation—



the values contained in the following table, which apply to the temperature  $440^\circ$ .  $p_0$  denotes the partial pressure of the hydrogen at the beginning of the experiment,  $p'_0$  is the corresponding value for the iodine gas, and  $x$  the proportion of hydrogen still free after the equilibrium has been established. It is evident from the numbers quoted that the observed values of  $x$  agree satisfactorily with those calculated. The measurements were carried out by collecting the gas mixture over water, which absorbs the acid formed, and the quantity of hydrogen was then determined eudiometrically. The reaction proceeds so slowly at the ordinary temperature that there is no disturbance of the equilibrium during the measurement.

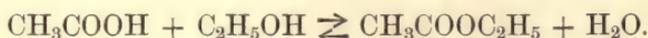
$p_0$ .	$\frac{p'_0}{p_0}$ .	$x$ (observed).	$x$ (calculated).
2.2 atmo.	1	0.240	0.280
2.33 "	0.784	0.350	0.373
2.33 "	0.527	0.547	0.534
2.31 "	0.258	0.774	0.754
1.15 "	1	0.255	0.280
0.37 "	1.36	0.124	0.184
0.45 "	1	0.266	0.280
0.41 "	0.623	0.676 (?)	0.470
0.45 "	0.58	0.614 (?)	0.497
0.46 "	0.56	0.600 (?)	0.510
0.48 "	0.53	0.563	0.535
0.48 "	0.26	0.794	0.756
0.25 "	1	0.250	0.280
0.10 "	1	0.290	0.280

Other similar equilibria, such as those represented by the following reactions—



have been studied, and in all cases a good agreement has been found between the calculated and observed results.

An example of a reaction between two liquids which is governed by Guldberg and Waage's law is the formation (or decomposition) of ethyl acetate—



This equilibrium was first studied experimentally by Berthelot and Péan de St. Gilles (9), and the results were afterwards calculated by Guldberg and Waage, and by van't Hoff (10).

The results are contained in the following table; in column *m* is given the number of molecules of alcohol which reacted on one molecule of acid, and *x* is the quantity of ester formed when equilibrium was established.

<i>m</i> .	<i>x</i> (observed).	<i>x</i> (calculated).
0.05	0.05	0.049
0.18	0.171	0.171
0.33	0.293	0.311
0.50	0.414	0.423
1.00	0.667	(0.667)
2.00	0.858	0.845
8.00	0.966	0.945

The agreement between observed and calculated values is very good. Experiments on various equilibria in solutions have also led to excellent agreement with, and a thorough confirmation of, the theory; for details the reader is referred to a text-book on physical chemistry.

In conclusion, it may be pointed out that in a *homogeneous* system the equilibrium relationships between *different* kinds

of molecules are controlled by Guldberg and Waage's law, whilst the equilibrium relationships of *one* kind of molecule between two phases of a *heterogeneous* system are determined by the law of distribution. With the help of these two laws every equilibrium can be calculated. They have been of immense service in the investigation of dissociation phenomena at high temperature, and we shall have to apply them later in our discussion of electrolytic dissociation.

**Clapeyron's Formula.**—For the process of evaporation, Clapeyron, in 1834, making use of Carnot's theorem, deduced the following connection:—

$$\frac{dp}{dT} = \frac{l}{(V - V_1)T}.$$

In this formula  $l$  is the heat of vaporisation of one gram of the liquid,  $T$  is the absolute temperature, and  $V$  and  $V_1$  are the volumes of one gram of the vapour and liquid respectively.

It is easy to alter this formula so that it applies to a gram-molecule. If we multiply numerator and denominator of the expression by the molecular weight  $M$  of the substance, we obtain in the numerator  $M \times l = \lambda$ , the molecular heat of vaporisation, and in the denominator  $(MV - MV_1) = v - v_1$ , the difference between the molecular volumes of the vapour and the liquid. Therefore—

$$\frac{dp}{dT} = \frac{\lambda}{(v - v_1)T}.$$

We have already (p. 48) made use of the formula in this form. If the temperature be sufficiently removed from the critical temperature, it is always permissible to neglect the molecular volume  $v_1$  of the liquid compared with that  $v$  of the gas, and by introducing at the same time  $pv = RT$  we obtain—

$$\frac{dp}{pdT} = \frac{\lambda}{RT^2}$$

or—

$$\frac{d \ln p}{dT} = \frac{\lambda}{RT^2}.$$

**Change of Solubility with Temperature.**—It has been shown that the solution of a substance corresponds exactly with the vaporisation of a liquid into a vacuum if the osmotic pressure be introduced in place of the vapour pressure; consequently for the solution there must be a connection analogous to that expressed by the Clapeyron formula, that is—

$$\frac{d \ln \pi}{dT} = \frac{\lambda}{iRT},$$

where  $\pi$  is the osmotic pressure of the saturated solution and  $i$ , as before, denotes the coefficient which occurs in the formula  $\pi V = iRT$  for the osmotic pressure. If we replace  $V$ , the volume, by  $\frac{1}{C}$ , the reciprocal of the concentration, we obtain—

$$\pi = iCRT,$$

and from this we further obtain—

$$d \ln \pi = d(\ln C + \ln T) = d \ln C + \frac{dT}{T};$$

one step more leads to—

$$\frac{d \ln C}{dT} = \frac{\lambda - iRT}{iRT^2} = \frac{\lambda_1}{iRT^2}.$$

$\lambda$  denotes the heat which is taken up when a gram-molecule of liquid passes into gas at constant pressure, *i.e.* with increase of volume, and the external work done amounts to  $iRT = 2iT$  (see p. 76). On the other hand, for the solution we consider the heat,  $\lambda_1$ , which is required when the process takes place without doing external work, *i.e.* at constant volume. During the solution the volume of the liquid is not appreciably altered.

Now,

$$\lambda_1 = \lambda - iRT,$$

*i.e.* the heat of vaporisation or of solution at constant volume differs from that at constant pressure by the amount of the external work done.

This connection between the heats under the different conditions was tested by van't Hoff (11), and was found to be experimentally confirmed, as the numbers in the following table show:—

Substance.	Temperature.		Solubility.		Heat of solution.		<i>i</i>
	<i>t</i>	<i>t</i> <sub>1</sub>	<i>s</i>	<i>s</i> <sub>1</sub>	obs.	calc.	
	°	°					
Succinic acid . . . . .	0	8.5	2.9	4.22	6.7	6.5	1
Benzoic acid . . . . .	4.5	75	0.182	2.193	6.5	6.7	1
Salicylic acid . . . . .	12.5	81	0.16	2.44	8.5	8.9	1
Oxalic acid . . . . .	0	10	5.2	8.0	8.5	8.2	1.25
Boric acid . . . . .	0	12	1.95	2.92	5.6	5.2	1
Lime . . . . .	15.6	54.4	0.13	0.103	-2.8	-2.8	2.6
Barium hydroxide . . . . .	0	10	1.5	2.22	15.2	16.3	2.7
Aniline . . . . .	16	35	3.1	3.6	0.1	0.7	1
Amyl alcohol . . . . .	0	18	4.23	3.0	-2.8	-3.3	1
Phenol . . . . .	1	45	7.1	10.2	2.1	1.4	1
Potassium oxalate (acid) . . . . .	0	10	2.2	3.1	9.6	9.8	1.8
Potassium bichromate . . . . .	0	10	4.6	7.4	17	17.3	2.36
Alum. . . . .	0	9.4	3	4.05	20.2	21.9	4.5
Potassium chlorate . . . . .	0	15.4	3.3	6.03	10	11	1.8
Borax . . . . .	0	10	2.83	4.65	25.8	27.4	3.6
Barium nitrate . . . . .	0	9	5.2	7.0	9.4	8.8	2.2
Mercuric chloride . . . . .	10	50	6.6	11.8	3	3	1.1

In the first column is given the substance experimented upon; under *t* and *t*<sub>1</sub> two temperatures at which the solubilities *s* and *s*<sub>1</sub> were determined (the solubility being expressed in percentage). Strictly, the solubility should be measured in grams per 100 c.c., but the values which would be obtained in this way do not differ much from those contained in the table, especially in those cases where the solubility is small. The heats of solution are given in large calories (1 Cal. = 1000 cal.); the observed values are mostly those found by Thomsen, and the calculated values are those obtained by van't Hoff according to the above law. Under *i* is given the value for the various substances at concentration  $\frac{s + s_1}{2}$  and temperature  $\frac{t + t_1}{2}$ . As is evident, the agreement between the observed and the calculated heats of solution is eminently satisfactory.

When the formula is integrated we obtain—

$$\ln \frac{1}{C_0} = \frac{\lambda_1}{2i} \left( \frac{1}{T_0} - \frac{1}{T_1} \right),$$

or—

$$C_1 = C_0 e^{\frac{\lambda_1}{2i} \cdot \frac{T_1 - T_0}{T_0 T_1}}.$$

Since  $T_0 T_1$  for a small temperature interval changes but little, and the variations of  $\lambda_1$  and  $i$  are not great, we may write with sufficiently close approximation—

$$C_1 = C_0 e^{A(t_1 - t_0)}$$

where  $A$  represents  $\frac{\lambda_1}{2i} \cdot \frac{1}{T_0 T_1}$  and  $t_1 - t_0 (= T_1 - T_0)$  is reckoned in Celsius degrees. The concentration of a saturated solution therefore increases with rise of temperature approximately proportionally to an exponential function, so that the solubility increases almost in the same ratio between  $0^\circ$  and  $5^\circ$  as between  $5^\circ$  and  $10^\circ$ , between  $10^\circ$  and  $15^\circ$ , etc. Attention was first called to this peculiarity by Nordenskiöld (*12*).

**Change of Homogeneous Equilibrium with the Temperature.**—Precisely the same relationships exist in the case of equilibria between a mixture of vapours and liquids as between a liquid and its vapour. As already pointed out, the volume of the liquid does not enter into the formula on account of its comparative smallness. Let us consider the equilibrium which exists in a mixture of ammonium chloride vapour, ammonia, and hydrochloric acid, the partial pressures of which are  $p_3$ ,  $p_1$ , and  $p_2$ . If a change of temperature takes place, the change of equilibrium—



produced is regulated by the above connection. It must, however, be observed that a gram-molecule of ammonium chloride disappears when a gram-molecule of ammonia and one of hydrochloric acid are formed. Van't Hoff's application (*13*) of the Clapeyron formula to this case gives—

$$\frac{d \ln p_1}{dT} + \frac{d \ln p_2}{dT} - \frac{d \ln p_3}{dT} = \frac{\mu}{RT^2}$$

where  $\mu$  denotes the heat absorbed when a gram-molecule of ammonium chloride is transformed into a mol of ammonia and a mol of hydrochloric acid. The condition for the applicability of this equation is that the pressure remains constant; if the change takes place at constant volume, then, as in the case of solutions, we may introduce the concentrations ( $C$ ) instead of the pressures, and obtain—

$$\frac{d(\ln C_1 + \ln C_2 - \ln C_3)}{dT} = \frac{\mu}{RT^2},$$

or—

$$\frac{d \ln \frac{C_1 C_2}{C_3}}{dT} = \frac{\mu}{RT^2}.$$

We know that at constant temperature—

$$\frac{C_1 C_2}{C_3} = K.$$

We therefore have for the change of  $K$  with change of temperature—

$$\frac{d \ln K}{dT} = \frac{\mu}{RT^2},$$

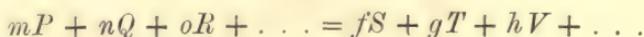
or integrated—

$$\ln K = \frac{\mu}{R} \left( \frac{1}{T_1} - \frac{1}{T_0} \right) + M$$

where  $M$  is a constant, or finally—

$$K = Me^{-\frac{\mu}{R} \cdot \frac{T_1 - T_0}{T_0 T_1}}$$

In general, for a reaction which takes place according to the chemical equation—



we have the equilibrium equation—

$$C_p^m \cdot C_q^n \cdot C_r^o \dots = K \cdot C_s^f \cdot C_t^g \cdot C_v^h \dots$$

where  $K$  is a constant and  $C_p, C_q$ , etc., denote the concentrations (or, more strictly, the osmotic pressures) of the substances  $P, Q$ , etc. Further, if  $\mu$  cal. are absorbed when  $m$  mols of substance  $P, n$  mols of substance  $Q$ , etc., react to form  $f$  mols of substance  $S$ , etc., then, provided that the volume does not change much with the temperature, we obtain for the change of the constant  $K$  with the temperature the same formula as in the above special case—

$$\ln K = \frac{\mu}{R} \left( \frac{1}{T_1} - \frac{1}{T_0} \right) + M,$$

or —

$$\log K = \frac{1}{2.3025} \cdot \frac{\mu}{R} \left( \frac{1}{T_1} - \frac{1}{T_0} \right) + M_1$$

when  $M$  and  $M_1$  are two integration constants, which give the value of  $\ln K$  and  $\log K$  at temperature  $T_0$ .<sup>1</sup> Since  $\mu$  is expressed in calories, the value of  $R$  is 1.99.

When  $\mu$  is positive, *i.e.* when in the reaction heat is absorbed, and  $T_1$  is greater than  $T_0$ ,  $\left( \frac{1}{T_1} - \frac{1}{T_0} \right)$  is evidently negative, and  $\ln K$  greater than  $M$ , indicating that, with rising temperature, the concentrations  $C_p, C_q$ , etc., diminish, whilst the concentrations  $C_s, C_t$ , etc., increase. From this we can draw the following general conclusion, which is applicable both to heterogeneous and homogeneous systems:—

*In an equilibrium that system of substances, the formation of which is accompanied by an absorption of heat, increases with rising temperature.*

Some examples illustrating this very important generalisation may be given. When a substance is melted, heat is absorbed, therefore the melted portion must increase when the temperature is raised.

As in this case the system is a condensed one, if the pressure is kept constant, the transition takes place suddenly when the melting point is passed. In the same way heat is absorbed when vaporisation takes place; consequently, if in a vessel there is an equilibrium between water and vapour,

<sup>1</sup> This signification of  $M$  and  $M_1$  is seen if  $T_1$  be set equal to  $T_0$ .

the quantity of the vapour must increase at the expense of the water when the temperature is raised. Most substances dissolve in water with an absorption of heat, and in these cases the solubility must increase as the temperature rises. Lime and many of the calcium salts, amyl alcohol, and other substances, behave in the opposite way, because heat is evolved when they are dissolved in water. As the decomposition of ammonium chloride into ammonia and hydrochloric acid is accompanied by an absorption of 44,500 cal., the dissociation of this must increase with the temperature. If in the above formula we set  $T = 0$ , we find that  $\ln K = \infty$ , *i.e.* one of the concentrations,  $C_s$ ,  $C_x$ , or  $C_v$ , must be zero. At the absolute zero, therefore, the substances must so react that the system which is formed with absorption of heat passes as completely as possible (until one of the reacting substances is fully used up) into the opposite system. At the absolute zero, therefore, the assertion of the older thermochemists, that that reaction occurs which is accompanied by an evolution of heat, is quite correct. For the ordinary temperature, which indeed does not lie very high above the absolute zero, most of the reactions examined do take place according to that view, but numerous exceptions are known. The assumption may, therefore, be of use to a certain extent in indicating what direction a reaction will probably take at normal temperature.

**Maxima and Minima in Equilibria.**—It is to be observed that the heat of transformation  $\mu$  often changes with the temperature. The connection between the heat of vaporisation of water at constant pressure,  $Q_p$  and the temperature can be represented, according to Regnault, by the formula (for 1 gram)—

$$Q_p = 606.5 - 0.695 t \text{ cal.}$$

If we transform this formula so as to make it apply to a gram-molecule, and to the absolute temperature, we obtain—

$$\mu_p = (10,917 - 12.51 t) = (14,332 - 12.51 T) \text{ cal.}$$

Let us assume that the vapour is evolved in a closed

space, then no work is done. As Regnault's formula refers to constant pressure, the heat of vaporisation  $\mu_v$  at constant volume must be smaller by  $2T$  cal. (see p. 91), *i.e.*—

$$\mu_v = (14,332 - 14.51 T) \text{ cal.}$$

According to this formula the heat of vaporisation should be equal to 0 at temperature  $T = \frac{14332}{14.51} = 715^\circ \text{ C}$ . As a matter of fact, the heat of vaporisation becomes equal to 0 at a much lower temperature, namely, at the critical temperature, which is about  $365^\circ \text{ C}$ .

Sometimes the sign of the value of  $\mu$  becomes changed at a particular temperature. In such cases the system possesses either a maximum or a minimum. According to the investigations of Étard and Engel (14), this behaviour is shown by the solubility of the sulphates, and at high temperatures by salts in general. Thus, ferrous sulphate has a maximum solubility at  $63^\circ$ , zinc sulphate at  $82^\circ$ , nickel sulphate at  $122^\circ$ , and copper sulphate at  $130^\circ$ . At the temperature at which this occurs it is frequently found that a change takes place in the solid whereby water of crystallisation is lost, and two different salts are present, the solubility curves of which cut each other. Thus, at  $34^\circ$  sodium sulphate passes from the modification  $\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$  (the ordinary crystallised Glauber salt) into the anhydrous salt  $\text{Na}_2\text{SO}_4$ . The former dissolves in water with absorption of heat (18,760 cal. according to Thomsen), the latter with a slight evolution of heat (4600 cal.). As the temperature rises, the solubility of the former salt increases, as the diagram (Fig. 20) shows, and that of

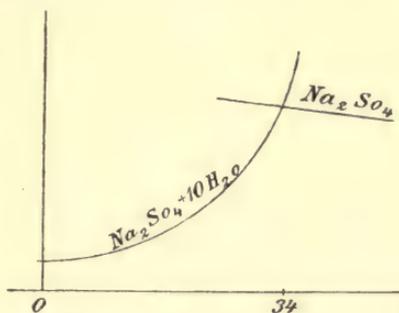


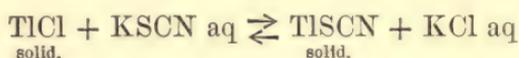
FIG. 20.

the latter salt diminishes; this gives rise to an (apparent) maximum solubility of Glauber salt at  $34^\circ$ . If we may

judge by the curves given by Étard and Engel, which all show sharp breaks, the maximum solubilities of the other salts are to be attributed to the same cause.

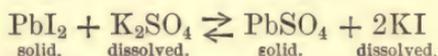
A true maximum in an equilibrium has been proved by Troost and Hautefeuille (15) for the dissociation of silicon chloride, and by Ditte (16) for the dissociation of hydrogen selenide. In these cases it must be assumed that the quantity of heat which is absorbed by the splitting up of the compound is at first positive, then at the maximum dissociation it changes its sign, so that at higher temperatures the decomposition is accompanied by an evolution of heat.

More recently an interesting example of a true recurring point has been found by Knüpffer (17) in the reaction—



at 32°.

The reaction expressed by the equation—



has been investigated by A. Klein (18); the electrical measurements show that below 8° the reaction is endothermic, *i.e.* is accompanied by an absorption of heat, and above 8° it is exothermic, *i.e.* takes place with evolution of heat.

The phenomenon that a chemical reaction at a sufficiently high temperature sometimes take place in the opposite direction to that in which it proceeds at the ordinary temperature is of the greatest importance in chemistry. Substances which are not stable at the ordinary temperature may be formed at high temperature, and in the same way substances may be formed at low temperature which at the normal temperature decompose with absorption of heat.

**Influence of Pressure.**—Besides the temperature we must also take into consideration the pressure when discussing the condition of a substance. As regards the influence of pressure the following statement is quite general—

*Diminution of pressure favours the formation of the system with the greater volume.*

At  $0^{\circ}$ , and under a pressure of 1 atmo., water and ice are in equilibrium. If the pressure is increased, the ice melts, because the specific volume of the melted water is smaller than that of the ice. Usually, however, a substance when fused has a greater volume than the same substance at the same temperature in the solid state. Consequently in most cases the melting point rises with increasing pressure, as Bunsen (19) proved for paraffin and spermaceti. As the pressure is increased this difference in volume seems to disappear, because in the liquid state the substance is more compressible than when solid. It is therefore not improbable that at very high pressures most substances would behave like water; as Tammann (20) has pointed out, at a certain pressure the fusion is not accompanied by a change of volume.

The influence of pressure on the solubility of salts has been studied by F. Braun (21), and has been found to be in agreement with the theory. Generally the influence of pressure on the equilibrium is only very small, as we are not in a position to apply excessively high pressures. It is otherwise, of course, when we consider the relationships in the interior of the earth or of the sun, where the pressure, on account of its enormously high value, plays an extremely important part.

## CHAPTER VII.

### Velocity of Reaction.

**Formation of the State of Equilibrium.**—When a chemical system is not in equilibrium it approaches this state with a greater or smaller velocity. Many reactions take place so very quickly that their course cannot be followed, whilst others proceed so slowly that their progress is not detectable. The influence of temperature in this respect is very great. For the establishment of an equilibrium in a mixture of hydrogen and iodine at  $265^{\circ}$  several months are required, at  $350^{\circ}$  about as many days, and at  $440^{\circ}$  about as many hours.

An explosive mixture of hydrogen and oxygen behaves in precisely the same way. Above  $580^{\circ}$  the reaction takes place with explosive violence, whilst at  $155^{\circ}$  it proceeds so slowly that it is only after months that combination has taken place to an appreciable extent [V. Meyer (1)]. At the normal temperature the mixture is apparently inactive, but in all probability this is not the case.

The following reactions, the velocities of which have been most fully studied, may serve as typical for others: the inversion of cane sugar under the influence of acids, the decomposition of ester into alcohol and acid, and the saponification of esters with bases.

**Inversion of Cane Sugar.**—The course of the inversion of cane sugar was first followed by Wilhelmy (2) in 1850. He found that the quantity of sugar inverted in unit time is, *ceteris paribus*, proportional to the amount of sugar in the solution. If the concentration of the sugar is  $A$  gram-molecules (mols), and, after time  $t$ ,  $x$  mols are inverted, then

at this point of time there are in the solution  $(A - x)$  mols of sugar. The quantity  $dx$  which is inverted in time  $dt$  is, according to Wilhelmy, proportional to  $(A - x)$ . We therefore have, if  $K$  is a constant—

$$\frac{dx}{dt} = K(A - x),$$

and by integration we obtain—

$$\ln \frac{A - x_0}{A - x_1} = K(t_1 - t_0).$$

The quantity of sugar present can be accurately determined by ascertaining the angle through which a definite length of the solution rotates the plane of polarised light. In the next table is given under  $t$  the time in minutes since the beginning of the reaction, under  $\alpha^\circ$  the angle of rotation produced by the solution on polarised light, and the third column contains the constant—

$$K = \frac{1}{t_1 - t_0} \log \frac{A - x_0}{A - x_1},$$

which is the specific velocity of the reaction. The original dextrorotation of the solution is due to the dextrorotatory cane sugar, and this passes into a lævorotation when the quantity of lævorotatory invert sugar becomes sufficiently great. When  $t = \infty$ , *i.e.* after a very long time, the inversion is as good as complete. The results given were obtained at  $25^\circ$  with a 20 per cent. cane sugar solution, which was also 0.5-normal with respect to lactic acid—

$t$	$\alpha^\circ$	$K$
0	34.50	—
1435	31.10	0.2348
4315	25.00	2359
7070	20.16	2343
11360	13.98	2310
14170	10.61	2301
16935	7.57	2316
19815	5.08	2291
29925	-1.65	2330
$\infty$	-10.77	—

**Saponification of an Ester.**—Since in the reaction just considered the quantity of one of the reacting substances remains constant, the concentration of only one kind of molecule changes, corresponding with the given equation—

$$\frac{dx}{dt} = K(A - x).$$

Van't Hoff terms such reactions *monomolecular*. Chemical reactions in which two of the reacting substances disappear in the course of the action are much more common. The best known example of such a *bimolecular* reaction is the saponification of an ester. This reaction proceeds according to the equation—



If we start with equivalent quantities,  $A$  mols per litre, of the two substances, then after time  $t$  the same quantity of the two substances,  $x$  mols, must have disappeared, and there will remain  $(A - x)$  mols of each in a litre. Now, the quantity of sodium acetate which is formed in unit time is proportional to the concentration of the ethyl acetate and that of the sodium hydroxide; therefore—

$$\frac{dx}{dt} = K(A - x)^2,$$

from which by integration can be obtained—

$$\frac{1}{A - x_0} - \frac{1}{A - x_1} = K(t_1 - t_0)$$

where  $K$ , a constant, represents the specific velocity of the reaction.

In order to prove the validity of this equation, we cite the following results obtained by Madsen ( $\beta$ ) in the investigation of the strengths of sugar, dextrose, and levulose as acids. The first column contains the time in minutes, the second the concentration of the base ( $\frac{1}{250}$   $n$ -solution being taken as unit), and the third the constant for the specific velocity of reaction.

The experiments were made at  $10.2^\circ$  with solutions which were 0.02485 normal with respect to ethyl acetate and sodium hydroxide.

$t$	$A - x$	$K$
0.0	4.60	—
3.8	3.98	2.23
7.3	3.52	2.28
12.3	3.03	2.28
16.3	2.74	2.28
20.1	2.53	2.23
24.0	2.28	2.28
27.1	2.17	2.23

**Velocity in Heterogeneous Systems.**—In the preceding chapter it was pointed out that the equilibrium of a system of molecules is to be regarded as “mobile.” The state of equilibrium is therefore attained in a chemical system when the two reactions proceeding in opposite directions have the same velocity. If the velocity of decomposition of the ester be represented by the formula—

$$-\frac{dC_{\text{ester}}}{dt} = kC_{\text{ester}}C_{\text{water}} - k^1C_{\text{alcohol}}C_{\text{acid}},$$

the equilibrium constant of the ester-hydrolysis,  $K$ , is equal to the quotient of the two velocity constants—

$$K = \frac{k}{k^1}.$$

It has been found by the study of vaporisation and solution that the relationship between velocity and equilibrium is just as simple in heterogeneous systems.

Equilibrium is attained between liquid and its vapour when the maximum tension  $P$  of the liquid is equal to the partial pressure  $p$  of its molecules in the vapour space, *i.e.* when  $P = p$ . The rate of evaporation is at every moment proportional to the difference between these two values, *i.e.* it is equal to  $k(P - p)$ .

Noyes and Whitney (4) have found that the rate of

solution of a solid substance is at any moment proportional to the difference between the concentration  $C$  when the solution is saturated, and the concentration  $c$  at that time *i.e.* the rate is equal to  $k(C - c)$ .

The velocity of crystallisation has recently been studied by Tammann (5). The velocity at first increases with the degree of super-cooling, reaches a maximum, then by further depression of the temperature decreases, and may thereafter become very small. H. A. Wilson (6) has shown that the velocity of crystallisation  $v$  can be represented by the equation—

$$v = K \frac{\theta_0 - \theta}{V}$$

where  $\theta_0 - \theta$  represents the super-cooling,  $V$  the viscosity of the liquid, and  $K$  a constant.

#### Influence of Temperature on the Velocity of Reaction.

—If we examine the influence of temperature on the specific velocity of a reaction, *e.g.* the saponification of ethyl acetate, we find that it can be approximately represented by the formula given on page 95 for the change of equilibrium. This is clearly seen from the results given in the following tables, in which are to be found:  $t$ , the temperature (Celsius);  $\rho$  (observed), the observed velocity of reaction; and  $\rho$  (calculated), the value calculated according to the formula mentioned:—

SAPONIFICATION OF ETHYL ACETATE.

$t$	$\rho$ (observed).	$\rho$ (calculated).
0		
3.6	1.42	1.48
7.2	1.92	(1.92)
12.7	2.87	2.82
19.3	4.57	4.38
23.6	6.01	5.78
28.4	8.03	7.81
34.0	10.92	(10.92)
37.7	13.41	13.59

## INVERSION OF CANE SUGAR.

$t$	$\rho$ (observed).	$\rho$ (calculated).
°		
25	9.67	(9.67)
40	73.4	75.7
45	139.0	144.0
50	268.0	(268.0)
55	491.0	491.0

The change of velocity constant with the temperature is evidently very great. The velocity of saponification is doubled for a rise of  $10^\circ$ , corresponding with an increase of 7 per cent. per degree. With cane sugar the increase is even greater, for a rise of temperature of  $15^\circ$  causes an increase of the velocity of inversion in the ratio  $1 : 8 = 1 : 2^3$ ; the velocity is therefore doubled by an increase of temperature through  $5^\circ$ , which is equivalent to an increase of 15 per cent. per degree. As is evident from the table, the increase is smaller at high temperatures than it is at low temperatures, and this is as would be expected from the formula.

Such an exponential increase with the temperature as that mentioned is scarcely ever met with for any other physical phenomenon except evaporation. A cubic centimetre of saturated water vapour at  $0^\circ$  contains double as much water, namely 4.9 grams, as the same volume at  $-10^\circ$  when the amount is only 2.4 grams. This consideration led me to construct the following hypothesis (7). The cane sugar solution contains two kinds of molecules, one sort of which can be attacked (inverted) by the acid, the other sort can not. The amount of the former sort is extremely small compared with that of the second, and both are in equilibrium. If we denote the concentrations of the two kinds by  $c_1$  and  $c_2$  respectively, we obtain—

$$\frac{c_1}{c_2} = K = Me^{\frac{\mu}{R} \left( \frac{T_1 - T_0}{T_0 T_1} \right)}$$

where  $\mu$  is the heat which is absorbed when ordinary sugar is transformed into the variety which can be attacked. Since  $R$ , expressed in calories, is equal to 2, we calculate for cane sugar  $\mu = 25,640$  cal. per gram-molecule. The corresponding number for ethyl acetate is 11,160 cal. per gram-molecule. According to this hypothesis, the velocity of the reaction should be directly proportional to the concentration of the molecules which can be attacked.

This view is supported by experiments on the rate of solution,  $\rho$ , of zinc in dilute (0.1-normal) hydrochloric acid. This velocity is hardly altered by change of temperature, as is shown by the results of Ericson-Aurén (8) contained in the following table:—

Temperature.	$\rho$
0	
9	0.107
16.5	0.122
23	0.117
28	0.116
32	0.105
40	0.109
50	0.110

In this case the velocity of reaction is, within the experimental error, independent of the temperature. This can be explained by assuming that the ordinary zinc molecules can be attacked, or are "active," or that the heat of transformation of the inactive into active molecules is zero. The first assumption seems the more probable.

Rothmund's results (9) on the influence of pressure on the velocity of reaction are in good agreement with the hypothesis.

It must be observed that at higher concentrations of the acid the temperature has a very great influence on the speed of solution of zinc, as Guldberg and Waage (10) found. This may be due to the formation of a layer of concentrated zinc salt solution round the metal, which protects it from further action if not removed by agitation. The agitation is

carried out by the gas evolution; it is the more perfect the greater the mobility of the solution, and, as is well known, this last factor increases with the temperature. A similar reasoning can be applied to other solution processes.

**Velocity of Reaction and Osmotic Pressure.**—It has been shown that in the inversion of cane sugar the quantity of sugar inverted is proportional to its concentration in the solution. This follows from the agreement between the calculated values and those found by Wilhelmy. However, this connection is only exact because during the reaction invert sugar is formed. If we start with different concentrations of cane sugar, we find that for a 40 per cent. solution the velocity constant is more than double that for a 20 per cent. solution. The following table contains the results obtained by Ostwald (11):—

INVERSION OF CANE SUGAR WITH 0·5-NORMAL HCl.

$C$	$\rho$	$\frac{\rho}{C}$	$E$	$\frac{\rho}{E}$
40 per cent.	11·68	0·292	3·41	3·43
20    ,,	4·54	0·227	1·37	3·32
10    ,,	2·07	0·207	0·612	3·38
4      ,,	0·768	0·192	0·228	3·37

The table contains under  $C$  the number of grams of sugar in 100 c.c. of solution, under  $\rho$  the velocity of reaction, in the third column the ratio of these two, in the fourth column the depression of the freezing point of a solution of the given concentration, and in the last column the ratio between velocity of reaction and the depression of the freezing point. This latter ratio is constant throughout, whilst the quotient  $\frac{\rho}{C}$  is entirely dependent on the concentration.

This result can be made clear by a kinetic consideration of the matter. The osmotic pressure at constant temperature is proportional to the number of collisions which the sugar molecules make with the sides of the containing vessel.

(This is quite evident if the walls consist of semi-permeable membranes which do not allow the sugar to pass through.) On the other hand, there is a proportionality between this number and the number of collisions of the sugar molecules with the active molecules of the inverting acid. As we shall see later, it is the hydrogen ions of the acid which must be considered. Now, since the concentration of the acid is constant during the experiment, the number of collisions between sugar molecules and acid molecules must be proportional to the osmotic pressure of the sugar. It has been assumed that the reaction only takes place when an acid molecule meets a molecule of sugar which can be attacked, and therefore we should take account only of the osmotic pressure of the sugar molecules in this condition. It is clear from what has previously been said (page 86), that if we denote the osmotic pressure of the ordinary sugar molecules by  $\pi_i$ , and that of the molecules which can be attacked by  $\pi_a$ , then—

$$K\pi_a = \pi_i$$

or—

$$(K + 1)\pi_a = \pi_i + \pi_a$$

where  $K$  is a constant, *i.e.* the osmotic partial pressure  $\pi_a$  of the molecules which can be attacked stands in a constant ratio to the osmotic pressure  $\pi_i + \pi_a$  of all the sugar molecules. From this it follows that the number of collisions per second between active molecules of acid and attackable molecules of cane sugar is proportional to the osmotic pressure of the sugar. Furthermore, the velocity of the reaction, *i.e.* the quantity of substance transformed in unit time, must be proportional to the number of such collisions, and consequently to the osmotic pressure of the sugar—a conclusion which is confirmed by experiment.

It would appear, therefore, in calculations concerned with the velocity of reaction to be more correct to use osmotic pressures and not concentrations, in the same way as has been pointed out for equilibria. The above example shows that using the former (theoretically more exact) method

correct results are obtained, whilst deviations amounting to as much as 40 per cent. occur when use is made of the concentrations. It has been found for the majority of reactions, that the velocity increases more quickly than it should do on the assumption that it is proportional to the concentration. The osmotic pressure shows the same behaviour, but a thorough investigation of the connection between these two phenomena has not yet been made.

**Action of Neutral Salts.**—The specific velocity of reaction  $\frac{\rho}{C}$  of a 10 per cent. solution of cane sugar which contains 10 per cent. of invert sugar, is the same as that of a 20 per cent. solution containing no invert sugar (p. 101). But for a 20 per cent. cane sugar solution  $\frac{\rho}{C}$  is  $1.11 \left( = \frac{22.9}{20.7} \right)$  times as great as for a 10 per cent. solution when no invert sugar is present. The relative speed of reaction is therefore increased by no less than 11 per cent. by the presence of 10 per cent. of invert sugar. It has been found that the addition of 0.4 gram-molecule of sodium chloride increases the speed of inversion by 26 per cent. Other salts exert a similar action. Tammann (*l.c.*) found that a solution which contained cane sugar and copper sulphate had an osmotic pressure greater than the sum of the osmotic pressures of the cane sugar without the copper salt and of the copper sulphate without the sugar. It is therefore probable that the osmotic pressure of the sugar is increased by the presence of foreign substances in the solution.

This gives us a probable explanation of the phenomenon which has been recognised for a long time, namely, that the specific velocity of reaction is increased by the addition of foreign substances (the so-called *action of neutral salts*, because the salts were first investigated in this connection).

## CHAPTER VIII.

### Electrolytes. Electrolytic Dissociation.

**Deviations shown by Electrolytes from van't Hoff's Law.**—In the preceding chapters a short sketch has been given of the laws which obtain for substances in solution. Attention has been called to the fact that many substances behave in accordance with van't Hoff's law, but that salts, strong acids and bases in aqueous or alcoholic solution exhibit deviations. These substances always have an osmotic pressure which is too high, whether this be found from the depression of vapour pressure or freezing point, or from the raising of the boiling point. These substances, too, are of very great interest, both in a chemical respect on account of their applications in analytical chemistry, and in a physical respect because of their conducting the electric current and being at the same time decomposed.

Since electrical measurements are the sharpest and most exact known in physical science, it was to be expected that a complete electrical examination of these substances would throw some light on their nature and peculiarities. As a matter of historical fact, the electrical examination led to the same point as van't Hoff's osmotic investigations, and it was only after the two studies were considered together that the problem of the nature of solutions was satisfactorily solved.

**Faraday's Experiments.**—We have already referred to Grotthuss' views, according to which the molecules in an electrolytic (*i.e.* salt) solution arrange themselves into a sort of chain between two metallic plates connected with

the poles of a battery and immersed in the solution. It was supposed that the oppositely charged constituents of the nearest salt molecules were attracted by the electrodes—for instance, in a solution of potassium chloride the chlorine was attracted by the positive pole and the potassium by the negative pole.

It was assumed that the electrical, decomposing force was only active near the poles, and that it decreased greatly with increasing distance from the poles, just as was assumed in the case of all forces which were regarded as actions at a distance.

Faraday, who strongly opposed the conception of action at a distance, showed in the following simple way that the electrical (electromotive) force is the same at all points of a parallel-sided trough through which a current is passing. By means of the wires  $C$  and  $D$  the poles of the battery  $B$  are connected with two poles immersed in a salt solution contained in the trough  $T$ . While

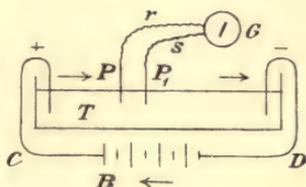


FIG. 21.

the current is passing through the solution two strips of platinum,  $P$  and  $P_1$ , which are kept at a fixed distance apart, are dipped into the solution. These strips are connected by the wires  $r$  and  $s$  with a galvanometer,  $G$ . The galvanometer shows a deflection indicating that a current is passing in the direction from  $P$  to  $P_1$  through  $G$ , and this current may be regarded as a branch of the main current passing through the trough  $T$ . It is found that the galvanometer-needle shows the same deflection at whatever point between the poles the strips  $P$  and  $P_1$  are placed, so long as a line joining these is parallel with the sides of the trough. This proves that the electromotive force between  $P$  and  $P_1$ , which causes the current through  $G$ , is the same at all points, and independent of the distance from the poles. Theoretically the experiment is simplest when the solution used is one of zinc sulphate, and the  $+$  and  $-$  electrodes as well as  $P$  and  $P_1$  consist of amalgamated zinc, because,

as will be later shown, no appreciable polarisation then takes place. The electrical condition in the trough can be graphically represented as in Fig. 22. At the point + the electric potential has a certain value, say  $A$ ; at the point - it has a lower value, say  $B$ ; consequently the (positive)

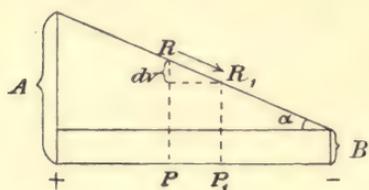


FIG. 22.

electric current flows in the direction from  $A$  to  $B$ , from higher to lower potential. The potential at any point,  $P$ , between + and - is found by joining the end points of  $A$  and  $B$ , and erecting at  $P$  a perpendicular which meets the line joining  $A$  and  $B$  at  $R$ .  $PR$  then gives the potential at  $P$ . In the same way  $P_1R_1$  represents the potential at point  $P_1$ , and the difference,  $dV$ , of the potentials  $PR$  and  $P_1R_1$  at points  $P$  and  $P_1$  is evidently the same throughout, so long as the distance  $PP_1$  is kept constant, because  $dV = PP_1 \tan \alpha$ , where  $\alpha$  is the inclination of the line joining  $A$  and  $B$  to the abscissæ-axis. The potential difference  $dV$  produces the current  $dI$  in the galvanometer; according to Ohm's law—

$$dI = \frac{dV}{M}$$

where  $M$  is the resistance in the circuit  $PGP_1$ . Since the resistance  $M$  does not vary, and  $dV$  is the same throughout, it is evident that the deflection of the galvanometer-needle must be the same at whatever distance from the poles  $P$  and  $P_1$  are placed.

Faraday further showed that chemical decomposition may also take place without metallic poles.

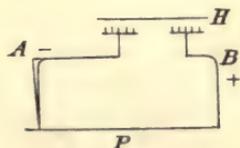


FIG. 23.

He connected a point,  $A$  (Fig. 23), with the negative pole of an electrical machine, and allowed negative electricity to stream from this against a strip of paper,  $P$ , which was moistened with a solution of sodium sulphate, made red with litmus, and which connected with the positive pole  $B$

of the machine. After some time the paper became blue immediately below *A*, proving that alkali had been formed.

A similar experiment described by Gubkin (*I*) is carried out as follows:—A solution of copper sulphate is placed under *A*, and a wire from *B* passes into the solution. When the negative electricity has passed across for some time, a thin film of copper is formed on the surface of the solution just below *A*.

Faraday proved, too, that chemical decomposition by an electric current may take place at a considerable distance from the poles. A layer of pure water was placed over a solution of magnesium sulphate, and an electric current was passed from a positive pole at the bottom of the solution to a negative pole near the surface of the water; it was found that a precipitation of magnesium hydroxide took place at the surface of separation of the solution and water. (This experiment was later studied more completely, and explained, by F. Kohlrausch.)

**The Ions.**—Faraday assumed that the ions were held together in the molecule by chemical forces, and that, further, the positive ion of one molecule was attracted by the negative ion of another molecule. This latter attraction, acting in conjunction with the electric force, was sufficient to overcome the attraction within the molecule.

Faraday, however, was astonished to find that those substances, like potassium or sodium chloride, or salts in general, which are the best conductors, are those in which the ions were supposed to be most firmly bound in the molecule. If all the molecules were really held together in the form of a Grotthuss chain so that a certain force would be necessary to break it, then a certain electromotive force would be required before electrolysis could take place. Apparently this is really the case, because polarisation often occurs at the electrodes.

If, however, the electrodes consist of unpolarisable metals, *i.e.* of the same metal as the positive ion of the salt, during the passage of the electric current the electrodes are

not altered, and a current can be obtained by using the smallest conceivable electromotive force. Even when working with polarisable electrodes it is only in order to transport the electricity from the electrode to the solution, or *vice versa*, that a certain electromotive force is required. In this case also the smallest fall of potential is sufficient to cause a current in the liquid. This fact was proved by Buff (2) with currents so small that it was only after months that a cubic centimetre of explosive mixture was obtained.

According to this, the very smallest force is sufficient to split the molecules in the Grotthuss chain. The behaviour of gases indicates what the relationships would be if the molecules of electrolytes were undecomposed. In order to keep a constant electric current passing through a gas a certain fall of potential per centimetre is necessary, and this is dependent on the pressure of the gas.

Faraday's view is therefore incorrect. The radicles of the salt molecule cannot be held together by a force of finite value. This was first appreciated by Clausius (1857), who was led to the assumption that in a solution of an electrolyte a constant exchange of ions is taking place between the molecules, or that, in special exceptional cases, free ions occur. According to this view the electrolyte is "electrolytically dissociated" into its ions, although these are present in such small quantity as not to be recognisable by chemical tests. Clausius arrived at these conclusions by the following considerations: According to the kinetic theory heat is due to the rapid motion of the molecules, and on the average the kinetic energy of a gram-molecule of every kind of gas molecule is the same. This motion is very great; at 20° the velocity of an oxygen molecule is 425 metre/sec., of a hydrogen molecule 1700 met./sec., and of a molecule of water vapour 566 met./sec.

It may be incidentally mentioned that a consequent development of the kinetic theory leads to the view that the velocity of dissolved molecules is about as great as that of gaseous molecules, because the osmotic pressure is about as

great as the gas pressure at the same temperature, the osmotic pressure being due to the impacts of the dissolved molecules against the semi-permeable membrane. For dissolved oxygen in aqueous solution at  $20^\circ$  the velocity of the molecule is therefore also 425 met./sec.

The dissolved molecules collide with the molecules of the solvent, and ultimately the mean value of the kinetic energy per gram-molecule will be the same for each. The velocity of the liquid molecules of the solvent must be the same as that in the gaseous state, therefore the velocity of water molecules in both conditions will be 566 met./sec., and the molecules of the solid should have the same velocity. The mean velocity increases proportionally to the square root of the absolute temperature. \*

Now, all molecules of one species do not possess the same velocity; thus, all water molecules at  $20^\circ$  do not have the velocity 566 met./sec., but this number represents the average value (1 in Fig. 24), and most of the velocities lie near this (Maxwell). Velocities ranging from 0 to very high values occur. However, the further any particular velocity is from the mean value the smaller is the number of molecules which possess this velocity, as is shown in the accompanying diagram. Amongst the water molecules there are therefore to be found some with a

velocity, *e.g.* 3 times as great as the mean velocity, and this corresponds with the mean velocity at a temperature 9 times higher than the temperature in question ( $273 + 20^\circ$ ), *i.e.* at the temperature  $2364^\circ$ . At this high

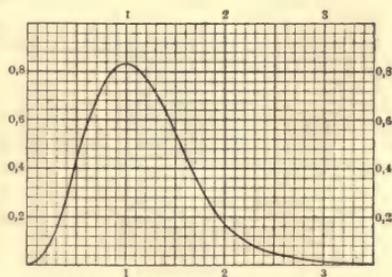


FIG. 24.

temperature water is partially dissociated into hydrogen and oxygen molecules, which indicates that the water molecules cannot withstand the rapid motion at this temperature without partly decomposing. A small part of the water at

the ordinary temperature ( $20^\circ$ ) must therefore be decomposed (dissociated) into hydrogen and oxygen molecules. According to the method of Helmholtz ( $\beta$ ) it can be calculated that, taking  $3 \times 10^{48}$  water molecules, two are dissociated into  $2\text{H}_2$  and  $\text{O}_2$ .

In the same way it can be shown that all possible combinations of hydrogen and oxygen, *e.g.* O, H, OH,  $\text{O}_2\text{H}$ , must occur in water. In a solution of potassium chloride, therefore, we must have the free ions  $\overset{+}{\text{K}}$  and  $\overset{-}{\text{Cl}}$ , but Clausius suggested that the quantity is so small as not to be recognisable by chemical methods. Nevertheless, the quantity was supposed to be sufficient to give an electric conductivity to the solution. When Clausius admitted that the number of free ions is so small, this proof lost much of its meaning when we consider that by the same reasoning we can show that even the compound  $\text{O}_2\text{H}$  occurs in the water in small quantity. For, although the correctness of the development cannot be doubted, it must yet be admitted that the substance  $\text{O}_2\text{H}$  does not really exist; if, for instance,  $10^{100}$  water molecules give rise to only one such molecule, then that has no practical significance. Furthermore, Clausius was not able to prove that the extremely small quantity of ions present in the salt solution was sufficient for the transportation of the electricity. \* N.C.

**Charging Current.** — If electricity be conducted through a trough containing an electrolytic solution, the

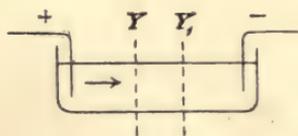


FIG. 25.

surface of the liquid receives a small charge during the first moment. After this has occurred, no further accumulation of electricity takes place either in the solution or at the surface. If we imagine two cross sections, Y and

$Y_1$ , of the solution (Fig. 25), then as much electricity must pass out from the liquid between these sections through  $Y_1$  as enters it through Y. In this way it can be proved that in any closed circuit the same quantity of electricity passes through every section after the charging current has ceased. \*

**Faraday's Laws.**—The relationship just mentioned was known to Davy. Faraday (4), working on this fact, investigated the behaviour of one and the same quantity of electricity when it passed through several water-decomposition apparatus which differed in having their poles unequal in size, divided into two, or consisting of different metals, such as platinum, zinc, or copper. These decomposition apparatus were connected in series in a circuit, an arrangement which ensures that the same quantity of electricity shall pass through all. By such experiments Faraday found that, no matter how the apparatus was arranged, the same quantity of explosive mixture (hydrogen and oxygen) was obtained in each of them. It was further observed that the same current passing through the apparatus in one case twice as long as in another gave twice as much of the explosive mixture. In other words, a given quantity of electricity corresponds with a certain definite quantity of explosive mixture. The quantity of electricity in coulombs is generally measured by its action on a magnetic needle. Kohlrausch (5) and Lord Rayleigh (6) have determined that for the evolution of 1 gram of explosive mixture 10,720 coulombs are required. From this and other determinations (with silver nitrate, etc.) it can be calculated that the charge for 1 gram-equivalent is 96,500 coulombs.

Faraday then sent the same current through several "voltameters" arranged in series, in one of which hydrogen was evolved, in another silver was deposited, in a third copper, etc. As a result of the experiment, he found that equal quantities of electricity decomposed chemically equivalent quantities of different substances.

This important result is known as Faraday's (second) law.

Faraday's first law, that the quantities of electricity are proportional to the quantity of decomposed substance, had already been suggested by Berzelius, but he had not been able to definitely prove it (compare pp. 7 and 18).

The simplest conception which can be derived from this

law is that the gram-equivalent of every ion carries a charge of 96,500 coulombs, and consequently all equivalents have the same charge. When the electricity passes through a liquid it is transported by the ions, the positive electricity being carried by the positive ions, and the negative by the negative ions. The electricity is firmly bound to the ions, and can only be given up at the electrodes, and the ions then cease to exist as such. It is easy to understand that equivalent quantities of different substances are charged with the same amount of electricity; for when we mix solutions of two electrolytes—for instance, calcium chloride ( $\text{CaCl}_2$ ) and sodium nitrate ( $\text{NaNO}_3$ ), partial exchange takes place, and there are formed sodium chloride ( $\text{NaCl}$ ) and calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ). Now, if one atom of calcium (= 2 equivalents) were not charged with the same quantity of electricity as two  $\text{NO}_3$  radicles, or the two sodium atoms originally combined with these, but had a greater positive charge, the molecules of calcium nitrate ( $\text{Ca}(\text{NO}_3)_2$ ) would be positively charged, and the sodium chloride molecules would be negatively charged, since the original solutions were electrically neutral. By evaporation or by some chemical means, one kind of molecule, *e.g.* the sodium chloride molecules, can be precipitated from the solution, or the two substances can be separated by diffusion. After this separation the solutions should be electrically charged. As not the slightest charge can be found on the solutions, we must assume that equivalent quantities of the various substances have the same charge.

**Composition of the Ions.**—Berzelius found that in the electrolysis of a solution of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ), or, as he wrote it,  $\text{Na}_2\text{OSO}_3$ , the base  $\text{NaOH}$  collected at the negative pole, and the acid  $\text{H}_2\text{SO}_4$  collected at the positive pole. He therefore regarded  $\text{Na}_2\text{O}$  and  $\text{SO}_3$  as the ions which, with water, formed  $2\text{NaOH}$  and  $\text{H}_2\text{SO}_4$ . Others were of the opinion that the decomposition of  $\text{Na}_2\text{SO}_4$  takes place in the same way as that of copper sulphate,  $\text{CuSO}_4$ , namely, into the metal  $\text{Na}$ , which, with water, forms  $\text{NaOH}$  with evolution

of hydrogen, and the acid radicle  $\text{SO}_4$ , which, with water, gives  $\text{H}_2\text{SO}_4$  and oxygen. In order to confirm this, Daniell \* filled two voltameters, *A* and *B* (Fig. 26), one (*A*) with a solution of sulphuric acid, the other (*B*) with a solution of sodium sulphate, and conducted a current through both. In both voltameters oxygen and hydrogen were evolved, and the same quantity of the corresponding gases in each, *i.e.*  $\text{O} = \text{O}_1$ , and  $\text{H} = \text{H}_1$ .

It was further found that in the voltameter containing the sodium sulphate solution there was an equivalent quantity of sodium hydroxide at the negative pole, and a corresponding quantity of sulphuric acid at the positive.

If Berzelius's view were correct—namely, that  $\text{Na}_2\text{O}$  and  $\text{SO}_3$  occurred as ions—the same quantity of electricity should have loosened double as many valencies (those of water and of sodium sulphate) in the voltameter *B* as in voltameter *A* (only the valencies of water). This is not in agreement with Faraday's law, or the law must be considerably modified and receive a particular formulation for the salts containing metals which decompose water. If no water is present, as when fused salts are employed, the metals, and not the oxides, are obtained. The later investigations of Hittorf and Kohlrausch on the migration of the ions and the conductivity of electrolytes have proved that Daniell's view is the only tenable one.

Much discussion of the topic has led to the conclusion that, in electrolytes, the hydrogen, the metals, or the radicles, such as ammonium ( $\text{NH}_4$ ), methylammonium ( $\text{CH}_3\text{NH}_3$ ), phenylammonium ( $\text{C}_6\text{H}_5\text{NH}_3$ ), uranyl ( $\text{UO}_2$ ), etc., which can replace a metal, form the positive ions; and the rest of the molecule, hydroxyl ( $\text{OH}$ ) in hydroxides,  $\text{SO}_4$  in sulphates,  $\text{NO}_3$  in nitrates,  $\text{Cl}$  in chlorides, forms the negative ion.

It was believed for a long time that in electrolytically conducting substances, besides the electricity transportation performed by the ions of the electrolyte, another sort of

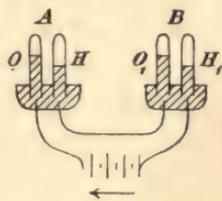


FIG. 26.

transportation, the so-called *metallic conduction*, went on simultaneously, and by this there was no decomposition of the substance. However, very exact investigations have proved that always so much salt is decomposed as is required by Faraday's law. Occasionally it is found that the quantity of hydrogen or oxygen evolved is too small, but this is due to the solubility of the gases in the liquid; and diffusion of the dissolved gases takes place, so that some of the hydrogen passes to the positive pole, and some oxygen to the negative pole, and there (by contact action of the platinum) partial recombination to water takes place.

Faraday termed an ion that product which is formed at a pole independently of whether it is the result of a primary or secondary action. Amongst the ions he therefore included not only chlorine and potassium, but also hydrochloric acid, caustic potash, and oxygen, but not the compound hydroxyl (OH), because this could not be obtained in the free state.

We now understand by ions those parts of an electrolyte which, electrically charged, wander through the liquid towards the electrodes, whether they suffer a secondary change at the electrodes or not.

**Application of Ohm's Law to Solutions.**—Let us again consider a current passing through a parallel-sided trough

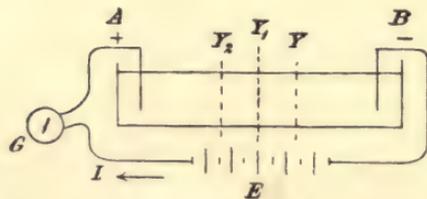


Fig. 27.

(Fig. 27) with two pole-plates, *A* being the positive, and *B* the negative. Suppose, further, that the electrodes are non-polarisable, as would be the case if we take amalgamated zinc plates in a

solution of zinc sulphate. The electricity is then transported by the ions  $Zn^{++}$  and  $SO_4^{--}$ , of which the former, the cation, goes to the negative pole *B*, and the latter, the anion, goes to the positive pole *A*.

If we now change the number of elements in the battery  $E$ , the current intensity  $I$ , measured by the galvanometer  $G$ , will be altered according to Ohm's law,

$$I = \frac{E}{R}, \quad e = \frac{K + E}{l}$$

where  $E$  is the potential difference between the anode and cathode, and  $R$  is the electrical resistance of the solution in the trough. According to the ordinary laws of electric forces the positively charged  $\text{Zn}^{++}$  ions pass from places at higher potential to places at lower potential, and the negatively charged  $\text{SO}_4^{--}$  ions travel in the opposite direction.

According to the doctrine of potential, the motive force for a substance carrying unit charge is the fall of potential per unit of length  $\frac{E}{l}$ , where  $l$  is the distance between the electrodes.

For an ion with the charge  $e$ , the motive force is therefore  $\frac{Ee}{l}$  (compare p. 6). Let us assume for the moment that the  $\text{SO}_4$  ions remain at rest, and that only the Zn ions transport electricity. If  $E$  is doubled, the quantity of electricity transported through the cross section  $Y$  in unit of time, will also be doubled. The quantity of electricity passing through the section  $Y$  of the electrolyte is bound to the zinc ions which travel in the direction from  $A$  to  $B$ . If, therefore, using the first current, all the zinc ions, which at time 0 are between section  $Y$  and  $Y_1$ , after one second—*i.e.* at time 1—have wandered through the cross section  $Y$ , then, using the second current, double as many zinc ions must have passed across the section  $Y$  after one second, *i.e.* all the zinc ions which at time 0 were contained between the cross sections  $Y_2$  and  $Y$ , if the distance  $Y_2Y = 2Y_1Y$ . In other words, in the first case the zinc ions which at time 0 lie at  $Y_2$  have passed in one second from  $Y_2$  to  $Y_1$ , in the second case from  $Y_2$  to  $Y$ . The velocity of the zinc ions is therefore

doubled when the fall of potential per unit of length  $\frac{E}{l}$ , *i.e.* the motive force, is doubled.

Now, not only the zinc ions, but also the  $\text{SO}_4$  ions, migrate under the influence of the fall of potential  $\frac{E}{l}$ , but they go in the opposite direction, namely from *B* to *A*. Hittorf's experiments, which will be considered in detail later, show that the migration velocity of the  $\text{SO}_4$  ions stands in a certain definite ratio to the velocity of the zinc ions, and this ratio is quite independent of the current strength *I*. It follows from this that the velocity of the sulphuric acid ions, like that of the zinc ions, is proportional to the value of the motive force  $\frac{E}{l}$ . This proportionality between velocity and motive force follows from the validity of Ohm's law for solutions.

Such a law as that the velocity with which a particle moves under the influence of a certain force is proportional to this force is valid for all liquid or gaseous particles moving between other liquid or gaseous particles so long as collisions constantly take place. This law can be derived from the principles of the kinetic theory of gases, as is proved in treatises on internal friction.

We must imagine the ions as particles of a liquid which receive an acceleration under the influence of some external force, electrical or osmotic, and the velocity imparted is proportional to the force acting. The ions, like liquid particles in general, become more mobile as the temperature rises; on the other hand, gas particles at high temperatures are more difficult to set in motion. On account of the similarity between the resistance experienced by ions in a solvent and the friction between liquid particles, the former phenomenon is called *galvanic friction*. This is, of course, different for different ions, and decreases with rising temperature.

**Standard Units for Resistance and Electromotive**

**Force.**—In Ohm's law we have two factors of great importance, namely, the resistance and the electromotive force or potential difference. Both of these are measured in units, which are determined by the magnetic effect of the electric current. As, however, these measurements are difficult to carry out, conventional values for the units have been adopted in a system in which they are easy to reproduce. As normal resistance we take the resistance offered by a column of mercury, at  $0^{\circ}$  and 760 mm. barometric pressure, 1 metre long and of 1 sq. mm. cross section. This choice has been made because it is comparatively easy to obtain pure mercury. This standard is called a Siemens' unit. The ratio adopted at the Paris Congress in 1881 between the ohm (*legal ohm*) and the Siemens' unit was 1 : 1.06. On account of more exact measurements, a meeting of deputies from Germany, Great Britain, and the United States in 1891 adopted the ratio : 1 ohm = 1.0630 Siemens' units (S.U.).

This new ohm (= 1.0630 S.U.) is called an *international ohm*, and will be used in the sequel.

The value of a volt is so determined that it is the potential difference produced by a current intensity of 1 ampere at the ends of a resistance of 1 ohm, because according to Ohm's law : 1 volt = 1 ohm  $\times$  1 ampere. In the course of time the volt has undergone the same changes as the ohm. In recent times no change has been made in the ampere (compare p. 4).

For the comparison of potential differences use is made of the electromotive force of a "constant" galvanic element. In order to construct such a constant element, *i.e.* one whose electromotive force does not change with time, polarisation of the poles must be rigorously avoided; the poles must be non-polarisable, and this is accomplished by making the electrodes of the same metal as the cation of the salt solution in contact with them. The first element of this type was constructed by Daniell; it consists of a copper pole in a solution of copper sulphate and, separated from

this by a porous cell, a solution of zinc sulphate (or dilute sulphuric acid, which soon forms zinc sulphate) containing a zinc pole. The electromotive force of this combination varies between 1.1 and 1.18 volts, according to the concentrations of the solutions. A more suitable "normal" or "standard" element, and that generally used, is the Clark cell. This is constructed as follows: A mixture of 90 per cent. mercury and 10 per cent. zinc (which,

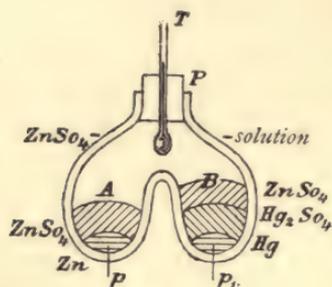


FIG. 28.

in an electromotive respect, acts like pure zinc) is put into the limb *A* of a vessel *AB* of the form shown in Fig. 28. This amalgam, which is easily fused, is allowed to solidify round the platinum wire *p*. Pure mercury is poured into the limb *B* over the platinum wire *p*<sub>1</sub>. A paste, made by rubbing together crystals of zinc sulphate ( $\text{ZnSO}_4$

$+7\text{H}_2\text{O}$ ), solid mercurous sulphate, mercury, and a concentrated solution of zinc sulphate, is poured on to the mercury to the depth of 1 cm., and this, as well as the zinc amalgam in *A*, is covered to a depth of at least 1 cm. with crystals of zinc sulphate. The vessel is now filled with a saturated solution of zinc sulphate, leaving only a small air bubble to allow for the expansion by heat of the solution; the vessel is then closed by a cork, *P*, through which passes the thermometer *T*. The electromotive force of this cell at 15° has been accurately determined to be 1.438 volts. Between 10° and 25° the E.M.F. decreases by 0.0012 volt for a rise of temperature of 1°. As the temperature coefficient of this cell is comparatively large, the Weston element (see Chap. XV.) has recently been used to a considerable extent as standard, and this seems to be quite justifiable, since the latest investigations prove that when the composition is correctly chosen (12 to 13 per cent. cadmium amalgam) the E.M.F. is very constant.

## CHAPTER IX.

### Conductivity of Electrolytes.

**Horsford's Method of Determining the Resistance** (1).—The experiment is carried out in a parallel-sided trough containing a salt solution and two non-polarisable electrodes (e.g. amalgamated zinc plates in a solution of zinc sulphate), the sizes of which are almost as great as the cross section of the trough. The electric current from a battery  $E$  (Fig. 29) is led to the anode  $A$ , and passes from this through the zinc

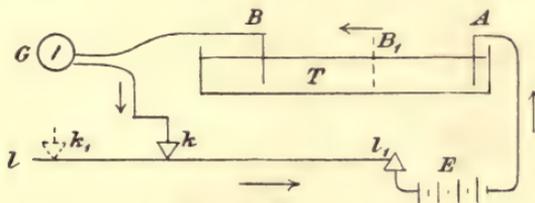


FIG. 29.

sulphate solution to the cathode  $B$ . From  $B$  it passes to a movable contact,  $k$ , and returns to  $E$  along the metal wire  $ll_1$ . The branch of the circuit between  $B$  and  $k$  contains a galvanometer  $G$ , and the deflection of the needle of this is proportional to the current strength.

If, now,  $B$  is brought to the position denoted by  $B_1$ , the resistance in the trough is diminished, and the galvanometer needle shows a greater deflection. If  $k$  is then slid along  $ll_1$  until the deflection of the galvanometer is the same as before, the total resistance in the circuit is evidently the same as originally, *i.e.* the resistance of the column of liquid  $BB_1$ ,

which has now been removed from the circuit, is the same as that of the wire between  $k$  and  $k_1$ , which has been introduced into the circuit. The resistance of the wire  $ll_1$  is determined beforehand by means of a Wheatstone bridge.

By measuring the resistance of columns of liquid of different lengths it is found that this is proportional to the length. If the quantity of liquid in the trough be changed, the cross section of the liquid column is changed, and it is found that the resistance is inversely proportional to the cross section.

These facts prove that the laws of resistance are the same for electrolytic solutions as for metals. The resistance of salt solutions, however, decreases as the temperature rises, about 2.4 per cent. per rise of temperature of one degree in the neighbourhood of  $18^\circ$ , whilst that of the metals increases with rising temperature. If the concentration of the zinc sulphate is varied, the resistance changes so that it becomes not quite double when the concentration is halved.

**Change of Conductivity with Dilution.**—Let us assume that in the trough  $T$  (Fig. 30) the zinc sulphate solution is so dilute that the number of salt molecules is negligible

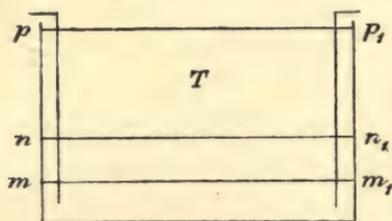


FIG. 30.

compared with the number of water molecules, and let this solution fill the vessel to the level  $mm_1$ . The resistance, or its reciprocal value the conductivity, of this solution depends both on the number of zinc and sulphate ions present and

on their specific powers of transporting electricity under the influence of a certain fall of potential.

This power of the ions depends only on the galvanic friction which they experience against the surrounding liquid. Since this surrounding liquid is water—the number of zinc sulphate molecules being, by supposition, small, and consequently not able to exert any power on the galvanic

friction—the “mobility” of the ions must remain unchanged when the solution is diluted with water. Let us now suppose that water is poured into the trough to the level  $nm_1$ , then if the number of zinc ions and sulphate ions were not altered by the dilution the conductivity would be the same as before, since the number and mobilities of the ions had remained constant.

This, however, is not the case. If we start, for instance, with a 0.01 normal solution of zinc sulphate, which contains 1.61 grams of  $ZnSO_4$  in a litre, then on dilution to double the volume, the resistance is reduced by 11.7 per cent., or the conductivity increased by about 13.2 per cent. ( $1.132 = \frac{1}{0.883}$ ). If the solution be diluted to four times its original volume, so that the level in the trough is  $pp_1$ , the conductivity is increased by no less than 26.3 per cent. To explain this phenomenon it must be assumed that the number of zinc and sulphate ions has been increased by 13.2 and 26.3 per cent. respectively by the dilutions. We must therefore conclude that *the quantity of the ions, and consequently also the degree of electrolytic dissociation, increases with dilution.*

**Specific and Molecular Conductivity.**—A large number of data has been collected on the subject of conductivity of solutions, and to express these some important units have been adopted, which will now be defined.

The *specific electrical resistance* of a conductor is that resistance offered by a column of it 1 metre long and of 1 sq. mm. cross section. Usually the resistance is expressed in Siemens' units, and the specific resistance of mercury at  $0^\circ$  is then equal to 1. If it be desired to express the specific resistance in ohms, the value in S.U. has to be divided by 1.063. Recent values of the specific resistance have been expressed as the resistance of a column 1 cm. long and of 1 sq. cm. cross section, measured in ohms. The specific resistance expressed in these units is  $100 \times 100 \times 1.063 = 10630$  times smaller than in the previously described

units. The specific resistance changes with the concentration, temperature, and pressure. The *specific electrical conductivity* is the reciprocal of the specific resistance. Expressed in the new units it is 10630 times greater than when the older units are used. The specific conductivity divided by the concentration gives the *molecular conductivity*. As unit of concentration, use is frequently made of the number of molecules in 1 c.c. instead of in 1 litre. The molecular conductivity expressed in this way is  $1.063 \times 10^7$  times greater than when expressed in the old units (S.U., column 1 metre long and of cross section 1 sq. mm., mols per litre). We shall here make use of the new units.

If the degree of dissociation of the solution did not change with dilution, *i.e.* if the percentage of molecules dissociated into ions were independent of the dilution, the molecular conductivity (the specific conductivity per gram-molecule) would also be constant. The changes in the value of the molecular conductivity give, therefore—for not too high concentrations—a measure of the increase in the dissociation by dilution.<sup>1</sup>

The specific electrical conductivity is denoted by  $\kappa$ . As this, however, changes with the dilution (*i.e.* with the volume  $v$  in litres in which a gram-molecule is dissolved), it is customary to add to  $\kappa$  an index denoting this volume, and  $\kappa_v$  then expresses the specific conductivity at dilution  $v$ . For the equivalent conductivity the symbol  $\lambda$  is used, and this also is provided with an index  $v$  indicating the dilution. According to the above definitions there exists the following connection between  $\kappa$ ,  $\lambda$ , and  $\eta$  (number of equivalents per c.c.):

$$\lambda = \frac{\kappa}{\eta}$$

$\lambda_v$  also changes with the dilution, and at infinite dilution

<sup>1</sup> When the concentrations are high (so that the number of dissolved molecules cannot be neglected) this alteration of the molecular conductivity cannot be used as a measure of the change of degree of dissociation. For  $\frac{1}{10}$ -normal and more dilute solutions, however, it is generally valid.

reaches the value  $\lambda_{\infty}$ , which is the equivalent conductivity at infinite dilution.

**The Wheatstone Bridge.**—For the determination of the specific conductivity of a metal the apparatus diagrammatically represented in Fig. 31 is used. The metal wire  $M$  to be investigated is introduced into the branch  $AB$  of the Wheatstone bridge, and between  $B$  and  $C$  there is a rheostat of known resistance. The two other branches  $AD$  and  $DC$  consist of a metal wire, generally platinum, along which the sliding contact  $D$  can be moved. A galvanometer is interposed between  $D$  and  $B$ . When the points  $A$  and  $C$  are connected with the poles of some source of electricity, the current distributes itself over the various parts of the bridge according to Kirchhoff's law. The galvanometer shows no deflection when the contact  $D$  is at a certain position on  $AC$ , and the ratio between the resistance sought (in  $AB$ ) and that in  $BC$  is then the same as the ratio of the resistance  $AD$  to  $DC$ . Since  $R$ ,  $AD$ , and  $DC$  are known, the resistance of  $M$  can be found from—

$$M = \frac{R \times AD}{DC}.$$

This method cannot, however, be used without modification for the determination of the resistance of an electrolytic solution, because the current is constantly passing in one direction, and this causes polarisation of the electrodes. This disturbing factor can be avoided in two ways: either non-polarisable electrodes are used (Fuchs and Bouty), or the direct current is replaced by an alternating current (F. Kohlrausch).

**Determination of the Resistance of Electrolytes.**—The method employed by Fuchs (2) and Bouty (3) is as follows: Two vessels,  $K$  and  $K_1$  (Fig. 32), are filled with zinc sulphate solution, and two non-polarisable zinc electrodes

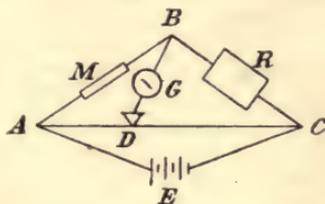


FIG. 31.

dip into the cells,  $A$  into  $K$  and  $B$  into  $K_1$ . The cells are connected by a narrow tube,  $M$ , which contains the solution whose resistance,  $R_1$ , is to be determined. The ends of this tube are usually closed by a piece of parchment paper or animal membrane, so that the contents do not mix with the solutions in  $K$  and  $K_1$ .

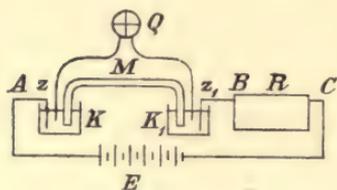


FIG. 32.

There dip also into the vessels two Sond electrodes,  $z$  and  $z_1$ , of amalgamated zinc, which are connected with the quadrant electrometer  $Q$ . The electrode  $B$

is connected with a known resistance (a rheostat), which is joined through  $C$  to the pole of a battery,  $E$ , the other pole being connected with the electrode  $A$ . The points  $B$  and  $C$  and  $z$  and  $z_1$  can alternately be connected with the electrometer. In the former case the deflection gives the potential difference  $V$  between  $B$  and  $C$ , and in the second case that  $V_1$  between  $z$  and  $z_1$ . If  $I$  is the current strength, then we have the following connections:—

$$V = IR, \quad V_1 = IR_1,$$

and therefore—

$$R_1 : R = V_1 : V,$$

from which  $R_1$  can be calculated.

In order to determine the specific resistance, the tube is first filled with a liquid of known specific resistance, and from the result obtained the constant for the tube is ascertained; this method is better than calculating from  $R$  and the dimensions of the tube. It is evident that the resistances of different liquids in the same tube bear the same ratio to each other as the specific resistances.

In place of the quadrant electrometer any other form of electrometer may, of course, be used, *e.g.* a capillary electrometer, provided that the conditions of the experiment are suitable.

Kohlrausch's method (4) more closely resembles that described for the determination of the resistance of metals. If a current be passed in the direction  $AB$  through a column of liquid lying between the electrodes  $A$  and  $B$  (Fig. 31), polarisation takes place, and the current is thereby weakened. If the direction of the current be now altered, *i.e.* passes in the direction from  $B$  to  $A$ , after it has produced its greatest polarisation effect, this polarisation intensifies the new current, which becomes stronger than it would be without the conjoint action of the polarisation. The new current, however, weakens the original polarisation, which depends on the separation of a small quantity of substance on the electrodes, and if it acts for a sufficient time, polarisation in the opposite sense takes place. By making the quantity of electricity which passes through the liquid small in comparison with the surface of the electrodes, whereby, according to Faraday's law, the quantity of substance separated per square centimetre, and consequently the polarisation, is inconsiderable, and at the same time applying an alternating current so that the polarisation of the principal current is intensified as often as it is weakened, the resistance of electrolytes can be measured according to the same principle as that used in the determination of the resistance of metals. This is the basis of the Kohlrausch method. The source of the electric energy  $E$  (Fig. 31) consists of a small induction-coil actuated by a galvanic element, and the galvanometer  $G$ , which is not suitable for alternating currents, is replaced by a telephone. The movable contact  $D$  is slid along  $AC$  until a tone minimum is established in the telephone, and then there exists the following relationship between the resistances :—

$$AB : BC = AD : DC.$$

The solutions are contained in "resistance" or "conductivity vessels," the form of which varies according to the magnitude of the resistance to be measured (Fig. 33,  $a, b, c, d$ ).

The vessel is filled to such an extent that the electrode is

completely immersed. The electrodes consist of platinum plates electrolytically covered with a film of platinum black, so that their surfaces become exceedingly great,<sup>1</sup> and the

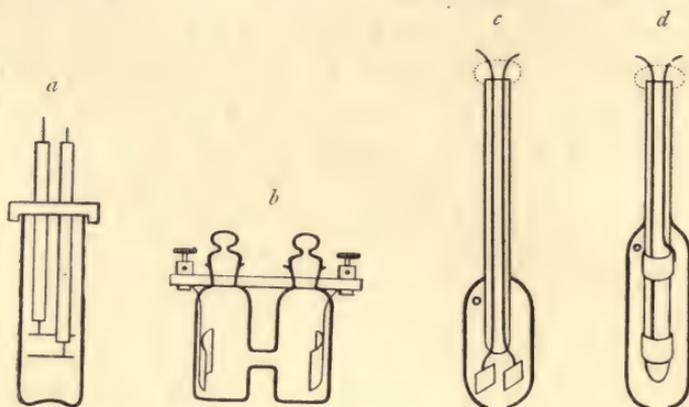


FIG. 33.

quantity of ions deposited per unit of surface is correspondingly small, and consequently also the polarisation.

The capacity of the resistance-cell is determined by measuring the resistance,  $\rho_1$ , offered by a solution of known resistance ( $m_1 = \frac{1}{\lambda_1}$ ). If the resistance of the solution under examination is  $\rho$ , the specific resistance and the conductivity are found from the relationship—

$$\rho : \rho_1 = m : m_1 = \lambda_1 : \lambda.$$

[The conductivity of electrolytes may also be measured satisfactorily in the following way, due to Stroud and Henderson (*Phil. Mag.*, 1897, **43**, 19). The detrimental effects of polarisation in the electrolytic cell are very largely reduced by inserting a second cell with a very different length of

<sup>1</sup> Kohlrausch found that the surface of an electrode covered with platinum black was several thousand times greater than that of the polished electrode. According to Lummer and Kurlbaum (5), the electrode should be platinised with a 3 per cent. solution of platonic chloride, containing about  $\frac{1}{10}$  per cent. of lead acetate.

electrolytic conductor in the corresponding arm of a Wheatstone bridge circuit. Further, any residual error arising from differential polarisation is effectively drowned by the employment of high potentials and high resistances.

The arrangement of the Wheatstone bridge circuit is as follows: One arm of the bridge is formed by the long-column electrolytic cell,  $C$ , in series with which is a resistance,  $R$ , forming the second arm. In parallel with these is the short-column electrolytic cell,  $c$ , and an adjustable resistance box,  $r$ ; these together form the third arm of the bridge, whose remaining arm consists of a resistance =  $R$ . If  $r$  be adjusted till there is no deflection of the galvanometer, the same current is traversing each cell, presumably producing, at all events approximately, the same polarisation, and  $r$  is equivalent to the resistance of a column of the electrolyte equal to the difference between the long and short columns. From the value of  $r$  the specific conductivity can be calculated. The voltage used is about 30, and the adjustable resistance about 20,000 ohms.]

**Experimental Results.**—Experiments carried out by the Kohlrausch method show that pure water has only a very inappreciable conductivity. When increasing amounts of an electrolyte are added to the water, the conductivity gradually increases, and finally reaches a maximum, provided that the solubility of the substance permits of reaching a sufficiently high concentration; as the concentration is further increased, the conductivity falls, and for pure electrolytes, *e.g.* hydrochloric acid or acetic acid, it has about the same value as for pure water. The observed conductivity consists of two factors, namely, that of the water used in making the solution, and that due to the dissolved electrolyte. The former is generally caused by dissolved impurities such as salts, ammonia, or carbon dioxide, and is only to a very slight extent due to the real conductivity of the pure water; in this connection it is of little theoretical interest. In practice, a correction is introduced by subtracting from the conductivity of the solution that of the water used as solvent. The





this with dilution indicates that, on addition of water, more ions capable of transporting electricity are formed at the expense of the undissociated molecules. In this respect we may consider as types, ammonia and acetic acid. With increasing dilution,  $\lambda_v$  assumes greater and greater values, and it is difficult to find that  $\lambda_v$  approaches a certain limit,  $\lambda_\infty$ , which, nevertheless, can be ascertained in an indirect manner.

The Clausius hypothesis aids us in this determination. When the part of the electrolyte dissociated into ions is only a small fraction of the whole number of molecules present, the quantity of ions, and therefore also  $\lambda_v$ , must increase on dilution from 10 to 100 by about the same amount as on dilution from 100 to 1000, etc., which is actually the case for the types of weak bases and acids mentioned.

The other substances mentioned— $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{MgSO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{CH}_3\text{COOK}$ ,  $\text{NaNO}_3$ ,  $\text{NaCl}$ , and  $\text{KCl}$ , which may be regarded as types of good conductors—behave otherwise. At high concentrations the increase in  $\lambda_v$  for dilution to double the volume is tolerably great; thus, *e.g.*, for  $\text{KCl}$  the difference  $\lambda_{10} - \lambda_5 = 4.07$ ; for  $\text{HCl}$ ,  $\lambda_{10} - \lambda_5 = 9$ . As the following numbers show, this increase diminishes at higher dilution:—

Substance.	$\lambda_{20} - \lambda_{10}$	$\lambda_{100} - \lambda_{50}$	$\lambda_{200} - \lambda_{100}$	$\lambda_{1000} - \lambda_{500}$	$\lambda_{2000} - \lambda_{1000}$	$\lambda_{10000} - \lambda_{5000}$
KCl	3.72	2.47	1.98	1.03	0.77	0.30
HCl	9	3	3	1	—	—

The increase of  $\lambda$  evidently approaches the value zero with increasing dilution, when the concentration is always changed in the same ratio, or in other words,  $\lambda$  converges with increasing volume ( $v$ ) to a limiting value  $\lambda_\infty$ . The same conclusion is arrived at, but perhaps not quite so clearly, by considering the conductivities of sulphuric acid and magnesium sulphate.

The only possible cause of the fact that the decomposition into ions reaches a certain limit is that ultimately all the molecules are dissociated; or we may say that at very great

dilution the dissociation is nearly complete, or the *degree of dissociation*, *i.e.* the proportion of molecules dissociated into ions, approaches the value 1.

From this we may conclude that the conductivity at infinite dilution, that is, when  $v$  becomes excessively large, has a value which is not very different from that for the highest measured dilution; it can be found by graphical extrapolation, and is denoted by  $\lambda_{\infty}$ . The extrapolation can also be calculated, *e.g.* for KCl, with the aid of the following differences:—

$$\begin{aligned}\lambda_{100} - \lambda_{10} &= 10.4. \\ \lambda_{1000} - \lambda_{100} &= 4.91. \\ \lambda_{10000} - \lambda_{1000} &= 1.73.\end{aligned}$$

These differences decrease almost in geometrical progression.

The value of  $\lambda_{\infty}$  for all highly dissociated electrolytes can be determined in the same way.

According to principles derived below from Kohlrausch's law, the values of the differences for various electrolytes are approximately the same. In the table on p. 135 the value of  $\lambda_{\infty}$  for some salts is given.

**Calculation of the Degree of Dissociation in Electrolytic Solutions.**—From what has been said, it is easy to see how the degree of dissociation of an electrolyte at any particular dilution  $v$  is to be calculated. If all the dissolved molecules took part in the conduction of the current,  $\lambda_v$  for each single salt would be independent of the dilution, and in the case of potassium chloride it would be equal to 130.11.

Since all the K ions transport the electricity at the same rate, and the same is true for the Cl ions, then if the value of  $\lambda$  is different from that of  $\lambda_{\infty}$ , the transportation of the electricity must be carried out by  $\frac{\lambda_v}{\lambda_{\infty}}$  ions, *i.e.* the degree of dissociation  $a$  is given by—

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

In this way the degree of dissociation can be determined for all salts of monovalent acids or bases, and for the strongest acids (hydrochloric, hydrobromic, hydriodic, nitric, chloric acids, etc.) and bases (potassium, sodium, calcium, strontium, barium hydroxides, ammonium bases, etc.). The value of  $\lambda_{\infty}$  (for a given temperature) is a measure of the mobility of the ion pair (K + Cl).

**Transport Number.**—It is of interest to learn to what extent the conductivity is due to each of the two ions of a “binary” electrolyte. Let us assume that a quantity of electricity corresponding exactly with 1 gram-equivalent (in this case 1 gram-molecule), *i.e.* 96,500 coulombs, passes between the electrodes *A* and *B* (Fig. 34) through a solution

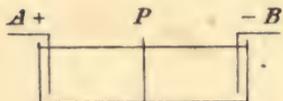


FIG. 34.

of potassium chloride. This quantity of electricity is transported partly by the K ions, which conduct positive electricity in the direction *AB*, and partly by the Cl ions, which carry the negative electricity in the opposite direction (*BA*). If the Cl ions remained stationary, *i.e.* did not aid the transportation of the electricity, a gram-equivalent (= 39.15 grams) of potassium would pass in the direction *AB* through any cross section *P* of the column of liquid. On the other hand, if the K ions remained stationary and the Cl ions alone transported the electricity, a gram-equivalent (= 35.45 grams) of chlorine would migrate through the section *P* in the direction *BA*. As a rule, however, both ions take part in the conduction. Let us assume that the K ions transport a fraction,  $u$ , of the electricity, then the Cl ions transport the remainder,  $(1 - u)$ . The fractions  $u$  and  $(1 - u)$  are termed the “transport numbers” or “migration numbers” of the potassium and chlorine ions respectively in the potassium chloride solution. There must then migrate across *P* in the direction *AB*  $u$  gram-equivalents ( $39.15 \times u$  grams) of potassium and in the direction *BA*  $(1 - u)$  gram-equivalents ( $= 35.45 - 35.45 \times u$  grams) of chlorine. In order to

ascertain experimentally the values of  $u$  and  $(1 - u)$  it is only necessary to divide the liquid column into two portions at  $P$  after the current has passed (*e.g.* by slipping into the trough a well-fitting glass plate), and then by chemical analysis to find by how much the quantity of potassium in the part  $BP$  has increased and by how much the amount of chlorine has increased in the part  $AP$ . As the original composition of the solution is known, it is sufficient to analyse the liquid in one part ( $AP$  or  $BP$ ) after the current has passed. In these experiments appreciable changes in concentration take place at the electrodes, and, besides, there is frequently an evolution of gas or deposition of long crystals (dendritic) which fall off and so stir up the liquid. The disturbances caused thereby can be avoided by various devices. The apparatus shown in Fig. 35, devised by Hopfgartner (6) from Hittorf's model, gives good results in determining the changes of concentration.

The vessel  $B$  fits into the neck of a thin-walled flask,  $A$ , which is provided with a tubulus,  $G$ .  $B$  is connected with the wide tube  $D$  by means of the U-tube  $C$ . By raising or lowering the plug  $F$  the vessel  $B$  may be opened or closed. The side tube  $K$  of the U-tube is closed by means of a rubber tube and clip. The anode is introduced through a rubber stopper through  $G$ , and mercury contained in  $E$  is used as cathode.

Hittorf (7) was the first to investigate the migration of the ions and prove that the anions and cations have different migration velocities. For the chlorine ion of a very dilute solution of potassium chloride the value of  $u$  generally accepted is 0.503, and consequently for the potassium ion 0.497.

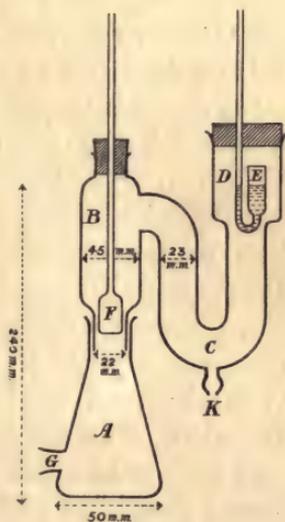


FIG. 35.

**Kohlrausch's Law.**—Since  $\lambda_{\infty}$  for potassium chloride evidently represents the sum of the transporting powers of the K and Cl ions, and since  $\lambda_{\text{KCl}_{\infty}} = 130.11$ , the part  $0.503 \times 130.11 = 65.44$  is due to the chlorine, and  $0.497 \times 130.11 = 64.67$  to the potassium. These numbers refer to the temperature  $18^{\circ}$ , and are termed the *mobilities* (or migration velocities) of the chlorine and potassium ions respectively. From the determinations of the conductivities  $\lambda_{\infty}$  of salts and the transport numbers it has been possible to ascertain the mobilities of other ions. The mobility of an ion, *e.g.* the chlorine ion, can evidently be obtained from the investigation of any chloride, and all the results must be the same. It is better, perhaps, to calculate the transport numbers from the mean value of the ionic mobilities, and see how the results agree with experiment. This is the method by which Kohlrausch proceeded to show the connection between transport numbers and conductivity.

Kohlrausch (8) stated the law that the molecular conductivity of an electrolyte (at infinite dilution) can be calculated as the sum of two numbers, one of which depends only on the cation and is independent of the anion, whilst the other depends on the anion and is independent of the cation with which it is combined in the original salt. Kohlrausch, however, could only prove this for certain groups of similarly constituted electrolytes, *e.g.* for those with two monovalent ions (so that 96,500 coulombs are transported per gram-ion). It appeared as if a chlorine ion, when present with a potassium ion, possessed a different mobility from that when it was the dissociation product of the barium salt the cation of which is divalent, *i.e.* is charged with  $2 \times 96,500$  coulombs per gram-ion. The difference in the mobilities of the  $\text{SO}_4$  ion was held to be much greater when it occurred with a monovalent than when with a divalent cation. At first it was not expected that the relationships would be so complicated; the presumption that the relationships are quite simple was afterwards confirmed, and so the general form given above was associated with the law. The connection expressed

in the law is also approximately true for the molecular conductivity at any given dilution,  $v$ , but only with each single group of electrolytes; attention was also called to this point by Kohlrausch.

**Transport Numbers and Ionic Mobilities.**—As already mentioned, Hittorf had confirmed his own views on this subject in his famous experiments on the migration of the ions. The data found by him refer for the most part to concentrations at which the transport numbers vary with the dilution. The data contained in the following table, which may be regarded as the most exact known at the present time, have been taken from the comprehensive investigations of Jahn (9) and his pupils, and refer to very dilute solutions at 18°. The table gives under  $u_c$  (observed) the observed transport number of the cation, and under  $u_c$  (calculated) the value calculated from Kohlrausch's results for  $\lambda_\infty$  and the Hittorf numbers—

Salt.	$u_c$ (observed).	Observer.	$u_c$ (calculated).
NaCl	0.396	Bogdan	0.399
KCl	0.497	"	0.497
KBr	0.496	"	
AgNO <sub>3</sub>	0.464	Metelka	0.478
	0.472	Mean value of various observers	
CuSO <sub>4</sub>	0.375	Metelka	0.412
BaCl <sub>2</sub>	0.447	"	0.465
CdCl <sub>2</sub>	0.433	"	0.40
CdI <sub>2</sub>	0.442	"	0.40

The influence of temperature on the transport number of some cations is shown by the following results obtained by Bein (10):—

Salt	Temperature.	$u_c$	Temperature.	$u_c$
	°		°	
NaCl	20	0.392	95	0.449
AgNO <sub>3</sub>	10	0.470	90	0.490
CuSO <sub>4</sub>	15	0.362	75	0.378
CdCl <sub>2</sub>	20	0.430	96	0.430
CdI <sub>2</sub>	20	0.360	75	0.40

It has been found that at higher temperatures the transport numbers approach the value 0.5, which indicates that with rising temperature the mobilities of the ions tend to become the same. This rule applies to all combinations of a positive and a negative ion. If we compare the salts of different positive ions with the same negative ion, the conductivities of these (provided that the degree of dissociation remains constant) must tend to a common value as the temperature rises. From this it follows that the worse the electrolyte conducts the greater is the percentage increase of conductivity with the temperature. This rule ought to apply only to the values of  $\lambda_{\infty}$ , but it has been found to be true for moderate dilutions of highly dissociated bodies.

In the following table are given the mobilities  $l_{\infty}$  at extreme dilution of the more important ions; the positive ions are given first, then the negative ions. The temperature coefficient for the ions K, Cl, Br, I,  $\text{NH}_4$ , Ag, and  $\frac{1}{2}\text{SO}_4$  is about 2.2 per cent. of the value at 18°. For the sodium ion and the ions of the organic acids the coefficient is about 2.7 per cent. per degree; for Li, 2.9 per cent.; for OH, 1.8 per cent.; and for H only 1.5 per cent.

The increase for the divalent ions Ca, Sr, Zn, Mg, and Cu is about 2.6 per cent., and for Ba, 2.5 per cent. From these numbers the temperature coefficients of the conductivities of most electrolytes—in dilute solution—can be calculated.

Cations.	$l_{\infty}$	Anions.	$l_{\infty}$
Hydrogen, H	314	Hydroxyl, OH	172
Potassium, K	64.67	Chlorine, Cl	65.44
Sodium, Na	43.55	Bromine, Br	66.4
Lithium, Li	33.44	Iodine, I	66.2
Ammonium, $\text{NH}_4$	63.6	Nitric acid, $\text{NO}_3$	61.78
Silver, Ag	55.0	Chloric acid, $\text{ClO}_3$	55.5
Barium, $\frac{1}{2}\text{Ba}$	56.6	Iodic acid, $\text{IO}_3$	33.87
Strontium, $\frac{1}{2}\text{Sr}$	53.3	Acetic acid, $\text{C}_2\text{H}_3\text{O}_2$	33
Calcium, $\frac{1}{2}\text{Ca}$	52.3	Sulphuric acid, $\text{SO}_4$	69
Magnesium, $\frac{1}{2}\text{Mg}$	48.3		
Zinc, $\frac{1}{2}\text{Zn}$	46.7		
Copper, $\frac{1}{2}\text{Cu}$	48.7		

**Abnormal Transport Numbers.**—It is evident that the transport number must lie between 0 and 1, for otherwise the positive ion would be travelling against the current or the negative ion with the current, and this is inconceivable. Nevertheless, Hittorf found for the transport number of iodine in a 4.8 per cent. solution of cadmium iodide in alcohol the value 2.1, and in a 3 per cent. solution the value 1.3. At a very high dilution the value would probably sink below 1, *i.e.* would lose its abnormality.

Hittorf explained this peculiar phenomenon as follows: He assumed that cadmium iodide forms complex molecules perhaps of the formula  $\text{Cd}_3\text{I}_6$ , which form the ions  $\text{Cd}_2\text{I}_6$  and  $\text{Cd}^{++}$ . For the sake of simplicity let us imagine that the cation  $\text{Cd}^{++}$  remains at rest, and that only the anion  $\text{Cd}_2\text{I}_6$  passes through the solution, in the direction opposite to that of the (positive) current. For every quantity of electricity  $2 \times 96,500$  coulombs, a gram-ion of  $\text{Cd}_2\text{I}_6$  (986 grams = 224 grams Cd + 762 grams I) must pass a cross section of the solution. Instead of 2 equivalents of iodine, which if iodine alone migrated would be sufficient to transport the same quantity of electricity, an amount three times as large must pass through the cross section. Consequently, if the transport number of the iodine in the former case were 1, it would in the second case be 3. Now, as the cation also migrates with a certain velocity, the transport number obtained for the anion will be less than 3. However, it is obvious that we have only to make the assumption of the existence of a particular molecular complex in order to be able to explain in this way any transport number. In the example quoted, if the transport number of the iodine is 3, that of the cadmium must be  $-2$ , since the sum must be equal to 1.

Cadmium iodide in concentrated solution behaves more anomalously than in dilute solution, and it must therefore be assumed that in concentrated solution there are more

complex molecules than in the dilute solution, a conclusion which indeed would be expected.

Hittorf (11) and Lenz (12) have proved that in aqueous solutions of cadmium iodide which are more concentrated than normal, the transport number of the iodine exceeds 1; for 3-normal solution it is 1.3, whilst for 0.03-normal solution it is 0.61.

For analogous reasons it is found that the transport numbers of the majority of electrolytes suffer a greater or less change with the concentration; this is shown by the results obtained by Goldhaber (13) for cadmium bromide at 18° contained in the following table, in which  $v$  indicates the volume of the solution in which a gram-molecule of the salt is dissolved, and  $u_c$  is the transport number for  $\frac{1}{2}\text{Cd}$ :—

$v$	$u_c$	$v$	$u_c$
1.99	0.218	16.01	0.430
3.98	0.355	23.99	0.433
7.80	0.399	48.02	0.431
11.99	0.423	79.75	0.431

On further dilution  $u_c$  remains constant.

In a 0.1-normal solution of copper sulphate, the transport number for the anion  $\text{SO}_4$  is 0.64, and in a 2-normal solution it is 0.73. In agreement with the explanation given, it is found from the depression of the freezing point that formation of molecular complexes does take place to a very considerable extent. A comparative investigation of the relationships obtained by these methods would be of great interest.

**Mobilities of Organic Ions.**—The values of the mobilities  $l_\infty$  at 25° have been determined by Ostwald and Bredig for a large number of organic ions, both positive and negative. Ostwald (14) found that the mobility of the negative ions decreases as the number of atoms in the ion increases. It is easy to see why this should be so, for as the number of atoms increases, so also does the surface of the ion, and consequently its friction against the liquid. However, this friction does not increase with the mass of the atoms.

On the contrary, it is found that in the two groups of atoms, Li, Na, and K on the one hand, and Ca, Sr, and Ba on the other, the heavier ions are the more mobile. And again, the ions Cl, Br, and I, which have very different masses, have almost the same mobilities.

From the table given below it can be seen that addition on to an atomic group exerts more influence on the smaller ions than on the larger. Were this not the case, then ions consisting of a large number of atoms would have the mobility 0, or even an impossible negative value.

Anion of	Formula.	$l_{\infty}$	Diff.
Formic acid . . . .	$\text{HCO}_2$	59.6	13.6
Acetic acid . . . .	$\text{CH}_3\text{CO}_2$	46.0	4.4
Propionic acid . . . .	$\text{C}_2\text{H}_5\text{CO}_2$	41.6	3.8
Butyric acid . . . .	$\text{C}_3\text{H}_7\text{CO}_2$	37.8	2.1
Valerianic acid . . . .	$\text{C}_4\text{H}_9\text{CO}_2$	35.7	1.5
Caproic acid . . . .	$\text{C}_5\text{H}_{11}\text{O}_2$	34.2	
Succinic acid . . . .	$\text{C}_4\text{H}_6\text{N}_2\text{O}_4$	33.4	
Phthalic acid . . . .	$\text{N}_7\text{H}_7\text{C}_9\text{O}_4$	31.2	
Phthalanilic acid . . . .	$\text{NH}_{10}\text{C}_{14}\text{O}_3$	30.9	

Similar regularities were found by Bredig (15) from his results with positive ions.

**Migration of Ions in Mixed Solutions.**—Before leaving Hittorf's work, an investigation which he made on the migration of ions in mixed solutions of potassium chloride and potassium iodide must be mentioned. When the current passes through this mixture only iodine appears at the anode, and the question arises whether the chlorine ions take any part in the conduction or not. According to our present views, of course, the answer is self-evident. Every ion must, on account of the charge which it carries, be set in motion when it is in an electrical field of varying potential. At the time when Hittorf carried out his investigation (1853-1859) the matter was not so clear, for the conducting molecules were then supposed to be joined together, and a large share in the current conduction was attributed to the water (solvent). Hittorf found that the

current is divided between the two dissolved electrolytes in the ratio of their conductivities. He regarded the separation of the chlorine, as well as the iodine, at the anode as the result of a primary action, but it immediately reacts with the potassium iodide, producing potassium chloride and free iodine. Hittorf's explanation has recently been confirmed by Schrader (16) for mixtures of potassium chloride and iodide, and copper sulphate and sulphuric acid, and further by Hopfgartner (6).

**Complex Ions.**—In his investigation of the so-called double salts, such as potassium argentocyanide ( $\text{KAg}(\text{CN})_2$ ), potassium ferrocyanide ( $\text{K}_4\text{Fe}(\text{CN})_6$ ), sodium platinichloride ( $\text{Na}_2\text{PtCl}_6$ ), and sodium aurichloride ( $\text{NaAuCl}_4$ ), Hittorf observed that the alkali metal always formed the positive ion, whilst the negative ion consisted of the rest of the molecule (termed a *complex ion*, on account of its composition). This observation was diametrically opposed to the chemical views then held, according to which, in consonance with the doctrine of valency, the formula  $\text{AgCN} + \text{KCN}$  was given to potassium argentocyanide, indicating that there is no close connection between the radicle  $\text{CN}$  of the potassium cyanide and the  $\text{AgCN}$ .

**Ionic Migration and the Theory of Dissociation.**—If we assume that the ions are perfectly free and transport the electricity quite independently of each other, it is quite natural to suppose that under the influence of the same force they will not pass through the solution with the same velocity; but rather a different friction against the liquid is *a priori* to be expected. Even if we suppose that the molecules are not dissociated in the solution, but that the ions influence each other in their migrations, it would be natural to imagine that they would travel with different velocities. To us at the present time, therefore, it seems incredible that Hittorf's doctrine of the unequal migrations of the ions was not at once accepted. As a matter of fact, however, the leaders in the science opposed Hittorf's views, and it was only after thirty years that these were adopted.

**Calculation of  $\lambda_{\infty}$  for Slightly Dissociated Electrolytes.**—The equivalent conductivity at infinite dilution of slightly dissociated substances, such as ammonia or acetic acid, cannot be estimated by extrapolation from the results at higher concentrations. If we know the values  $l_{\infty}$  for the mobilities of the ions, however, we can easily calculate the value of  $\lambda_{\infty}$ . From what has been said, it follows that  $\lambda_{\infty}$  is made up of the sum of the mobilities of the two ions  $l_{M_{\infty}}$  and  $l_{A_{\infty}}$  of the salt MA; thus, at 18° for potassium chloride,  $\lambda_{\infty} = l_{K_{\infty}} + l_{Cl_{\infty}}$  ( $130.11 = 64.67 + 65.44$ ); for acetic acid,  $\lambda_{\infty} = 347.7$ ; and for ammonia,  $\lambda_{\infty} = 236.2$ .

In order to determine the value of the conductivity at infinite dilution of a weak electrolyte, the corresponding value for one of its salts is estimated, and from the value so obtained the number sought may be calculated by substitution. Thus, to find the value of  $\lambda_{\infty}$  for benzoic acid,  $\lambda_{\infty}$  is determined for potassium benzoate, and from the result the value of  $l_{K_{\infty}}$  is subtracted, and that of  $l_{H_{\infty}}$  added.

**Absolute Velocity of the Ions.**—As we have seen, the galvanic conducting power of a solution depends on the number of ions present, and on their mobilities, *i.e.* on their capability of wandering through the solution. The ions exert a kind of friction against the liquid, which can be calculated from the conductivity of the solution. This "electrolytic friction" is measured by the force required to impel a gram-ion (1 gram of  $H^+$  or 35.45 grams of  $\bar{Cl}$ ) at a speed of 1 cm. per second. Imagine a column of a normal solution of hydrochloric acid at 18°,  $PP_1$  in Fig. 36, of 1 sq. cm. cross section. Suppose two planes, *A* and *B*, laid through this column perpendicularly, at a distance of 1 cm. apart, and a current flowing in the direction *AB*, driven by a potential difference between the two planes of *V* volts. The current strength is then—

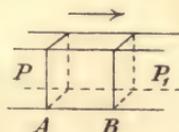


FIG. 36.

$$I = V \times \kappa$$

where  $\kappa$  is the specific conductivity of the normal solution. If hydrochloric acid were completely dissociated in normal solution, then at  $18^\circ$   $I$  would be  $\frac{(314 + 65.44)}{1000} = \frac{379.44}{1000}$ , or, roughly, 0.380 ampere per volt; of this the first part is conditioned by the mobility of the hydrogen ion, and the second part by that of the chlorine ion. That part of the current strength due to the migration of the hydrogen ion is  $I_H = V \times 0.314$  amperes. Now, a gram-ion carries with it 96,500 coulombs, and between  $A$  and  $B$  there is 1 c.c. of normal solution, and therefore, assuming complete dissociation, 0.001 gram-ion. This quantity of hydrogen ion carries a charge of 96.5 coulombs. Since the current strength due to the hydrogen ions is  $I_H = 0.314 \times V$  amperes (coulombs per second), the time—

$$\frac{96.5}{0.314 \times V} = \frac{307.3}{V} \text{ seconds}$$

must elapse before all the hydrogen ions between  $A$  and  $B$  have passed through the plane  $B$ . If  $V = 1$  volt, the hydrogen ions require about 307 seconds to pass through 1 cm.; their velocity is, therefore, 0.00325 cm. per second.

Under the same external conditions, the velocity of the chlorine ions is 0.000678 cm. per second, and that of the other ions is of the same order of magnitude.

The assumption that the hydrochloric acid is completely dissociated has no influence on the result of the calculation. Since the velocity of the ions is proportional to the mobility and to the fall of potential per unit length, and this seldom reaches the value of 1 volt per centimetre, it is usually found that the velocity of the ions, and of the electricity with which they are charged, is extremely small, scarcely amounting to 0.01 mm. per second. The following numbers give the absolute velocities,  $U$  and  $V$ , of the most commonly occurring cations and anions at  $18^\circ$ , under the influence of a fall of potential of 1 volt per centimetre:—

Cation.	$U \times 10^5$ .	Anion.	$V \times 10^5$ .
H	3250	OH	1780
K	670	Cl	678
Na	451	I	685
Li	347	NO <sub>3</sub>	640
NH <sub>4</sub>	660	CH <sub>3</sub> CO <sub>2</sub>	350
Ag	570	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub>	320

From these data we can calculate the mechanical force necessary to drive a gram-ion through the water with a certain velocity. The volt is so defined that the work  $10^7$  ergs is required to transport 1 coulomb against this potential difference. Inversely, if the fall of potential is 1 volt per centimetre, then  $10^7$  dyne-cms. (ergs) are required to transport 1 coulomb through 1 cm. against this fall, *i.e.* the force necessary for 1 coulomb is  $10^7$  dynes = 10.18 kilograms. The force required for a gram-ion charged with 96,500 coulombs against this same fall of potential is therefore  $96,500 \times 10.18 = 983,000$  kilograms. This force drives a gram-ion of hydrogen with the velocity  $325 \times 10^{-5}$  cms. per second. The force required in order that the velocity may be 1 cm. per second must be  $\frac{10^5}{325}$  times greater, *i.e.* it must be  $\frac{983,000 \times 10^5}{325} = 302 \times 10^6$  kilograms. The following table gives the force in million kilograms required to drive 1 gram-ion through water at 18° with a velocity of 1 cm. per second:—

K . . . 1467	NH <sub>4</sub> . . 1490	Cl . . . 1450	OH . . . 552
Na . . . 2180	H . . . 302	I . . . 1435	CH <sub>3</sub> CO <sub>2</sub> . 2810
Li . . . 2833	Ag . . . 1725	NO <sub>3</sub> . . 1536	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> . 3110

From these numbers it can be seen what enormous mechanical forces are required to move the ions through the solvent with an appreciable velocity. As the temperature rises, these values, which are a measure of the friction, decrease in about the same ratio as that in which the mobilities

of the ions increase, *i.e.* for most ions about 2.5 per cent. per degree.

The electrolytic friction of the ions is greater in other solvents than in water. The addition of a very small quantity of another non-conductor to the water appreciably increases the friction of the ions, and consequently decreases the conductivity of the solution, just as the internal friction of the liquid is altered by a similar addition. The action of foreign substances on the internal friction runs almost parallel with that on the electrolytic friction. Thus I have found (17) that the addition of one per cent. by volume of the non-conductors mentioned in the following table raises the internal friction, and the electrolytic friction of the commonly occurring ions at 25° by the amount given in the table. If greater quantities be added, there is a proportional increase in the electrolytic friction, but also a diminution of the degree of dissociation of the electrolyte, particularly if a concentrated solution of this is used. On this subject Walker (18) has made an interesting investigation on the action of alcohols on diethylammonium chloride. It appears that the degree of dissociation is most affected by those substances which contain relatively least hydroxyl.

Percentage increase of the internal and ionic friction by addition of 1 per cent. by volume of the non-conductor.	Methyl alcohol.	Ethyl alcohol.	Isopropyl alcohol.	Ether.	Acetone.	Cane sugar.
	%	%	%	%	%	%
Internal friction of the water	2.1	3.0	3.6	2.6	1.9	4.6
H ion . . . . .	1.6	1.77	1.91	1.55	1.54	2.32
OH ion . . . . .		1.76	1.87			
Monovalent salt ions . . . . .	1.75	2.34	2.56	1.99	1.62	2.99
SO <sub>4</sub> , CO <sub>3</sub> , etc. (divalent negative ions) . . . . .	2.06	2.65	2.95	2.27	2.14	3.64
Ba, Zn, etc. (divalent positive ions) . . . . .	1.86	2.45	2.85	2.21	1.73	3.21

As the addition increases, the function of the water as solvent gradually diminishes, and we obtain electrolytic

solutions in another solvent than water. Only few investigations have been carried out with a view to ascertaining the relationships in this respect. Kablukoff (19) investigated solutions of hydrochloric acid in various media, and found that benzene and other hydrocarbons give the poorest conductors; solvents in which the conduction is better are ethyl ether and higher alcohols; and in ethyl alcohol, methyl alcohol, and water the salts conduct best. This influence is, however, not solely dependent on the differences of the frictions against the various liquids, but depends far more on the degree of dissociation of the electrolyte in the solvent; only after these two actions have been differentiated will it be possible to gain some exact knowledge about the influence of additions on the friction of the ions in solution. The same may be said of the conductivity of fused salts.

Many attempts have been made to directly measure the velocities of the ions, particularly by Lodge and Whetham. Lodge (20), for instance, filled a long glass tube, *R* (Fig. 37), with sodium chloride solution, which was deeply coloured with some alkali and phenolphthalein.

In order to avoid disturbances in the solution, agar-agar was added. This is a gelatinous substance which acts like a fine network in the pores of which is the solution, like water in a sponge. The ends of the tube were immersed in sulphuric acid solution, contained in the vessels *S* and *S*<sub>1</sub>.

A current from the battery *B* was sent in the direction from *S* to *S*<sub>1</sub> through *R*, so that the hydrogen ions of the sulphuric acid gradually passed along *R*, and caused decolorisation as they went. The results obtained for the velocity of migration of the ions in the tube *R* corresponded with those predicted by theory.

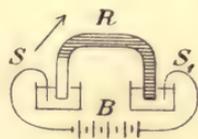


FIG. 37.

It must be noted that in these experiments it is not the true ionic mobility which is measured, but the product of ionic mobility and degree of dissociation, because the free

ions are being constantly changed. For example, if half of the molecules of an electrolyte are dissociated, then during the first half of a definite interval of time all the ions are to be regarded as combined, and during the next half they are free. Consequently, although the fall of potential only acts on the free ions in every infinitely small interval of time, yet in a finite time all the molecules will be similarly moved, inasmuch as during the first half of this time they migrate as ions, and in the second half they remain at rest in the undissociated state. The apparent velocity will in this case be only half of the actual. In agreement with this, Whetham (21) found a much lower velocity for the hydrogen ions from acetic acid than for the same ions from hydrochloric acid, corresponding with the lower degree of dissociation of acetic acid.

Recently ionic mobilities and degrees of dissociation in other solvents than water have been determined by Völlmer (22), Carrara (23), Euler (24), Walden (25), and others.

**Diffusion.**—Besides the electrical, other forces may be active in causing the movement of the ions. Of these the osmotic pressure is the most important. On account of this pressure a phenomenon called diffusion (hydrodiffusion) may be observed. Consider a solution in a parallel-sided trough of

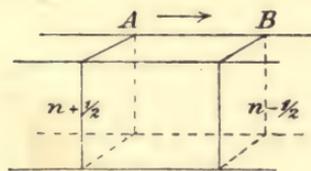


FIG. 38.

1 sq. cm. cross section (Fig. 38), and imagine two planes,  $A$  and  $B$ , perpendicular to the column of liquid, 1 cm. apart. Let the solution at  $A$  be  $(n + \frac{1}{2})$  normal and that at  $B$   $(n - \frac{1}{2})$  normal.

The osmotic pressure at  $A$  is then greater than that at  $B$ , and if the molecules of dissolved substance are not dissociated the excess of pressure at  $A$  is equal to the osmotic pressure of a normal solution, *i.e.*  $84.688 \times 273 = 23,120$  grams per sq. cm. at  $0^\circ$  (compare pp. 26 and 30). This excess of pressure drives the dissolved molecules in the

direction  $AB$ . It acts on all the molecules in the cubic centimetre between  $A$  and  $B$ , and as the solution is (taken as a whole) normal, it acts on  $\frac{n}{1000}$  gram-molecules. If the force necessary to drive a gram-molecule of the dissolved substance with a velocity of 1 cm. per sec. is  $P$  kilograms—this force is known as the *coefficient of friction* of the substance—the velocity  $v$ , which is proportional to the force acting on a gram-molecule, is given by—

$$v = \frac{23 \cdot 12}{P} \cdot \frac{1000}{n} (1 + at) \text{ cm. per second.}$$

The factor  $(1 + at)$ , the temperature coefficient, allows the formula to be applied for other temperatures than  $0^\circ$ . The quantity of dissolved substance which passes  $B$  in one second is found from the number of molecules lying between the plane  $B$  and another plane  $v$  cm. distant. The number of milligram-molecules in this volume ( $v$  c.c.) is  $v \times n = N$ .  $N$  is therefore given by—

$$N = \frac{23 \cdot 12(1 + at)}{P} \cdot 1000,$$

and is the number of (milligram-) molecules which are driven through 1 cm. per second, when the fall of concentration is 1, *i.e.* when the concentration changes by 1 unit per centimetre.  $N$  is called the *diffusion coefficient*.

This coefficient is 1000 times greater than the osmotic pressure per sq. cm. of a normal solution at the given temperature divided by the friction  $P$  in kilog. of a gram-molecule of the substance.

If we have an electrolyte instead of a non-conductor in the solution, then, as this is completely dissociated in dilute solution, the osmotic pressure is double that calculated. The friction  $P$  is made up of two factors,  $P_1$  the friction of the positive ion, and  $P_2$  that of the negative ion (see below). At  $18^\circ$  we find the value of the numerator of the expression for  $N$  to be  $46,240 (1 + \frac{18}{273}) = 49,289$ .

According to the table on p. 149, the value of  $P_1$  for Na is  $2180 \times 10^6$  kilograms, and that of  $P_2$  for Cl,  $1450 \times 10^6$  kilograms; therefore for sodium chloride (NaCl)  $P = P_1 + P_2 = 3630 \times 10^6$  kilograms. If we take the day instead of the second as the unit of time, the number given has to be multiplied by the number of seconds in a day ( $60 \times 60 \times 24 = 8.64 \times 10^4$ ). We then obtain for sodium chloride at  $18^\circ$ —

$$N = \frac{49,289 \times 8.64 \times 10^4}{3,630 \times 10^6} = 1.17.$$

Nernst (26),<sup>1</sup> who first developed this theory, showed that the calculated numbers agree well with those found by experiment, as can be gathered from the next table. The difference between the observed and calculated values is mainly due to the fact that solutions of such concentration were used that the dissociation was not complete; and so the osmotic pressure was actually smaller than the value employed in the calculation; it will be observed that the calculated values are generally higher than those found from experiment.

#### DIFFUSION COEFFICIENTS AT $18^\circ$ .

(Unit of time, the day.)

	Obs.	Calc.		Obs.	Calc.
HCl . . . . .	2.30	2.43	NaNO <sub>3</sub> . . . . .	1.03	1.15
HNO <sub>3</sub> . . . . .	2.22	2.32	NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> . . . . .	0.78	0.84
KOH . . . . .	1.85	2.07	NaCHO <sub>2</sub> . . . . .	0.95	1.02
NaOH . . . . .	1.40	1.55	NaC <sub>6</sub> H <sub>5</sub> SO <sub>3</sub> . . . . .	0.74	0.74
NaCl . . . . .	1.08	1.17	KCl . . . . .	1.29	1.46
NaBr . . . . .	1.10	1.13	KBr . . . . .	1.40	1.47
NaI . . . . .	1.05	1.12	KI . . . . .	1.34	1.47
KNO <sub>3</sub> . . . . .	1.22	1.42	LiBr . . . . .	1.05	1.00
NH <sub>4</sub> Cl . . . . .	1.30	1.44	LiI . . . . .	0.94	1.00
LiCl . . . . .	0.97	0.99	AgNO <sub>3</sub> . . . . .	1.27	1.29

It is easy to see that the temperature coefficient of the diffusion must be the sum of the temperature coefficients of

<sup>1</sup> In his calculation Nernst used other figures than here employed, and obtained for  $N$  1.12 instead of 1.17.

the osmotic pressure, which is about 0.0034 at 18°, and of  $P_1$  and  $P_2$ , which for the common salts is about 0.024. According to this the diffusion coefficient should increase by 2.7 per cent. per degree at 18°, and this has been experimentally confirmed.

The friction coefficient of non-conductors cannot be determined by an electrical method; but its value can be estimated from the diffusion constant. From Graham's results, Nernst has calculated the following values:—

Diffusing substance.	Formula.	Number of atoms.	Molecular weight.	Coefficient of friction.
Urea . . . .	$\text{CO}(\text{NH}_2)_2$	8	60	$2,500 \times 10^6$ kg.
Chloral hydrate	$\text{CCl}_3\text{CH}(\text{OH})_2$	10	165	3,800 "
Mannitol . . .	$\text{C}_6\text{H}_{14}\text{O}_6$	26	182	5,500 "
Cane sugar . .	$\text{C}_{12}\text{H}_{22}\text{O}_{11}$	45	342	6,700 "
Gum arabic . .	$n(\text{C}_6\text{H}_{10}\text{O}_5)$	very great		16,000 "
Tannic acid . .	—	"	"	20,000 "
Egg albumen . .	—	"	"	33,000 "
Caramel . . .	—	"	"	44,000 "

The friction evidently increases with the molecular weight of the substance.

According to a calculation made by Euler (27), the friction of a gram-molecule is approximately proportional to the square root of the molecular weight of the substance examined. This gives very good values for substances of known molecular weight, provided that the molecular volume does not vary too much. If we apply this method to calculate the molecular weight,  $M$ , of the four colloids examined by Graham, we find the following values:—

Gum arabic	( $n = 11$ ) $M =$	1,750
Tannic acid		2,730
Egg albumen		7,420
Caramel		13,200.

These results are particularly interesting because we have no method free from objection for determining the

molecular weight of a pure colloid. It is very certain, as other investigations have also shown, that the molecular weights of these substances are very high.

It might appear strange that a force of  $302 \times 10^6$  kilograms is required to move a gram of hydrogen ion in water with a velocity of 1 cm. per second. However, it is known that the more finely divided a suspended substance is, the slower does it deposit under the influence of some force, *e.g.* gravity (or rather the difference between the specific gravity of the suspended solid and that of the liquid). A good example of this is offered by the fat globules in milk. The ions being infinitely smaller than the particles of suspended matter, it is therefore not so astonishing that these move so slowly under the influence of tolerable forces.

## CHAPTER X.

### Degree of Dissociation and Dissociation Constant.

**Strong and Weak Electrolytes.**—Before proceeding further it will be advisable to classify the electrolytes into two groups—those highly dissociated and those dissociated only to a slight extent, or, shortly, strong and weak electrolytes. All salts belong to the first class, with a few exceptions which have not yet been thoroughly investigated (copper acetate, mercury salts, potassium antimonyl tartrate, and possibly some compounds closely allied to these); and to this class belong also many of the inorganic mono- and di-valent acids and bases. The organic acids and bases (but not exclusively these) are weak electrolytes; as examples we may quote the already-mentioned cases of acetic acid and ammonia. These latter substances at moderate dilution are only dissociated to the extent of a few per cents. There are, of course, substances which stand roughly between these two groups, but their number is comparatively small.

#### Degree of Dissociation of some Typical Electrolytes.

—In order to give some idea of the behaviour of various electrolytes, the following table contains the degree of dissociation of some commonly occurring salts:—

$\frac{1}{v}$ .	HCl.	KCl.	KC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .	‡BaCl <sub>2</sub> .	‡K <sub>2</sub> SO <sub>4</sub> .	‡ZnSO <sub>4</sub> .
0·0001		0·992	0·990	0·992	0·992	0·989
0·001	0·992	0·979	0·973	0·962	0·959	0·890
0·01	0·974	0·941	0·931	0·886	0·873	0·664
0·1	0·924	0·861	0·830	0·759	0·713	0·418
1	0·792	0·755	0·628	0·579	0·534	0·241

Of the substances mentioned hydrochloric acid is the most highly dissociated.

The other monovalent strong acids, like nitric, hydrobromic, hydriodic, chloric acids, etc., have about the same degree of dissociation; the strong bases, such as potassium, sodium, lithium, and thallium hydroxides, and the ammonium bases, etc., are also dissociated to about the same extent. The salts formed from monovalent acids and monovalent bases have a slightly lower degree of dissociation, as seen from the numbers given for potassium chloride and potassium acetate. The degree of dissociation is much smaller for salts formed from divalent acids with monovalent bases and for those formed from monovalent acids and divalent bases; the degrees for these two classes of salts are very similar (compare potassium sulphate and barium chloride in the table). Salts produced from a divalent acid and a divalent base (zinc sulphate) have a still lower degree of dissociation.

We know the mobilities,  $l_{\infty}$ , of almost all ions and the degree of dissociation for various *salts* (from the investigations of Kohlrausch (1), Ostwald, and Bredig), and with the aid of these we can calculate the conductivity of any salt solution. We cannot, however, make the calculation for solutions of *weak* bases and acids. These compounds are much less dissociated than the salts. From the table on p. 135 we find the following degrees of dissociation,  $\alpha$ , for acetic acid and ammonia:—

Acetic acid.		Ammonia.	
$\frac{1}{c}$	100 $\alpha$ .	$\frac{1}{v}$	100 $\alpha$ .
0.0001	30.8	0.0001	28.0
0.001	11.8	0.001	11.9
0.01	4.11	0.01	4.07
0.1	1.32	0.1	1.40

We shall return later to these weak electrolytes, which appeared at first to show the least agreement, but which later exhibited more regularities than the strong electrolytes.

**Comparison between the Results of the Osmotic and the Electric Determinations of the Degree of Dissociation.**—Solutions of salts give what appeared to be anomalous results with respect to the lowering of the freezing point, or the vapour pressure, and the raising of the boiling point, or the osmotic pressure, inasmuch as the influence of the salts was greater than that of other substances (see the preceding chapters). As mentioned on p. 59, these facts can be explained by assuming that the salt is partially dissociated. From the values obtained in any of these determinations the degree of dissociation can be calculated, and there arises the question whether the degrees found in this way are the same as those obtained from the electrical measurements. In 1887 I showed (2) that in the case of about a hundred solutions there was a good agreement between the degrees of dissociation calculated from Raoult's results for the freezing point and from Kohlrausch's measurements of the conductivity.

The following tables contain the degrees of dissociation found by the two methods. The value obtained from the conductivity is given under  $a_1$ , and under  $a_2$  is the result calculated from the freezing point of a 1 per cent. solution of the substance. The following consideration shows how the latter calculation is made: If a substance in solution has the molecular weight  $M$  which corresponds with its chemical formula, then a solution which contains  $M$  grams of the substance in 100 grams of solvent should have the freezing point  $-18.6^\circ$  (the molecular depression of the freezing point of water), and a solution containing 1 gram in 100 grams of solvent should freeze at  $-\frac{18.6^\circ}{M}$ . Instead of this the solution freezes at  $-A^\circ$ , which is lower than the temperature already indicated. The depression of the freezing point caused by the dissolved substance is therefore too great, indicating that the solution contains more molecules than has been assumed, *i.e.* a part of the dissolved molecules has been split up into smaller ones (the ions), so that the number

of molecules dissolved is greater than that calculated simply from the chemical formula. Now, if a molecule can be dissociated into  $n$  ions (for  $\text{KCl} = \text{K} + \text{Cl}$ ,  $n = 2$ ; for  $\text{K}_2\text{SO}_4 = 2\text{K} + \text{SO}_4$ ,  $n = 3$ ; for  $\text{K}_4(\text{CN})_6\text{Fe} = 4\text{K} + (\text{CN})_6\text{Fe}$ ,  $n = 5$ ), and if  $a_2$  denotes the fraction of the whole number of molecules which are dissociated, then in the solution there must be for every gram-molecule dissolved  $1 - a_2$  undissociated molecules and  $a_2n$  ions, which are to be regarded as free molecules. From every gram-molecule, therefore, we obtain  $1 - a_2 + na_2 = 1 + (n - 1)a_2$  molecules, and the observed freezing point  $-A^\circ$  must be greater than that calculated according to the chemical formula  $-\frac{18.6^\circ}{M}$  in this ratio ( $f$ ).

That is to say—

$$f = A \div \frac{18.6}{M} = 1 + (n - 1)a_2,$$

from which  $a_2$  can be calculated.

Non-electrolytes.			Bases.			Acids.		
	$\alpha_1$	$\alpha_2$		$\alpha_1$	$\alpha_2$		$\alpha_1$	$\alpha_2$
Methyl alcohol . . .	0.00	0.06	Barium hydroxide	0.84	0.85	Hydrochloric acid	0.90	0.98
Ethyl alcohol . . .	0.00	0.06	Calcium hydroxide	0.80	0.80	Nitric acid . . .	0.92	0.94
Butyl alcohol . . .	0.00	0.07	Lithium hydroxide	0.83	1.02	Chloric acid . . .	0.91	0.97
Glycerol . . .	0.00	0.08	Sodium hydroxide	0.88	0.96	Sulphuric acid . .	0.60	0.53
Mannitol . . .	0.00	0.03	Potassiumhydroxide	0.93	0.91	Phosphoric acid .	0.08	0.44
Cane sugar . . .	0.00	0.00	Ammonia . . .	0.01	0.03	Hydrogen sulphide	0.00	0.04
Phenol . . .	0.00	0.16	Methylamine . . .	0.03	0.00	Boric acid . . .	0.00	0.11
Acetone . . .	0.00	0.03	Trimethylamine .	0.03	0.09	Formic acid . . .	0.03	0.04
Ethyl ether . . .	0.00	0.10	Ethylamine . . .	0.04	0.00	Butyric acid . . .	0.01	0.01
Ethyl acetate . . .	0.00	0.04	Propylamine . . .	0.04	0.00	Oxalic acid . . .	0.25	0.13
Acetamide . . .	0.00	0.04	Aniline . . .	0.00	0.17	Malic acid . . .	0.07	0.08

Salts.			Salts.		
	$\alpha_1$	$\alpha_2$		$\alpha_1$	$\alpha_2$
Potassium chloride . .	0.86	0.82	Barium chloride . . .	0.77	0.81
Potassium nitrate . .	0.81	0.67	Lead nitrate . . .	0.54	0.51
Sodium nitrate . . .	0.82	0.82	Copper sulphate . . .	0.35	0.03
Potassium acetate . .	0.83	0.86	Mercuric chloride . .	0.05	0.11
Potassium carbonate .	0.69	0.63	Cadmium iodide . . .	0.56	0.06
Potassium sulphate . .	0.67	0.56			

In dilute solution, too, unexpected results have been obtained. These, however, are to be attributed for the most

part to errors of experiment with which the methods are infected. Thus, Jones (3) found for a 0.75 per cent. solution of cane sugar a molecular depression of the freezing point which was too great by 27 per cent., and all the older observations on dilute solutions are subject to similar deviations. Nernst and Abegg (4) have shown that this want of agreement is partly attributable to the fact that the freezing out of the solid solvent does not take place instantaneously, and in consequence the observed temperature is to a certain extent influenced by the temperature of the surrounding freezing mixture. The ideal method would therefore be to work with a freezing mixture the temperature of which is only infinitesimally lower than the freezing point to be determined. Interesting observations in this respect have been made by Jones, Loomis, Raoult, and others.

The salt which has been most thoroughly investigated cryoscopically is potassium chloride, which possesses the great advantage that the internal friction of the solution differs but slightly from that of pure water, so that a correction for the influence of this friction on the conductivity, within the limits of concentration employed, can safely be neglected. Loomis (5) found the following freezing points for solutions of this salt:—

Concentration, <i>m.</i>	Freezing point, <i>G.</i>	$\frac{G}{m}$	$(i + a)1.86.$	Diff. in per cent.
0.01	-0.0360°	3.60	3.59	+ 0.3
0.02	0.0709	3.55	3.56	- 0.3
0.03	0.1055	3.52	3.53	- 0.3
0.035	0.1235	3.53	3.52	+ 0.3
0.05	0.1749	3.50	3.50	0.0
0.10	0.3445	3.445	3.441	+ 0.1
0.20	0.6808	3.404	3.386	+ 0.5
0.40	1.3411	3.353	3.305	+ 1.5

For concentrations up to 0.2-normal the agreement is perfect (within the experimental error). The data obtained by Loomis have been fully confirmed by Jones, Abegg, Barnes,

and Raoult. For higher concentrations  $\frac{G}{m}$  is always greater than the calculated value; the following salts, however, which are known to partially form double molecules in concentrated solution, behave exceptionally in this matter: cadmium iodide, magnesium sulphate, zinc sulphate, copper sulphate, etc. (compare p. 143).

The more recent determinations by Hausrath (6) show that the degrees of dissociation at high dilution obtained from the freezing point experiments agree well with those found from the conductivities.

**Dissociation Equilibrium of Weak Electrolytes.**—The laws mentioned in Chapter VI. for ordinary dissociation must also obtain for the equilibrium between an electrolyte and its ions. As already shown, the dissociation of a substance AB which decomposes into the components A and B is regulated by the law of mass action—

$$K \times C_{AB} = C_A \times C_B$$

where  $K$  is a constant.

If we dissolve an electrolyte, for instance, acetic acid, it partially dissociates into the ions  $\overset{+}{H}$  and  $\overset{-}{CH_3CO_2}$ , and the above law can be applied to this decomposition. This was done by Ostwald, and almost simultaneously by van't Hoff (7), whose results for acetic acid at 14.1° are given in the next table.  $\mu$  denotes the molecular conductivity, and  $a$  (observed) the degree of dissociation calculated from this. Under  $a$  (calculated) is given the degree of dissociation calculated by means of the above formula, setting  $C_A = C_B$ , since both ions must occur in equal quantities;  $v$  is the dilution, *i.e.* the volume in litres in which a gram-molecule (60 grams) of acetic acid is dissolved.

Since—

$$a = \frac{\mu_r}{\mu_\infty}, C_{AB} = \frac{1-a}{v}, \text{ and } C_A = C_B = \frac{a}{v}$$

the formula  $K \times C_{AB} = C_A \times C_B = \left(\frac{a}{v}\right)^2$  can be transformed into—

$$K \frac{1 - \frac{\mu_v}{\mu_\infty}}{v} = \frac{\left(\frac{\mu_v}{\mu_\infty}\right)^2}{v^2} \text{ or } K = \frac{\left(\frac{\mu_v}{\mu_\infty}\right)^2}{\left(1 - \frac{\mu_v}{\mu_\infty}\right)v}$$

The relationship expressed in this formula is known as Ostwald's law, or the *law of dilution* (8).

The constant  $K$  is termed the electrolytic dissociation constant of acetic acid.

ACETIC ACID AT 14.1°.

$v$ .	$\mu_v$ .	100 $\alpha$ (observed).	100 $\alpha$ (calculated).
0.994	1.27	0.402	0.42
2.02	1.94	0.614	0.60
15.9	5.26	1.66	1.67
18.9	5.63	1.78	1.78
1500	46.6	14.7	15.0
3010	64.8	20.5	20.2
7480	95.1	30.1	30.5
15000	129	40.8	40.1
$\infty$	316	100	100

$$\log K = 5.25 - 10(5.25). \quad K = 0.0000178.$$

As is evident from the numbers given, the calculated and observed degrees of dissociation agree extremely well. In no other field in which the law of mass action has been applied have so good results been obtained.

This agreement between theory and practice, however, is only found for weak electrolytes, of which Ostwald investigated the acids and Bredig the bases (9).

It is just possible that even in this case the law of mass action is not undisturbed by other factors. The deviation from the law seems to be greater the stronger the acid is. Amongst the stronger organic acids deviations occur, *e.g.* with formic acid, and to an even greater extent with the

nitrobenzoic acids and the chloracetic acids. (Phosphoric acid, which may be regarded as a transition electrolyte to the strong acids, also shows great deviations.) We shall return later to a possible explanation of this unexpected phenomenon.

#### Dissociation Equilibrium of Strong Electrolytes.—

Up till the present it has unfortunately not been possible to bring the dissociation of strong electrolytes (salts, strong acids, and bases) into perfect agreement with the law of mass action. For this class of substances Rudolphi (10) has changed the Ostwald formula into—

$$K = \left( \frac{\frac{\mu_v}{\mu_\infty}}{1 - \frac{\mu_v}{\mu_\infty}} \right) \sqrt{v},$$

*i.e.* he has replaced the factor  $v$  in the denominator by  $\sqrt{v}$ . As an example we may give the numbers for silver nitrate. In this case the formula gives values which are in perfect agreement with the experimental results, and the same is true for many other strong electrolytes. The connection expressed in the formula is purely empiric, and no reason can be given for its validity. This anomaly in connection with strong electrolytes is the most difficult problem of the dissociation theory, and several experienced investigators have endeavoured to solve it, but so far without success.

SILVER NITRATE AT 25°.

$v$ .	$\mu_v$ .	$\alpha$ (observed).	$K$ .
16	102.3	0.828	1.00
32	108.0	0.875	1.08
64	111.0	0.899	0.96
128	114.3	0.926	1.03
256	116.9	0.947	1.05
512	118.7	0.962	1.07
	123.5	1.00	

$$K \text{ (mean value)} = 1.03.$$

Another, and still more exact formula connecting the

dissociation of salts with the dilution has been suggested by van't Hoff (11), namely—

$$K = \frac{C_i^2}{C_s}$$

whilst Ostwald's formula can be expressed in the form—

$$K = \frac{C_i^2}{C_s}$$

$C_i$  denotes the concentration of each ion (it is the same for both) expressed in gram-ions per litre, and  $C_s$  is the concentration of the undissociated part of the electrolyte expressed in gram-molecules per litre.

Others, among them Storch (12), have expressed the dilution law in the form—

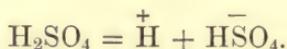
$$K = \frac{C_i^n}{C_s}$$

and have experimentally determined the value of the exponent  $n$ , which has been found to vary for electrolytes of different strengths, but in general is not very different from the value 1.5 contained in van't Hoff's form.

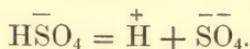
A possible explanation of this peculiar deviation from the law of mass action is that the addition of the ions of a strong electrolyte considerably increases the dissociating power of the water. If this be correct, the dissociation constant of the dissolved substance should be an increasing function of the quantity of salt ions dissolved in the water. This action of the ions recalls the much weaker and opposite effect of some non-electrolytes (see p. 150). The assumption is supported by some experiments in which the dissociation equilibrium of weak acids was determined in presence of salts (13). These experiments show that the dissociation constants of the weak acids increase in the same way with increasing salt concentration as do the constants for the salts; there is, however, a quantitative difference, and in the case of the salts their own ions form the active material. Whatever be the explanation, it may be regarded as certain

that the deviation from the law of mass action is only apparent.

**Divalent Acids.**—The above formulæ apply to electrolytes formed from two monovalent ions. When the concentration is great, a strong divalent acid, such as sulphuric acid, appears to dissociate according to—



As the solution is diluted, the  $\overset{-}{\text{HSO}}_4$  ions suffer further dissociation—



Each of these dissociations is regulated by a particular equation, and the equilibrium is so masked thereby that it cannot be determined. The same applies to salts consisting of polyvalent ions.

In the case of most of the di- and poly-valent acids (sulphuric acid is almost the only exception) only the first phase of the dissociation takes place at the dilutions at which we commonly work, *i.e.* only the first hydrogen ion is split off. The other possible dissociation can therefore be neglected, and with a fair degree of exactitude we can apply Ostwald's formula, although this is only rigidly applicable to electrolytes consisting of two monovalent ions.

**Influence of Substitution on the Dissociation of Acids.**—It has been known for a very long time that an acid, such as acetic acid, becomes stronger by replacement (substitution) of one hydrogen atom by a chlorine atom; monochloroacetic acid ( $\text{CH}_2\text{ClCOOH}$ ) is considerably stronger than acetic acid ( $\text{CH}_3\text{COOH}$ ); dichloroacetic acid ( $\text{CHCl}_2\text{COOH}$ ) is stronger than monochloroacetic acid; and trichloroacetic acid ( $\text{CCl}_3\text{COOH}$ ) is the strongest of the substitution products. The series of strengths can be recognised from the dissociation constants,  $K$ , because the greater this constant is the greater is the quantity of substance dissociated at a particular dilution,  $v$ , or the degree of dissociation of the acid, and it

is upon this alone that the strength of the acid depends (see Chap. XII). For the four acids mentioned, Ostwald (14) has determined the dissociation constants to be—

$\text{CH}_3\text{COOH}$	$\text{CH}_2\text{ClCOOH}$	$\text{CHCl}_2\text{COOH}$	$\text{CCl}_3\text{COOH}$
$1.80 \times 10^{-5}$	$155 \times 10^{-5}$	$5140 \times 10^{-5}$	$121000 \times 10^{-5}$

Bromine, iodine, cyanogen, oxygen, and the nitro group, when introduced into the radicle of an acid in place of hydrogen, increase the dissociation constant, and consequently the strength, of the acid; substitution by hydrogen or the amino group weakens the acid. In the case of the benzene derivatives, substitution in the ortho position exerts a stronger influence than substitution in the meta or para positions, which act about equally. These regularities are of great interest in organic chemistry, and have been much utilised to solve questions concerning constitution and grouping of the atoms in the molecule.

## CHAPTER XI.

### Conclusions from the Dissociation Theory. Additive Properties of Solutions.

**General Remarks.**—The properties of a solution may be regarded as the sum of the properties of the substances present in the solution. A solution of cane sugar contains two substances; that which is present in excess is generally termed the solvent, and the other the dissolved substance; the physical, chemical, physiological, and other properties of the solution can be regarded as approximately the sum of the corresponding properties of the two substances mixed (water and sugar).

Now, since salts are highly dissociated in aqueous solution, the properties of the solution will be equal to the sum of the properties of the solvent (water), of the ions, and of the undissociated substance. For dilute solutions the undissociated part is comparatively small, and it appears in many cases that its properties, when they differ appreciably from those of the two ions (*e.g.* with reference to reactivity and occasionally with reference to colour, etc.), are not striking. For such cases it is usual to say that the properties of the salt solution are equal to the sum of the properties of the two ions, and leave the properties of the solvent out of account. This rule enables us to review the properties of the numerous salts in solutions (dilute), because the number of ions obtained from these salts is comparatively small. The experimental confirmation of this rule may be regarded as a strong support of the view that the salts are electrolytically dissociated.

**Specific Gravity of Electrolytic Solutions.**—When we dissolve a substance, *e.g.* cane sugar, in water, the specific gravity of the solution deviates more and more from 1 as the concentration increases. In the case of most electrolytes the specific gravity increases. When we examine the dependence of the specific gravity on the normality  $n$ , we find that it can be represented by a function of the form—

$$S = S_0 + an + a_1n^2.$$

Thus, for sugar solutions at  $17.5^\circ$ , we find, if the density of water at  $17.5^\circ$  be taken as unit—

$$S = 1 + 0.1328n - 0.002n^2.$$

The first part of the following table shows how exactly the specific gravity may be obtained from a formula of this type—

% Cane sugar.	Normality.	Specific gravity (observed).	Specific gravity (calculated).
0	0	1	1
10	0.3041	1.0402	1.0402
20	0.6336	1.0833	1.0833
30	0.9908	1.1296	1.1296
40	1.3794	1.1794	1.1793
50	1.8025	1.2328	1.2328
60	2.263	1.2899	1.2903
70	2.765	1.3510	1.3520
10	0.3041	1.0402	1.0399
20	0.6336	1.0833	1.0832
30	0.9908	1.1296	1.1301

The numbers in the lower part of the table have been calculated from the simpler formula—

$$S = 1 + 0.1313n,$$

which gives the specific gravities up to normal concentration (30 per cent.) sufficiently accurately for most purposes.

If, now, the specific gravity of solutions of a substance,  $A$ , can be found from—

$$S = 1 + an,$$

and that of solutions of another substance,  $B$ , from—

$$S = 1 + \beta n,$$

then for solutions containing both substances,  $n$ -normal with respect to  $A$ , and  $n_1$  normal with respect to  $B$ , we have—

$$S = 1 + an + \beta n_1.$$

If we take the case of a highly dissociated salt, *e.g.* sodium chloride, we may for the present purpose assume that it is completely dissociated in dilute solution. The solution contains in unit volume a certain number ( $n$ ) of sodium ions, and the same number of chlorine ions. Let us now set the coefficient of the chlorine ions =  $a$ , of the sodium ions =  $\beta$ , and, further, the coefficients for bromine ions =  $\gamma$ , and for ammonium ions =  $\delta$ , then we obtain for 0.1-normal solutions of the salts sodium chloride (a), sodium bromide (b), ammonium chloride (c), and ammonium bromide (d) the equations—

$$S_a = 1 + 0.1(a + \beta),$$

$$S_b = 1 + 0.1(\beta + \gamma),$$

$$S_c = 1 + 0.1(a + \delta),$$

$$S_d = 1 + 0.1(\gamma + \delta).$$

Consequently—

$$S_a - S_b = S_c - S_d.$$

This illustrates a typical additive property. If we have numerical data of a property for equally concentrated solutions of four salts,  $A_1K_1$ ,  $A_1K_2$ ,  $A_2K_1$ , and  $A_2K_2$ , which are formed from a pair of positive ions,  $K$ , and a pair of negative ions,  $A$ , then the difference in the value of this property for the salts  $A_1K_1$  and  $A_1K_2$  is the same as the difference between the salts  $A_2K_1$  and  $A_2K_2$ . We may put this in the form—

$$A_1K_1 - A_2K_1 = A_1K_2 - A_2K_2.$$

If we arrange a series of  $m$  negative ions,  $A_1, A_2, \dots, A_m$ , in a horizontal row, and a series of  $n$  positive ions,  $B_1, B_2, \dots, B_n$ , in a vertical row, then by combination of these ions  $mn$  salts  $AB$  can be obtained, as the following scheme shows:—

	$A_1$	$A_2$	$\dots$	$A_m$
$B_1$	$A_1B_1$	$A_2B_1$	$\dots$	$A_mB_1$
$B_2$	$A_1B_2$	$A_2B_2$	$\dots$	$A_mB_2$
	$\dots$	$\dots$	$\dots$	$\dots$
	$\dots$	$\dots$	$\dots$	$\dots$
$B_n$	$A_1B_n$	$A_2B_n$	$\dots$	$A_mB_n$

In this scheme we may write in place of each salt  $AB$  the numerical value of one of its properties in, for example, normal solution, and this property is to be regarded as additive if the following relationship exists between the differences—

$$A_1B_1 - A_1B_2 = A_2B_1 - A_2B_2 = \dots A_mB_1 - A_mB_2.$$

Expressed in words, this may be stated thus: The differences between two values which are in the same vertical column and two certain horizontal rows must be the same (within the experimental error) for all the vertical columns if the property in question is additive.

Exactly the same must hold good for the differences between the horizontal rows and, of course, for any concentration, provided this is the same for all the salt solutions. By constructing such a table (the so-called additive scheme) and calculating the differences between the rows and the columns, it is easy to decide whether the particular property of the dissolved salt is additive or not.

According to Valson (1), additive properties can also be expressed by moduli. As an example, we give below the moduli for the specific gravities. Valson chose as his starting

point the specific gravities of ammonium chloride solutions, which have the following values:—

## AMMONIUM CHLORIDE.

Concentration, <i>n.</i>	Specific gravity, $\frac{18}{18}$	Concentration, <i>n.</i>	Specific gravity, $\frac{18}{18}$
0	1.0000	3	1.0451
1	1.0157	4	1.0587
2	1.0308	5	1.0728

The following numbers multiplied by  $10^{-4}$  are the moduli for the various ions:—

$\text{NH}_4$	K	Na	Li	$\frac{1}{2}\text{Ba}$	$\frac{1}{2}\text{Sr}$	$\frac{1}{2}\text{Ca}$	$\frac{1}{2}\text{Mg}$	$\frac{1}{2}\text{Mn}$	$\frac{1}{2}\text{Zn}$
0	289	238	78	735	500	280	210	356	410
$\frac{1}{2}\text{Cd}$	$\frac{1}{2}\text{Pb}$	$\frac{1}{2}\text{Cu}$	Ag	H	Cl	Br	I	$\text{NO}_3$	$\frac{1}{2}\text{SO}_4$
606	1087	434	1061	16	0	373	733	163	206
				$\text{C}_2\text{H}_3\text{O}_2$		OH			
				— 15		20			

The specific gravity of, *e.g.* a  $3n$   $\frac{1}{2}\text{CaBr}_2$  solution, would be calculated to be—

$$S = 1.0451 + 3(280 + 373) \cdot 10^{-4} = 1.0431 + 0.1959 = 1.2397,$$

and by experiment 1.2395 has actually been found.

With the aid of these moduli the specific gravities of quite concentrated solutions can be obtained fairly accurately, although, as the example given proves, the salt is not by any means nearly completely dissociated.

**Compressibility, Capillarity, and Internal Friction of Solutions.**—Other properties of solutions besides the specific gravity show the same regularities. As an example, we may take the compressibility, *i.e.* the volume change suffered by 1 c.c. when the pressure is raised from 1 atmo. to 2 atmas.

Röntgen and Schneider (2) found the numbers contained in the following table for 0.7-normal solutions at the

ordinary temperature, and it will be seen that the differences for each column are constant. Water and ammonia, which are not very much dissociated, form exceptions, and ought, therefore, not to be included. The compressibility of water is set = 1000, and the numbers refer to this standard.

	H.	Δ.	NH <sub>4</sub> .	Δ.	Li.	Δ.	K.	Δ.	Na.
I. . . . .	—	—	954	14	940	8	932	8	924
NO <sub>3</sub> . . . . .	981	27	954	20	934	4	930	8	922
Br . . . . .	981	28	953	19	934	4	930	7	923
Cl . . . . .	974	29	945	17	928	9	919	2	917
OH . . . . .	1000	(8)	992	(97)	895	11	884	3	881

The capillarity and internal friction of solutions are also additive properties. In proof of this we subjoin some results obtained by Reyher (3) for the internal friction of normal salt solutions referred to that of water at 25° as unity.

	Cl.	Br.	ClO <sub>3</sub> .	NO <sub>3</sub> .	ClO <sub>4</sub> .	H <sub>2</sub> PO <sub>4</sub> .	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .
Na . . . . .	1·099	1·062	1·089	1·052	1·035	1·476	1·400
H . . . . .	1·070	1·038	1·053	1·022	1·002	1·285	1·127
Difference . . . . .	0·029	0·024	0·036	0·030	0·033	0·191	0·273

The difference Na - H is on the average about 0·030, except in the case of phosphate and acetate, and this is due to the fact that the corresponding free acids have only a low degree of dissociation, and therefore do not fit properly into the scheme.

**Refractive Index of Solutions.**—According to the formula—

$$n = N_x + (a + b)x$$

we can calculate the refractive index *n* of a salt solution if the normality (*x*) be known; *N<sub>x</sub>* is the refractive index of another salt solution (taken as standard) of the same concentration, and *a* and *b* are the moduli, *M*, of the refractive index.

Bender (4) used a solution of potassium chloride for comparison, and found the following refractive indices for the  $H_{\alpha}$ , D,  $H_{\beta}$ , and  $H_{\gamma}$  lines of the spectrum:—

z.	$H_{\alpha}$ .	D.	$H_{\beta}$ .	$H_{\gamma}$ .
	Refractive index for KCl.			
1	1.3409	1.3428	1.3472	1.3505
2	1.3498	1.3518	1.3565	1.3600
3	1.3583	1.3603	1.3651	1.3689

Moduli of the refractive index  $M \times 10^{-4}$  for

K, Cl	0	0	0	0
Na	2	2	2	2
$\frac{1}{2}$ Cd	38	—	40	41
Br	37	38	41	43
I	111	114	123	131

From this we can calculate, for instance, the refractive index of a 2-normal solution of sodium bromide for light of wave-length  $H_{\alpha}$ :

$$n = 1.3498 + \frac{2(2 + 37)}{10,000} = 1.3576.$$

The experimental value is 1.3578. It should, however, be noted that the agreement is not always so good. Le Blanc (5) has shown that weak acids and bases do not fit into this additive scheme.

**Magnetic Rotation of Solutions.**—Jahn (6) found the following values for the power of salt solutions to rotate the plane of polarisation in a magnetic field. He determined the angle through which the plane of polarisation of sodium light was turned in passing through a column of water of definite length in a strong magnetic field. This angle was taken as equal to 100. Working under precisely the same external conditions, he determined the angle for normal solutions of various electrolytes. From this he subtracted

the angle of rotation for the water contained in the solution, and obtained the following values for the ions:—

	Cl.	Br.	I.	NO <sub>3</sub> .	4SO <sub>4</sub> .	4CO <sub>3</sub> .
H . . . . .	4.67	—	—	—	—	—
Li . . . . .	4.61	—	—	—	1.53	—
Na . . . . .	5.36	9.19	18.46	1.37	1.77	1.76
K . . . . .	5.66	9.36	18.95	1.35	1.79	1.78
$\frac{1}{2}$ Ca . . . . .	4.70	8.80	—	—	—	—
$\frac{1}{2}$ Sr . . . . .	4.86	9.08	—	—	—	—
$\frac{1}{2}$ Ba . . . . .	5.05	9.27	—	—	—	—
$\frac{1}{2}$ Cd . . . . .	5.89	9.85	20.45	—	2.58	—
$\frac{1}{2}$ Mn . . . . .	4.52	—	—	—	1.14	—

If we take the differences between two vertical rows, we find that these are nearly constant, *e.g.* for Br - Cl—

Na	K	$\frac{1}{2}$ Ca	$\frac{1}{2}$ Sr	$\frac{1}{2}$ Ba	$\frac{1}{2}$ Cd
3.83	3.70	4.10	4.22	4.22	3.96.

The simplest relationships are found when the particular property is due exclusively, or, at any rate, for the greater part, to one of the two ions.

In such cases all salts, which in dilute solution contain the same quantity of the particular ion, have the same value for the property in question whatever be the nature of the other ion present. As examples of this, we may cite the molecular magnetism of the magnetic salts (particularly iron salts), the natural power of rotating plane polarised light, the colour and the light absorption.

**Molecular Magnetism.**—Experiments on magnetic salt solutions were made by G. Wiedemann (?). The liquid to be investigated was placed in a small flask, which was suspended at one end of the horizontal rod of a Coulomb torsion balance, and this was equipoised by means of a weight. A strong electromagnet was placed near the flask, and when the current was started, the flask was attracted on account of the induced magnetism in the solution. This attraction was measured for several solutions, and was found to vary. By

measuring the attraction suffered by the flask empty, and when filled with water, then from the value obtained with the solution, the part due to the dissolved salt can easily be calculated. The attraction is proportional to the quantity of dissolved salt. If the flask contains 1 gram-molecule of dissolved salt, the attraction is a direct measure of the molecular magnetism. In the same way the atomic magnetism of a gram-atom of iron can be determined. Wiedemann found that all the ferrous salts possess the same molecular magnetism; thus he obtained for the sulphate, the nitrate, and the chloride, the relative numbers, 3900, 3861, and 3858; whilst for the ferric salts he obtained as mean value, 4800. The nitrate, sulphate, and chloride of nickel gave 1433, 1426, and 1400; manganous sulphate, nitrate, acetate, and chloride gave 4695, 4693, 4586, and 4700; and cupric nitrate, acetate, and chloride, 480, 489, and 477.

If we set the atomic magnetism of iron in ferric salts = 100, we obtain the following values for the magnetism of a gram-atom of the metal in the salts: in manganous salts, 100·4; in ferrous salts, 83·1; in cobaltous salts, 67·2; in nickelous salts, 30·5; in didymium salts, 22·6; in cupric salts, 10·8; in ceric salts, 10·3; and in chromic salts, 41·9.

It is noteworthy that the temperature coefficient for the temporary magnetism is almost the same for all salt solutions; it is given by—

$$m_t = m_0(1 - 0\cdot00325 t)$$

where  $t$  is the temperature (centigrade), and  $m_t$  and  $m_0$  the temporary magnetisms at  $t^\circ$  and  $0^\circ$ .

Recent and more exact determinations by du Bois and Liebknecht (*8*) have proved that the atomic magnetism is not strictly additive, but, on the other hand, the additivity mentioned is so general that it can be applied not only to solutions, but also to crystallised salts, in which the dissociation is very small if it takes place at all.

**Natural Rotatory Power in Solution.**—Some few organic compounds are capable of rotating the plane of polarisation of light passed through them. If, therefore, we

combine say an anion possessed of this power with an inactive cation, which in combination with most ions gives inactive salts, equivalent quantities of all the salts of this anion must, in dilute solution, have equal rotatory powers. This has been confirmed in one or two instances; the salts of quinic acid in  $\frac{1}{7}$ -normal solution give the following molecular rotations :—

Potassium . . . . .	48·8°	Barium . . . . .	46·6°
Sodium . . . . .	48·9	Strontium . . . . .	48·7
Ammonium . . . . .	47·9	Magnesium . . . . .	47·8.

The differences are quite inconsiderable. For the sake of comparison, it may be added that the molecular rotation of a  $\frac{1}{7}$ -normal solution of quinic acid, which is very little dissociated, is 43·4°.

The molecular rotation of tartaric acid (little dissociated) is 15° at 20°, that of the salts is from 26·30° to 27·62°. Oudemans (9) and Landolt (10) have examined these salts of optically active acids and bases.

**Light Absorption of Solutions.**—Another optical property of dilute solutions which is of great importance is their power of absorbing light. Ostwald, who carried out experiments in this direction, applied a photographic method (11). He produced on the same photographic plate spectral images of different solutions, which contained the same “coloured” ion in equivalent quantities with various cations. In most cases these absorption spectra are identical; Fig. 39 shows the absorption spectra of 0·002-normal solutions of permanganates,  $MnO_4$  with 10 different cations. Only in a few cases were

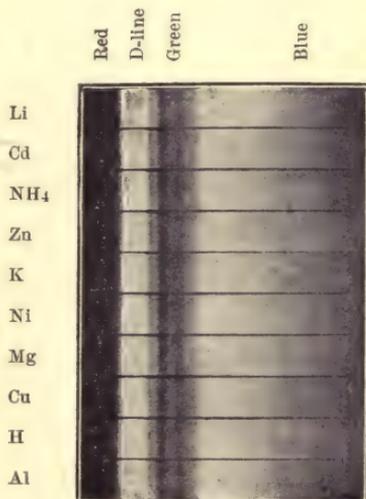


FIG. 39.

deviations from this observed, and these could be attributed to disturbing factors. Since the colour, *i.e.* the absorption, of a compound suffers a very considerable change by a comparatively small chemical change, such as the replacement of bromine by chlorine, the constancy observed with the salt solutions can hardly be otherwise explained than by assuming that the salt molecules have decomposed into ions. Further, since a spectrum consists of several parts, and the agreement in all parts is perfect, Ostwald's investigation, which covered 4 positive and 13 negative, "coloured" ions, may be mentioned as strong evidence in favour of the dissociation theory.

This is the reason why all salts containing the same ion have the same colour in dilute solution. All nickelous salts in dilute solution are green, all cupric salts blue, all manganous salts pink, all ferrous salts green, and all ferric salts colourless. The last-mentioned solution has a yellow colour due to the presence of colloidal ferric hydrate. The ferrous and ferric salts are differently coloured, because they contain different ions, namely,  $\text{Fe}^{++}$  and  $\text{Fe}^{+++}$ ; in the same way the ferrocyanide and the ferricyanide ions have different colours. A large number of examples are known, particularly amongst organic compounds.

The application of indicators in the titration of acids and bases is based on this colour of the ions. Phenolphthalein, which behaves as a weak acid, is colourless in solution, whilst its salts (in solution) possess a brilliant pink colour. The acid is hardly dissociated, and therefore does not show the colour of the anion, for this does not exist in acid solution. In the same way, litmus is a weak acid with a red colour, whilst the anion produced from the dissociation of its salts is blue.

**Chemical Properties of the Ions.**—In mentioning indicators we have touched upon one of the most important additive properties of salt solutions; one which is the basis of analytical chemistry. Let us consider a solution containing

chlorine. On the addition of a reagent, usually silver nitrate, it is found that the solution gives a reaction characteristic for chlorine, inasmuch as a curdy precipitate of silver chloride is formed. It can easily be proved that this reaction will not detect every chlorine atom, but only those existing as ions, for a number of substances containing chlorine, such as potassium chlorate, monochloroacetic acid, and other organic and inorganic compounds in which the presence of chlorine can otherwise be proved, do not give this characteristic reaction. These substances do not dissociate to give chlorine ions. When a substance, such as mercuric chloride, gives only a small amount of chlorine ion, then on addition of silver nitrate this is removed from the solution as silver chloride. By the removal of the chlorine ion the dissociation equilibrium is disturbed, and in order to re-establish it more chlorine ion must be formed at the expense of undissociated mercuric chloride molecules. Consequently, one part of the chlorine after another is precipitated, until the whole of it is completely removed from the solution. If, however, the number of chlorine ions at the beginning is extremely small, it may happen that on the addition of silver nitrate the solubility product of silver chloride is not reached, and consequently there will be no precipitation of this substance. The reagent silver nitrate can nevertheless be used to detect the presence of a certain extremely small quantity of chlorine ion in solution. This and other chemical means are often very delicate, and are therefore of great use in determining the occurrence of ions in solutions in which the electric conductivity gives no certain result on account of the presence of other ions.

The same sort of behaviour is exhibited by most of the chemical reagents generally used in ordinary "wet" analysis.

An example, to which I (12) called attention in 1884, is the behaviour of the ferrocyanides, which, although they contain iron, do not give the reactions characteristic of iron, or rather of the iron ions. Cases like this were previously

classed amongst those in which the "retention of the type" takes place against the ordinary chemical rules. By the action of other salts, where exchange of ions takes place, a ferrocyanide always gives a ferrocyanide, and not a cyanide and a ferrous salt. In order to bring about such a rearrangement, more energetic chemical means must be employed; in this case, for instance, potassium ferrocyanide may be heated (fused), and it is decomposed into potassium cyanide, nitrogen, and iron carbide, and this last compound, on treatment with hydrochloric acid, gives ferrous chloride.

As a rule the ions are much more reactive than other chemical substances. The exchange of ions in precipitation and similar reactions takes place, as far as we can judge, instantaneously, whilst other reactions often take place very slowly and only at high temperature with a measurable velocity. We might even go so far as to say that only ions can react chemically. However, it would be difficult to definitely prove this; but we may assume that in the case of reactions which take place very slowly ions are present, although not in measurable quantity so far as our present methods are able to detect them.

Gore (13) has shown that absolutely anhydrous hydrochloric acid, which does not conduct an electric current, does not react with the oxides or carbonates of magnesium and the alkaline earth metals, whilst in aqueous solution these substances are violently attacked. Concentrated sulphuric acid does not act upon iron until water is added.

**Physiological Action of the Ions.**—The physiological actions of different salt solutions as curative agents or poisons are of great practical interest. It has been known for a long time that morphine given in the form of sulphate, chloride, acetate, etc., always has the same effect when used in equivalent quantities. The negative ion present with the morphine has no physiological influence. Similar observations have been made with other substances, such as quinine, etc.

Mention may here be made of some observations with

poisons. It was found that potassium chlorate is poisonous, and this led to an investigation of the action of other potassium salts. Solutions of a definite strength were introduced into living organisms, and the degree of poisonousness was determined by the length of time required to kill the organism. The result of this investigation was to show that all potassium salts, with the exception, of course, of those containing a poisonous negative ion, like potassium cyanide, have nearly the same poisonous effect in solutions of equal concentration.

Recently Kahlenberg (14) and Loeb (15), as well as Paul and Krönig (16), have investigated the action of salts on bacteria and spores. All the results obtained agree very perfectly with what would be expected from the dissociation theory. Paul and Krönig exposed spores for a certain length of time to the action of salt solutions at 18°, and determined the vitality of the spores by the number of bacteria colonies formed when placed under conditions favourable to their growth. The degree of dissociation of the following mercuric salts in equivalent solution decreases in the order given: chloride, bromide, thiocyanate, iodide, cyanide, and it was found that their powers of killing spores of the anthrax bacillus were in the same order, so that the cyanide has the least action. The influence of complex salts is still smaller, *e.g.* potassium mercuricyanide,  $K_2(CN)_4Hg$ , which gives hardly any mercuric ions. Similar relationships were found for gold and silver salts. By the addition of neutral salts, such as sodium chloride and potassium chloride, both the degree of dissociation and the poisonousness are diminished. In some other cases, for instance with acids, not only does the hydrogen ion exert a poisonous influence, but also the negative ion with which it is present, so that the action of hydrofluoric acid is greater than that of hydrochloric acid, although the latter is dissociated to the greater extent. Nevertheless, the weak acids, formic and acetic acids, have the smallest effect of any acids so far examined, whilst phenol shows peculiar relationships.

### Catalytic Action of Hydrogen and Hydroxyl Ions.—

As mentioned in Chapter VII., cane sugar in aqueous solution is converted in presence of acids into invert sugar.

Now, since the characteristic of all acids is the presence of hydrogen ions, it might be supposed that the hydrogen ion was the cause of this change. Further, since the degree of dissociation of an acid is proportional to its molecular conductivity and inversely proportional to its conductivity at infinite dilution, it might be expected, since this latter value is nearly the same for all acids, that the velocity of inversion of cane sugar would be proportional to the conductivity of the acid added if equivalent quantities of different acids were employed. In 1884 I (12) showed on theoretical grounds that this velocity must be proportional to the conductivity of the catalysing acid, and shortly afterwards Ostwald (17), who was then investigating reaction velocities, experimentally confirmed this conclusion. Ostwald obtained the numbers given in the next table for the conductivity ( $l$ ) and the velocity of inversion ( $\rho$ ) of different acids at the same concentration; the conductivity of hydrochloric acid (in normal solution) is set = 100, and the velocity of inversion caused by this same acid (in 0.5-normal solution) is also set = 100.

Acid.	$l$ .	$\rho$ .	$\sigma$ .
Hydrochloric acid . . . . .	100	100	100
Nitric acid . . . . .	100	100	92
Chloric acid . . . . .	100	104	94
Sulphuric acid . . . . .	59.5	54	55
Benzenesulphonic acid . . . . .	—	104	99
Trichloroacetic acid . . . . .	—	75	68
Dichloroacetic acid . . . . .	33.0	27.1	23
Monochloroacetic acid . . . . .	6.41	4.84	4.3
Acetic acid . . . . .	0.67	0.4	0.34
Formic acid . . . . .	2.3	1.5	1.3

The values given under  $\sigma$  are for the velocity of saponification of esters in presence of 0.67-normal solutions of the acids mentioned.

From the numbers it can be seen that there is a good parallelism between the conductivities and the effects on the inversion. However, a more exact and thorough investigation seemed advisable. I carried out an investigation (18) on this velocity of inversion, and it was afterwards extended by Palmaer (19). The result of these experiments was to show that at high dilution of the acids and constant sugar concentration the velocity of inversion is proportional to the concentration of the hydrogen ion present. At higher concentrations deviations are observed of the same nature as those caused by the addition of neutral salts, the so-called action of salts (see p. 109). By addition of a large quantity of acid, the osmotic pressure of the cane sugar is increased so that the velocity of reaction  $\rho$ , instead of being proportional to the quantity  $m$  of hydrogen ion present, is regulated by the formula—

$$\rho = am + bm^2.$$

The coefficient  $a$  is the same for all acids, *i.e.* it is independent of the nature of the anion;  $b$ , on the other hand, is dependent on the anion, for this ion also acts so as to increase the osmotic pressure of the sugar, and all anions do not act to the same extent in this direction. The fact that  $a$  is the same for all acids evidently indicates that (at low concentration) all hydrogen ions exert the same influence independently of the acid from which they are formed. It is therefore possible to calculate the velocity with which any acid can invert sugar if we know the velocity in the case of another acid, say hydrochloric acid, and the "salt action" of the various ions (which can be determined by other methods). The following table gives the reaction velocities for several concentrations of the acids. Under  $\rho$  (observed) are given the numbers found by Ostwald.

	Concentration.	$\rho$ (observed).	$\rho$ (calculated).
HCl . . . . .	0.5	20.5	20.1
	0.1	3.34	3.41
	0.01	0.317	0.318
HBr . . . . .	0.5	22.3	22.2
	0.1	3.41	3.50
	0.01	0.318	0.324
H <sub>2</sub> SO <sub>4</sub> . . . . .	0.25	10.7	11.1
	0.05	2.08	2.09
	0.005	0.265	0.256
HCOOH . . . . .	0.5	0.332	0.345
	0.1	0.135	0.134
	0.01	0.0372	0.0360
CH <sub>3</sub> COOH . . . . .	0.5	0.1005	0.1005
	0.1	0.0430	0.0409
	0.05	0.0771	0.0750
C <sub>2</sub> H <sub>5</sub> COOH . . . . .	0.1	0.0341	0.0325
	0.01	0.0097	0.0095
	0.5	0.0791	0.0749
C <sub>3</sub> H <sub>7</sub> COOH . . . . .	0.1	0.0362	0.0355
	0.01	0.0100	0.0095
	0.25	0.1210	0.1280
C <sub>2</sub> H <sub>4</sub> (COOH) <sub>2</sub> . . . . .	0.05	0.0536	0.0531
	0.005	0.0202	0.0190

Similar relationships are shown in the case of other reactions, the velocities of which are accelerated by acids, but they have not been so fully investigated.

In the saponification by bases it has been found that all strong bases exert about the same action. The velocity of reaction at 9.4° is—

NaOH . . . . .	2.31	Sr(OH) <sub>2</sub> . . . . .	2.20
KOH . . . . .	2.30	Ba(OH) <sub>2</sub> . . . . .	2.14
Ca(OH) <sub>2</sub> . . . . .	2.29		

The numbers are for  $\frac{1}{40}$ -normal solutions, in which the strong bases may be regarded as completely dissociated; in equivalent quantity they should exert the same action, which, according to the above numbers of Reicher (20), they actually do. The corresponding value for the weakly dissociated ammonia is 0.011.

**Objections to the Assumption of Electrolytic Dissociation.**—However it may be with some details not yet

explained, it is quite certain that the degree of dissociation found from the osmotic method generally agrees closely with that found by the electrical method. Such an agreement was essential, in order that the idea of electrolytic dissociation might be valid.

The most important objection which has been raised by chemists is that salts in solution show a higher osmotic pressure than corresponds with their chemical formulæ, and this seems to correspond with the phenomenon that a gas—as, for instance, ammonium chloride—shows a higher gas pressure than would be expected from the composition of the molecule  $\text{NH}_4\text{Cl}$ . In this latter case it was admitted that the deviation from the gas laws was only apparent and due to the decomposition of the molecule into simpler constituents ( $\text{NH}_3$  and  $\text{HCl}$ ). However at that time it could be shown that the products of dissociation might be separated by diffusion, and the question arose why it is not possible to effect a similar separation by diffusion of the products of dissociation of sodium chloride (sodium and chlorine).

The explanation of our inability to effect this separation lies in the extraordinarily high charge of 96,500 coulombs per equivalent which the products of electrolytic dissociation, *i.e.* the ions, receive, whilst the products from an ordinary dissociation remain unelectrified. If we had a layer of pure water over a solution of sodium chloride, then if this charge had no influence, the chlorine, which is appreciably more mobile than the sodium (in the ratio 68 : 45), would be found to be in excess in the upper layer. Let us assume that  $10^{-12}$  gram-equivalents more of chlorine than of sodium have diffused into the pure-water layer, then this would have a negative charge of  $\frac{96,500}{10^{12}}$  coulombs, or 290 electrostatic units, a quantity of electricity which, if brought on to a sphere of 10 cms. radius, would be able to give a spark 0.2 cm. long. Now, it can easily be shown that the electric (electromotive) forces which would be exercised by even so small a quantity ( $10^{-12}$  gram-equivalent) would far exceed

all osmotic forces, whereby the sodium would receive an acceleration, but the chlorine a retardation. As the unit of electromotive force is equal to 300 volts when expressed in electrostatic units, the 290 electrostatic units mentioned would possess a potential of  $\frac{290 \times 300}{10} = 8700$  volts. This

charge, when communicated to a solution in the form of a cube, the length of whose side is 10 cms., would be at a tension of the same order of magnitude, or, in round numbers,  $10^4$  volts.

Let us consider a column of 1 sq. cm. cross section and 1 cm. high, one end of which, *A* (Fig. 40), has a potential of  $10^4$  volts, whilst at the other end, *B*, the potential is 0. Let the liquid between *A* and *B* contain dissolved sodium chloride, so arranged that at *A* the concentration is 0, at *B* 1-normal, *i.e.* *in toto* 0.5-normal. And, further, we assume that the sodium chloride is completely dissociated. The chlorine ions are acted on (compare p. 121)

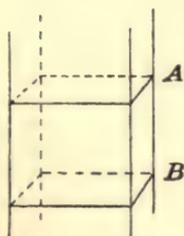


FIG. 40.

by an electric force  $\frac{V}{l}e$ , where  $\frac{V}{l}$  is the fall of potential per centimetre, in this case equal to  $10^4$  volts, and  $e$  denotes the number of coulombs with which the chlorine ions are charged, here equal to  $\frac{1}{2000}96,500 = 48.2$ , since the cubic centimetre of the solution contains  $\frac{0.5}{1000}$  gram-ions. The force acting is therefore (see p. 6)—

$$48.2 \times 10^4 \text{ volt-coulombs per cm.} = 48.2 \times 10^{11} \text{ dynes.}$$

The osmotic force acting on the same chlorine ions is given by the difference between the osmotic pressure of the normal solution at *B*, and that of concentration 0 at *A*. According to p. 26, this is for the temperature  $18^\circ = 291^\circ$  abs.—

$$84,688 \times 291 \times \frac{982}{1000} = 2.42 \times 10^7 \text{ dynes.}$$

The force is therefore  $2 \times 10^5$  times smaller than the

former, and an excess of  $0.5 \times 10^{-5} \times 10^{-12}$  gram-ions of chlorine over the number of sodium ions should be sufficient to prevent a further separation of the chlorine ions by diffusion. Such small quantities ( $5 \times 10^{-18}$  gram-equivalent) cannot be detected by chemical means.

Since a millivolt can be detected by an electrometer, the  $10^{-7}$ th part of the charge mentioned can be determined. The smallest weighable quantity is usually 0.1 milligram, so that if the equivalent weight is 100,  $10^{-3}$  milligram-equivalent, or  $10^{-6}$  gram-equivalent can be measured. The electro-metric analysis is therefore in this case  $10^{13}$  times more delicate than the chemical method.

In the diffusion the more mobile chlorine moves slightly quicker than the sodium, and the liquid becomes negatively charged at *A* where pure water is, and positively charged at *B*, so that an electric current can be obtained when unpolarisable electrodes are placed at the ends and joined by a wire. We return later to these so-called concentration currents. The separation of the ions can, at any rate, be effected by taking from them their electric charges, as is done in electro-analysis.

Since electric forces come into play when electrolytic dissociation takes place and do not in the case of ordinary dissociation, the number of phenomena which accompany the former is greater than that associated with the latter. On account of the delicacy of the electrical methods of measurement, no other dissociation has been so thoroughly studied, and from so many points of view, as that of electrolytes into ions.

## CHAPTER XII.

### Equilibrium between Several Electrolytes.

**Isohydric Solutions.**—In Chapter X. we have discussed the equilibrium between the ions and the undissociated part of an electrolyte; but, of course, when several electrolytes are simultaneously present in the solution the relationships become somewhat more complicated.

Let us consider aqueous solutions of two acids which obey Ostwald's dilution law (see p. 162). Let there be  $a$  gram-ions of one acid,  $A$ , in volume  $V_A$ , and  $\beta$  gram-ions of the other acid,  $B$ , in volume  $V_B$ . Then if  $\frac{a}{V_A} = \frac{\beta}{V_B}$ , no change in the dissociation will occur when the two solutions are mixed. For if  $K_A$  is the dissociation constant of the first acid, then for the solution we have the following equation:—

$$\left(\frac{a}{V_A}\right)^2 = K_A \cdot \frac{n - a}{V_A}$$

where  $n$  is the number of gram-molecules of the acid (which is supposed to be monovalent). After mixing, the quantity  $a$  of the anion from acid  $A$  will be changed to  $a_1$ , and the quantity  $\beta$  of the anion of acid  $B$  becomes  $\beta_1$ . The quantity of positive (H) ion from  $A$  becomes  $a_1 + \beta_1$ , and the volume is changed from  $V_A$  to  $V_A + V_B$ . Consequently, after mixing, we have—

$$\frac{a_1}{(V_A + V_B)} \cdot \frac{a_1 + \beta_1}{(V_A + V_B)} = K_A \cdot \frac{n - a_1}{(V_A + V_B)}$$

If  $\frac{\beta_1}{V_B} = \frac{a_1}{V_A}$ , the two equations are similar, only  $a$  is replaced by  $a_1$ . Therefore  $a$  is equal to  $a_1$ , and in the same way it can be shown that  $\beta$  is equal to  $\beta_1$ . This relationship, developed for weak acids, can also be applied to strong electrolytes. Solutions which on mixing do not change their dissociations (and consequently their other properties) are extremely important, and are called *isohydric solutions*. The conductivity of a mixed solution can thus be easily arrived at; we have only to think of the solvent water so distributed between the dissolved substances that the solutions formed are isohydric, *i.e.* contain the same number of gram-ions per litre. If the substances contain a common ion, no change in dissociation takes place on mixing, and the conductivity can be calculated as the sum of the conductivities of the several ions.

If two salts, as, for instance, potassium chloride and sodium nitrate, have not a common ion, there are formed in the mixed solution the other two possible salts, in this case potassium nitrate and sodium chloride. It can easily be proved that for the four salts  $KCl$ ,  $KNO_3$ ,  $NaCl$ , and  $NaNO_3$ , present in the quantities  $M_1$ ,  $M_2$ ,  $M_3$ , and  $M_4$ , and whose degrees of dissociation are  $a_1$ ,  $a_2$ ,  $a_3$ , and  $a_4$ , there exists the following relationship:—

$$a_1M_1 \times a_4M_4 = a_2M_2 \times a_3M_3.$$

**Precipitation.**—The connection just mentioned is valid for homogeneous systems, but it must be slightly modified when one of the reacting substances is difficultly soluble. Silver acetate in water is a case in point. The saturated solution of this substance at  $18.6^\circ$  is 0.0593-normal, and the difficult solubility is due to the fact that water can dissolve only little of the undissociated part of this salt. The dissolved quantity of the salt may as a close approximation be assumed to be constant; let it be represented by  $C(AgCH_3COO)$ . If a foreign substance be added to the solution, which substance on dissolving gives (silver ions or)

acetate ions, we have, according to the law of mass action, before the addition—

$$C_0(\text{Ag}) \times C_0(\text{CH}_3\text{COO}) = K \times C(\text{AgCH}_3\text{COO}),$$

and after the addition—

$$C_2(\text{Ag}) \times C_1(\text{CH}_3\text{COO}) = K \times C(\text{AgCH}_3\text{COO}).$$

$C(\text{AgCH}_3\text{COO})$  is the same in both cases. On the other hand,  $C_1(\text{CH}_3\text{COO})$  is greater than  $C_0(\text{CH}_3\text{COO})$  on account of the addition of  $\text{CH}_3\text{COO}$  ions from sodium acetate or other compound. Consequently  $C_2(\text{Ag})$  must be just as much smaller. The amount of dissolved silver is therefore smaller in the second case than in the first. This agrees with the long-known fact that the solubility of many difficultly soluble salts is decreased by the addition of neutral salts with a common ion. Apparent exceptions to this rule, *e.g.* increase of solubility of silver cyanide by the addition of potassium cyanide, are due to the formation of double salts (such as  $\text{KAg}(\text{CN})_2$ ). In order to effectively precipitate difficultly soluble salts, *e.g.* barium sulphate, it is usually recommended in analytical descriptions to add excess of the precipitant, in this case barium chloride or sulphuric acid.

Van't Hoff (1) first suggested that the product of the ionic concentrations of a difficultly soluble electrolyte is constant.

As already mentioned (p. 164), salts deviate from the law of mass action so that their dissociation constants,  $K$ , must be replaced in this relationship by a function of the quantity of the ions present, therefore the equations given cannot claim an absolute exactitude.

Another circumstance aids the deviation of the equations from exactness. The solubility of these difficultly soluble substances (in water) is frequently considerably influenced by the presence of even quite small quantities of foreign substances, such as alcohols, cane sugar, glycerol, etc. Euler (2) and Rothmund (3) have shown from their own and previous experiments that ions possess in a marked

degree the power of influencing the solubility of other substances present in the solution. It might well happen that the undissociated part of the silver acetate in the example cited did not remain constant after increasing quantities of sodium acetate had been added. As a matter of fact, experiments indicate that the solubility of undissociated silver acetate is appreciably depressed by the addition of sodium acetate.

These two disturbing factors act in opposite directions. They thus partially compensate each other (in cases so far investigated almost exactly), so that the view of the constancy of the ionic products is far more applicable than might have been supposed.

#### Distribution of a Base between Two Acids (Avidity).

—The condition of equilibrium

$$a_1M_1 \times a_4M_4 = a_2M_2 \times a_3M_3$$

is of very great importance for determining the relative strengths of acids and bases. If, for instance, acetic acid is added to a solution of sodium formate, some formic acid and some sodium acetate will be formed. By applying the above equation we obtain as result that the ratio between the quantity of formate and that of acetate is equal to the ratio of the square roots of the dissociation constants of the corresponding acids. The ratio between the degrees of dissociation of the two acids at equal concentrations is also the same. The distribution of a base between two acids can easily be calculated by means of this rule. Thomsen and Ostwald have experimentally ascertained the value of this distribution for several cases. Thomsen (4) observed the heat change which accompanied the addition of an acid to the solution of a salt of the other acid, whilst Ostwald (5) determined the change of volume or of the refractive power under the same conditions. The fact that a change does take place indicates that a reaction has occurred, and from the magnitude of the change the extent of the reaction can be calculated. The following table contains some distribution ratios. The

value 0.76 for the ratio between nitric acid and dichloroacetic acid signifies that on mixing three equal volumes of normal solutions of these two acids and sodium hydroxide, 76 per cent. of the alkali is converted into nitrate and 24 per cent. into dichloroacetate. The calculated values are given as well as those found by experiment. According to Thomsen's phraseology, nitric acid has an *avidity*  $\frac{76}{24} = 3.17$  times greater than that of dichloroacetic acid. Except in the case of the ratio between formic acid and glycollic acid, the experimental values agree well with those calculated, and this exception is no doubt due to an error of observation.

The numbers given were obtained by Ostwald, and apply to the ordinary temperature.

	Observed.	Calculated.
Nitric acid : Dichloroacetic acid . . . . .	0.76	0.69
Hydrochloric acid : " " . . . . .	0.74	0.69
Trichloroacetic acid : " " . . . . .	0.71	0.69
Dichloroacetic acid : Lactic acid . . . . .	0.91	0.95
Trichloroacetic acid : Monochloroacetic acid . . . . .	0.92	0.91
" " : Formic acid . . . . .	0.97	0.97
Formic acid : Lactic acid . . . . .	0.54	0.56
" " : Acetic acid . . . . .	0.76	0.75
" " : Butyric acid . . . . .	0.80	0.79
" " : Isobutyric acid . . . . .	0.79	0.79
" " : Propionic acid . . . . .	0.81	0.80
" " : Glycollic acid . . . . .	0.44	0.53
Acetic acid : Butyric acid . . . . .	0.53	0.54
" " : Isobutyric acid . . . . .	0.53	0.54

**Strength of Acids and Bases.**—For a long time it has been customary to determine the strength of acids by measuring their avidities, which, as shown above, are proportional to their degrees of dissociation. Now, since the strength of acids varies a good deal, it was assumed, in agreement with the conception formulated by Bergman, that the stronger acids replaced the weaker from their salts. Berthelot (6) has given us a large amount of data as to which of two acids is the stronger, or, according to his view, which

completely displaces the other from its salts. He found that the acid which conducts best is the stronger. This suggested to me (in 1884) that the strength of an acid is proportional to its conductivity ( $\gamma$ ), or, more correctly, to its degree of dissociation (according to our more recent theories). A corresponding connection is shown by bases.

**The Dissociation of Water.**—In my theoretical discussions ( $\gamma$ ) of 1884 I regarded water as either a weak acid or a weak base. If we dissolve alkali salts of weak acids, such as carbonic acid or hydrocyanic acid, in water, the solutions have an alkaline reaction indicating the presence of free alkali. Water, HOH, therefore replaces part of the weak acid HCN from the KCN and forms the compound KOH, just as any recognised weak acid would do. This view has been confirmed by later investigations. Shields (8) found 2·4 per cent. of free alkali in a  $\frac{1}{40}$ -normal solution of potassium cyanide, and 7·1 per cent. in a sodium carbonate solution of the same concentration, whilst in a 0·1-normal solution of sodium acetate he found 0·008 per cent. of alkali. These determinations were made by ascertaining the powers of the solutions to effect the decomposition of ethyl acetate.

Shields determined the extent of decomposition of an acetate solution into acid and base, the so-called *hydrolysis*, and from this we can calculate the strength of water (as an acid) compared with that of acetic acid. Since the degree of dissociation of acetic acid is known, it is possible to calculate the degree of dissociation of water. I (9) have calculated this to be  $2\cdot03 \times 10^{-9}$  at  $25^\circ$ , so that in a litre of water there is  $1\cdot113 \times 10^{-7}$  dissociated gram-molecule.

In aqueous solution methyl acetate is slowly decomposed into methyl alcohol and acetic acid. In this case it is the hydroxyl ion of the water which is the active agent. By comparing the action of water with that of a solution of sodium hydroxide, Wijs (10) determined the number of dissociated gram-molecules in a litre of water to be  $1\cdot2 \times 10^{-7}$  at  $25^\circ$ , which agrees well with the value given above.

From the electromotive force of the element  $H_2(Pt) | \text{Base} | \text{Acid} | H_2(Pt)$ , Ostwald (11) determined the degree of dissociation of water, and found  $7 \times 10^{-7}$  to  $7.4 \times 10^{-7}$ .

From the hydrolysis of aniline hydrochloride, Bredig (12) found the degree of dissociation  $6 \times 10^{-7}$ . These two last values do not agree so well with those found by Wijs and myself.

By repeated distillation of water in a vacuum, Kohlrausch and Heydweiller (13) obtained water much purer than any which had previously been prepared, and found that it conducted about 20 times worse than the best sample of water distilled in the air. The conductivity at  $18^\circ$  was  $386 \times 10^{-10}$  (expressed in the new units).

Since  $\lambda_\infty$  for  $OH = 172$  and for  $H$  it is  $314$ , the number of dissociated gram-molecules per litre at  $18^\circ$  is  $0.8 \times 10^{-7}$ . At  $25^\circ$  the value is  $1.05 \times 10^{-7}$ . The degree of dissociation, which is  $55.5$  times smaller, has therefore the value  $1.4 \times 10^{-9}$  at  $18^\circ$ , and  $1.9 \times 10^{-9}$  at  $25^\circ$ .

The agreement between the values found by these different methods for the dissociation of water is extremely good, and Kohlrausch regards this as the best proof of the correctness of the dissociation theory. Kohlrausch and Heydweiller give the following numbers for the number of gram-ions of hydrogen ( $A$ ) in a litre of water at the various temperatures:—

Temp.	$0^\circ$	$10^\circ$	$18^\circ$	$26^\circ$	$34^\circ$	$42^\circ$	$50^\circ$
$10^7 A$	0.35	0.56	0.80	1.09	1.47	1.93	2.48.

**Heat of Dissociation of Water.**—The influence of temperature on the dissociation of water can be calculated as follows. According to the result arrived at on p. 94, the equation—

$$\frac{d \ln K}{dT} = \frac{\mu}{RT^2}$$

can be applied to the dissociation of water, where  $K$  is the dissociation constant,  $T$  the absolute temperature, and  $\mu$  the heat of dissociation. The value of  $R$  is  $1.99$  cal. (see p. 13)

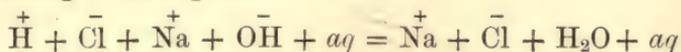
For water, which contains 55.5 gram-molecules in a litre, we have—

$$K \times 55.5(1 - a) = (55.5a)^2,$$

or, since the degree of dissociation,  $a$ , is small in comparison with 1—

$$d \ln a = \frac{1}{2}d \ln K.$$

Therefore, if we know  $\mu$ , *i.e.* the heat which is absorbed when a gram-molecule of water dissociates into hydrogen and hydroxyl ions, we can calculate the change of  $a$  with temperature. In order to find  $\mu$  we make the following consideration. Suppose we have 1 gram-molecule of hydrochloric acid and 1 gram-molecule of sodium hydroxide each in such dilution that we may assume without appreciable error that they are completely dissociated. Leaving the water out of account, these solutions contain 1 gram-equivalent of each of the ions  $\overset{+}{\text{H}}$  (1 gram) and  $\bar{\text{Cl}}$  (35.45 grams), and of the ions  $\overset{+}{\text{Na}}$  (23 grams) and  $\bar{\text{OH}}$  (17 grams) respectively. When these two solutions are mixed, sodium chloride in the dissociated condition, *i.e.*  $\overset{+}{\text{Na}} + \bar{\text{Cl}}$ , and water are formed according to the equation—



where  $aq$  denotes the water present in the system in large quantity. The only change, therefore, which has actually taken place is the union of a gram-ion of  $\overset{+}{\text{H}}$  with a gram-ion of  $\bar{\text{OH}}$  to form a gram-molecule of water. The heat developed was determined by Thomsen to be 14,247 cal. at 10.14° and 13,627 cal. at 24.6°. Evidently this is the same quantity of heat ( $\mu$ ) which would be absorbed when a gram-molecule of water dissociates into  $\overset{+}{\text{H}}$  and  $\bar{\text{OH}}$ . Kohlrausch was then able to calculate the change of  $K$  and  $a$  with temperature after I had pointed out the meaning of the heat of neutralisation. The agreement between the calculated

and observed conductivities of water as found by Kohlrausch and Heydweiller is very perfect, as the numbers in the following table show. The equivalent conductivity ( $\lambda_{\infty}$ ) is taken as equal to  $340 + 8t$ .

SPECIFIC CONDUCTIVITY ( $\kappa$ ) OF WATER.

Temperature.	$10^{\circ}\kappa$ (observed).	$10^{\circ}\kappa$ (calculated).
$-2^{\circ}$	0.0107	0.0103
$+4^{\circ}$	0.0162	0.0158
$10^{\circ}$	0.0238	0.0236
$18^{\circ}$	0.0386	0.0386
$26^{\circ}$	0.0606	0.0601
$34^{\circ}$	0.0890	0.0901
$42^{\circ}$	0.1294	0.1305
$50^{\circ}$	0.1807	0.1839

**Heat of Neutralisation.**—From the description given above, it follows that the heat of neutralisation must be the same for all dilute strong acids and bases, independent of the nature of the acid and base, since in all cases only the  $\overset{+}{\text{H}}$  and  $\overset{-}{\text{OH}}$  combine to form  $\text{H}_2\text{O}$ . This fact, which had been known for a very long time, seemed peculiar until the dissociation theory (1884)<sup>1</sup> gave the key to the explanation.

The development can, however, only be applied to strong acids and bases, because at the dilutions at which we commonly work the weak acids and bases are only dissociated to a slight extent. For these also, however, the heat of neutralisation can be determined from electrical measurements.

If we investigate a solution of succinic acid, for example, we find that in 0.28-normal solution (the concentration used by Thomsen) the acid is only dissociated to the extent of 1.5 per cent. at  $21.5^{\circ}$ . In order, therefore, to compare this acid with the strong acids, we must first supply so much heat as is necessary for the dissociation of the remaining 98.5 per cent.

<sup>1</sup> It may not be out of place here to rectify the common belief that the dissociation theory was suggested in 1887. As a matter of fact, it was, in a less perfect form, propounded by Arrhenius in his Inaugural Dissertation in 1884.—TR.

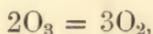
Then the process would become exactly like the former. The heat of dissociation,  $\mu$ , of the succinic acid can be calculated from the change of the dissociation constant with the temperature, by means of the same equation as we have applied to water. If  $\mu$  thus found be multiplied by 0.985, and the product subtracted from the heat of neutralisation of strong acids, we must obtain the correct value for the neutralisation of succinic acid. I (*14*) have calculated the heat of neutralisation of several acids in this way, and have obtained values which agree with those determined calorimetrically by Thomsen.

## HEAT OF NEUTRALISATION AT 21.5°.

Acid.	Observed.	Calculated.
Hydrochloric acid . . . . .	13,447	13,740
Hydrobromic acid . . . . .	13,525	13,750
Nitric acid . . . . .	13,550	13,680
Acetic acid . . . . .	13,263	13,400
Propionic acid . . . . .	13,598	13,480
Butyric acid . . . . .	13,957	13,800
Succinic acid . . . . .	12,430	12,400
Dichloroacetic acid . . . . .	14,930	14,830
Phosphoric acid . . . . .	14,959	14,830
Hypophosphorous acid . . . . .	15,409	15,160
Hydrofluoric acid . . . . .	16,320	16,270

The heat of neutralisation of most acids is evidently greater than the heat of dissociation of water, which I have calculated to be 13,212 cal. at 21.5°. The cause of this is that the heat of dissociation of most acids is negative, *i.e.*  $\frac{d \ln K}{dT}$  is negative, or, in other words, the dissociation constant, and consequently also the degree of dissociation, decreases with rising temperature. This may appear strange since in the ordinary dissociations the degree increases with rising temperature. But cases of ordinary dissociation are known, *e.g.* the decomposition of hydrogen selenide and hydrogen telluride into the elements, in which, at any rate at

certain temperatures, the dissociation decreases as the temperature rises. The decomposition of ozone into oxygen—



which takes place with evolution of heat, is another example. The fact that the degree of dissociation of electrolytes as a rule decreases with rising temperature is perhaps connected with the fact that the dielectric constant of water decreases as the temperature rises (by about 0.6 per cent. per degree at 0°, according to Abegg). According to the theory of J. J. Thomson (15) and Nernst (16), the degree of dissociation should increase with the dielectric constant. It must be noted, however, that the heat of neutralisation of many acids is smaller than the heat of dissociation of water, and therefore their degree of dissociation must increase with rising temperature, as is the case with succinic acid, and to a greater extent with hydrocyanic acid (heat of neutralisation 3000 cal.).

**Electrolytes with a Negative Temperature Coefficient for the Conductivity.**—As the degree of dissociation of several acids, as well as that of some salts, decreases with rising temperature, it may happen that the product  $\alpha\lambda_{\infty}$  which is equal to  $\lambda_{\infty}$ , *i.e.* that the equivalent conductivity, and with it the specific, diminishes as the temperature rises; in other words, that the temperature coefficient becomes negative, although as a rule  $\lambda_{\infty}$  (for acids) increases by about 1.7 per cent. per degree. It is to be expected that this will most probably be the case with acids which have a high heat of neutralisation. The theory also predicts that this will happen more readily at high than at low temperatures. Experiment shows that the temperature coefficient for hypophosphorous acid above 54° and for phosphoric acid above 74° (both in normal solution) is negative. These results were quite unexpected, for it was formerly supposed that the conductivity of all electrolytes must increase as the temperature was raised.

**Neutralisation Volume.**—On mixing a solution of an

acid with one of a base, a change of volume ensues which amounts to 19 c.c., when each solution (dilute) contains a gram-equivalent. This is the *neutralisation volume*. This regularity, like that of the heat of neutralisation, only holds good for strong acids and bases. For weak electrolytes a correction must be introduced, the dissociation volume, *i.e.* the change of volume which takes place when a gram-molecule of acid splits up into its ions. This volume can be theoretically derived from the formula developed by Planck (17)—

$$RT \frac{d \ln K}{dp} = \Delta_v$$

where the constant  $R$  has the value 81.8 (atmospheres per square centimetre, see p. 26),  $p$  denotes the pressure in atmospheres,  $K$  the dissociation constant of the acid, and  $\Delta_v$  the dissociation volume in c.c. at the absolute temperature  $T$ .

Fanjung (18) investigated the influence of pressure on the dissociation constant of weak acids, and calculated the values of  $\Delta_v$  from his results. He found that  $\Delta_v$  is always negative, which proves that the ions occupy a smaller volume than the undissociated molecules, and from this it follows that the dissociation increases with rising pressure (see p. 99). These results were compared with those calculated from Ostwald's experiments on the increase of volume on neutralisation, and, as the following table shows, a very perfect agreement was found:—

NEUTRALISATION VOLUMES.

Acid.	Calculated by Fanjung.	Observed by Ostwald.
	c.c.	c.c.
Formic acid . . . . .	8.7	7.7
Acetic acid . . . . .	10.6	10.5
Propionic acid . . . . .	12.4	12.2
Butyric acid . . . . .	13.4	13.1
Isobutyric acid . . . . .	13.3	13.8
Lactic acid . . . . .	12.1	11.8
Succinic acid . . . . .	11.2	11.8
Malic acid . . . . .	10.3	11.4

It is remarkable that the ions in the solution occupy a smaller volume than the compound molecules. In this branch of our subject, however, many peculiarities are to be found, as, for instance, the fact that certain substances (sodium hydroxide, etc.) cause such a contraction of the water that the solution has a smaller volume than the solvent used.

It can easily be seen that all strong acids and bases must have almost the same neutralisation volume; that this is actually the case may be gathered from the following numbers:—

Acid.	$\Delta_v$ on neutralising with	
	KOH	NaOH
HNO <sub>3</sub>	20.05	19.77
HCl	19.52	19.24
HBr	19.63	19.34
HI	19.80	19.54

For ammonia the volume change on neutralising with a strong acid amounts to 26 c.c.

The opinion of Nernst and Drude (19) is that the ions influence the volume of the water on account of the strong electric field which they give rise to. All liquids, whose dielectric constant is increased by pressure—and this is probably always the case (20)—suffer a contraction in a strong electric field. This phenomenon is known as *electrostriction*. The ions in water, alcohol, or other solvent cause such an electrostriction.

## CHAPTER XIII.

### Calculation of Electromotive Forces.

**Introduction.**—We have treated in the preceding chapters, with the aid of the theory of electrolytic dissociation, of the several physical and chemical properties of homogeneous electrolytic solutions; and we have developed the laws which regulate the equilibrium which obtains between two phases of a heterogeneous system. We now pass on to the consideration of the free energy which can be obtained when an electrolyte passes from one solution to another, or from one phase to another, and shall study particularly those cases in which the transport of material is associated with a transport of electricity. In such cases the whole of the mechanical energy may be transformed into electric energy, and the latter can be very easily estimated by measuring the electromotive force produced simultaneously with the mass transport.

This mass transport (or transport of material) may consist partly in removing ions from one solution to another, and partly in the separation of the ions at the electrodes. The ions are always accompanied by their electric charges, but when they separate at the electrode they are quickly transformed into uncharged molecules, and give up their electricity to the electrode. In practice, this latter process is by far the more important, although the theory has been most completely developed for the former.

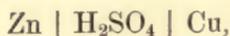
The greatest progress in the theory of this subject has been made by Helmholtz and Nernst. By applying the second law of thermodynamics, Helmholtz showed the connection between

the heat absorbed in a galvanic element, its electromotive force, and the change of this with temperature. He succeeded also in calculating, on thermodynamic principles, the electromotive force of certain concentration cells.

Nernst treated the subject more from a kinetic point of view, and, by means of the theory of osmotic pressure, calculated the electric forces associated with the transport of the ions. Here, too, the kinetic view gives us a better picture of the process, but the thermodynamic method gives more trustworthy results. Nernst showed how, by the kinetic method, we can calculate the single electromotive force at the surface of contact of two liquids, whilst by the other method only the total effect can be obtained.

**Galvanic Elements.**—These may consist of a combination of conductors of the first and second class, metals and electrolytes, or, as in the liquid cells, only of electrolytes. It is true that in the liquid cells there are always places of contact between metals and electrolytes, but these are so arranged that they exactly balance each other. Liquid elements are of great interest, because Nernst first gave the mechanical description of the production of an electromotive force for them. They are not, however, practically used as sources of electricity.

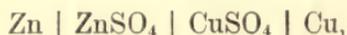
Of the so-called hydro-elements, the best known is the Volta pile—



in which zinc passes into solution and hydrogen separates at the copper pole. This is a type of the *irreversible elements*. The hydrogen is evolved and the original condition is not re-established when a current is passed through the element in the opposite direction; in this case copper is dissolved and hydrogen is evolved at the zinc pole when the current is passed from copper to zinc through the solution.

In the theoretical respect, the so-called *reversible elements* behave much more simply; in these the electrodes are non-polarisable, *i.e.* surrounded by an electrolyte, the positive ion

of which is the same as the metal of the electrode. The commonest of these elements is the Daniell cell—



in which zinc is dissolved with formation of zinc sulphate, and copper is deposited from the copper sulphate. When a current is passed in the opposite direction, *i.e.* from the copper to the zinc through the solutions, the deposited copper is dissolved and zinc is separated, so that the original condition can be re-established. Combinations of the type of the Clark cell (see p. 124) are also reversible. The commonly used Bunsen and Leclanché cells belong to the group of irreversible elements.

In order to express electric energy in the ordinary units, we recall what has already been said (pp. 6 and 11). Electrical work is expended when a given quantity of positive electricity,  $q$  coulombs, is brought from a place of lower potential,  $V_0$  volts, to a place of higher potential,  $V_1$  volts. The work done then amounts to—

$$q(V_1 - V_0) \text{ volt-coulombs.} \quad E = J.$$

The same work has to be done to bring the quantity  $q$  of negative electricity from the higher potential  $V_1$  to the lower potential  $V_0$ , and the calculation for the simultaneous transport of the two electricities (positive and negative) can be made in an analogous manner.

Now, according to definition, the value of a volt-coulomb is—

$$\begin{aligned} 1 \text{ volt-coulomb} &= 10^7 \text{ ergs} = 0.1018 \text{ kilogram-metres} \\ &= 0.239 \text{ cal.} \end{aligned}$$

To separate a gram-equivalent of a metal 96,500 coulombs are required; the work done for such a quantity of electricity is therefore—

$$23,070(V_0 - V_1) \text{ cal.}$$

**Transformation of Chemical into Electrical Energy in**

**a Daniell Cell. Thomson's Rule.**—We may now go more fully into the processes which take place in a Daniell element. If this develops 96,500 coulombs, then at the same time a gram-equivalent (32·7 grams) of zinc is dissolved, and a gram-equivalent (31·8 grams) of copper is deposited. A certain amount of heat is evolved during this change, and can be determined calorimetrically; it amounts to 25,065 cal. If the electric work done by the element were exactly equal to the quantity of heat evolved, or, in other words, if the heat evolved in the Daniell cell were completely changed into electric work, it could move the 96,500 coulombs against an electromotive force  $V_0 - V_1$ , which is given by the relationship—

$$23,070(V_0 - V_1) = 25,065.$$

The value of  $V_0 - V_1$  would then be 1·086 volts, *i.e.* the element would be able to bring the unit charge of 96,500 coulombs from potential 0 to potential 1·086 volts. If we connect the zinc pole of the cell with the earth, and the copper pole with a condenser at potential  $P$ , the electricity can pass to this condenser, *i.e.* the condenser can be charged, so long as  $P$  is smaller than the electromotive force of the element. The greatest work which an element can do in this way is to charge a condenser to the same potential as the electromotive force of the element.

If our assumption be correct, that the Daniell element changes the whole of the chemical energy used up into electrical energy, then its electromotive force must be 1·086 volts. Experiment shows that the electromotive force almost reaches this value (1 dll. = about 1·10 volts, see p. 124), and on this account it was for a long time believed that the electromotive force of an element could be calculated from the heat value (per gram-equivalent) of the chemical process taking place by simply dividing this (expressed in gram-calories) by the number 23,070. According to this, if  $E$  is the electromotive force and  $H$  the quantity of heat developed by the chemical reaction per gram-equivalent, then—

$$E = \frac{H}{23,070}$$

This idea was first suggested by Helmholtz (1), and was afterwards taken up by Lord Kelvin (W. Thomson) (2), and is known as the Thomson rule.

Several attempts, notably by Raoult and J. Thomsen, have been made to confirm the Thomson rule, and it has been found that in the cases investigated the experimental values agree well with the theory. Thus, Thomsen (3) obtained the following values for the electromotive forces of several elements, 1 dll. being taken as unit:—

Element.	Heat evolution.	Electromotive force.	
		Calculated.	Observed.
Zn   H <sub>2</sub> SO <sub>4</sub> + 100 aq   CuSO <sub>4</sub>   Cu	25065	1.00	1.00
Zn   H <sub>2</sub> SO <sub>4</sub>   CdSO <sub>4</sub>   Cd . . .	8295	0.33	0.33
Zn   HCl   AgCl   Ag . . . . .	27040	1.08	1.06
Zn   H <sub>2</sub> SO <sub>4</sub>   HNO <sub>3</sub>   C . . . . .	48040	1.92	1.86
Zn   H <sub>2</sub> SO <sub>4</sub>   HNO <sub>3</sub> + 7H <sub>2</sub> O   C . . . . .	41405	1.65	1.69
Cu   H <sub>2</sub> SO <sub>4</sub>   K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> + H <sub>2</sub> SO <sub>4</sub>   C	49895	1.99	1.85
Cu   H <sub>2</sub> SO <sub>4</sub>   HNO <sub>3</sub>   C . . . . .	22995	0.92	0.88
Cu   H <sub>2</sub> SO <sub>4</sub>   HNO <sub>3</sub> + 7H <sub>2</sub> O   C . . . . .	16340	0.65	0.73
Fe   FeCl <sub>2</sub>   Fe <sub>2</sub> Cl <sub>6</sub>   C . . . . .	22215	0.89	0.90

When concentrated nitric acid was used, Thomsen assumed that nitrogen peroxide (N<sub>2</sub>O<sub>4</sub>) was formed, and remained dissolved in the liquid; when more dilute nitric acid (HNO<sub>3</sub> + 7H<sub>2</sub>O) was used, he assumed that nitric oxide (N<sub>2</sub>O) was produced. Consequently there was a different heat evolved when these were employed. In the chromic acid cell it was assumed that chromic oxide was formed, and in the ferric chloride cell that ferrous chloride was produced.

**Criticism of Thomson's Rule.**—When the Thomson rule was more fully examined difficulties arose. The cause of the deviations was sought for in so-called secondary processes by which heat is evolved, but which were supposed to have no influence on the electromotive force.

At that time it was believed, as Volta had assumed, that the seat of the electromotive force was at the place of contact of the two metals, in the Daniell cell at the place of contact of the copper and the zinc; the electromotive force between these two metals was supposed to be about 1 volt. Edlund (4) determined how much heat is evolved when a definite quantity of electricity is passed through a junction of copper and zinc (the Peltier effect). According to the above principle we should be able to calculate this quantity of heat. The observed result was, however, very much smaller than expected, the potential difference for  $\text{Cu} \mid \text{Zn}$  being only 0.006 volt instead of 1 volt. This result induced Edlund to investigate the correctness of the Thomson rule.

In his discussion he made use of some results which had been obtained by Raoult. Raoult observed that in the electrolysis of water in a voltameter, besides the evolution of gases, there is a local heating which is not due to the friction of the ions against the liquid, and is therefore different from the Joule effect. In these experiments Raoult also measured the electromotive force.

Edlund gave the following explanation. In the voltameter a back electromotive force,  $e$ , is produced. If 96,500 coulombs are moved against this force, then for each volt there will be an evolution of heat amounting to 23,070 cal. (23,900 cal. for 1 dll., according to the numbers then accepted). In one case, for instance, the back electromotive force was 2.04 dll., and there should therefore be an evolution of 48,756 cal. If we subtract from this the quantity of heat, 34,462 cal., required for the decomposition of the water, we obtain for the local heating 14,294 cal., whilst Raoult found 14,898 cal. Several similar experimental results of Raoult were calculated with the same success (1869). Edlund later showed that in the electrolysis of silver salts a local cooling may take place. Now, if Thomson's rule were correct, such local heat effects should not occur, but the heat necessary for the decomposition should be exactly sufficient to produce the electromotive force of the element.

Braun (5) made a number of observations with elements which do not follow the Thomson rule, which continued to be supported by Fr. Exner. W. Gibbs (6) proved that with electrodes which can be used at their melting points (bismuth, lead, tin) there is no change of the electromotive force at this point, as there should be according to the Thomson rule.

**Helmholtz's Calculation.**—In 1882 Helmholtz (7) gave the following simple deduction from the second law of thermodynamics. In the diagram (Fig. 41)  $V$  represents the electromotive force of an element, and the quantity of electricity,  $q$ , which passes through the element is chosen as abscissa. The work is measured by the product  $q \cdot V$ . In the first place, let the quantity of electricity  $q$  pass through the element, which is supposed to be a perfectly reversible one, at the absolute temperature  $T + dT$ , and so do the greatest possible (maximum) work. If the electromotive force of the element is  $P$  at the temperature  $T$ , then at  $T + dT$  it is—

$$P + \frac{dP}{dT} \cdot dT = P + dP.$$

The work done by the element at  $T + dT$  is therefore—

$$A + dA = \left( P + \frac{dP}{dT} dT \right) q.$$

The temperature of the element is now allowed to fall to  $T$ , and by doing mechanical work (say, by a dynamo) the quantity  $q$  is forced through the element in the opposite direction. The electromotive force of the element is now reduced to  $P$ , therefore the work expended by the dynamo is—

$$A = P \cdot q.$$

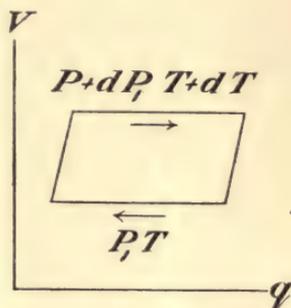


FIG. 41.

$dW =$

The completely reversible element has now returned to its initial condition, leaving the temperature out of account, for the same quantity of electricity has passed through it in both directions. Practically no work has to be done to raise its temperature by  $dT$ .

Let the quantity of electricity  $q$  be 96,500 coulombs, and the heat evolved in the chemical process be  $W$ , then at the temperature  $T + dT$  the quantity of heat  $\{(P + dP)23,070 - W\}$  cal. is taken from the element (and therefore from the surrounding medium which keeps the temperature of the element constant). At the temperature  $T$  the quantity of heat  $(P \times 23,070 - W)$  cal. is introduced into the element, whilst the quantity  $23,070 \cdot dP$  is transformed into work. Now, if a quantity of heat,  $Q$  cal., passes from the temperature  $T + dT$  to  $T$ , and if the work done thereby is  $dA$  cal., then, according to the second law of thermodynamics—

$$\frac{dA}{Q} = \frac{dT}{T}$$

In the case taken,  $dA = 23,070dP$ , and  $Q = P \times 23,070 - W$ . Therefore—

$$\frac{23,070dP}{23,070P - W} = \frac{dT}{T}$$

If  $\frac{dP}{dT} = 0$ , *i.e.* if the electromotive force of the element does not change with the temperature—

$$P = \frac{W}{23,070}$$

and in this case Thomson's rule is correct. As a matter of fact, the electromotive force of a series of elements is almost independent of the temperature, for instance, the Daniell element, and for these Thomson's rule is applicable.

Elements are known which, when functioning, absorb heat—their electromotive force increases with rising

temperature—and others are known which give up heat to the surrounding medium, and their electromotive force decreases as the temperature rises.

Helmholtz's deduction has been fully confirmed by experiment, most thoroughly by Jahn (8), who measured the heat evolution by means of an ice calorimeter. The following table gives the results of his experiments. In the column headed *Calc.* are given the values of  $23,070 \times P - W$ , calculated by Helmholtz's method from the observed temperature coefficients, and in the column headed *Obs.* the calorimetrically observed values are given. The experiments were made at  $0^\circ$  ( $273^\circ$  absolute).

Element.	P.	23070P.	W.	23070P - W.	
				Obs.	Calc.
Cu   CuSO <sub>4</sub> + 100H <sub>2</sub> O   ZnSO <sub>4</sub> + 100H <sub>2</sub> O   Zn .	1.096	25263	25055	208	214
Cu   Cu(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> + 100H <sub>2</sub> O   Pb(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> + 100H <sub>2</sub> O   Pb .	0.476	10980	8261	2718	2422
Ag   AgCl   ZnCl <sub>2</sub> + 100H <sub>2</sub> O   Zn . . . . .	1.031	23753	26085	-2330	-2574
Ag   AgCl   ZnCl <sub>2</sub> + 50H <sub>2</sub> O   Zn . . . . .	1.017	23448	24541	-1093	-1322
Ag   AgCl   ZnCl <sub>2</sub> + 25H <sub>2</sub> O   Zn . . . . .	0.974	22454	23573	-1169	-1270
Ag   AgBr   ZnBr <sub>2</sub> + 25H <sub>2</sub> O   Zn . . . . .	0.841	19386	19968	-582	-667
Ag   AgNO <sub>3</sub>   Pb(NO <sub>3</sub> ) <sub>2</sub>   Pb . . . . .	0.932	25435	21490	3975	3945
Ag   AgNO <sub>3</sub>   Cu(NO <sub>3</sub> ) <sub>2</sub>   Cu . . . . .	0.458	15020	10560	4460	4460
Hg   Hg <sub>2</sub> O   KOH   KCl   HgCl   Hg (Bugarszky)	0.328	7566	-3820	11386	11276

From the numbers quoted, it can be seen that the value of  $23,070P$  is sometimes greater and sometimes smaller than  $W$ , the difference amounting to even as much as 50 per cent. Indeed, in Bugarszky's element these two values have different signs. It is noteworthy that such a small addition of water to the zinc chloride in the element Ag - Zn is able to produce such a great change in its behaviour.

**Free and Bound Energy.**—As already mentioned, the view was previously entertained that the whole heat energy of an element might be transformed into electric energy. Helmholtz, however, showed by the above reasoning that this is not always the case, and he therefore introduced the idea of *free energy* as that part of the total energy which can be completely transformed into mechanical work. The energy  $23,070 \cdot P$  in the above case, is evidently of this kind, for

electric energy can (theoretically) be totally converted into mechanical work. (Practically, of course, the energy transformation cannot be carried out without loss of work, because no machine works ideally; the best electric motors give a yield of about 95 per cent. in mechanical work.) The free energy of an element amounts therefore to  $23,070 \cdot P$  for every gram-equivalent decomposed, when  $P$  is the electromotive force of the element in volts. If  $W$  is the corresponding total energy, measured by the heat change, the difference,  $W - 23,070 \cdot P$ , is the *bound energy*.

The free energy of a system plays a very important part; it gives, so to say, the maximum work which the system is capable of doing when a certain change takes place. The complete using up of the free energy is only conceivable in the case of reversible processes; and in this connection it must be noticed that in reality any process can only be carried out more or less approximately in a reversible manner; part of the free energy is always lost in overcoming unavoidable friction resistances. The free energy of a system always decreases when a spontaneous process takes place in it. It corresponds with the amount of work stored in the system. Thermochemists formerly believed (erroneously) that this store of work was represented by the total heat, in which case Thomson's rule would be quite valid.

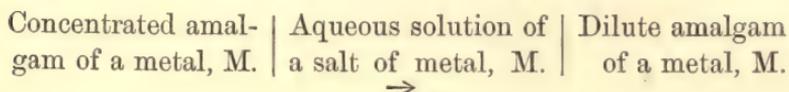
The rule has a certain practical importance, for it may be applied in estimating the electromotive force of a new galvanic combination, the corresponding heat change of the reaction being generally known from direct measurements.

**G. Meyer's Concentration Element.**—The work which can be obtained by the decomposition of a gram-equivalent in an element is given by  $23,070 \cdot P$ . Occasionally this work  $A$  can be measured in another way. Then from the equation—

$$A = 23,070 \cdot P$$

the electromotive force of the element can be calculated.

A case of this nature was studied by G. Meyer (9). The arrangement of the element used by him was—



He examined the metals—zinc, cadmium, lead, tin, copper, and sodium. Now, if one mol of one of these metals passes from the concentrated amalgam of concentration  $C_1$  to the dilute amalgam of concentration  $C_2$ , the work done will be (see Chap. VI. p. 77)—

$$A = RT \ln \frac{C_1}{C_2}.$$

If the work is measured in gram-calories,  $R = 1.99$ . An element of this kind, which depends for its action on differences of concentration, is called a *concentration element*.

If, now, the circuit of a combination of two amalgams be closed by a metal wire, a current passes through the solution in the direction indicated by the arrow, so that metal is dissolved from the concentrated amalgam, and just as much is deposited at the dilute amalgam. The total result of the process is that, simultaneously with the transportation of 96,500 coulombs, one gram-equivalent of metal passes from one amalgam to the other, and the concentration of the solution between the two remains unaltered.

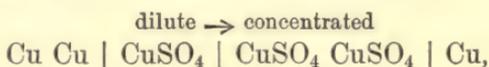
If a gram-molecule contains  $n$  equivalents, the same work will be done by the motion of  $\frac{1}{n}$  gram-molecule. The work obtainable is, therefore, in general—

$$A = 23,070P = \frac{1}{n} RT \ln \frac{C_1}{C_2}.$$

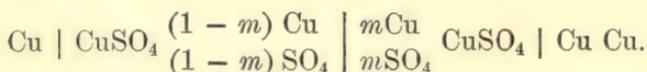
By measuring the electromotive force  $P$ , Meyer verified this result. From this he determined the value of  $n$ , and found numbers which agree well with those arrived at by

Tammann, Heycock and Neville (10), and others. The metals examined were found to be monatomic.

**Helmholtz's Concentration Element.**—In his theoretical deductions (1877) Helmholtz (11) considered a combination consisting of two copper sulphate solutions of different concentrations, which were in contact, and into each of which was immersed a copper electrode. For the sake of simplicity, let us imagine that the difference of concentrations of the two solutions is infinitesimally small, so that the concentration of one may be represented by  $C$ , and that of the other by  $C + dC$ . Let the Hittorf transport number for copper be  $m$ , then that for  $\text{SO}_4$  will be  $(1 - m)$ ; and, further, let the potential difference between the two electrodes be  $dV$ . If we pass through the combination—



$2 \times 96,500$  coulombs (because a mol of  $\text{CuSO}_4$  corresponds with two gram-equivalents) in the direction indicated by the arrow, the concentration will then be represented by the following scheme:—



In the direction of the current (from left to right)  $m$  gram-ions of copper have passed through the surface of separation of the two solutions, and  $(1 - m)$  gram-ions of  $\text{SO}_4$  have passed through in the opposite direction. A gram-ion of copper has dissolved from the left electrode, and this same quantity has been deposited on the right electrode. This latter change is connected with no expenditure of work, for it consists simply in moving 63.6 grams of copper in a horizontal plane (if the copper electrodes were not at the same height, the work, which appears in the so-called gravitation elements, might be neglected, provided the difference in the heights is not great).

The principal change consists in moving  $(1 - m)$

gram-molecule of copper sulphate from the concentrated solution to the more dilute one. The electrical work amounts to—

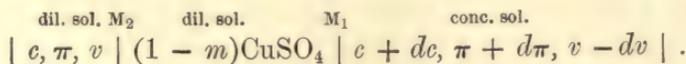
$$dA = 2 \times 23,070 dV \text{ cal.},$$

or, in general, when the electrolyte used contains  $n$  gram-equivalents per gram-molecule—

$$dA = n \times 23,070 dV \text{ cal.}$$

This work may be used to re-establish the old conditions of concentration, which is done by separating so much of the dilute solution as contains  $(1 - m)$  mol of copper sulphate, and evaporating water partly from this and partly from the concentrated solution at constant temperature until the old concentration is reached. This quantity of water vapour is now compressed until it reaches the same concentration as the vapour over the dilute solution, and it is then forced into this solution. The only work done in this process is used in the compression of the water vapour at low pressure over the concentrated solution to the high pressure over the dilute solution. This was the method used by Helmholtz in his deduction.

The same result can be attained more simply by making use of semi-permeable membranes, which allow water, but not salt, to pass through. Let the concentration of the solution to the left, which contains 1 mol of copper sulphate, be  $c$ , its osmotic pressure  $\pi$ , and its volume  $v = \frac{1}{c}$ , and let this be separated from the solution to the right by a semi-permeable membrane,  $M_1$ ; further, let the characteristics for this second solution be  $c + dc$ ,  $\pi + d\pi$ , and  $v - dv$ . Another semi-permeable membrane,  $M_2$ , is used to separate from the remainder such a quantity of the dilute solution as contains  $(1 - m)$  gram-molecule dissolved copper sulphate. The arrangement can then be expressed by the following scheme:—



In the first place, we force through  $M_2$  towards the left  $(1 - m)dv$  c.c. of water. This process takes place against an osmotic excess pressure which rises from 0 to  $d\pi$ , because at the beginning the concentration in the middle partition is the same as that to the left, and at the end it is the same as that to the right. The corresponding work is—

$$dA_1 = \frac{1}{2}d\pi \cdot dv \cdot (1 - m),$$

or, since the osmotic pressure  $\pi$  of a copper sulphate solution is regulated by vant Hoff's equation (see p. 76)—

$$\pi v = iRT \text{ or } \pi = RTci,$$

therefore—

$$dA_1 = \frac{1 - m}{2} dv \cdot d(RTci).$$

Now let  $M_1$  be removed, and so much water forced from right to left as was contained between  $M_2$  and  $M_1$ , namely  $(1 - m)(v - dv)$  c.c. This requires the work—

$$dA_2 = (1 - m)(v - dv)d(RTci).$$

Since  $dv$  can be neglected, on account of its smallness compared with  $v$ , the whole work done is expressed by—

$$dA_1 + dA_2 = (1 - m)RT \frac{d(ci)}{c} = (1 - m)RT \left\{ di + i \frac{dc}{c} \right\}$$

since  $v = \frac{1}{c}$ .

Now,  $dA$  must be equal to  $dA_1 + dA_2$ . Consequently—

$$dV = \frac{RT}{n \cdot 23,070} (1 - m) \frac{d(ci)}{c} \text{ volts.}$$

We may imagine a whole series of solutions of only slightly differing concentrations placed side by side, so that between the two end ones there is a finite difference of concentration. The total electromotive force,  $V$ , between these

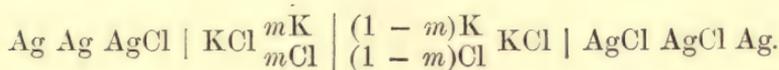
end solutions must be equal to the sum of all the  $dV$  values for the various contiguous solutions, and therefore—

$$V = \frac{RT}{n \cdot 23,070} \left\{ \int_{c_0}^{c_1} (1 - m) di + \int_{c_0}^{c_1} (1 - m) id \ln c \right\} \text{ volts.}$$

If we had used a concentration element of the following composition—



where the unpolarisable electrodes are of the second order, and if  $n \cdot 96,500$  coulombs were conducted through the combination in the direction indicated, we should have found the following result :—



The principal action in this case would be that  $m$  gram-molecules of the salt would be transported from the concentrated to the dilute solution. In a similar way we should calculate the electromotive force by means of the expression—

$$V = \frac{RT}{n \cdot 23,070} \left\{ \int_{c_0}^{c_1} m di + \int_{c_0}^{c_1} mid \ln c \right\} \text{ volts.}$$

In the example given  $n = 1$  (for KCl). In concentration elements with unpolarisable electrodes of the second order, the electromotive force strives to drive the current through the liquid from the concentrated to the dilute solution; with unpolarisable electrodes of the first order the current is driven in the opposite direction. (It is assumed that  $m$  is a proper fraction, which is generally the case: see pp. 137 and 143.)

Elements of the latter kind have recently been exactly studied by Jahn (12). The liquids used were dilute

solutions of potassium chloride, sodium chloride, and hydrochloric acid. According to the results obtained by Loomis and Hausrath, we may set  $i = 1 + a$  (approximately), where  $a$  is the degree of dissociation calculated from the conductivity. In the following table Jahn's experimental values ( $E$ , observed) are given along with those calculated ( $E$ , calculated). The concentrations (in gram-molecules per litre) of the solutions used are given in the columns headed  $x_1$  and  $x_2$ .

Electrolyte.	$x_1$ .	$x_2$ .	$E$ (observed).	$E$ (calculated).	Difference.
KCl	0.03349	0.00167	0.07028	0.07173	- 2.0%
"	0.01669	"	0.05424	0.05539	- 2.1
"	0.01114	"	0.04497	0.04579	- 1.8
"	0.00833	"	0.03844	0.03885	- 1.1
"	0.00670	"	0.03330	0.03364	- 1.0
"	0.00557	"	0.02895	0.02920	- 0.9
HCl	0.03342	0.001665	0.11955	0.12122	- 1.4
"	0.01665	"	0.09235	0.09334	- 1.1
"	0.01113	"	0.07664	0.07710	- 0.6
"	0.00831	"	0.06487	0.06534	- 0.7
"	0.00669	"	0.05614	0.05652	- 0.7
"	0.00556	"	0.04884	0.04906	- 0.4
NaCl	0.03344	0.001674	0.05614	0.05679	- 1.1
"	0.01673	"	0.04360	0.04395	- 0.8
"	0.01117	"	0.03608	0.03636	- 0.8
"	0.00836	"	0.03073	0.03089	- 0.5
"	0.00669	"	0.02652	0.02663	- 0.4

The agreement between the observed and calculated values is very satisfactory. The observed values are always somewhat smaller (on the average about 1 per cent.), which points to a constant experimental error.

The formulæ given above for  $V$  are perfectly exact, but they are more or less inconvenient, since they cannot be directly integrated. They can, however, be integrated if we assume that they are constant, and that the law of mass action—

$$\frac{g^r}{c - g} = \text{const.}$$

is valid, where  $r$  is the number of ions contained in a molecule of the salt, and  $\frac{g}{c}$  denotes the degree of dissociation. We then obtain—

$$i = 1 + (r - 1)\frac{g}{c}$$

$$\frac{d(ci)}{c} = \frac{d(c + (r - 1)g)}{c} = \frac{dc + (r - 1)dg}{c}$$

By differentiating the equation for mass action we obtain—

$$\frac{rg^{r-1}dg}{c-g} - \frac{g^r}{(c-g)^2}d(c-g) = 0$$

$$r(c-g)dg = gdc - g^2dg$$

$$\frac{rcdg}{g} = dc + (r-1)dg$$

$$\frac{d(ci)}{c} = \frac{rdg}{g},$$

from which it follows that—

$$V_1 = \frac{RT \cdot 2.3025}{n \cdot 23,070} \cdot r \cdot (1 - m) \log \frac{g_1}{g_0}$$

$$V_2 = \frac{RT \cdot 2.3025}{n \cdot 23,070} \cdot r \cdot m \cdot \log \frac{g_1}{g_0}$$

where  $V_1$  is applicable for concentration elements with unpolarisable electrodes of the first order, and  $V_2$  for those with unpolarisable electrodes of the second order (log denotes the ordinary logarithm). Without appreciable error we may set  $\frac{2.3025}{23,070} = 10^{-4}$ . These formulæ, which are convenient for calculating, agree with those of Nernst. The product of concentration and degree of dissociation,  $g$ , is a measure of the concentration of the ions. For electrolytes consisting of two monovalent ions  $r = 2$  and  $n = 1$ . Most of the determinations which have been carried out were made with such electrolytes.

**Nernst's Calculation of the Electromotive Force at the Surface of Separation of Two Solutions of the Same Salt (13).**—We begin with salts which

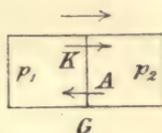


FIG. 42.

consist of two monovalent ions. Suppose two solutions in contact, in which each of the two kinds of ions have the osmotic pressures  $p_1$  and  $p_2$  respectively (Fig. 42). Let us calculate the work necessary to move the quantity of electricity 96,500 coulombs through the surface of separation  $G$ ; this work corresponds with the electromotive force at this surface. If the migration velocity of the cation  $C$  is  $u$ , and that of the anion  $A$  is  $v$ , then  $\frac{u}{v+u}$  equivalents of  $C$  pass through the contact plane to the right, and  $\frac{v}{u+v}$  equivalents to the left. The work done, expressed in heat units, is for the cation—

$$W_c = 1.99T \frac{u}{u+v} \ln \frac{p_1}{p_2},$$

and for the anion—

$$W_A = 1.99T \frac{v}{u+v} \ln \frac{p_2}{p_1}.$$

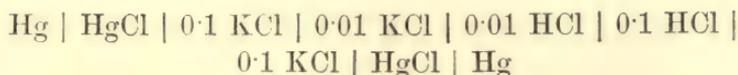
The total work must be equal to  $23,070\pi$ , where  $\pi$  is the required potential difference (expressed in volts) at  $G$ . Therefore—

$$23,070\pi = W_c + W_A = 1.99T \frac{u-v}{u+v} \ln \frac{p_1}{p_2}$$

$$\text{or } \pi = 86T \cdot 10^{-6} \frac{u-v}{u+v} \ln \frac{p_1}{p_2} = 1.99 \cdot 10^{-4} T \frac{u-v}{u+v} \log \frac{p_1}{p_2}.$$

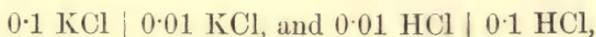
These electromotive forces come into play in liquid elements in which the electrodes are so arranged that there are no resulting electromotive forces between the metals and the liquids.

Thus, for instance, in the element—



the two electromotive forces at the ends exactly balance each other, since they are equal, but act in opposite directions.

Furthermore, the electromotive force between  $0.1 \text{ HCl} \mid 0.1 \text{ KCl}$  must be equal to that between  $0.01 \text{ KCl} \mid 0.01 \text{ HCl}$ , but with the opposite sign, since the electromotive force depends on the ratio of the concentrations of two solutions, and not on the absolute values. The remaining electromotive forces are therefore—



which can be calculated according to the above formulæ. Nernst (13) has made a large number of observations with such elements, and we give below some of his results. The experiments were carried out at  $18^\circ$ , and in this case we obtain—

$$\pi = 86T \cdot 10^{-2} \left\{ \frac{u-v}{u+v} - \frac{u_1-v_1}{u_1+v_1} \right\} \ln 10,$$

from which we find—

$$\pi = 5.78 \cdot 10^{-6} \left( \frac{u-v}{u+v} - \frac{u_1-v_1}{u_1+v_1} \right).$$

Electrolytes.	$\frac{u-v}{u+v} - \frac{u_1-v_1}{u_1+v_1}$	$\pi$ (observed).	$\pi$ (calculated).
KCl, NaCl . . . . .	+ 0.237	0.0111	0.0137
KCl, LiCl . . . . .	0.366	0.0183	0.0211
KCl, $\text{NH}_4\text{Cl}$ . . . . .	0.019	0.0004	0.0011
$\text{NH}_4\text{Cl}$ , NaCl . . . . .	0.218	0.0098	0.0126
KCl, HCl . . . . .	- 0.688	- 0.0357	- 0.0397
KCl, $\text{HNO}_3$ . . . . .	- 0.719	- 0.0378	- 0.0414
KCl, $\text{HO}_3\text{SC}_9\text{H}_{11}$ . . . . .	- 0.902	- 0.0469	- 0.0520

The calculated values are all about 12 per cent. higher than those observed. A deviation of about 5 per cent. can be explained by incomplete dissociation, but the cause

of the remainder of the deviation has not yet been found. For some silver salts the disagreement was still greater; the observed values were 0.0214 and 0.0146 volt, whilst calculation gives 0.0109 and 0.008 respectively.

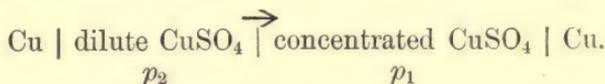
If the above combination consists of  $n$ -valent ions, then for each mol  $n \cdot 96,500$  coulombs must be passed through the element, and we obtain for the electric work—

$$n23,070\pi = 1.99T \frac{u-v}{u+v} \ln \frac{p_1}{p_2}.$$

Consequently  $n$  passes into the denominator of the final formula, and we have—

$$\pi = \frac{1.99}{n} \cdot 10^{-4} \cdot T \frac{u-v}{u+v} \log \frac{p_1}{p_2}.$$

**Nernst's Calculation of the Electromotive Forces of Concentration Elements (14)**—Let us again consider the Helmholtz combination—



When a current passes through this element in the direction indicated by the arrow, the following changes occur:—

(1) A gram-ion (63.6 grams) of copper is dissolved from the copper electrode in contact with the dilute copper sulphate solution, and is transformed from the metallic to the ionic condition;

(2) At the surface of separation of the two solutions the same process takes place as described in the previous case; and

(3) A gram-ion (63.6 grams) of copper is deposited from the concentrated solution on the copper electrode in contact with it, the copper passing from the ionic to the metallic condition.

The final result of processes (1) and (3) is that a gram-ion of copper passes from the concentrated to the dilute solution.

If the work which can be gained from this be measured in gram-calories, the corresponding electromotive force can be calculated from the equation—

$$23,070 \cdot n \cdot \pi = 1.99 \cdot T \cdot \ln \frac{p_1}{p_2},$$

or 
$$\pi = \frac{1.99 T \cdot 10^{-4}}{n} \log \frac{p_1}{p_2}.$$

To this we must add the process (2), which is analogous to that already described (p. 218), but which takes place in the opposite direction. In the former case the cation moves from the solution of osmotic pressure,  $p_1$  (osmotic pressure with reference to the cation), to that of osmotic pressure,  $p_2$ ; here the motion takes place in the opposite direction, and gives rise to the electromotive force—

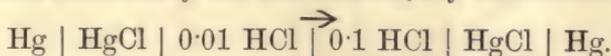
$$\pi_1 = \frac{1.99 T \cdot 10^{-4}}{n} \cdot \frac{v - u}{v + u} \cdot \log \frac{p_1}{p_2}.$$

By adding together  $\pi$  and  $\pi_1$ , we obtain the total electromotive force  $P$ —

$$P = \pi + \pi_1 = \frac{1.99 T \cdot 10^{-4}}{n} \cdot \frac{2v}{u + v} \cdot \log \frac{p_1}{p_2}.$$

The direction of the current is always from the dilute to the concentrated solution, since it is in this way that the concentration difference can disappear.

Instead of an element of this type with *unpolarisable electrodes of the first order*,<sup>1</sup> we may consider a type with *unpolarisable electrodes of the second order*, say the combination—



When a quantity of electricity  $n \cdot 96,500$  coulombs (in this

<sup>1</sup> By unpolarisable electrodes of the first order, we mean electrodes in an unsaturated solution of a salt containing a cation, the same as the metal of the electrode; by an unpolarisable electrode of the second order, is meant a metal in a solution of one of its salts, which by being in contact with excess of solid salt, is always kept saturated.

case  $n = 1$ , since the electrolyte HCl consists of monovalent ions) is passed through the element in the direction of the arrow, *i.e.* from the dilute to the concentrated solution, the following changes take place:—

(1) A gram-equivalent of mercury combines with an equivalent of chlorine from the calomel, and forms HgCl;

(2) The gram-equivalent of mercury thus set free from the calomel combines with an equivalent of chlorine from the 0.01-normal HCl solution. This latter solution, therefore, loses a gram-ion of chlorine;

(3) At the contact surface of concentrated and dilute solution the same process takes place as in the above example;

(4) A gram-equivalent of hydrogen from the 0.1-normal HCl solution combines with an equivalent of chlorine from the adjacent calomel solution, and forms a gram-molecule of hydrochloric acid. The concentration of the latter solution is thereby increased; and

(5) The gram-equivalent of mercury, which becomes free on account of process (4), is deposited at the mercury electrode.

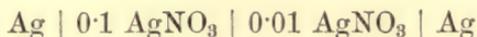
The result of these processes may be summed up as follows:—

By processes (1) and (5) the left side loses and the right side (in the diagram) gains a gram-ion of mercury. The old equilibrium can be re-established by allowing this quantity of mercury to flow back from right to left, and no work is required for this. This part of the whole process cannot, therefore, cause any electromotive force. By processes (2) and (4) a gram-ion of chlorine is brought from the dilute to the concentrated solution. This process is therefore the same, but in the opposite direction, as when unpolarisable electrodes of the first order are used, and consequently the same electromotive force occurs, but with the other sign. By process (3) we obtain the same electromotive force at the surface of contact as in the former example. The total electromotive force is therefore given by—

$$P_1 = \pi + \pi_1 = - \frac{1.99 \cdot T \cdot 10^{-4}}{n} \cdot \frac{2u}{u+v} \cdot \log \frac{p_1}{p_2}$$

The negative sign indicates that the electromotive force strives to drive the electricity in the opposite direction to that assumed in the development of the formula, *i.e.* the electricity goes through the element from the concentrated to the dilute solution.

**Experimental Confirmation of the Theory.**—In his investigations Helmholtz only considered concentration elements with unpolarisable electrodes of the first order. His results were experimentally confirmed by Moser (15) and Miesler. Similar experiments were later carried out by Nernst (16). Nernst found for the element—



the electromotive force 0.055 volt at 18°, whilst the theory leads to—

$$\begin{aligned} \pi &= 1.99 \times 291 \cdot \frac{2 \times 61.8}{55.0 + 61.8} \cdot 10^{-4} \cdot \log 10 \\ &= 1.99 \times 291 \times 1.058 \times 10^{-4} = 0.0613 \text{ volt,} \end{aligned}$$

when  $T = 291$ ,  $u = 55.0$ , and  $v = 61.8$  (see p. 142).

The agreement is satisfactory. Now, since the dissociation is in reality not complete, as is assumed, we may introduce a correction for this disturbing factor, and then obtain the value 0.0574 volt.

Nernst has measured a large number of electromotive forces with elements which are reversible with respect to the anion, that is to say, with unpolarisable electrodes of the second order. His results are given in the following table, where  $c_1$  and  $c_2$  denote the normalities of the concentrated and dilute solutions, and  $\epsilon$  obs. and  $\epsilon$  calc.<sub>2</sub> the electromotive forces, the latter calculated by means of Nernst's formula:—

Electrolyte.	$c_1$ .	$c_2$ .	$\epsilon$ obs.	$\epsilon$ calc. <sub>1</sub> .	$\epsilon$ calc. <sub>2</sub> .
HCl . . . . .	0.105	0.018	0.0710	0.0717	0.0736
HCl . . . . .	0.10	0.01	0.0926	0.0939	0.0962
HBr . . . . .	0.126	0.0132	0.0932	0.0917	0.0940
KCl . . . . .	0.125	0.0125	0.0532	0.0542	0.0565
NaCl . . . . .	0.125	0.0125	0.0402	0.0408	0.0429
LiCl . . . . .	0.10	0.01	0.0354	0.0336	0.0355
NH <sub>4</sub> Cl. . . . .	0.10	0.01	0.0546	0.0531	0.0554
NaBr . . . . .	0.125	0.0125	0.0417	0.0404	0.0425
NaOH . . . . .	0.235	0.030	0.0178	0.0183	0.0188

In the calculation of  $\epsilon$  calc.<sub>1</sub>, Nernst took account of the incomplete dissociation, and set the ratio of the osmotic pressures of the two solutions equal to the ratio of their conductivities, and not to that of their concentrations. The values calculated in this way agree very well with those observed directly.

The activity of a concentration element can be easily shown; this is best done by the experiment made by Bucholz in 1804. A glass cylinder is half filled with a strong solution of stannous chloride (layer *b* in Fig. 43), and this is covered by a layer of pure water (*a*). A tin rod is immersed in the liquid. A current is produced which passes from the lower end of the rod upwards; this causes solution of the tin at the upper end, and dendritic crystals of tin are formed at *b*.

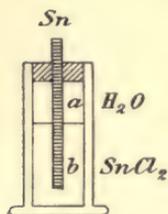
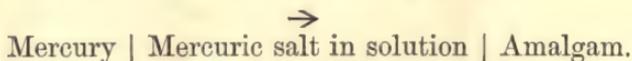


FIG. 43.

Another kind of concentration cell has been suggested by von Türlin (17). This has the combination—



In order that the mercury may not expel the dissolved metal in the amalgam, it is necessary that this be "nobler" than mercury: for example, gold. In this arrangement mercury will be transported through the solution from left to right. This corresponds exactly with a distillation of

mercury to the amalgam, the vapour pressure of which must necessarily be lower than that of the pure substance. The electromotive force is evidently proportional to the depression of the vapour pressure, and this again is proportional to  $\frac{n}{N}$ , where  $n$  is the number of dissolved molecules, and  $N$  the number of solvent (mercury) molecules. By measuring the electromotive force of such an element, the molecular weight of the dissolved metal can be determined (compare Meyer's concentration element, p. 210).

**Solution Pressure of Metals.**—In concentration elements we have three electromotive forces, which act at the three contact surfaces. For one of these, namely, that between the concentrated and dilute solution, Nernst has deduced (see p. 218) the expression—

$$\pi_1 = \frac{1.99 \times 10^{-4}}{n} \cdot T \cdot \frac{u - v}{u + v} \cdot \log \frac{p_1}{p_2},$$

where  $p_1$  and  $p_2$  denote the osmotic pressures of the two solutions,  $u$  and  $v$  the migration velocities, and  $n$  is the valence of the ions. For the other two electromotive forces we have obtained (see p. 221)—

$$\pi = \pi_0 + \pi_2 = 1.99 \cdot 10^{-4} T \cdot \log \frac{p_1}{p_2}.$$

It would be of interest to ascertain the value of each of these electromotive forces, *e.g.* between Cu and dilute  $\text{CuSO}_4$ , and between Cu and concentrated  $\text{CuSO}_4$ , and not only, as the above formula gives us, their sum.

In order to obtain some analogy with the other formulæ, the form—

$$\pi_0 + \pi_2 = 1.99 \cdot 10^{-4} T \cdot \log \frac{P}{p_2} - 1.99 \cdot 10^{-4} T \cdot \log \frac{P}{p_1}$$

has been given to the above one.

The factors containing the expression  $\log \frac{P}{p}$  give the

electromotive forces between copper and dilute copper sulphate, and between copper and concentrated copper sulphate.

In order to explain a formula of this sort, Nernst introduced the following conception, which was afterwards further developed by Ostwald (18).

Suppose we have a substance, *e.g.* sugar, in contact with a liquid, *e.g.* water, the solid dissolves until a saturated solution is formed. This process corresponds exactly with the vaporisation of a liquid, which goes on until the vapour space is saturated and the vapour possesses a certain pressure—its maximum pressure at the particular temperature.

On account of this analogy the osmotic (partial) pressure exerted by the saturated solution of sugar is termed the solution pressure, or solution tension, of the sugar at the particular temperature (according to van't Hoff's law).

Now, if we consider the metals—for instance, zinc in sulphuric acid—we see that they do not pass into solution unchanged, but that they strive to dissolve as ions. It seems natural to suppose that the metal passes into solution until the concentration of the ions, and with it the osmotic pressure, has reached a certain value, which pressure is termed the *electrolytic solution pressure*.

We shall denote this pressure by  $P$ . Let us suppose that a gram-ion (65 grams) of zinc passes into solution in the form of ions, and in the solution the zinc ions have the osmotic pressure  $p$ ; this process can be conducted reversibly by dissolving the zinc at constant pressure  $P$ , whereby no work is done (just as when water evaporates into a vacuum), and then by expanding the zinc ions from pressure  $P$  to pressure  $p$ , whereby the work done is—

$$\int_P^p p dv = RT \int_P^p \frac{dv}{v} = -RT \int_P^p \frac{dp}{p} = -RT \ln \frac{p}{P}.$$

The total work done is therefore—

$$RT \ln \frac{P}{p}.$$

The electric work which can be obtained from this is  $n \cdot 96,500 \cdot \pi_0$ , where  $\pi_0$  is the electromotive force at the surface of contact; therefore when  $p = p_2$  (see p. 218)—

$$\pi_0 = \frac{RT}{n \cdot 96,500} \cdot \ln \frac{P}{p} = \frac{86 \cdot T \cdot 10^{-6}}{n} \cdot \ln \frac{P}{p_2}$$

This applies to the pole at which the zinc dissolves; at the other pole (where  $p = p_1$ ) an electromotive force in the opposite direction is set up, and this, consequently, has the opposite sign. We have, therefore—

$$\pi_2 = - \frac{86 \cdot T \cdot 10^{-6}}{n} \cdot \ln \frac{P}{p_1}$$

The sum of  $\pi_0$  and  $\pi_2$  is—

$$\pi_0 + \pi_2 = \frac{86 \cdot T \cdot 10^{-6}}{n} \cdot \ln \frac{p_1}{p_2} = \frac{1.99 \cdot T \cdot 10^{-4}}{n} \cdot \log \frac{p_1}{p_2},$$

which is the same expression as we found above.

**Planck's Formula.**—Nernst only developed the expression for the electromotive force at the contact surface between two solutions of the same electrolyte at different concentrations. Planck (19), taking a more general view of the problem, has deduced a formula for the electromotive force at the contact surface between any two electrolytic solutions. If—

$$\begin{aligned} U &= up + u_1p_1 + u_2p_2 + \dots \\ \text{and—} \quad V &= vq + v_1q_1 + v_2q_2 + \dots \end{aligned}$$

where  $u, u_1, u_2$ , etc., are the transport numbers of the positive ions;  $v, v_1, v_2$ , etc., those of the negative ions;  $p, p_1, p_2$ , etc., and  $q, q_1, q_2$ , etc., the osmotic pressures of these ions; and if  $c$  is the total concentration of all the positive ions, and therefore of all the negative ions, provided that all the ions are monovalent, then we have to find expressions for  $U_1$  and  $U_2$ ,

$V_1$  and  $V_2$ ,  $c_1$  and  $c_2$ , which are applicable to each of the solutions which are in contact.

Planck found that the electromotive force at such a surface of contact can be expressed by—

$$\pi = 1.99 \cdot 10^{-4} \cdot T \cdot \log \xi,$$

where  $\xi$  is given by the equation—

$$\frac{\xi U_2 - U_1}{V_2 - \xi V_1} = \frac{\ln \frac{c_2}{c_1} - \ln \xi}{\ln \frac{c_2}{c_1} + \ln \xi} \cdot \frac{\xi c_2 - c_1}{c_2 - \xi c_1}.$$

When two solutions of the same electrolyte are examined—

$$U_1 = uc_1; \quad U_2 = uc_2; \quad V_1 = vc_1; \quad V_2 = vc_2,$$

and by introducing these values into Planck's formula, we obtain that of Nernst (see p. 218)—

$$\pi = 1.99 \cdot 10^{-4} \cdot T \frac{u - v}{u + v} \log \frac{c_1}{c_2}.$$

A further simplification occurs when  $c_1 = c_2$ , *i.e.* when the total concentration is the same on both sides of the contact surface. In this case we have—

$$\xi = \frac{U_1 + V_2}{V_1 + U_2}$$

and— 
$$\pi = 1.99 \cdot 10^{-4} \cdot T \cdot \log \frac{U_1 + V_2}{V_1 + U_2}.$$

For a solution of one electrolyte,  $U_1 = up$ , and  $V_1 = vp$ ; and for that of another electrolyte,  $U_2 = u_1p$ , and  $V_2 = v_1p$ . Several combinations of this type were examined by Nernst, and his results, as well as those calculated by Planck's formula, are contained in the following table:—

Solutions.	$\pi$ (observed).	$\pi$ (calculated).
HCl, KCl . . .	0.0285	0.0282
HCl, NaCl . . .	0.0350	0.0334
HCl, LiCl . . .	0.0400	0.0358
KCl, NaCl . . .	0.0040	0.0052
KCl, LiCl . . .	0.0069	0.0077
NaCl, LiCl . . .	0.0027	0.0024

The agreement between observed and calculated values is very satisfactory.

Similar experiments carried out later by Negbaur (20) also showed a very perfect agreement with the theory.

## CHAPTER XIV.

### Potential Difference between Two Bodies.

**Electrical Double-layer.**—When a zinc plate is immersed in a solution of zinc sulphate, it tends to send more ions into the solution, provided that the osmotic pressure  $p$  of the zinc ions is smaller than the electrolytic solution pressure  $P$  of the metal.

The solution becomes positively charged by these positive zinc ions, and the zinc plate, which was formerly neutral, takes on a negative charge. At the surface of separation a highly charged double-layer is formed, corresponding with a Franklin condenser one side of which consists of the negatively charged zinc and the other of the positively charged ions in the zinc sulphate solution.

On the other hand, if we have a metal whose electrolytic solution pressure,  $P$ , is smaller than the osmotic pressure  $p$  of the corresponding cations in the salt solution, say copper in copper sulphate solution, some of the positive ions are deposited on the metal, which thereby becomes positively charged, whilst the solution becomes negatively charged. The two parts of the Franklin condenser are then the positive metal and the solution which, on account of the excess of negative ions, is negatively charged. This sort of charged contact surface has been termed by Helmholtz an *electrical double-layer*.

In the first case, the smaller the osmotic pressure of the zinc ions in the solution, the more ions must go into solution when this is in contact with the metal, and the stronger will

be the negative charge on the zinc. When the charge has reached a certain value, solution of the zinc ceases; this takes place when the potential difference due to the charges attains the value—

$$\pi_0 = \frac{86 \times 10^{-6}}{n} \cdot \ln \frac{P}{p},$$

for then it exactly counterbalances the effect of the solution pressure of the metal.

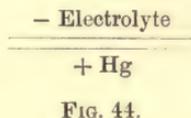
**Potential Difference between a Metal and a Liquid.**

—When there is a potential difference  $V$  between two condenser plates of area  $S$  which are at distance  $d$  apart, and when the insulator is the light ether, the quantity of electricity on the condenser is given by—

$$q = \frac{VS}{4\pi d}.$$

If we know  $q$ ,  $V$ , and  $S$  for one plate, which is polarised in an electrolyte, then  $d$  can be calculated,  $d$  being the distance between the polarised plate and the nearest layer of ions. Thus, Helmholtz ( $I$ ) found in the case of polarised platinum  $0.4 \times 10^{-7}$  to  $0.8 \times 10^{-7}$  cm., which corresponds almost with molecular dimensions.

If we use a liquid metal, for instance mercury, the surface tension comes into play—that is to say, the surface of separation between mercury and an electrolyte in contact with it tends to decrease. If the contact surface is charged, the electricity tends to bring about the opposite effect. The electricity strives to spread itself over as large a surface as possible, and since it is bound at the surface it tends to increase this. Consequently, if we have an electrical double-layer at the contact between mercury and an electrolyte, the surface tension—*i.e.* the force with which the surface tends to diminish itself—is determined by the natural surface tension of the metal diminished by the force with which the electric charge



tends to increase the surface. The latter increases with the magnitude of the charge.

**Capillary Electrometer.**—In order to observe the change of surface tension, the mercury is put into a tube which is drawn out to a capillary, slightly conical point,  $R$  (Fig. 45), so that the pressure of the mercury column acts on the contents of the capillary. The lower meniscus of the mercury is in contact with a saturated solution of mercurous sulphate in sulphuric acid contained in the vessel  $K$ , in the bottom of which is placed a layer of mercury. If the

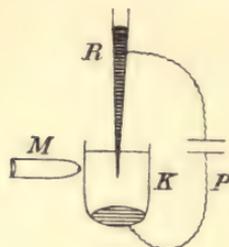


FIG. 45.

charge at the contact surface be altered by introducing a potential difference (electromotive force) at  $P$ , there is a simultaneous change of surface tension. If this tension is decreased, the mercury meniscus in  $R$  falls; if it increases, the mercury rises in  $R$ , and the movement can be observed with a microscope,  $M$ . An instrument of this kind, called

a *capillary electrometer*, was first constructed by Lippmann (?). It can be used to determine when the potential difference reaches the value 0, and is therefore useful for comparing potential differences. It is most commonly employed as a null instrument in the form shown in Fig. 46.

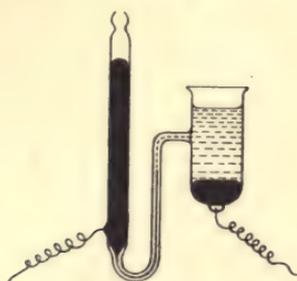


FIG. 46.

At the beginning of the experiment let the potential difference be zero, *i.e.*  $P = 0$ . If now  $P$  be so altered that the mercury in the tube becomes negatively charged, the mercury rises in the tube, *i.e.* the surface tension increases. The cause of this is that the original charge of the mercury is diminished, which proves that this was positive. Mercury, therefore, in contact with sulphuric acid becomes positively charged, and the acid negatively.

If the contact surface be now charged with increasing

electromotive forces which conduct negative electricity to the mercury, the surface tension of the metal rises until the charge of the double-layer becomes equal to 0. When this limit is exceeded, the mercury becomes negatively charged, whilst the sulphuric acid receives a positive charge. This occurs when  $P$  has a value of about 1 volt. Mercury in the ordinary condition exhibits, when in contact with sulphuric acid, a potential difference towards it of about 1 volt, the mercury being positively and the acid negatively charged.

A. König (3) arrived at practically the same result by examining the curvature of mercury drops in sulphuric acid; this method also permits of the determination of the surface tension. It is, however, not easy to ascertain the maximum surface tension in this way.

**Dropping Electrodes.**—From these results, Helmholtz came to a conclusion which led to the construction of the so-called *dropping electrodes*. Let us suppose that we have a quantity of mercury which can be allowed to flow out through a fine tube into an electrolyte. If the mercury is positively charged, the surface of contact will be vastly increased by the flowing out, and the charge must become smaller. The charge, however, will only diminish provided that no new mercury ions pass from the solution into the mercury, and thus recharge the mercury electrode; the solution in contact with mercury always contains some mercury salt. With an arrangement of this kind Helmholtz (4) found that the dropping mercury possesses the same potential as a drop of mercury which is polarised to the maximum surface tension. Ostwald repeated these experiments, but Paschen (5) was the first to successfully construct dropping electrodes, which he did by arranging the tube so that the stream of mercury is broken up into drops just at the surface of the electrolyte under examination. The opening of the tube should be from 0.02 to 0.05 mm. in diameter.

According to Nernst (6), the action of dropping electrodes can be explained as follows. Mercury is a "noble"

metal (see below), *i.e.* it possesses a low solution pressure. Now, if a liquid,  $W$  (Fig. 47), in which there hangs a mercury drop,  $A$ , from a capillary electrometer,  $K$ , contains mercury ions, even in

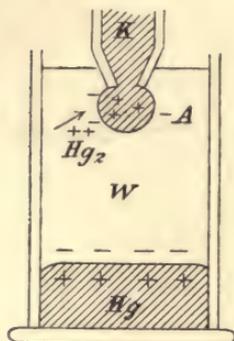


FIG. 47.

minute quantity, then, provided that its osmotic pressure is greater than  $10^{-15}$  atmos., this pressure is higher than the solution pressure of the mercury. A sufficient number of mercury ions pass into solution to establish this condition by oxidation and solution of the small amount of the mercury which has fallen from the dropping electrode and rests at the bottom of the liquid  $W$ . This

determines that mercurous ions,  $\overset{++}{\text{Hg}}_2$ , must separate from the liquid  $W$  and deposit on the falling drop, which thereby becomes positively charged; this positive electricity is carried to the layer of mercury at the bottom, and the solution becomes negatively charged. By this process the liquid near the place where the drops are formed loses mercurous ions, and consequently mercury salt, whilst that at the bottom of the vessel becomes more concentrated, as Palmaer (7) has directly proved.

This process should theoretically continue until the concentration of the mercury ions in the liquid at  $A$  has decreased to a certain value corresponding with the solution pressure of the mercury; this condition can be nearly attained by allowing the drops to form quickly, but it cannot be perfectly reached on account of diffusion of mercurous ions from the lower to the upper part of the vessel. Suppose this condition has been established, then evidently no more ions would pass from the solution to the drop, no double layer would be produced, and the mercury would have the same potential as the liquid.

An analogous process takes place when any other metal of low solution pressure—copper, silver, etc.—is brought into

contact with an aqueous solution. A small quantity of oxide is formed; this dissolves, and ions are then able to deposit on the metal, which thus becomes positively charged, whilst the solution receives a negative charge. The opposite effect is produced when a metal of high solution pressure is immersed in a solvent. The ions then pass from the metal, leaving this negatively charged and communicating a positive charge to the liquid.

**The Volta Effect.**—The above method of viewing the process explains the Volta effect for combinations of metals and liquids. If we are concerned with two liquids, the charges are due to the dissimilar mobilities of the ions (see p. 218). However, the Volta effect is also produced between metals and insulators, as, *e.g.*, varnish. In this case the varnish may be conceived as a medium (a solvent) in which traces of metal oxides or salts dissolve. When air is the insulator, it is simplest to imagine that the metal reacts with the oxygen ions (of the air), and is thus oxidised, whereby the metal becomes negatively electrified and the air positively.

Now, if we have, as in Volta's original experiment, two metals, *A* and *B*, in the air, these are oxidised to different extents according to their "chemical affinities" for oxygen. As a consequence of this the potential difference between the metal *A* and the air will be different from that between the metal *B* and the air. In other words, there is a certain potential difference between the two metals, so long as they are not in metallic contact, and the potential difference is such that the more easily oxidisable metal is negatively electrified.

If the two metals be joined by a wire, the difference of potential disappears by positive electricity passing to the more easily oxidisable metal, and negative electricity passing to the more "noble" metal. If the metals be in the form of plates, and if they be brought close together, so that the distance between them is small, a condenser is produced, as in Volta's experiment, and therefore the electricities

“bind” each other, so that fresh and comparatively large quantities of electricity collect on the plates in order to maintain the electrical equilibrium.

Now let the connecting wire be removed, and the plates separated from each other. The previously “bound” electricities become free, and the more easily oxidisable metal is found to be positively electrified, and the “nobler” metal negatively. This explains why the metals can be arranged in an “electromotive series” (with reference to one and the same gas), and why the most easily oxidisable metals occur at the beginning of the series, and the least oxidisable at the end.

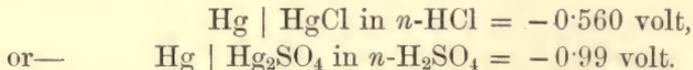
If we use other gases which act on the metals we obtain a different series (*e.g.* with chlorine, hydrogen sulphide, etc.), as J. Brown (8) has proved.

The actual potential difference between two metals is ascertained by conducting a known quantity of electricity through the junction and determining the heat developed (the so-called Peltier effect). Since 1 volt-coulomb = 0.239 cal., the potential difference can easily be calculated in volts; these differences of potential seldom reach so much as a few hundredths of a volt.

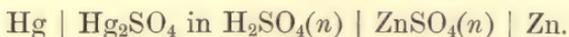
**Pellat's Method.**—A fourth method of determining when the potential difference between mercury and a liquid in contact with it becomes zero was devised by Pellat (9), who observed, in a capillary electrometer, the polarised mercury surface, which could be increased in  $R$  (Fig. 44) by suction. The potential difference  $P$  could be altered as desired.

If there is a difference of potential between the mercury and the solution, and the surface of contact be suddenly increased, a current flows through a galvanometer,  $G$ , placed at  $P$ , to the newly formed parts of the surface, so as to charge these to the same potential as the original parts. If, however, the contact surface is uncharged, no current is produced. This occurs when  $P$  is equal to the potential difference,  $\text{Hg} \mid \text{Hg}_2\text{SO}_4$  in  $\text{H}_2\text{SO}_4$ . Pellat, by altering  $P$  until this point was reached, obtained the value  $P = -0.97$  volt.

**Results of Experimental Determinations.** By means of these various methods the difference of potential between mercury and electrolyte can be determined. The starting-point chosen by Ostwald (*l*o) was—



If one potential difference is known, then all the others can be measured by a suitable combination of galvanic elements. Thus, if it be required to ascertain the tension between zinc and normal zinc sulphate solution, we should form the element—



The electromotive force of this element has been found to be 1.514 volts. If we subtract from this 0.99 volt for Hg | *n*-H<sub>2</sub>SO<sub>4</sub>, we obtain as remainder 0.524 volt for Zn | ZnSO<sub>4</sub>. (For a correction, see p. 240.)

The potential differences given below between metals and normal solutions of their salts have been determined in this way.

From the values so obtained the electrolytic solution pressure *P* for metals in normal solutions of their salts can be calculated by means of the formula—

$$\pi = \frac{RT}{nE} \ln \frac{P}{p}$$

The values for  $\pi$  and *P* contained in the following tables have been obtained by Ostwald:—

POTENTIAL DIFFERENCE,  $\pi$ , BETWEEN METALS AND THEIR SALTS IN NORMAL SOLUTION.

	Volts.		Volts.
Magnesium . . . . .	+1.22	Lead . . . . .	-0.10
Zinc . . . . .	+0.51	Hydrogen . . . . .	-0.25
Aluminium . . . . .	+0.22	Copper . . . . .	-0.60
Cadmium . . . . .	+0.19	Mercury . . . . .	-0.99
Iron . . . . .	+0.06	Silver . . . . .	-1.01
Nickel . . . . .	-0.02		

SOLUTION PRESSURE,  $P$ , OF THE METALS IN ATMOSPHERES.

	Volts.		Volts.
Magnesium . . . . .	$10^{44}$	Lead . . . . .	$10^{-2}$
Zinc . . . . .	$10^{18}$	Hydrogen . . . . .	$10^{-4}$
Aluminium . . . . .	$10^{13}$	Copper . . . . .	$10^{-12}$
Cadmium . . . . .	$10^7$	Mercury . . . . .	$10^{-15}$
Iron . . . . .	$10^3$	Silver . . . . .	$10^{-15}$
Nickel . . . . .	$10^{-0}$		

The elements used in these determinations were (the sum of Metal | Zn and Zn | ZnSO<sub>4</sub> is taken as equal to 0.518 volt : see p. 240)—

	Volts.		Volts.
Zn   ZnSO <sub>4</sub>   MgSO <sub>4</sub>   Mg	= -0.725	∴ Mg   MgSO <sub>4</sub>	= 1.243
Zn   ZnSO <sub>4</sub>   CdSO <sub>4</sub>   Cd	= 0.360	∴ Cd   CdSO <sub>4</sub>	= 0.158
Zn   ZnSO <sub>4</sub>   FeSO <sub>4</sub>   Fe	= 0.440	∴ Fe   FeSO <sub>4</sub>	= 0.078
Zn   ZnSO <sub>4</sub>   PbAc <sub>2</sub>   Pb	= 0.607	∴ Pb   PbAc <sub>2</sub>	= -0.089
Zn   ZnSO <sub>4</sub>   CuSO <sub>4</sub>   Cu	= 1.100	∴ Cu   CuSO <sub>4</sub>	= -0.582
Zn   ZnSO <sub>4</sub>   Ag <sub>2</sub> SO <sub>4</sub>   Ag	= 1.539	∴ Ag   Ag <sub>2</sub> SO <sub>4</sub>	= -1.024
Zn   ZnSO <sub>4</sub>   H <sub>2</sub> SO <sub>4</sub>   H <sub>2</sub> (Pd)	= 0.760	∴ H <sub>2</sub>   H <sub>2</sub> SO <sub>4</sub>	= -0.240

**Heat of Ionisation.**—As Ostwald has shown, we can calculate  $W$ , in this case the heat of ionisation, from the formula already given—

$$23,070 \frac{dP}{dT} = \frac{23,070P - W}{T}$$

if we know  $P$ , the potential difference between metal and solution. The value of  $\frac{dP}{dT}$  can easily be determined by arranging in opposition to each other two surfaces, Metal | Salt solution kept at different temperatures. Thus we find for Copper | Copper acetate,  $\frac{dP}{dT} = 0.000774$  volt; for Copper | Copper sulphate, 0.000757 volt, or as the mean value 0.000766 volt per degree. Therefore, if  $T = 290^\circ$ —

$$23,070 \times 0.000766 \times 290 = 23070 \times 0.60 - W,$$

from which—

$$W = 13,842 - 5124 = 8718 \text{ cal.}$$

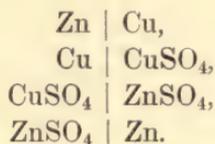
The above formula is valid for the condition that  $q = 96,500$  coulombs, *i.e.* for an equivalent, so that the heat of ionisation obtained refers to a gram-equivalent of copper ( $= 31.8$  grams). For a gram-ion ( $63.6$  grams), the heat is, of course, twice as great; *i.e.* for the transformation of  $63.6$  grams of copper from the metallic to the ionic condition,  $2 \times 8718$  ( $= 17,436$ ) cal. are required.

As a rule, heat is evolved when ions are formed; that is to say, the heat of ionisation is negative. If we know the heat of ionisation of one metal, that of any other metal can be calculated from the thermochemical data. For instance, when copper is displaced from copper sulphate by zinc,  $25,055$  cal. are evolved per equivalent. This process consists partly in the transformation of an equivalent of zinc from the metallic to the ionic condition, and partly in the transformation of an equivalent of copper from the ionic to the metallic condition. The heat evolution for the latter has been shown to be  $8718$  cal. For the former, therefore, there remain  $16,337$  cal. Now, since the heat changes which occur when one metal displaces another from its salts are known from thermochemical measurements, it is easy to calculate in the above manner the heats of ionisation, as has been done by Ostwald (*10*), whose values for equivalent quantities are contained in the following table. The heat of ionisation of hydrogen is almost zero; it amounts to  $550$  cal. The heat of ionisation of a metal is, therefore, equal to the negative heat of solution of the metal in an acid less  $550$  cal.

HEATS OF IONISATION IN CALORIES (SMALL).

Potassium . . . . .	- 61,000	Cobalt . . . . .	- 7,300
Sodium . . . . .	- 56,300	Nickel . . . . .	- 6,800
Lithium . . . . .	- 62,000	Zinc . . . . .	- 16,300
Strontium . . . . .	- 57,800	Cadmium . . . . .	- 8,100
Calcium . . . . .	- 53,500	Copper, divalent . . . . .	+ 8,800
Magnesium . . . . .	- 53,400	Mercury . . . . .	+ 20,500
Aluminium . . . . .	- 39,200	Silver . . . . .	+ 26,200
Manganese . . . . .	- 24,000	Thallium . . . . .	- 1,000
Iron, divalent . . . . .	- 10,000	Lead . . . . .	+ 500
Iron, 2-3 valent . . . . .	+ 12,100	Tin . . . . .	- 1,000

**Seat of the Electromotive Force in a Daniell Element.**—From what has been said it is easy to form a conception of the mode of action of a Daniell element,  $\text{Cu} \mid \text{CuSO}_4 \mid \text{ZnSO}_4 \mid \text{Zn}$ . In this there occur four potential differences, namely—



Of the first of these electromotive forces we may assume that its value can be measured by the Peltier effect, according to Edlund (11), and it is therefore a few thousandths of a volt (0.006 volt). The potential difference between the liquids is, according to Planck (see p. 228), of the same order of magnitude. In the case cited, when the concentrations are the same, it is almost zero, because copper and zinc sulphates have nearly the same transport numbers. When the concentrations are different, the difference of potential may rise to a few millivolts. When the two solutions are of about the same concentration, therefore, the electromotive forces referred to cannot contribute much to the total electromotive force, which reaches the value of 1.114 volts. There remain the other two potential differences between metals and solutions. The values of  $\pi$  in the table on p. 237 have been corrected for these two small electromotive forces.

If the solution pressure of copper is  $P_1$ , the osmotic pressure of the copper ions in the copper sulphate solution  $p_1$ , and if the corresponding values for zinc are  $P_2$  and  $p_2$ , the total electromotive force is given by—

$$\begin{aligned} E &= \frac{1.99 \times 10^{-4}}{2} T \left( \log \frac{P_1}{p_1} - \log \frac{P_2}{p_2} \right) \\ &= \frac{1.99 \times 10^{-4}}{2} T \left( \log \frac{P_1}{P_2} - \log \frac{p_1}{p_2} \right). \end{aligned}$$

In this case  $E$  has a high negative value, since  $P_2$ , the

solution pressure of zinc, is very much greater than  $P_1$ , that of copper. The value of  $\log \frac{p_1}{p_2}$  can, as a rule, be neglected.

It shows, however, that the electromotive force of the element will be the greater according as the value of  $p_2$  is great and that of  $p_1$  small. In spite of the difficulties attending the experiments on account of the smallness of the potential differences, this has been directly proved. If a Daniell element contains solutions of zinc sulphate and copper sulphate of such concentrations that  $p_1$  and  $p_2$  are equal, whilst in another case the solutions are of such concentration that  $p_1 = 1000p_2$ , the difference in the electromotive forces is only—

$$\frac{1.99 \times 10^{-4}}{2} \cdot 291 \times \log 1000 = 0.087 \text{ volt.}$$

It can, therefore, be seen that quite large differences of concentration exert only a comparatively small influence. When the zinc sulphate in a Daniell element is replaced by sulphuric acid, the potential difference must evidently become higher; this is due to the fact that in this case  $p_2$  is exceedingly small, particularly at the beginning.

From the formula given we may conclude that the potential difference in such an element depends mainly (almost exclusively) on the ratio of the solution pressures. Some exceptions will be later considered in detail.

This rule, gained by experience, has been confirmed by the following numbers found by Streintz (12). Nevertheless, varying numbers have been obtained for the same metals, the differences amounting in some cases to as much as 0.2 volt, and further investigation on this subject is required to clear up the cause of these peculiarities.

The following table gives the magnitudes of the electromotive forces of some elements of the type of the Daniell cell, that is, with unpolarisable electrodes of the first order. The salts used in these elements, in normal solution, are indicated by their negative ions. The numbers in brackets

are those obtained 48 hours after the element had been put together, the others were obtained immediately after the element had been constructed.

	ZnCu.	MgCu.	CdCu.	ZnCd.
SO <sub>4</sub> . . . .	100·0	167·5	67·6	32·6
NO <sub>3</sub> . . . .	100·0(100·0)	159·1(179·7)	81·8(68·1)	17·5(32·0)
Cl . . . .	90·0	180·4(177·8)	79·6(75·9)	20·2(25·0)

**Very Small Ionic Concentrations.**—Occasionally the values of  $p_1$  and  $p_2$  are extremely small, namely, when the salt is very difficultly soluble, and when double salts are formed. As an example of the former case, we may take the silver halides. Quite different values are obtained when these are used from those found when a salt solution of finite concentration is employed. Wright and Thompson found the following values for the electromotive forces of elements constructed on the plan: silver | silver salt | zinc sulphate | zinc, when different silver salts were used:—

Sulphate . . . . .	Volts.	1·54	Chloride . . . . .	Volts.	1·10
Nitrate . . . . .	1·53	Bromide . . . . .	0·91		
Acetate . . . . .	1·49	Iodide . . . . .	0·71		

In this case the silver corresponds with the copper in a Daniell element. Consequently the electromotive force of the element is the greater the higher the concentration of silver ions in the neighbourhood of the silver. For the three comparatively easily soluble silver salts, sulphate, nitrate, and acetate, the electromotive force is almost the same, but for the difficultly soluble chloride, bromide, and iodide it is decidedly lower.

In other experiments the solution contained, besides the silver halide, other chlorides, bromides, or iodides, which depress the solubility of the silver salt. As a consequence of this, it was found that the electromotive forces were appreciably smaller, the smallest being obtained with the

iodide. The same remarks apply to the chlorides, bromides, and iodides of lead and mercury.

Double salts behave in quite the same way. In the element  $\text{Cu} \mid \text{KCN} \mid \text{ZnSO}_4 \mid \text{Zn}$  the current does not go in the usual direction from zinc, through the solution, to copper, but in the opposite direction. The reason for this is that the osmotic pressure of copper ions in potassium cyanide solution is exceedingly small. When copper dissolves in this solution, the double salt  $\text{K}_2(\text{CN})_4\text{Cu}$  is formed with the ions  $2\text{K}$  and  $\text{Cu}(\text{CN})_4$ , and only a trifling quantity of  $\text{Cu}(\text{CN})_2$  is produced, which dissociates into  $\overset{++}{\text{Cu}}$  and  $2(\overset{-}{\text{CN}})$ .

The osmotic pressure  $p_1$  of the copper ions thus becomes so small that the expression  $\log \frac{p_1}{p_2}$  counterbalances the expression  $\log \frac{P_1}{P_2}$ .

Measurements of the electromotive force may be used to determine the solubility of difficultly soluble salts or the degree of dissociation of double salts. The alkalis, their sulphides, thiocyanates, ferrocyanides, and similar salts, behave, in aqueous solution, like potassium cyanide. If the electromotive force of the element, silver  $\mid$  potassium cyanide  $\mid$  potassium nitrate  $\mid$  silver nitrate  $\mid$  silver, is 1.14 volts at  $17^\circ$  ( $T = 290^\circ$ ), it follows that—

$$1.14 = 0.0002 T \log \frac{p_1}{p_2}.$$

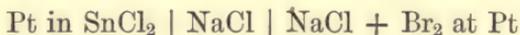
Now, if the silver nitrate solution is 0.1-normal,  $\log p_1 = -1$ , therefore  $p_2 = 10^{-20.7}$ , *i.e.* 108 grams of silver are contained in  $10^{20.7}$  litres of potassium argentocyanide in the form of silver ions.

Since, in a Daniell element, the solution pressure of the zinc is very much greater than that of the copper, the zinc replaces the copper dissolved as ions, and we may rightly regard the Daniell element as a machine which is driven by osmotic pressure (really, solution pressure).

## CHAPTER XV.

### Oxidation and Reduction Elements. Secondary Elements.

**Becquerel's Experiments.**—Becquerel (1) has shown that when two platinum or gold electrodes are surrounded, one with an oxidising and the other with a reducing agent, a current passes in the liquid from the reducing to the oxidising agent. Ostwald and his pupils have made a study of these so-called *oxidation and reduction elements*. Bancroft (2) found an electromotive force for the element—



of 1.171 volts.

In place of stannous chloride, any reducing agent, such as sulphurous acid or ferrous sulphate, may be used; and instead of bromine, any oxidising agent, like gold or mercuric chloride, potassium permanganate, etc.; in this way quite considerable electromotive forces can be obtained. Bancroft arranged the oxidising and reducing agents examined in this way in a series which describes well their chemical position.

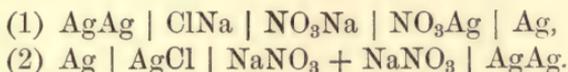
In these elements we have evidently a direct transformation of chemical into electrical energy. Ostwald terms this "chemical action at a distance." The oxidation and reducing agents which, when mixed, react chemically on each other, are here separated, and can only react when an electric current passes through the liquid and brings

hydrogen ions to the oxidising agent, and negative ions to the reducing agent.

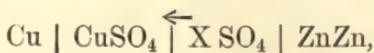
In a similar way, the chemical energy which is obtained when solutions of sodium chloride and silver nitrate are brought into contact (silver chloride being precipitated, and sodium nitrate remaining in solution) may be transformed. This can be done in the element—



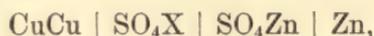
This may be viewed as a concentration element. The osmotic pressure of the silver ions in the sodium chloride solution is very small, therefore silver ions pass into solution there, and silver is separated from the silver nitrate solution. A layer of silver chloride is formed evidently at the expense of the silver nitrate and sodium chloride solutions, with simultaneous production of sodium nitrate, as shown by the scheme—



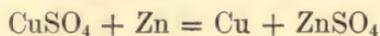
It is a characteristic of all galvanic elements that at the poles two (or more) substances are present which, when brought into contact, react with one another chemically, but which are so separated in the element by one (or more) electrolyte from each other that no chemical action takes place between them except that due to unavoidable diffusion. By means of the current, ions are transported from the separating electrolytes, and so the chemical action becomes possible. In a Daniell element, for instance, the reacting substances are zinc and copper sulphate, which are at the poles, but are separated from each other by sulphuric acid, zinc sulphate, or some other sulphate—magnesium sulphate in Meidinger's modification ( $\beta$ ) of the element. By putting the poles in metallic connection, a current is spontaneously produced, which transports the ions according to the scheme—



so that we obtain—



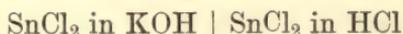
where X is divalent, hydrogen ( $\text{H}_2$ ) or zinc in the Daniell element, magnesium in Meidinger's element. On account of the passage of the current, the chemical reaction—



between zinc and copper sulphate takes place in the element through the medium of the ions, although the two reacting substances are spatially separated from each other. On account of the charges on the ions, electricity is transported during the reaction, and so the ion may be regarded as a sort of machine for transforming chemical into electrical energy.

We can imagine Bancroft's measurements carried out as follows. Several platinum wires, each surrounded by its oxidising or reducing agent (*A, B, C, D*, etc.), are immersed in a conducting liquid. The potential difference between *A* and *D* will then be equal to the sum of the differences between *A* and *B*, *B* and *C*, and *C* and *D*. All the substances examined may be arranged in a series, starting with the strongest reducing agent, stannous chloride in potassium hydroxide solution, and ending with the most energetic oxidising agent, potassium permanganate in sulphuric acid. The numbers in this series (see the following table) give the potential differences between the compound indicated and the last in the series, potassium permanganate in sulphuric acid. It may be noticed that quite considerable potential differences exist between stannous chloride in potassium hydroxide and stannous chloride in hydrochloric acid, between chlorine in potassium hydroxide and chlorine in potassium chloride, etc. In the first case, stannic chloride is formed, which decomposes into  $4\text{HCl}$  and  $\text{Sn}(\text{OH})_4$ , and the hydrochloric acid is neutralised by the potassium hydroxide present. Consequently, in presence of potassium hydroxide more chemical energy is capable of being

transformed into electrical energy than in presence of hydrochloric acid. According to this view,

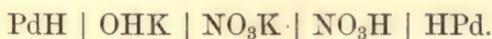


is a kind of concentration element with respect to hydrogen ions, which are present to a large extent in the hydrochloric acid solution, but only occur in small quantity in the alkali solution.

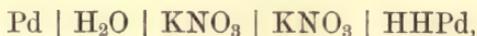
Chlorine in potassium hydroxide behaves in the same way towards chlorine in potassium chloride. In the former solution it is reduced by the hydrogen ions to hydrochloric acid.

	Volts.		Volts.
SnCl <sub>2</sub> in KOH . . . . .	2·06	NaHSO <sub>3</sub> . . . . .	1·10
NaSH . . . . .	1·86	H <sub>2</sub> SO <sub>3</sub> . . . . .	1·04
Hydroxylamine in KOH . . . . .	1·83	Ferrous sulphate in H <sub>2</sub> SO <sub>4</sub> . . . . .	0·97
Chromous acetate in KOH . . . . .	1·79	Potassium ferrioxalate . . . . .	0·91
Pyrogallic acid in KOH . . . . .	1·68	Iodine in KI . . . . .	0·88
Hydroquinone in KOH . . . . .	1·53	Potassium ferricyanide . . . . .	0·78
Zinc hydrosulphite . . . . .	1·49	Potassium bichromate . . . . .	0·70
Potassium ferro-oxalate . . . . .	1·48	Potassium nitrite in H <sub>2</sub> SO <sub>4</sub> . . . . .	0·63
Chromous acetate . . . . .	1·40	Chlorine in KOH . . . . .	0·58
Potassium ferrocyanide . . . . .	1·29	Ferric chloride . . . . .	0·52
Iodine in KOH . . . . .	1·28	Nitric acid . . . . .	0·51
SnCl <sub>2</sub> in HCl . . . . .	1·27	KClO <sub>4</sub> in H <sub>2</sub> SO <sub>4</sub> . . . . .	0·50
Potassium arsenite . . . . .	1·26	Br <sub>2</sub> in KOH . . . . .	0·45
NaH <sub>2</sub> PO <sub>2</sub> . . . . .	1·25	H <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> . . . . .	0·37
Cu <sub>2</sub> Cl <sub>2</sub> . . . . .	1·20	KClO <sub>3</sub> in H <sub>2</sub> SO <sub>4</sub> . . . . .	0·35
Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> . . . . .	1·19	Br <sub>2</sub> in KBr . . . . .	0·34
Na <sub>2</sub> SO <sub>3</sub> . . . . .	1·18	KIO <sub>3</sub> in H <sub>2</sub> SO <sub>4</sub> . . . . .	0·27
Na <sub>2</sub> HPO <sub>3</sub> . . . . .	1·17	MnO <sub>2</sub> in HCl . . . . .	0·14
FeSO <sub>4</sub> . . . . .	1·13	Cl <sub>2</sub> in KCl . . . . .	0·10
Hydroxylamine in HCl . . . . .	1·12	KMnO <sub>4</sub> in H <sub>2</sub> SO <sub>4</sub> . . . . .	0·00

**Neutralisation Element.**—In the following element electrical energy is produced on account of the neutralisation process which takes place :—



It gives—



and therefore the process consists of the transformation of

$\text{KOH} + \text{HNO}_3$  into  $\text{KNO}_3 + \text{H}_2\text{O}$ . On the basis of older experiments with platinum instead of palladium, Ostwald (4) assumes that the electromotive force is about 0.74 volt. This electromotive force ( $E$ ) is governed by the formula—

$$E = 0.0002 T \log \frac{p_a}{p_b} = 0.0002 T \log \frac{C_a}{C_b}$$

where  $p_a$  and  $C_a$  are the osmotic pressure and the concentration of hydrogen ions in the acid,  $p_b$  and  $C_b$  the corresponding values for the hydrogen ions in the solution of potassium hydroxide. Since  $C_a$  is known, the value of  $C_b$  can be calculated. If the concentration of the hydroxyl ( $\text{OH}$ ) ions in the alkali, which is known, be denoted by  $C^1_b$ , the equation of equilibrium (see p. 87) is—

$$C_b C^1_b = K C_{\text{H}_2\text{O}}$$

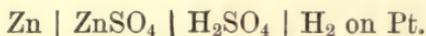
where  $C_{\text{H}_2\text{O}}$  is the concentration of the water in the solution, and it may be regarded as constant (55.5 gram-molecules per litre). From this,  $K$ , the dissociation constant of water, may be calculated.

For water, in which the number of hydrogen ions is equal to the number of hydroxyl ions ( $C_0$ ), we have the equation,  $C_0^2 = K C_{\text{H}_2\text{O}}$

However, in the element cited, electromotive forces appear at the surfaces of separation of  $\text{KOH}$  and  $\text{KNO}_3$ , and at that between  $\text{KNO}_3$  and  $\text{HNO}_3$ , and, according to Planck's formula, the combined value for these is 0.065 volt, which must be subtracted from the total electromotive force in order to give that due to the neutralisation. From the data obtained in this way we arrive at the result that the number of gram-ions of hydrogen in a litre of water is  $0.8 \times 10^{-7}$ , a value which agrees excellently with that found by Kohlrausch,  $0.8 \times 10^{-7}$  at  $18^\circ$  (see p. 194).

**Irreversible Elements.**—If we construct an element according to the scheme  $\text{Zn} \mid \text{H}_2\text{SO}_4 \mid \text{Pt}$ , we find that it gives rise to a current which, however, soon ceases because  $\text{H}_2$  is

deposited at the platinum electrode, and we then really have the element—



The current is weakened because the hydrogen bubbles diminish the conductivity, but this we may neglect. It is further weakened on account of the deposited hydrogen, which possesses a higher solution pressure than the platinum. This solution pressure is, moreover, proportional to the pressure of the evolved hydrogen; it may easily be imagined that if this pressure is sufficiently great, the solution pressure of the zinc would not exceed that of the hydrogen, and the current would stop. This would take place only at an enormously high pressure, and it cannot be realised. The quantity of hydrogen in the neighbourhood of the electrode can be diminished by addition of an oxidising agent, such as chromic acid (Poggendorff's element,  $E = 2.0$  volts), nitric acid (Grove's, Bunsen's element,  $E = 1.9$  volts), manganese dioxide (Leclanché's element,  $E = 1.48$  volts), etc. The greater the intensity with which the oxidising agent reduces the pressure of the hydrogen at the platinum, the greater does  $\log \frac{P}{p}$  become, where  $P$  is the solution pressure of the zinc, and  $p$  that of the hydrogen gas, and the higher is the electromotive force of the element. These elements may, therefore, be regarded as a kind of oxidation elements. If the current strength becomes too great it may happen that the oxidising agent does not diffuse sufficiently quickly to the platinum in Grove's element, or to the carbon in Bunsen's element, to allow of complete depolarisation. This is particularly the case when manganese dioxide is used as depolariser, for in this case the separated hydrogen must diffuse to the oxide in order to be oxidised. Consequently, too much current must not be drawn from these elements if it be required that the electromotive force is not to sink too greatly. A small diminution of the electromotive force always takes place, because the oxidising agent gradually

becomes used up. Nevertheless, these elements are largely used in practice, for with them a fair yield of current can be obtained at an almost constant electromotive force comparatively cheaply. Before the introduction of accumulators the commonest element in use was the Bunsen :  $\text{Zn} \mid \text{H}_2\text{SO}_4 \mid \text{HNO}_3 \mid \text{C}$ . The great disadvantage possessed by this element is that it gives off unpleasant nitrous fumes.

Leclanché's element differs from these others, inasmuch as the electrolyte is not sulphuric acid, but a concentrated solution of ammonium chloride. In common with acids, this substance possesses the power of dissolving metal oxides ( $\text{ZnO}$ ) which are formed during the passage of the current; water and ammonia are formed, and this latter combines partially with the metal chloride simultaneously produced. Ammonium chloride is also used in other elements, such as Pollak's regenerative element, which consists of porous (air-absorbing) carbon coated on the under side with galvanically deposited copper, ammonium chloride solution, and zinc. The copper is first oxidised by the absorbed oxygen, and then dissolved by the ammonium chloride with formation of cupric chloride. Zinc then dissolves with production of zinc chloride, and an equivalent quantity of copper is deposited at the positive pole (the carbon), thus giving rise to the current. When the element is at rest the copper is again oxidised.

Alkalis can also dissolve certain metallic oxides, and therefore may replace acids in a Volta pile. This is made use of in the element of Lalande and Chaperon (copper element) (5), which consists of a metal (iron or copper) coated with copper oxide, 40 per cent. potassium hydroxide solution, and zinc. In order to prevent absorption of carbon dioxide by the alkali this must be covered tightly, or protected from the access of air by a film of petroleum. The chemical process which takes place is that zinc is oxidised by the copper oxide, and the zinc oxide dissolves in the alkali, with formation of potassium zincate. Copper is deposited at the negative pole, and by roasting this in the air it can again be oxidised.

As already mentioned, these irreversible elements never possess an absolutely constant electromotive force; for the measurement of electromotive forces we must, therefore, use reversible, so-called normal, elements.

**Normal Elements.**—The first element which was designed to fulfil this purpose was the Daniell cell. It was, however, soon found that the electromotive force varied with the concentration of the solutions, and so standard solutions were adopted. The normal Daniell element consists of pure copper, copper sulphate solution of sp. gr. 1·195 at 18°, solution of pure sulphuric acid of sp. gr. 1·075 at 18°, and amalgamated pure zinc. Results obtained with this element give—

$$1 \text{ normal Daniell} = 1\cdot176 [1 + 0\cdot0002(t - 18)] \text{ volts.}$$

One disadvantage of this element is that the copper sulphate gradually diffuses to the zinc where copper is deposited, and so the element is spoiled. It must, therefore, be freshly set together immediately before use.

The only negative metal (according to Volta's designation) which by deposition on amalgamated zinc (the positive metal) does not change the electromotive force of this is mercury; it unites with the amalgam at the surface of the zinc, and by dissolving a corresponding quantity of fresh zinc leaves the positive metal unaltered.

For this reason all the other normal elements contain mercury as negative metal. In order to diminish the diffusion as much as possible, the mercury is covered with an excess of a difficultly soluble mercurous salt, so that the mercury forms an unpolarisable electrode of the second order. An example of this kind of normal element is the Helmholtz calomel element (6), in which the positive mercury pole is covered with a paste of mercurous chloride and 10 per cent. zinc chloride solution. The electromotive force of this element is—

$$1 \text{ normal Helmholtz} = 1\cdot074 [1 + 0\cdot0001(t - 20)] \text{ volts.}$$

This element suffers from the disadvantage that the concentration of the zinc chloride may change by evaporation, and from the fact that when current is drawn from it the concentration of the salt may alter on account of zinc dissolving.

To avoid these disturbing factors, a zinc salt easy to prepare pure and in the crystalline form is used for making up the solution, and a layer of this salt is placed over the zinc.

The most suitable salt which has so far been used is the sulphate, which is employed in the normal Clark cell (7), already referred to (p. 124). The electromotive force of this is—

$$1 \text{ normal Clark} = 1.433[1 - 0.0084(t - 15)] \text{ volts.}$$

In the Weston element (8) the zinc is replaced by the closely related metal, cadmium. This cell consists of mercury, mercuric sulphate paste, saturated cadmium sulphate solution, and cadmium amalgam covered with cadmium sulphate crystals. The cadmium amalgam is made up of six parts of mercury and one part of cadmium. The electromotive force of the element is—

$$1 \text{ normal Weston} = 1.019[1 + 0.00004(t - 20)] \text{ volts.}$$

This element has the great advantage of possessing a very small temperature coefficient, so that it is unnecessary to exactly determine the temperature when it is used (it is sufficient to state that the experiment was carried out at the ordinary room temperature). For the composition of the cell, see p. 124.

The elements mentioned, containing difficultly soluble mercury salts, cannot withstand very appreciable current strengths, for such cause the deposition of the small quantity of mercury ion, and it requires a considerable time before a sufficient amount of salt dissolves to re-establish the necessary mercury ion concentration. Of the normal elements the calomel cell can stand the greatest current strength, and this

is due to the fact that mercurous chloride is appreciably more soluble at the ordinary temperature than mercurous sulphate.

**Secondary Elements.**—Secondary elements produced by the polarisation of two electrodes may be regarded as a special type of oxidation and reduction elements. If we connect two plates of platinum (or other metal not attacked), which are immersed in an electrolytic solution, with the poles of a galvanic battery, a separation takes place at each plate. If the electrolyte is a base, an oxygen acid, or the alkali salt of an oxygen acid, hydrogen is separated at the cathode and oxygen at the anode. If, after disconnecting the battery, the two plates be joined by a wire, we obtain a current in the opposite direction to that of the polarising current (see p. 1). We may therefore regard the two pole plates as electrodes of different metals, and the whole as a galvanic element. Such *gas elements* were suggested by Ritter at the beginning of the nineteenth century, and have been much studied since then.

**Polarisation Current.**—The strength of the polarising current falls quickly when a small electromotive force (under 1 volt) is used for the polarisation. It never, however, completely disappears, because the polarised plates become gradually depolarised by diffusion, so that new quantities of gas must be separated in order to maintain the polarisation near the polarising electromotive force. By breaking the circuit and examining the electromotive force of polarisation at different times, it has been found that the speed with which the polarisation spontaneously disappears by diffusion of the separated gases, partly in the liquid and partly in the electrodes (particularly if these be platinum or palladium), is not only dependent on the nature of the electrodes, but also on that of the liquid. The smallest current strength required to replace the gas which is lost by diffusion is called the *polarisation current*.

**Smale's Experiments.**—When higher electromotive forces (1.062 volts) are used, Smale (9) found some comparatively simple relationships. He electrolysed sulphuric

acid between palladium electrodes, which, as is well known, have the power of absorbing the separated gases, particularly hydrogen, and noticed a slight evolution of gas. The gas element thus produced was found to be reversible, for by discharging it fairly quickly, it showed the same electromotive force as the polarising element had to overcome during charging.

Since the combustion of a gram-equivalent of hydrogen is accompanied by the evolution of the quantity of heat ( $W$ ) 34,200 cal., Thomson's rule requires for this element an electromotive force of  $\frac{34200}{23070} = 1.480$  volts, which is higher by 0.418 than that found by Smale. The change of electromotive force of this element with temperature was found to be at 20°—

$$\frac{dP}{dT} = -0.00142 \text{ volt per degree,}$$

from which, by the Helmholtz relationship (see p. 208), we find—

$$\begin{aligned} \frac{23,070P - W}{23,070} &= P - \frac{W}{23,070} = T \frac{dP}{dT} \\ &= 293(-0.00142) = -0.416 \text{ volt;} \end{aligned}$$

whilst by experiment the difference was—

$$P - \frac{W}{23,070} = 1.062 - 1.480 = -0.418 \text{ volt,}$$

which shows a very good agreement with the value calculated. From this it can be gathered that the element is reversible.

Bose (10), too, found that the hydrogen-oxygen cell works reversibly, although he found a somewhat higher electromotive force (about 1.11 volts) than Smale did.

**Helmholtz's Investigation on the Influence of Pressure.**—When platinum electrodes are used it is found that higher electromotive forces are required to produce an

evident evolution of gas. Since the gas must have a pressure at least equal to the external pressure in order to be able to leave the electrode in the form of bubbles, it is clear that the electromotive force, as in Meyer's concentration element, will be the greater the higher the external pressure is. Helmholtz (11) investigated the relationship by varying the pressure from  $P_0 = 10$  mm. of water to  $P_1 = 742$  mm. of mercury. The ratio of these pressures is 1 : 1000, therefore  $\log \frac{P_1}{P_0} = 3$ . The concentration of the gas in the liquid must be in the same ratio, according to Henry's law, and the difference in the electromotive force for the hydrogen electrode will be (see the formula on p. 211)—

$$dE = \frac{1}{2} \cdot \frac{2T}{23,070} \ln 1000 = 0.0879.$$

A molecule of hydrogen ( $H_2$ ) contains two equivalents (H), therefore in the formula  $n = 2$ .

For the oxygen the corresponding difference  $dE_1$  is only half as great (for  $n = 4$ ), and we therefore obtain—

$$dE + dE_1 = 0.0879 + 0.0440 = 0.1319 \text{ volt,}$$

whilst Helmholtz actually found that the electromotive force of polarisation rose from 1.635 volt to 1.805 volt;  $dE + dE_1$  was, therefore, 0.17 volt, which is in tolerable agreement with the requirement of the theory.

If the electromotive force of polarisation is known for a certain pressure, we may evidently calculate how great the partial pressure of the hydrogen and of the oxygen must be in order that the polarisation may become zero. Now, since the concentration of hydrogen and oxygen in water is regulated by Henry's law at a given external pressure, and the absorption coefficients of the two gases are known, we may easily calculate what quantities of the gases are contained in unit volume of the liquid when the electromotive force is zero, assuming that the hydrogen and oxygen are present in equivalent quantities. If we are below this limit, the back electromotive force is negative, *i.e.* by the

decomposition of the water work is done. In other words, the water spontaneously decomposes until this concentration is reached; the liquid therefore contains  $0.7 \times 10^{-27}$  gram-molecules of hydrogen, and half as much oxygen per litre at  $20^\circ$ . In this calculation Smale's result,  $E = 1.062$ , and Bunsen's absorption coefficients of the two gases in water have been used.

If the concentration of the oxygen, by being in equilibrium with the oxygen of the air, is kept constant ( $2.5 \times 10^{-4}$  gram-molecules per litre at  $20^\circ$ , according to Bunsen), the quantity of hydrogen is also determined ( $0.1 \times 10^{-50}$  gram-molecule per litre), for the product of the concentrations must, at any given temperature, be constant (see p. 85).

**Strength of the Polarisation Current.**—Suppose we work with an electromotive force,  $E$ , which is not sufficient to produce an evident separation of gas. Further, suppose that the quantity of dissolved oxygen in the water near the anode is kept constant by being in equilibrium with the oxygen of the air. The electromotive force  $E$  then increases proportionally to the logarithm of the concentration of the hydrogen ( $f$ ) near the cathode, so that—

$$E = A + T \times 10^{-4} \log f,$$

where  $A$  is a constant.

A polarisation current is produced by the diffusion of the dissolved hydrogen from the cathode into the water, which, according to our assumption, contains less hydrogen. The quantity of hydrogen which diffuses in a second must, *ceteris paribus*, be proportional to the excess pressure of the hydrogen at the cathode over that in the liquid (see p. 153). This latter is so small that it may be entirely neglected. The quantity of hydrogen which diffuses is replaced by that separated by the polarisation current in one second, and this is proportional to the current strength  $i$  of the polarisation current. We therefore obtain—

$$i = \text{const. } f, \text{ and } E = A_1 + T \times 10^{-4} \log i,$$

where  $A_1$  is a new constant.

According to theory, therefore, the strength of the polarisation current must increase proportionally with an exponential function of the electromotive force—

$$i = \text{const. } e^{cE}$$

where  $c$  denotes a constant.

In reality the intensity of the polarisation current increases enormously quickly with the polarising electromotive force until visible gas evolution occurs, when, of course,  $f$  cannot further rise. It has, nevertheless, been found that even after this point has been reached,  $E$  increases with the strength  $i$  of the polarising current. This phenomenon may be due to a sort of supersaturation of hydrogen taking place in the water. (The same applies, of course, to the oxygen.) Jahn (12) assumes that this supersaturation is proportional to the current density, and obtains for visible electrolysis a formula analogous to the above one, only with different constants ( $c$  is greater than in the former case). As a matter of fact, it is observed that immediately after the beginning of the gas evolution there is a much greater increase of the current density for the same increase of the polarising electromotive force ( $E$ ) than before.

**Le Blanc's Investigations.**—By means of a galvanometer or capillary electrometer the value of  $E$  can be determined at the decomposition-point.

Le Blanc (13) found, as required by theory, that the electromotive force of polarisation is independent of the nature of the electrolyte, provided that the substance separated at the platinum electrodes is the same, a condition which is fulfilled when the ordinary oxygen acids or bases are used. The values obtained by him for  $E$  were—

	Volts.		Volts.
Sulphuric acid . . . . .	1.67	Sodium hydroxide . . . . .	1.69
Nitric acid . . . . .	1.69	Potassium hydroxide . . . . .	1.67
Phosphoric acid . . . . .	1.70	Ammonia . . . . .	1.74
Monochloroacetic acid . . . . .	1.72	Methylamine . . . . .	1.75
Dichloroacetic acid . . . . .	1.66	Diethylamine . . . . .	1.68
Malonic acid . . . . .	1.69	Tetramethylammonium hy-	
Perchloric acid . . . . .	1.65	droxide . . . . .	1.74
Tartaric acid . . . . .	1.62		

On the other hand, if the products of the electrolysis are not the same, as is the case with hydrochloric acid ( $H_2$  and  $Cl_2$ ), hydrobromic acid ( $H_2$  and  $Br_2$ ), hydriodic acid ( $H_2$  and  $I_2$ ), different tensions are obtained: in these three cases, 1.31, 0.94, and 0.52 volt respectively for normal solutions. In the case of some organic acids, such as oxalic acid, trichloroacetic acid, etc., deviating results were obtained, because in these instances the secondary processes which take place at the electrodes play an important part.

For these acids, which all show a lower value for  $E$  than 1.67 volt, corresponding with the separation of hydrogen and oxygen at the platinum electrodes, the influence of the secondary processes diminishes with rising dilution, and at the same time the reduction of the separated oxygen does not take place so readily. The polarisation for a normal solution of oxalic acid is 0.95 volt, whilst for a 0.067-normal solution it rises to 1.04 volts. A similar behaviour is exhibited by hydrochloric acid solutions, in which more and more oxygen instead of chlorine is separated as the dilution increases. Thus a normal solution of hydrochloric acid shows the tension of polarisation  $E = 1.31$  volts, and for a  $\frac{1}{22}$ -normal solution,  $E = 1.69$  volts, *i.e.* as great as for oxygen acids. The oxygen acids show no appreciable change of electromotive force with dilution, so that  $E = 1.67$  volts both for a normal and for a  $\frac{1}{50}$ -normal solution of sulphuric acid.

The alkali salts of the oxygen acids behave somewhat differently. With these the decomposition products are not only  $O_2$  and  $H_2$ , but base and acid as well, *i.e.*  $OH$  and  $H$  ions. Consequently more work is required for the electrolysis of these than for acids, but about the same for all salts. Using platinum electrodes, Le Blanc found the following polarisation electromotive force  $E$ :—

	Volts.		Volts.
Sodium nitrate . . . . .	2.15	Sodium sulphate . . . . .	2.21
Potassium nitrate . . . . .	2.17	Potassium sulphate . . . . .	2.20
Lithium nitrate . . . . .	2.11	Sodium acetate . . . . .	2.10
Strontium nitrate . . . . .	2.28	Ammonium nitrate. . . . .	2.08
Calcium nitrate . . . . .	2.11	Ammonium sulphate . . . . .	2.11
Barium nitrate . . . . .	2.25		

These decomposition tensions exceed those of the acids by 0·47 volt on the average. The difference between the decomposition tensions of the chlorides, bromides, and iodides and the corresponding acids is somewhat greater, as can be seen from the following values found by Le Blanc :—

	Volts.		Volts.
Sodium chloride . . . .	1·98	Barium chloride . . . .	1·95
Potassium chloride . . . .	1·96	Sodium bromide . . . .	1·58
Lithium chloride . . . .	1·86	Potassium bromide . . . .	1·61
Calcium chloride . . . .	1·89	Sodium iodide . . . .	1·12
Strontium chloride . . . .	2·01	Potassium iodide . . . .	1·14

The difference amounts to about 0·87 volt for the chlorides, 0·67 volt for the bromides, and 0·61 volt for the iodides when these are compared with normal solutions of the acids. If for comparison we take a  $\frac{1}{2}$ -normal solution of hydrochloric acid, the difference for the chlorides would only be 0·49 volt. It is difficult to give the preference to one or other concentration of the acid on any rational basis. If the difference of the decomposition products between the halogen acids and their salts were the same as between the oxygen acids and their salts, then the difference in the electromotive force would necessarily be the same in both cases.

**Maximum Polarisation.**—It was formerly supposed that, with increasing current strength, the value of  $E$  rose asymptotically to a maximum. From Jahn's results this conclusion is rendered doubtful; he found that  $E$  increases almost proportionally with  $\log i$ . The increase, however, takes place so slowly that we may assume for the currents which are used practically that there is a maximum electromotive force of polarisation; without appreciable error we may take the value of this to be 2·5 volts for acids and bases, and 3·3 volts for the salts of oxygen acids.

**Polarisation by Deposition of Solid Substances.**—When a solution of copper sulphate is electrolysed between platinum plates, copper is deposited at the cathode, and  $\text{SO}_4$  at the anode, and this latter, by reaction with the water, gives  $\text{H}_2\text{SO}_4$  and  $\text{O}_2$ . If the electrolysis be carried to a certain

point, the platinum cathode becomes covered with a film of copper, and in an electromotive respect behaves like a copper plate. However, the deposited film must assume a certain (although very small) thickness before it acts quite like pure copper. Oberbeck (14) found that when the deposited film on the platinum electrodes is 2·7 millionths of a millimetre thick in the case of zinc, and 1·9 millionths of a millimetre in the case of cadmium, the same electromotive force is obtained as when the pure metals (zinc or cadmium) are used. This phenomenon is also termed polarisation, and we therefore say that the electromotive force of polarisation in the decomposition of copper sulphate is for the cathode the same as the electromotive force  $\text{Cu} \mid \text{CuSO}_4$ .

**Grove's Investigations.**—Grove (15) immersed in a dilute solution of sulphuric acid two platinum plates covered with films of different gases. Between the platinised platinum plates charged with different gases and a platinum electrode saturated with hydrogen, he obtained the following tensions in volts (the unit adopted by Grove = 2 volts):—

	Volt.		Volt.
Chlorine . . . . .	0·63	Cyanogen . . . . .	0·42
Bromine . . . . .	0·56	Carbon dioxide . . . . .	0·42
Oxygen . . . . .	0·48	Nitric oxide . . . . .	0·41
Iodine . . . . .	0·48	Air . . . . .	0·41
Nitrous oxide . . . . .	0·43	Pure platinum . . . . .	0·40

In the form used by Grove these elements are by no means reversible, otherwise he would have found the same potential difference as Smale (9) did for the combination oxygen  $\mid$  hydrogen at a palladium electrode, whilst he only obtained something less than half this value.

**Cathodic and Anodic Polarisation.**—In studying polarisation phenomena, the action of the cathode can be distinguished from that of the anode by comparing the potential of each electrode with that of a so-called normal electrode, generally mercury under calomel and a 0·1-normal solution of potassium chloride, the polarisation vessel being connected with the normal electrode by means of a

fine syphon or wet thread containing 0.1-normal KCl. Any unpolarisable electrode may be used as a normal electrode. Since the polarisation diminishes rapidly after the circuit is broken, it should be measured as soon as possible (within 0.01 second) after the current is stopped: the measurement can best be made with an electromagnetic tuning-fork.

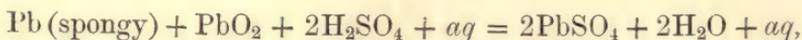
**Accumulators.**—The accumulators constructed by Planté (16) in 1859 are a particular kind of secondary elements. The simplest form consists of two lead pole plates immersed in a 15 to 30 per cent. solution of sulphuric acid. When a current is conducted through this element, hydrogen is separated at one side, and oxygen at the other, which gradually oxidises the positive plate to lead peroxide. When this process has taken place for some time, the current is reversed, so that the lead peroxide is reduced to lead oxide, which, with the sulphuric acid, forms lead sulphate, and this, by further reduction, leads to a spongy mass of lead. At the same time the surface of the other plate becomes covered with a film of lead peroxide. By repeatedly reversing the direction of the current, the lead peroxide permeates deeper and deeper into the positive plate, which becomes more porous. This successive charge and discharge necessary to “form” the accumulator plates requires a very long time, and formerly about a year was spent on this process. Chemical and mechanical means were afterwards introduced for treating the lead plates, so that the change into spongy lead was so far accelerated that the process may now be carried out in about fourteen days, or even less. In order to still further aid the “forming” of the plates, Faure (17) introduced the process of mechanically fixing litharge, or red lead, upon the lead plates. This succeeds well, for both litharge and red lead form a sort of cement with sulphuric acid, which (on account of the formation of lead sulphate) assumes a solid consistency, and, according to the process of Sellon and Volekmar (18), a mixture of this sort is brought into properly disposed cuts on the lead plates. Finely divided lead, moistened with water and sulphuric acid,

behaves similarly, and may be used to fill the rills of the lead plates. The cuts are now made so deep that the lead plate has the appearance of a sort of framework (or grid), with the spaces filled with the mixture described. These plates are "formed" against an ordinary plate. An objection to such plates is that the substance of the electrode does not hold together well, and cannot withstand high current strengths. The passage of the current is accompanied by chemical processes, which take place with change of volume; if these occur quickly, pieces of the filling material break off from the plates, and fall to the bottom of the containing vessel. [In the Tudor process the positive grid is constructed by pickling it in a bath of sulphuric acid containing nitric acid, and then obtaining the stratum of lead peroxide by electrolysis, using an ordinary plate as cathode. The negative plate is an open grid, pasted with litharge, but not reduced before leaving the factory.]

The liquid in the accumulator must be free from certain impurities, such as chlorine, nitrates, and foreign metals, for if these are present the lead plates are violently attacked; [the presence of arsenic is particularly detrimental]. If foreign metals are present, local currents are set up, provided that the metal deposited on the lead plate during the charging is more negative (as, *e.g.*, copper) than lead. It is particularly important that the water used in filling up the vessel to replace that lost by evaporation should be entirely free from chlorides and nitrates.

In charging an accumulator, a certain current density, which depends on the kind of plates, should not be exceeded. Formerly, 0.6 ampere per square decimetre was recommended. According to more recent experience, the current density may safely be raised to 1 amp./sq. dm., and, with the best plates (prepared by the Planté method), it may even be as high as 2.6 amp./sq. dm. In discharging, too, the current density must be maintained within the same limits. At the beginning of the charging, the back electromotive force (the pole tension) has a value of about 2.07 volts, which rises slowly to 2.20 volts,

and then quickly to about 2.5 volts. When the charging is nearly complete, persulphuric acid is formed at the peroxide plate, and this partially decomposes into sulphuric acid and oxygen. The oxygen evolves (the accumulator "boils"), and when this occurs it shows that the accumulator is fully charged; at the same time hydrogen is evolved at the other plate; according to Darrieus (19), the former plate is then permeated by persulphuric acid, and the latter has absorbed hydrogen. During the discharge the comparatively small quantities of these substances are used up, and this causes the electromotive force to sink to about 2 volts. Thereafter the principal reaction is—



which evolves, according to the measurement of J. Thomsen, 43,500 cal. for every gram-equivalent of spongy lead which is transformed. During the course of this reaction, the electromotive force falls slowly to 1.9 volts, and then more quickly to 1.8 volts, provided that the discharge does not take place too fast. If the discharge is carried out very rapidly, the electromotive force, after a certain time, falls to a lower value than that mentioned, and this is probably due to a kind of polarisation, inasmuch as the chemical action cannot, so to say, keep up with the electrical process. When the voltage has been reduced to 1.8, no more current should be drawn from the cell, as this is apt to spoil it. If the discharge, however, be carried further, the electromotive force very rapidly decreases. This shows that by slowly discharging an accumulator more electricity (calculated in ampere-hours, at 3600 coulombs) can be obtained than when it is quickly discharged; for in the latter case the voltage more quickly reaches the value 1.8, *i.e.* after a shorter number of ampere-hours.

The number of ampere-hours (at the rate of 3 to 5 amperes per sq. dm. of the positive plate) which an accumulator can yield determines its *capacity*. This is, therefore, greater for weak currents than for strong ones; it

amounts, for instance, to 140 ampere-hours when the discharge takes 10 hours, and only to 100 ampere-hours when the cell is discharged in 3 hours. A discharged element should not be kept in this condition for any length of time, because the lead sulphate formed easily sets to a hard mass, which can only with difficulty be transformed during charging.

It is of interest to learn what is the economic value or the so-called efficiency of an accumulator. This can be judged, on the one hand, by the number of ampere-hours which the element can give compared with the number required for charging it. On the other hand, the efficiency may be determined by the quantity of energy, generally estimated in watt-hours at 3600 coulombs, which the element can yield compared with that absorbed by it during charging. According to the former method, the efficiency amounts to from 82 to 94 per cent., whilst by the latter method it is from 75 to 83 per cent. [and is frequently as low as 60 per cent.], depending on the current density. If an accumulator be left for some time unused, it spontaneously loses part of its charge, *i.e.* its efficiency diminishes.

By means of Thomson's rule we calculate that the electromotive force of an accumulator is  $\frac{43500}{23070} = 1.886$  volts. On the basis of Helmholtz's theorem the temperature coefficient of the electromotive force must be taken into account; this amounts, however, to only 2 to 4 millionths per degree, and so the correction does not exceed 0.001 volt. Now, the electromotive force of an accumulator during the principal reaction is, on the average, 1.9 volts, *i.e.* slightly higher than the calculated value, and even more so at the beginning of the principal reaction when the electromotive force may be as high as 2 volts. The reason for this difference is that the sulphuric acid of the element is more concentrated than was assumed by Thomsen in his calculation. Streintz (20) found that the electromotive force of an accumulator at the beginning of the principal process is given by the formula—

$$E = 1.850 + 0.917 (S - 1),$$

where  $S$  is the specific gravity of the sulphuric acid used. In practice, sulphuric acid of 20 to 24 per cent. with specific gravity varying from 1.144 to 1.173 is employed. [In the Tudor cell acid of specific gravity 1.20 is used.]

It is easy to see why the electromotive force of an accumulator increases with the concentration of the sulphuric acid. Suppose we have two accumulators,  $A$  and  $B$ , filled with 25 per cent. and 15 per cent. sulphuric acid respectively, and suppose that they are so connected that their electromotive forces are opposed to each other, as shown in Fig. 48.

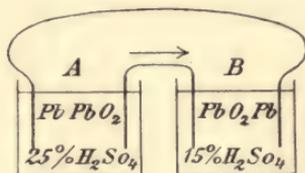


FIG. 48.

Just as the concentration of a layer of 25 per cent. sulphuric acid tends by diffusion to come into equilibrium with a layer of 15 per cent. acid with which it is in contact, so in the system depicted a current arises which tends to establish the same equilibrium, *i.e.* the common concentration of 20 per cent. Now, since on the discharge of an accumulator water is formed and sulphuric acid disappears, whilst the opposite reaction takes place during charging, the accumulator  $A$  must discharge in order to establish the equilibrium, and at the same time this charges  $B$ . It can easily be found thermodynamically how much work can be gained by transferring 18 grams of water from  $B$  to  $A$ , and 98 grams of sulphuric acid from  $A$  to  $B$  (see p. 75). Dolezalek (21) has ascertained in this way the electromotive force of the above combination, and from this calculated how the electromotive force of an accumulator changes with varying concentration of the sulphuric acid. The calculation is in good agreement with the result found by Streintz.

On account of the many advantages possessed by accumulators, they have almost entirely replaced in practice all the older galvanic elements, with the exception of those of Leclanché [and of Daniell], which are more suitable for cases when only a weak current is required, and that for only a

short time, as with bells, telephones, in telegraphy, etc. In scientific work, too, accumulators have been of great service, both for producing comparatively large currents and for obtaining high potentials. For the latter purpose a large number of small elements is used; these elements are constructed with small preparation tubes containing sulphuric acid and strips of lead. In charging, a large number of elements is arranged in parallel, whilst on discharging all the cells are connected in series. Batteries of this sort, which, on account of the smallness of the electrodes, have only a small capacity, are frequently used for the study of electrical phenomena in gases, insulators, and poor conductors.

Certain disadvantages also attend the use of accumulators. The lead of which the electrodes consist must be used in fairly large pieces if any degree of rigidity is to be obtained, and this, of course, means a considerable weight. Furthermore, lead is very easily attacked chemically. In order to avoid these objections, attempts have been made to use lead containing small amounts of foreign metals; 4 per cent. of antimony (so-called Julien metal) and other metals have been tried.

Every reversible element is in a certain sense an accumulator. For instance, if a current is impressed through a Daniell cell in the direction opposite to that of its own electromotive force, zinc is deposited from the zinc sulphate, and copper dissolves to copper sulphate. When left to itself, the process takes place in the opposite direction. In this case, however, the reversibility is more of a theoretical than of a practical nature, because, on account of diffusion of the two electrolytes, copper is deposited on the zinc. This gives rise to a vigorous "local action," whereby the zinc is rapidly destroyed, and there is an evolution of hydrogen in the short-circuited element consisting of zinc, deposited copper, and sulphuric acid (or sulphate solution). A similar disturbance vitiates the usefulness of the copper element (which it was hoped would prove a valuable accumulator), because

some of the copper oxide dissolves in the alkali and diffuses to the zinc. In this respect mercury takes up an exceptional position (see p. 251). Attempts have, therefore, been made to use mercury as the positive pole plate of accumulators, but no practical success has been attained by this. Since in lead accumulators no fear of disturbances due to diffusion need be entertained, the distance between the plates may be made very small, and in this way the internal resistance reduced to a minimum. According to Streintz (20), lead peroxide conducts like a metal, and this also tends to reduce the internal resistance of lead accumulators.

In this latter respect aluminium stands in sharp contrast to lead. At the ordinary temperature an anode of this metal becomes covered with a film of oxide, which offers such a large resistance that the passage of the current is almost entirely stopped. Based on this property, Graetz (22) has constructed a commutator of some theoretic interest. In a trough

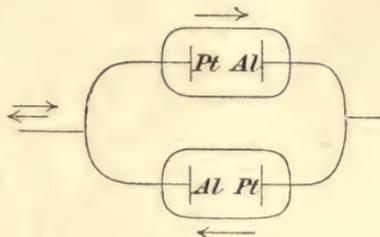
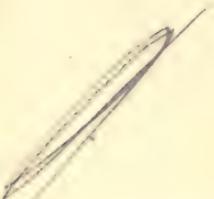


FIG. 49.

filled with a salt solution, in which are a platinum and an aluminium electrode, the current can only pass in the direction from the platinum through the solution to the aluminium, on account of the property mentioned. If we introduce into the circuit of an alternating current two such troughs arranged as in Fig. 49, the current goes through each branch almost entirely in the direction indicated by the arrows.



## CHAPTER XVI.

### Electro-analysis.

**Determination of the Quantity of Salt in a Solution by measuring the Conductivity.**—If we know the conductivity of solutions of a particular salt at various concentrations, then inversely by determining the conductivity we can find the concentration.

If we have a solution containing two given salts, then by making two determinations we find the quantity of each present; one of the determinations may be the conductivity, the second some other property, such as the total weight of dry substance. Erdmann (*1*) determines in this way the quantity of potassium chloride in presence of potassium iodide or rubidium chloride, etc.

In many cases the proportions of the constituents present are nearly constant; this is the case, for instance, with different samples of sea water containing varying total amounts of dissolved substance. In such cases the determination of the resistance is sufficient to indicate the quantities present, and this method of analysis has actually been employed.

Occasionally non-electrolytes are present in the solution to be analysed (for instance, in the estimation of the ash of cane sugar or molasses), and these diminish the conductivity. When this happens a correction must be introduced, and the magnitude of this can be ascertained either from the data given on p. 150, or it has to be found by a special experiment.

For some salts, *e.g.* silver chloride, the conductivity is

not known from direct experiment, but in these cases the molecular conductivity at infinite dilution can be ascertained, as also the degree of dissociation which is set equal to that of some closely allied salt (here, silver nitrate) at the same dilution. The concentration of a given solution of silver chloride can be estimated from the conductivity, and if a saturated solution be used we obtain the solubility. The solubilities of several difficultly soluble salts, such as silver chloride, silver bromide, silver iodide, barium sulphate, calcium sulphate, strontium sulphate, and various silicates have been determined in this way by Kohlrausch and Rose (2) much more exactly than could be done by ordinary analysis.

At high dilution all salts when applied in equivalent quantity conduct almost equally well. Consequently when it is desired to find approximately how many gram-equivalents of salt are present in a water (*e.g.* a well water), this can be done simply by determining the resistance.

**Application of the Electrometer as an Indicator.**—Behrend (3) introduced this instrument for the titration of mercury. Suppose we have two solutions of mercurous nitrate over mercury in two beakers, and that the concentration of one of the solutions is known (*e.g.* 0.1-normal), whilst that of the other is to be found. The two solutions are connected by a syphon tube containing nitric acid, and two platinum wires dip into the mercury in the vessels—the wires are fused through glass tubes, so that only the ends remain free. The platinum wires are connected with the poles of an electrometer; and the electromotive force of the concentration element thus constructed is measured with the electrometer. To the solution whose concentration is to be determined a standard solution of a chloride, *e.g.* potassium chloride, is added, and the mercury is precipitated as calomel. This causes the electromotive force to change slowly until almost all the mercury has been thrown out of solution. The logarithm of the concentration, the value of which determines the electromotive force, then changes very

quickly and most suddenly, just when the last quantity of mercury is precipitated. The electrometer then indicates a spring of about 0.1 volt, and may thus be used as an indicator. This kind of analysis, which can be applied in other similar cases, has not been used in practice to any extent.

**Analysis by Metal Deposition.**—The electrolytic deposition of metal, on account of the ease with which it can be carried out, is the most frequent electrical method of analysis. For the separation of a metal a certain electromotive force (see p. 257) and a definite quantity of electricity are required. The former can be ascertained from the polarisation, the latter by means of Faraday's law, according to which 1 gram-equivalent of any substance is precipitated by a current strength of 1 ampere in 96,500 seconds, *i.e.* 26 hours 48 minutes. If we used an electromotive force for the separation exactly equal to the back electromotive force of polarisation, it would require an infinitely long time to carry out the deposition. In practice, therefore, it is customary to use an appreciably higher electromotive force (higher by 1 to 2 volts). The potential difference between the cathode and anode determines what electromotive force must be used, and between these an electrometer is interposed in a branch circuit. In order to obtain a good, coherent deposit, the current density (given below in amperes per square decimetre) must be judiciously chosen. In order to be able to control this an ammeter is introduced before the decomposition cell. To regulate the current density, a metal wire rheostat is used, and arranged so that different lengths of wire can be interposed at will. The electromotive force is best obtained from a battery of accumulators (only few elements are required, for the electromotive force never exceeds 5 volts). The instruments do not need to be very exact, for an approximate measurement of the electromotive force and the current density suffices.

When the times required for the deposition are calculated by Faraday's law, it is always found that they are too small.

In many cases it is necessary to prolong the electrolysis for five times as long as the time indicated by Faraday's law. The reason for this is that a large part of the current is used up for other processes than the metal deposition. To determine when the deposition is complete, it is, therefore, advisable to withdraw small portions of the solution from the cell, and by means of some delicate reaction ascertain when all the metal has been precipitated from the solution. The quantity of solution taken out must, of course, be exceedingly small, so that the solution may not be robbed of an appreciable amount of the metal.

The solution to be electrolysed should not be more than about 100 c.c., and should be placed in a perfectly clean platinum basin of 10 cm. diameter, which serves as cathode. If the basin is not clean, a good deposit cannot be obtained. In order to cause the deposit to cling well to the basin, this is often provided with a matt surface. The basin is placed on a metal ring, which is carried by an upright stand, the two being united by means of an insulator, and the ring is connected with the negative pole of the battery. The form of the anode may be a perforated plate, a wire spiral, a cylinder of foil or a foil cone of platinum. This anode is held by the same stand which carries the cathode ring, by means of a metal arm connected with the positive pole of the battery. If the electrolysis be carried out in a glass vessel, the cathode should have the form of a cylinder or cone. The anode must not possess any surface to which large bubbles of gas may cling, because when these are ultimately evolved they might easily carry away some of the liquid to be electrolysed. For safety a glass funnel should always be inverted over the basin to catch any drops which may be spirted out of the liquid.

Most of the processes for electrolytic analysis proceed better at a somewhat elevated temperature (50 - 60°) than at the ordinary temperature. For this purpose a small burner is placed below the basin, so that a current of hot air ascends and warms the solution. It is convenient to have the burner fixed to the stand carrying the cell. The

efficacious action of the heat may be in part due to the convection current, to which it gives rise in the liquid.

When the electrolysis is complete the cathode basin is washed out. The deposit should be washed three times with about 50 c.c. of cold water, then three times with about the same quantity of alcohol, after which it is placed for about five minutes in an air bath at  $80^{\circ}$ , dried in a desiccator, and finally weighed when cold. It frequently happens that the liquid in the basin (acid liquids particularly) exerts a dissolving action on the deposited metal so soon as the current is stopped. In these cases the liquid must be removed from the basin by means of a syphon while the current is still passing. Occasionally some substance is added to the liquid in the basin in order to diminish the rate of solution, *e.g.* sodium acetate to a sulphuric acid solution from which copper has been deposited. The sulphuric acid is replaced by the acetic acid, and in this wise the solution process is as good as prevented. Sometimes the adjuncts for washing out are mounted on the stand along with the electrodes.

After the deposit has been weighed it is removed by some chemical solvent, which, as a rule, offers no difficulty. In certain cases the deposit adheres closely to the platinum surface, *e.g.* with zinc or tin, and the platinum becomes more or less porous when the deposit is dissolved off. To prevent this the basin may first be coated with a thin film of copper or silver. Precipitated gold is best removed by chromic anhydride dissolved in a saturated solution of sodium chloride.

Should the level of the liquid sink during the electrolysis, part of the deposited metal will be exposed, and probably suffer oxidation. This may easily be avoided by replacing any water lost by evaporation.

It is characteristic of the depositions used for analytical purposes that they almost all result from secondary processes (see p. 282). So much substance should be taken for the analysis that a deposit of 0.1 to 0.4 gram of metal

will be obtained. In order to assist the secondary electrolysis various electrolytes may be added. In the simplest case, the corresponding acid is added to the solution of the electrolyte. Here a considerable part of the metal is deposited primarily. This method is employed in the following analysis: for the deposition of cadmium (slightly acid ( $\text{H}_2\text{SO}_4$ ) solution,  $t = 70 - 80^\circ$ , current density per square decimetre,  $D = 0.6 - 1$  amp.), copper (solution containing 8 - 10 per cent. of nitric or sulphuric acid,  $D = 1 - 1.5$  amp. in warm or cold solution; in sulphuric acid solution the addition of 0.5 gram of hydroxylamine sulphate, or 1 gram of urea, assists the formation of a good, coherent deposit; chlorides must be entirely absent), mercury (5 per cent. nitric acid,  $D = 0.5$  amp.), bismuth (deposited as amalgam when the solution contains a corresponding quantity of mercury salt; if the electromotive force is less than 1.3 volts only mercury is separated), platinum (with 3 per cent. of sulphuric acid gives a coherent deposit at  $t = 65^\circ$  and  $D = 0.05$ , but platinum black (or sponge) at the ordinary temperature when  $D = 0.1 - 0.2$ ,  $E = 1.2$  volts), and palladium (conditions the same as for platinum).

In other cases double salts are used. The double salts of nickel and cobalt with ammonium sulphate give good deposits in ammoniacal solution (30 - 40 c.c. of ammonia solution,  $t = 50^\circ$ ,  $D = 0.5 - 1.5$ ) according to Fresenius and Bergmann.

The majority of the heavy metals give with ammonium oxalate double salts which are suitable for deposition. The methods in these cases have been mostly worked out by Classen (4). In depositing iron, the absence of nitrates is essential. The solutions should be kept slightly acid with oxalic acid when zinc, cadmium, copper, and tin are being separated. An equivalent quantity of ammonium oxalate is about the amount to be added to the salt solution.

The following metals are deposited in this manner:—  
Iron ( $t = 20 - 40^\circ$ ,  $D = 1 - 1.5$ ,  $E = 3.6 - 4.3$  volts), cobalt

( $t = 60 - 70^\circ$ ,  $D = 1$ ,  $E = 3.1 - 3.8$  volts), nickel ( $t = 60 - 70^\circ$ ,  $D = 1$ ,  $E = 2.9 - 3.1$  volts), zinc ( $t = 50 - 60^\circ$ ,  $D = 1$ ,  $E = 3.5 - 4.8$  volts), cadmium ( $t = 70^\circ$ ,  $D = 0.5 - 1$ ,  $E = 3 - 3.1$  volts), copper ( $t = 80^\circ$ ,  $D = 1$ ,  $E = 2.5 - 3.1$  volts), mercury (ordinary temperature,  $D = 0.1 - 1$ ,  $E = 2.5 - 3.5$  volts), and tin (ordinary temperature,  $D = 0.2 - 0.6$ ,  $E = 2.7 - 3.8$  volts). From such solutions aluminium and uranium are deposited as hydrates; chromium is oxidised to chromic acid, and beryllium is converted into acid carbonate.

The double cyanides, so much used in the technical deposition of metals, are also of considerable importance in electro-analysis. Potassium cyanide is added to the solution until the precipitate at first formed is re-dissolved, after which a slight excess of it is added. The following metals can be deposited in this way: Zinc ( $t = 50^\circ$ ,  $D = 0.5 - 1$ ), cadmium ( $t = 20^\circ$ ,  $D = 0.5$ ), copper ( $t = 20 - 60^\circ$ ,  $D = 0.2 - 0.5$ ,  $E = 2.5$  volts), silver ( $t = 20 - 60^\circ$ ,  $D = 0.2 - 0.5$ ,  $E = 3.7 - 4.8$  volts), mercury ( $t = 20 - 60^\circ$ ,  $D = 0.5 - 1$ ,  $E = 3.7 - 4.5$  volts; washing with alcohol must be avoided), and gold ( $t = 50 - 60^\circ$ ,  $D = 0.3 - 0.8$ ,  $E = 2.7 - 4$  volts).

The sulpho-salts of antimony and tin also give good deposits on electrolysis (for antimony  $t = 70 - 80^\circ$ ,  $D = 1 - 1.5$ ,  $E = 1 - 1.8$  volts; for tin  $t = 50 - 60^\circ$ ,  $D = 1 - 2$ ,  $E = 4 - 5$  volts). The sodium salt is recommended for antimony, the ammonium salt for tin.

Occasionally the double tartrates are used, for instance, with zinc (addition of sodium potassium tartrate and sodium hydroxide,  $t = 40 - 50^\circ$ ,  $D = 0.4 - 0.7$ ), and with tin (6 grams of tartaric acid, 6 grams of ammonium acetate, and 1 gram of hydroxylamine chloride or sulphate are added for each gram of stannous chloride,  $t = 60 - 70^\circ$ ,  $D = 0.7 - 1.0$ ).

Zinc can also be deposited well from the double lactates, and copper from the sodium phosphate double salt.

**Peroxide Precipitates.**—Lead and manganese cannot be deposited conveniently at the cathode. The former is separated quantitatively, but it oxidises extremely readily

during washing and drying. On the other hand, the peroxides of both metals can be produced at the anode in a stable, coherent form. To obtain the best results a matt platinum basin should be used. When a lead salt is electrolysed, at least 10 per cent. of nitric acid must be added, which completely prevents deposition of lead at the cathode ( $t = 50 - 60^\circ$ ,  $D = 1.5$ ,  $E = 2.5$  volts). The precipitate must be washed before the current is stopped, and in order to get rid of hydrate water it must be dried at  $180 - 190^\circ$ . The presence of chlorides or metals precipitable by hydrogen sulphide should be avoided.

In depositing manganese as peroxide, about 10 grams of ammonium acetate and 2 grams of chrome alum are added to 0.7 gram of manganous sulphate, and the electrolysis is carried out at  $80^\circ$  with a current density of about  $0.6 - 0.9$  amp./sq. dm. ( $E = 3 - 5$  volts). The chrome alum removes the oxygen separated at the anode, which would otherwise prevent the deposition of a coherent precipitate. After washing, the precipitate, which consists of a hydrated peroxide, is converted into mangano-manganic oxide,  $Mn_3O_4$ , by heating the platinum basin with the point of a blow-pipe flame. It is advisable also to rewash this residue in order to free it from chromic acid. When other metals are present which would be precipitated on account of the existence of the chromium in the solution, the chrome alum is replaced by 5 - 10 c.c. of alcohol ( $t = 70^\circ$ ,  $D = 0.15$ ,  $E = 1.2$  volts). Good results can only be obtained in the absence of chlorides.

**Reduction of Nitric Acid to Ammonia.**—Another secondary process which has been used in analysis is the cathodic reduction of nitric acid to ammonia. According to Ulsch (5), the best method of carrying out the reduction is to add to the nitrate solution a known excess of sulphuric acid, and to use a copper wire spiral as cathode, and a platinum wire held in the centre of this as anode. The current density at the cathode, which at the beginning may be about 1.5 amp./sq. dm., gradually sinks as the amount of acid becomes smaller. In the earlier parts of the process the hydrogen

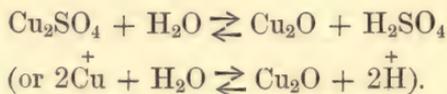
is wholly used up in reducing the nitric acid, but after a time it begins to be evolved at the cathode. When evolution of hydrogen has taken place for a short time (ten minutes if a 2 per cent. nitric acid solution be used), the reduction may be assumed to be complete.

**Copper Refining.**—The different behaviours of solutions of various metals on electrolysis have led to methods for separating the metals from each other. Some metals, like aluminium and uranium, are not deposited by the current, some of low solution pressure are deposited by an electromotive force between the pole plates which is insufficient to separate those of high solution pressure. As an example of this type of separation we may take the technically important deposition in the refining of copper which has recently been fully studied by Neumann (6).

In the refining of this metal thin plates of copper are used as cathode, and the anode is a piece of crude cast copper. These are suspended in a wide vessel containing copper sulphate solution and sulphuric acid. When the current is passed, copper deposits in a coherent form on the cathode, and the crude copper is dissolved from the anode. The electromotive force may be from 0.25 to 0.7 volt, and as a rule the tension between the electrodes is 0.35 volt; the current density is generally between 0.2 and 0.9 ampere per square decimetre. The optimum temperature for the process is about 40°. The impurities in the crude copper, metals of higher solution pressure (iron, zinc, nickel, and cobalt), gradually dissolve, so that the solution in the bath becomes richer in the sulphates of these metals, and poorer in copper sulphate. The other impurities, such as gold, silver, bismuth, antimony, and lead, remain undissolved, or form insoluble compounds (principally basic salts), and falling from the anode, collect in the so-called anode slime. Arsenic, and also antimony and bismuth partially, pass into solution, and must occasionally be removed from the bath by the addition of copper oxide. (Tin also may pass into solution, but is without influence on the nature of the copper deposit.)

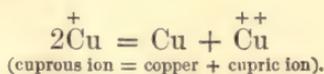
It might be supposed that it would be advantageous to separate all the copper at the cathode. According to Neumann, however, this is attended with poor results, for the deposit is then very spongy. In these investigations, Neumann used as anode a metal containing 50 per cent. copper and 50 per cent. nickel in one case, and in another 65 per cent. copper and 35 per cent. zinc. In the former case the electrolyte contained 46 grams of copper and 150 grams of sulphuric acid, in the latter case 23 grams of copper and 40 grams of sulphuric acid. The temperatures were  $30^{\circ}$  and  $50^{\circ}$  respectively, and the electromotive force 0.5 volt. From these data we may conclude that only about 2 per cent. of the current passed through the copper sulphate, and therefore the greater part of the copper must have been deposited as the result of a secondary process. The current density, which at the beginning was 2.0 or 1.3, gradually diminished to 1.0 or 0.6 amp./sq. dm. respectively. Until the quantity of nickel or zinc in the bath became double that of the copper, the deposit was extremely good. If the proportion of copper is further decreased, the deposit becomes bud-like or warty, and later very spongy on account of the simultaneous separation of hydrogen; at the same time the yield obtained from the current is greatly diminished. When this happens, a fresh quantity of electrolyte should be taken, and the copper in the old solution separated from the impurities by means of hydrogen sulphide. On account of secondary actions more metal is dissolved than is precipitated. Consequently the concentration of the sulphuric acid diminishes (provided that the volume of the liquid does not decrease by evaporation of water). In the technical refining of copper insoluble sulphates are formed, and these sink to the bottom of the cell. The mode of action of the acid can be seen from the results obtained by Förster (?). It may first be mentioned that the acid greatly increases the conductivity of the electrolyte in the bath, and therefore prevents a good deal of loss of energy in the form of Joule heat. In the solution,

however, the principal part is played by the cuprous ions. When the current density is very small (less than 0.01) cuprous sulphate is formed at the anode (at the ordinary temperature). As the current density increases, greater quantities of cupric sulphate are produced. The relative proportion of cuprous to cupric sulphate formed increases with rising temperature, so that at 100° and with current densities up to 0.3 amp./sq. dm. cuprous salt is almost exclusively formed. This cuprous salt is highly detrimental to the electrolysis; for it decomposes partially according to the equation—



The more acid (*i.e.* hydrogen ion) is present, the higher may the cuprous ion concentration be without this decomposition occurring.

On the other hand, the cuprous ions are in equilibrium with the cupric ions—



At a certain acid (hydrogen ion) concentration, which increases with rising temperature, no cuprous oxide is precipitated. When it does deposit partially at the cathode and forms badly conducting spots, it gives rise to the warty appearance of the deposited copper. The copper is therefore less coherent, and the separation of the cuprous oxide should consequently be prevented by addition of sulphuric acid. The formation of cuprous oxide may also be hindered by the addition of certain organic substances (*e.g.* alcohol). Probably the organic substance simply acts in a reducing capacity. Oettel (*8*), who studied the accuracy of the copper voltameter, found that an addition of 5 per cent. of alcohol is sufficient to prevent the disturbing effect of cuprous oxide at the cathode when the current density is small. In practice sulphuric acid is used, for the

organic substance would be too costly. The concentration of the sulphuric acid and the current density must not be too high, for otherwise so much hydrogen is separated at the cathode that it is not completely removed by the secondary processes, and the deposited copper becomes spongy and pulverulent. Small changes can be brought about in the deposited metal by altering the current density, and these have a great influence on the hardness and electrical conductivity of the copper; use is made of this fact in practice.

The smaller the number of cupric ions the lower is the concentration of cuprous ions; according to the above equation the concentration of the latter is proportional to the square root of that of the cupric ions. The concentration of the cupric ions is greatly reduced by the addition of the acid, and to a still greater extent by the addition of salts which are able to form copper double salts. It may easily be conceived that similar relationships hold good for other metals. In the deposition of silver, organic substances are frequently added to the bath "to increase the polish of the metal."

**Precipitation of Metal from a Solution containing Two Metal Salts.**—If a solution contains two metals of different solution pressures, say silver and copper as nitrates, two cases may occur on electrolysis. The electromotive force used is either so great (over 1.14 volts) that it exceeds the solution pressures of both silver and copper, or it is sufficient (between 0.7 and 1.14 volts) just to overcome the solution pressure of one of the metals. This leads to a method, suggested and applied by Freudenberg (9), for the separation of one metal from another analytically. The method is not good when the solution pressures of the two metals lie close together. In technical work, too, great use has been made of this principle, for instance in the separation of gold from the platinum metals (the gold being much more readily deposited from hydrochloric acid solution), or of silver from copper and other metals (from nitric acid solution). The

refining of copper also belongs to this category of processes.

If the electromotive force is sufficient to precipitate both metals, both are generally deposited simultaneously. Very often, however, after the primary deposition a secondary reaction takes place between the metal of higher solution pressure and the salt of the other metal. Thus, *e.g.*, if a solution containing copper and zinc sulphates be electrolysed, both metals are deposited, but a secondary reaction then takes place, in which zinc dissolves and an equivalent amount of copper is separated. This sort of action occurs particularly when the deposition is carried out very slowly, *i.e.* when the current density is small. If the solution contains much zinc and little copper, it may easily happen that all the deposited zinc cannot re-dissolve, for the copper ions only diffuse slowly to the cathode, and in this way a mixed metal is obtained. It is worthy of note that brass can be prepared in this electrolytic manner. The preparation is more successful if potassium cyanide solutions of the two metals be used, because then their positions in the electromotive series are close together. A sufficiently high current density (about 0.6 amp./sq. dm.) must, however, be used if equal quantities of the two metals (zinc and copper) are dissolved in the bath, so that the copper may not be deposited in too large an amount. A piece of brass is used as anode, and this dissolves to replace the metals deposited from the solution.

**Position of Hydrogen in Deposition.**—Since aqueous solutions are used almost exclusively, a secondary separation of hydrogen occurs so soon as a metal is deposited whose solution pressure exceeds that of hydrogen (a primary deposition also occurs, provided that no acid is present, but on account of the low conductivity of water this is very small).

It is, therefore, impossible, without some particular device, to deposit the alkali metals, magnesium, or aluminium, from aqueous solution, and these are consequently prepared from their fused salts. By collecting the alkali metals at a

mercury electrode, a small amount of the metal may be obtained as amalgam; but as soon as a fair quantity of it has separated, a secondary decomposition of the solvent-water takes place, and hydroxide is formed—a process which is used in Kellner's method of preparing hydroxides of the alkali metals.

If the solution pressure of the deposited metal (*e.g.* zinc and nickel) is not so high as that of the metals mentioned, it can be separated from aqueous solution (say, solution of the sulphate) without any appreciable disturbance by secondary processes. In technical work, however, the metal obtained in these two cases is frequently spoiled on account of the formation of a small quantity of oxide, and the nickel appears yellowish and the zinc spongy. This formation of oxide can be prevented by addition of acid, which, however, must not give rise to a strong primary separation of hydrogen. In the electrolysis of nickel salts, a weakly dissociated acid is added, such as citric, lactic, or boric acid (or even phosphoric acid), and the nickel obtained has then a pure white colour. For the deposition of zinc a small amount of sulphuric acid is added to the solution, about 0.01 per cent., or of aluminium sulphate, which is highly hydrolysed, and a high current density is used (over 1 amp./sq. dm.) in order to avoid a secondary evolution of hydrogen. If too much hydrogen does separate in these cases, the nickel appears leafy, and the zinc is not compact.

**Analytical Separation of the Metals.**—It has already been mentioned (p. 276) that the precipitation of copper from an acid solution of its sulphate cannot be made complete if other metals, particularly of the iron group or zinc, are present. This process cannot, therefore, be used for the quantitative separation of copper from more positive metals. For similar reasons several of the processes referred to above, which are quite good for the deposition of the metal from a pure solution, cannot be used for the separation from other metals. With the electro-analysis we therefore have, as a rule, to combine the ordinary analytical methods. For

instance, to determine iron in presence of nickel or cobalt, both metals are completely deposited, and the weight ascertained; the mixed metal is then dissolved in sulphuric acid, and by titration with potassium permanganate the quantity of iron present is determined.

Zinc, which under ordinary circumstances cannot be separated electro-analytically from the metals of the iron group, can be separated (it deposits first) if we use a potassium cyanide solution. Zinc, iron, nickel, and cobalt can be separated from aluminium and chromium, because these two latter elements are not deposited in the metallic condition.

In potassium cyanide, double oxalate, or sulphuric acid solution, cadmium can easily be separated from zinc ( $E = 2.4 - 3.6$  volts). Silver can be separated from copper in nitric acid solution by using an electromotive force of 1.36 volts, in potassium cyanide solution by using 2.3 - 2.4 volts. Mercury behaves similarly to silver. Copper can be separated from cobalt, and nickel from copper in hot oxalate solution ( $60^\circ$ ), and from manganese in presence of free oxalic acid ( $t = 80^\circ$ ). Copper is deposited from sulphuric acid solution when the electromotive force is 1.85 volts, whilst cadmium remains dissolved. Mercury can easily be separated from iron, cobalt, nickel, zinc, or cadmium in nitric acid solution.

Antimony, in presence of arsenic (as arsenic acid, into which form the arsenic is transformed by the current, provided that alkali is present) and tin, are precipitated from a concentrated sodium sulphide solution. Arsenic can best be separated from tin by chemical means. These three metals should first be separated from other metals by ammonium sulphide, and the mixture then analysed by electrolysis.

#### **Primary and Secondary Deposition of Metal.—**

More than forty years ago, Bunsen observed that metals deposited secondarily have a much more even and brighter surface than those which are primarily separated. It has also been observed that primarily evolved hydrogen leaves

the solution in large bubbles, whilst in the secondary formation of this, *e.g.* in the electrolysis of an alkali salt solution with a mercury cathode, a fine cloud of very small bubbles is produced. This peculiarity is supposed to be due to the fact that the substance separates more easily on already present parts of the same substance than on foreign substances, on account of the work done in surface formation. In an analogous way a salt, such as Glauber salt, may be maintained in supersaturated solution, so long as crystals of it are not present, but, if these be added, the salt deposits on the crystals. Consequently, if silver be primarily deposited from silver nitrate solution, the metal appears in a granular crystalline form, because it tends to separate on the already formed crystals of metal. On the other hand, if the silver be deposited secondarily from potassium cyanide solution, the positive ion of this salt, potassium, is primarily separated, and this secondarily precipitates the silver. The silver thrown out of solution in this way will naturally deposit at the spot where the primarily separated potassium was. The potassium has no reason for separating at any particular spot (on the silver, for instance), and therefore the deposit of silver is more uniform, and a smooth film is formed on the electrode. In these cases the current density does not require to be large; indeed, smaller current densities frequently give better results. Thus in silvering with potassium argentocyanide a current density of 0.15 – 0.5 amp./sq. dm. is used, and in gilding with potassium auricyanide 0.2 – 0.25 amp./sq. dm.

For the reasons given, a secondary deposition is almost always used in electro-plating where the essential is a uniform deposit of the metal; the double cyanides are used in the cases of silver, gold, and copper, and the ammonium sulphate double salts in the deposition of nickel and iron. Particularly in gilding, the process is often carried out at a high temperature, which aids the secondary deposition.

It is a matter of experience that comparatively small amounts of organic substances, such as alcohol, sugar, or

gelatine, improve certain properties (density, lustre, and elasticity) of the deposited metal. The influence exerted by these has not yet been satisfactorily explained. Possibly they are connected, like the cases previously mentioned, with surface phenomena (see p. 279).

**Difference of the Temperature Influence in Primary and Secondary Processes.**—As has been repeatedly mentioned, the velocity of a chemical reaction increases considerably with rise of temperature. As we have seen above, the secondary processes are of a purely chemical nature, and an increase of temperature therefore promotes their influence. It is true that an exception is known to this, namely, the evolution of hydrogen from an acid in very dilute solution (0·1-normal and weaker) by zinc, particularly at high temperature. However, so dilute solutions are seldom used in practice, and we may therefore disregard this deviation (see p. 106).

In contradistinction to the secondary processes, primary electrolytic deposition depends solely on the current strength, which varies with the temperature only in so far as the resistance in the bath diminishes on heating. If a primary process is disturbed by a secondary one, the disturbance can be increased or diminished by raising or lowering the temperature. In the electrolysis of potassium sulphate with a mercury cathode potassium is primarily deposited at the mercury with formation of potassium amalgam, from which hydrogen is afterwards evolved secondarily. The higher the temperature is, the sooner does this latter process occur. When a normal solution of potassium sulphate was electrolysed by using 0·053 ampere and a circular mercury cathode 3·7 mm. in diameter, hydrogen was evolved after 25 seconds at 20°, but after 7·6 seconds at 83°.

These temperature relationships are of importance in practice. Thus, in the deposition of bronze (copper and zinc), where the deposited zinc seeks to dissolve and precipitate copper, the temperature must not, according to Fontaine (10), exceed 36°.

The temperature exerts no appreciable influence on primary processes taking place with organic substances, as Tafel (11) has proved in the case of the electrolytic reduction of caffeine and other difficultly reducible substances.

In many cases it is sought to favour the secondary process, and for this too low a temperature must not be chosen. Thus, in electro-gilding (with potassium auricyanide) it is recommended that the bath be kept at 70–75°, and in the deposition of nickel from ammonium nickel sulphate the temperature should be from 50° to 90°, according to circumstances. It has further been found that the optimum temperature for the preparation of iodoform from a solution of potassium iodide and dilute alcohol containing sodium carbonate, is about 60°; hydriodic acid and carbon dioxide are also formed.

In the analogous preparation of chloral from potassium chloride and alcohol the temperature must be raised to 100°. Many other organic electrolytic processes, of which Elbs (12) has studied a large number, proceed best at comparatively high temperatures.

Occasionally several secondary processes take place simultaneously, *e.g.* in the electrolysis of potassium chloride solution with a platinum anode. Chlorine is primarily separated at the anode, and this gives rise to a secondary formation of hypochlorite, chlorate, and oxygen. The hypochlorite is formed in largest quantity at low temperature, the chlorate and oxygen particularly at high temperature.

The relative quantities of the different electrolytic products can therefore be regulated by altering the temperature.

As a rule the secondary process is favoured by stirring the liquid as well as by elevating the temperature. The effect of stirring is to bring fresh quantities of the unionised substances into contact with the ions primarily separated at the electrodes, and thus aid the secondary action. Since the introduction of heat always causes a stirring in the liquid of the bath, the secondary process is helped both by the stirring and by the rise of temperature.

**Voltameter.**—The principle of the voltameter, used for the measurement of current, is based on the separation of gases or metals. The oldest of these instruments is the electrolytic gas voltameter, in which hydrogen and oxygen are separated, and collected either singly in calibrated tubes or together in one tube. Formerly the electrolyte used was dilute sulphuric acid. Secondary reactions, however, arise in this case inasmuch as, at the expense of the oxygen, persulphuric acid, ozone, and hydrogen peroxide are formed. The sulphuric acid was first replaced by phosphoric acid, but later, potassium hydroxide solutions were introduced, and the electrodes were made of nickel instead of platinum. Using sulphuric acid, only the hydrogen should be collected, since the disturbances occur at the pole where the oxygen is separated. The gas volume must be reduced to normal temperature and pressure, and due allowance made for the water vapour present. One coulomb corresponds with 0.174 c.c. of electrolytic gas, or 0.116 c.c. of hydrogen. One ampere evolves 6.96 c.c. of hydrogen per minute.

On account of the inaccuracies of the electrolytic gas voltameter, its place has now been taken by silver or copper voltameters. In the silver voltameter a platinum crucible is used as cathode, and a rod of silver in the centre serves as anode. In order to prevent pieces (particularly of peroxide) of the anode from falling into the crucible, the rod should be wrapped in filter paper, or a small glass basin should be suspended beneath it. The formation of peroxide can be most judiciously prevented by adding some alcohol to the silver nitrate solution (15–30 per cent.) used as electrolyte. The current density may be very variable.

In the copper voltameter two thick copper plates serve as anode, and a thin sheet of copper hung between them is the cathode; the electrodes are suspended in a solution of about 15 per cent. copper sulphate, 5 per cent. sulphuric acid, and 5 per cent. alcohol, contained in a beaker. If the current density is less than 0.4 amp./sq. dm., oxidation by the air has a disturbing effect. When the current density is small, the

voltameter should be provided with a cover, and a current of hydrogen passed over the surface of the liquid. One coulomb corresponds with the deposition of 1.118 milligrams of silver, or 0.3284 milligram of copper. One ampere deposits 0.06708 gram of silver, or 0.0197 gram of copper in one minute on the cathode, which is weighed after being washed.

## CHAPTER XVII.

### Development of Heat by the Electric Current.

**Review.**—When electricity passes through a circuit consisting of one or several conductors, a quantity of heat,  $W$ , is evolved which can be calculated from the formula (see pp. 11 and 203)—

$$W = 0.24i\epsilon \text{ cal.}$$

where  $i$  is the current strength (in amperes), and  $\epsilon$  the potential difference (in volts) between the two ends of the conductor. If the conduction takes place along a uniform metal wire, or through a column of liquid, the heat is developed uniformly throughout the conducting material. If the circuit is not homogeneous, *i.e.* if we have surfaces of contact of different substances, then the heat is not equally distributed over all parts.

In the former case the formula given can also be written—

$$W = 0.24 i^2 m = 0.24 \frac{\epsilon^2}{m} \text{ cal.}$$

where  $m$  is the resistance between the ends of the circuit. This quantity of heat, developed in a uniform conductor by resistance analogous to friction, is called Joule heat. Besides this there occurs a change of heat at contact surfaces, *e.g.* between metals, which is known as the Peltier effect, and which is measured by the expression—

$$W_1 = 0.24\pi i \text{ cal.}$$

where  $\pi$  is the electromotive force of the Peltier effect.

It has also been shown by Lord Kelvin (1) that an electromotive force occurs between differently tempered parts of the same metallic conductor, and this strives to conduct heat from the warmer to the cooler part.

This so-called Thomson effect is very inappreciable for metals; it occurs in liquids and probably also in gases. It has not yet been very thoroughly investigated, and may here be neglected. In galvanic elements and electrolytic decomposition cells, besides the Joule heat, a quantity of heat,  $\omega$ , is evolved for each equivalent of substance taking part in the chemical change, and this is partially used up in doing work to send the current through the circuit, which part is measured by the expression  $23,070P$ . ( $P$  denotes the electromotive force of the element, or of the decomposition cell, see p. 205.)

The quantity of heat—

$$W_2 = \omega - 23,070P$$

is termed *local heat* (or internal heat), and, like the Joule heat, remains in the element or vessel (voltameter) in which the electrolytic process takes place.

In elements  $\omega$  is generally positive, as also is  $P$ ; in decomposition cells it is negative.

**Arc Light.**—The greatest development of heat takes place when the electricity passes through gases. The passage may be disruptive, as in the spark discharge and outflow of electricity from points, or it may be continuous with formation of an arc light. In the former case the quantity of electricity transported is very small.

The arc light, or Volta arc, which is now so much used for illuminating purposes, was discovered by Volta in 1808, and afterwards thoroughly studied by several investigators.

Edlund (2) showed that the potential difference  $\epsilon$  between two carbon points between which the arc is playing is given by the formula—

$$\epsilon = a + bl$$

where  $a$  and  $b$  are coefficients which gradually increase with the current strength, and  $l$  is the length of the arc.

If  $l$  becomes very small (0.5 mm.), an arc can be obtained with a potential difference of only 25 to 30 volts. It is difficult, however, to keep such an arc going. A spongy elevation of carbon, transferred from the positive carbon, forms on the negative carbon; by this loss the well-known crater-like depression is formed in the positive carbon. If the deposit on the negative carbon increases much, the two carbon points come into contact, and, on the other hand, if it falls off, the length  $l$  suddenly increases, and the arc goes out. Ordinary arc lights have a length of at least 2 mm., and generally 4 to 5 mm., and require a potential difference of 40 to 45 volts.

Arc lights produced by a potential difference of only 30 to 40 volts do not burn uniformly, and make a hissing noise.

A certain minimum current strength is also required to produce a steady arc light. Arc lights have been successfully produced with 1 to 2 amperes and 40 to 45 volts, but a very fine and delicate regulation of the length is necessary, and on this account such small current strengths are never used in practice. To produce arcs with small current strengths a very good, hard, thin carbon rod is required. For arc lamps the current strength used lies between 4 and 25, and is most frequently 8 amperes, and the potential difference is about 42 volts, the carbon rods having a diameter of 8 to 18 mm.

According to measurements carried out at the Electrical Exhibition at Frankfort-a-M. in 1891, the maximum length  $l$  of an arc when fed with a current of  $i$  amperes is given in the following table:—

$i$ amp.	$l$ mm.	$i$ amp.	$l$ mm.
10	25	60	94
20	51	70	102
30	68	80	104
40	81	90	112
50	90	100	114

The length of the arc at first increases rapidly with the current strength, then more slowly. The carbon used is of such a size that there is about 0.1 ampere per square millimetre of the section.

Uppenborn (*3*) determined  $a$  for an arc between carbon rods of 12 mm. diameter to be 38 volts, 32.5 for the positive, and 5.5 for the negative pole; for  $b$  he found about 1 volt per millimetre. From this it can be understood that the greater heat development takes place at the positive pole, which radiates 85 per cent. of the whole light emitted. Nevertheless, according to measurements by Violle (*4*) the carbon cannot be heated above  $3500^{\circ}$  at the ordinary pressure, for at this temperature it volatilises without previous fusion. The glowing gases in the arc are heated to a greater extent, their temperature being estimated by Rosetti (*5*) at about  $4800^{\circ}$ .

Of the good conducting substances so far investigated, carbon resists the heat best, with the exception of some oxides used in the Auer-, Jablochhoff-, and Nernst-lamps; carbon may be heated to  $3000^{\circ}$  without appreciably gasifying, at a somewhat higher temperature it becomes soft, and may be welded.

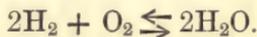
The arc light may be interrupted for a short time, about 0.1 second, without losing its conductivity; consequently the arc may be produced by an alternating current, which is to be preferred in electrochemical practice when we are concerned with the production of heat. In this case, of course, the carbons are equally heated, and become equally corroded.

The possibility of concentrating the heat in a small space has led to the adoption of electrical heating methods for the production of high temperatures, and by the aid of these certain reactions can be brought about which only take place when the temperature is very high.

#### **Influence of Temperature on Chemical Reactions.**

—As has been stated in previous chapters, the temperature exerts a double influence on chemical reactions. On the

one hand, the velocity of reaction is generally very greatly increased with rising temperature. As an example of this we may cite the formation of water from a mixture of hydrogen and oxygen, which hardly proceeds at all at the ordinary temperature, but which takes place with explosive violence above  $580^{\circ}$ . On the other hand, a change of temperature causes a displacement of the equilibrium which is established between the components of every chemical system. Again, we may take water and a mixture of hydrogen and oxygen as an example. Theory (see p. 256) requires that at  $20^{\circ}$  a litre of water contains  $0.65 \times 10^{-27}$  gram-molecules of hydrogen, and half as many gram-molecules of oxygen. This quantity of mixed hydrogen and oxygen cannot be detected by chemical methods, but from electrical observations, such as those of Helmholtz (6), it can be calculated. Now, there must be an equilibrium between the water and the mixture of gases dissolved in it—



If we denote the concentrations of the three substances by  $C_{\text{H}}$ ,  $C_{\text{O}}$ , and  $C_{\text{H}_2\text{O}}$ , the following equations should be valid (see pp. 85 and 94):—

$$C_{\text{H}}^2 \cdot C_{\text{O}} = KC_{\text{H}_2\text{O}},$$

$$\log K = \frac{\mu}{2.3025 \times R} \left( \frac{1}{T_1} - \frac{1}{T_0} \right) + M,$$

where  $\mu$  is the quantity of heat which is absorbed when two mols of hydrogen and one mol of oxygen combine to form liquid water ( $-136,800$  cal.).

The value of  $K$  applies to the temperature  $T_1$ . At  $T_0$ ,  $\log K = M$ . Now, at  $20^{\circ}$ ,  $T_0 = 293$ ;  $C_{\text{H}_2\text{O}} = 55.5 (= 1.08^{\text{g}})$ ;  $C_{\text{H}} = 0.65 \times 10^{-27}$ ; and  $C_{\text{O}} = 0.33 \times 10^{-27}$ . From this we obtain—

$$M = 2 \times 0.81 - 2 \times 28 + 0.51 - 28 - 2 \times 1.74 = 0.65 - 86$$

and—

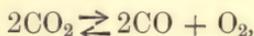
$$\begin{aligned}\log K &= M - \frac{136,800}{1.99 \times 2.3025} \cdot \frac{1}{293} \left( \frac{T_0}{T_1} - \frac{T_1}{T_1} \right) \\ &= M + 101.3 \left( \frac{T_1 - T_0}{T_1} \right).\end{aligned}$$

In the neighbourhood of  $20^\circ$   $\log K$  increases for every degree by  $\frac{101.3}{293} = 0.346$ , since  $C_{H_2O}$  may be regarded as constant, and  $\log K$  increases three times as quickly as  $\log C_H$ , consequently  $\log C$  becomes greater by  $0.1153$  for each degree;  $C_H$  therefore increases in the proportion  $1 : 1.3$  per degree, and reaches a tenfold value by raising the temperature by  $7.7^\circ$ . At  $100^\circ$  the quantity of hydrogen has risen to  $1.15 \times 10^{-20}$ , and at the critical temperature ( $365^\circ$ ) to  $1.23 \times 10^{-9}$  gram-molecules per litre.

So long as water is present in the liquid condition there is only an exceedingly small dissociation into hydrogen and oxygen. From the above formula it would appear also that  $\log K$  may never reach a higher value than  $M + 101.3 = 15.95$ , however high the temperature be raised, *i.e.* according to the theory, even at the highest temperature the dissociation cannot go beyond a certain limiting value. In this, however, it is assumed that no change of volume occurs, otherwise the pressure relationships would have to be taken account of. Now, since in the dissociation of water into hydrogen and oxygen two molecules give rise to three, *i.e.* the volume increases (provided that the pressure is constant, and that all the substances are present in the gas state), the decomposition must increase when the volume becomes greater. If the pressure be kept constant, the volume steadily increases with rising temperature. Consequently the gaseous dissociation of water vapour (at constant pressure) increases with the temperature, and the increase in the degree of dissociation is unlimited. It has been experimentally found (Deville) that above  $2000^\circ$  water vapour is appreciably dissociated (?). This dissociation at the high temperature is the reason

why, in the explosion of a mixture of hydrogen and oxygen, the temperature does not rise so high as would be expected from the calculation.

As an example of a similar, but more thoroughly studied, displacement of the equilibrium by temperature and pressure, we may consider the decomposition of carbon dioxide into carbon monoxide and oxygen, which takes place according to—



with evolution of 136,000 cal. The volume change is the same as in the dissociation of water vapour, and the heat change does not differ very appreciably from that found for water vapour, 116,000 cal. The two equilibria must therefore be similar in character, since the dissociations at a corresponding point (with respect to temperature and pressure) are of the same order of magnitude (at 2000°, and 1 atmo. pressure carbon dioxide is dissociated to the extent of 5 per cent., water to a slightly greater extent).

Le Chatelier has calculated that, of 100 molecules of carbon dioxide, the following number is dissociated at the temperature and pressure given:—

Pressure in atmos.	1000°.	1500°.	2000°.	2500°.	3000°.	3500°.	4000°.
0·001 . . .	0·7	7	35	81	94	96	97
0·01 . . .	0·3	3·5	18*	58*	80	86*	90
0·1 . . .	0·13	1·7	10*	36*	60	70	80
1 . . .	0·06	0·8	5*	19	37*	53	63
10 . . .	0·03	0·4	2·5*	9	18*	32	45
100 . . .	0·015	0·2	1·2*	4	8	15	25

Since the heat of dissociation of water vapour is lower (in the ratio 12 : 14) than that of carbon dioxide, the

\* As in the calculations for the temperature 2000°, an error has evidently been made in the original paper, the numbers indicated by an asterisk \* are taken from the curve given by Le Chatelier (*Zeit. physikal. Chem.*, 1888, 2, 785) instead of from the table.

dissociation of water must increase more slowly (in the ratio 12 : 14) with rising temperature than does that of carbon dioxide. Most substances (gases) on decomposition suffer an increase of volume—the number of molecules, as a rule, is increased by the decomposition—consequently, heat, which alone would not be able to bring about the dissociation, is frequently assisted by the simultaneous volume increase which takes place when the temperature is raised.

From this circumstance it is easy for us to see that in the visible layers of the sun's atmosphere, which possess a very high temperature and a relatively low pressure, the substances are all decomposed into their ultimate elements. The metals, whose presence in the sun has been detected by spectrum analysis, occur there in the form of simple atoms, just as is the case with these substances in solution at the ordinary temperature. In other words, in the sun there are formed as many, and as light, molecules as possible. It may well be, however, that in the interior of the sun, where quite enormous pressure probably obtains, compounds like water are capable of existence.

**Fused Electrolytes. Heroult's Furnace.**—For the preparation of aluminium Heroult (*S*) constructed a furnace which consists essentially of a large iron crucible, *F*, provided with plates of carbon, *C* (Fig. 50). This is filled with a mixture, *B*, of two parts of sodium chloride and one part of cryolite ( $\text{Na}_3\text{AlF}_6$ ), which is fused by being heated from below. When the mass has fused, a bundle of carbon rods, *A*, is introduced, and this serves as anode, the carbon plates, *C*, being used as cathode.

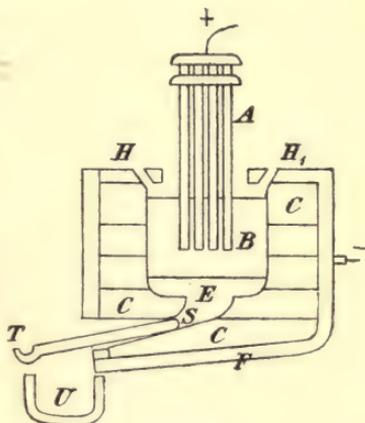


FIG. 50.

When the current has begun to pass through, the heat developed is sufficient to keep the whole mass molten. As the aluminium is separated, alumina (clay or bauxite) or some other appropriate material is introduced through the openings  $H$  and  $H_1$ . The metal formed is allowed to flow into the receiver  $U$  from time to time, through the hole  $S$ , which can be closed by the rod  $T$ .

It was soon found that the aluminium formed in this way was contaminated by particles of carbon from the cathode  $C$ . In order to prevent such contamination, iron or copper is added, and this collects at the bottom,  $E$ , of the crucible. In this way valuable aluminium alloys can be obtained. It was afterwards found that pure aluminium could be obtained by making the melt more mobile in various ways, as by the addition of lithium fluoride or potassium fluoride [Hall (9)], or by keeping only the central part of the salt fused, so that a solid, non-conducting crust remains on the walls of the crucible, except at the very lowest points. When the latter device is adopted, a special hollowed-out copper cathode is set in the bottom of the crucible, and this is kept cool by the circulation of water, so as to prevent it from fusing (Borchers). The possibility of concentrating the heat in a small part of the mass, and thus avoiding contamination from the walls of the crucible, which become coated with a solid crust of the electrolyte, is one of the most important advantages which electrical heating possesses over the ordinary method; this advantageous property of the electric furnace has been particularly called attention to by Borchers (10), who has made much use of it.

In order to avoid the inconvenient preliminary heating of the material, a small quantity of the mixture is fused in the crucible  $C$ , by placing the anode  $A$  in contact with the bottom of the crucible, and fresh electrolyte is then added until the whole is full. This introduction of material is occasionally regulated by an apparatus similar to that used in arc lights. When the resistance between the electrodes diminishes the current strength increases, and in

order to keep this approximately constant  $A$  is automatically raised.

Many arrangements, similar to that used in the Heroult process, have been successfully employed in the electrolysis of fused salts. Thus, for instance, lead is used in order to take up alkali metals, and several models of crucibles have been constructed by Borchers for the preparation of the alkali metals from the fused salts.

**Non-electrolytic Processes with Electrical Heating. Cowles' Furnace.**—So long ago as 1815 Pepys carried out experiments on the electric cementation of iron (conversion of iron into steel, by allowing carbon to diffuse into the iron at a high temperature). In this process the iron was raised to the necessary temperature by means of an electric current. The brothers Cowles (in 1884) (11) were the first to introduce the extensive applications of the electric furnace. The furnace, named after them, and which is so highly prized in the aluminium industry, has the construction shown in Fig. 51. A hollow block of fire-proof material,  $A$ , is

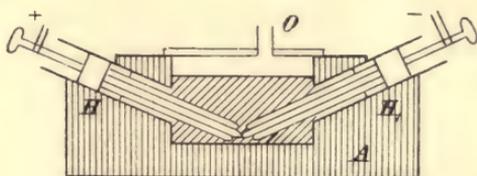


FIG. 51.

provided with holes,  $H$  and  $H_1$ , on opposite sides; through these pass two movable carbon electrodes, which, at first, are in contact. The crucible is furnished with an iron lid, and gases can escape through an opening,  $O$ , in this. The carbon electrodes generally consist of several (9) rods, each 65 mm. in diameter, fastened together, and these, connected by two strong cables to the source of the current, can be moved by means of screws. The mixture of alumina (bauxite), wood, charcoal or coke, and copper or iron clippings is placed round the electrodes. At first the contact surface of the electrodes becomes warm, and these are then drawn apart, so that an arc is formed or the current passes through the mixture in contact with the

electrodes. In any case the mixture becomes exposed to such a high temperature, that the iron or copper fuses, and the alumina is reduced by the carbon to aluminium, which is taken up by the fused iron or copper. The electrodes are gradually drawn further and further apart, so that the current strength, read off on an interposed ammeter, remains approximately constant—about 5000 amperes are usually employed.

In the course of some hours the whole of the mixture will have undergone reaction; the furnace is then allowed to cool, and the melt withdrawn. One disadvantage of the process is that the activity of the furnace is intermittent, and consequently a good deal of heat is lost on cooling.

It has been stated that the Heroult process, which is in use amongst other places at the aluminium works at Neuhausen, is more economical than the Cowles' process which has been introduced at the works at Stoke-on-Trent.

In the Cowles' process direct currents can be used just as well as alternating currents without in any way interfering with the yield obtained from the current. This shows clearly that the electrolytic process plays no real part in the action, which depends only on the high temperature (essential for the reduction of the alumina) attained by means of the electric current. In such cases alternating currents are to be preferred to direct ones, because then the process takes place uniformly at the two poles, and alternating currents of suitable electromotive force and strength can readily be obtained by the use of a transformer. If a polyphase current is employed, as many electrodes should be used as the current has phases, *e.g.* three with a three-phase current.

In the lighting of a Cowles' furnace we are reminded of the lighting of an arc lamp, and Maxim (*l.c.*), in the furnace devised by him, has introduced lighting on the same principle as that made use of in Jablochhoff's electrical candle. Two

parallel rods of carbon<sup>1</sup> are placed near the long side of the furnace, and each is connected at one of the short sides by means of a conducting cable with the source of electricity. In the neighbourhood of the opposite short side the two carbon electrodes are connected by a small rod or a small piece of compressed carbon powder, which is quickly used up, and the carbon electrodes are gradually drawn out of the furnace as the mass of material suffers progressive reaction.

### Resistance Furnaces. The Carborundum Process.—

Instead of conducting the current through the contents of the furnace, and thus heating the substance which is to undergo reaction, the electricity may be passed through a relatively large carbon resistance, which becomes hot, and passes the heat on to the material near it.

The simplest furnace of this type is that designed by Borchers (10). A thin carbon rod, *C* (Fig. 52), lies between two larger ones, *A* and *B*.

The material to be heated surrounds *C*, and a strong current is passed from *A* to *B*. *A* and *B* should be so thick that the current density does

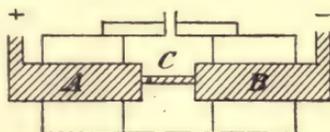


FIG. 52.

not amount to more than 0.1 amp. / sq. mm. The size of the rod *C* depends on the temperature to which it is desired to heat the mass. A red heat is obtained if the current density in *C* amounts to 0.5 amp. / sq. mm. If it is ten times as large, a temperature can be attained at which calcium carbide can be produced, and if the current density reaches 10–15 amp. / sq. mm., temperatures of 3000 to 3500° can be reached. Borchers has stated that there is no oxide which can resist reduction when the current density is 10 amp. / sq. mm. The carbon electrodes *A* and *B* are introduced through the sides of the furnace, which is made of fire-proof material, and is covered in the usual way.

<sup>1</sup> When a three-phase current is used, three electrodes are introduced, but otherwise the arrangement is the same.

In the preparation of carborundum [Mühlhaeuser, (13)] the two thick electrodes, *A* and *B* (Fig. 53), are joined by a train 2 to 3 metres long of coke powder, *C* (of 4 to 5 mm.

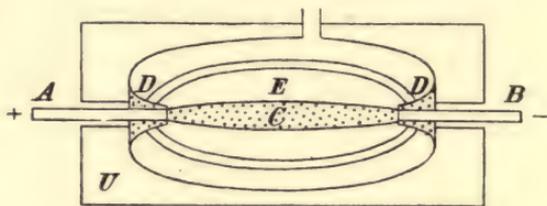
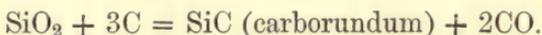


FIG. 53.

diameter granules). At the ends of this train there is placed some finer coke powder, *D*, in order to ensure good contact with the electrodes. The carbon electrodes are embedded, by means of asbestos packing, in the walls of the fire-proof furnace *U*. Under the influence of the current the train *C* more or less runs together to a conducting mass. The mixture to be heated, which consists of 100 parts of carbon (coke powder), 100 parts of sand, and 25 parts of common salt, is placed round *C*. Occasionally 12 parts of sawdust are added to the mixture, and the quantity of sand may then be increased to 140 parts. Reaction occurs according to the equation—



The salt serves to bake together the unattacked portions of the mixture. The process is generally carried out with an alternating current, and when it is finished it is found that round *C* there is an elliptical mass, *E*, of crystallised carborundum, but at the ends of *C* the substance is amorphous. Outside this kernel there remains a layer of unattacked mixture, and this in turn is surrounded by a layer of almost pure salt. Quite close to *C* there is generally a thin layer of graphite, which is probably produced as a decomposition product of the carborundum at the excessively high temperature. After cooling, the carborundum is removed from the

furnace and freed from small amounts of metallic sulphides, phosphides, and carbides by treatment with acid—the impurities come from the foreign substances present in the coke and sand used.

**Arc Light Furnaces.**—In recent times the enormous heat developed by the arc light has been used for bringing about such chemical processes as require an extremely high temperature. This was first applied in the melting and refining of difficultly fusible metals. As there is a greater development of heat at the positive pole than at the negative the substance to be fused is placed in direct contact with the the positive pole. Many special constructions have been suggested for carrying this out. In many cases it is necessary to provide the electrodes with some form of interior cooler, in order to make them last (see p. 296).

The arc light furnaces are, however, far more important, both in industry and science, when so arranged that the heat of the arc itself is the active factor. In such furnaces use is made of the property which the arc, like all movable conductors through which a current is passing, possesses of being influenced by an electro-magnet. A conductor through which a current is passing, and which is perpendicular to the lines of force of a magnetic field, moves so as to cut the lines of force from right to left as seen by a person supposed to be swimming in the direction of the current, and facing in the direction opposite to that of the lines of force.

If the magnetic field is very strong, and the current producing the arc light comparatively weak, the arc may be so much affected by this attraction that it goes out. (Tesla's method of preventing a series of consecutive electric sparks from following a track is based on this phenomenon.)

The electromagnet is so arranged that the arc is attracted downwards, and thus comes into contact with the material to be heated. The longest path through which the arc is deflected is met with in Zerener's "electric blowpipe" (14),

where a strong current circulating between two carbon poles, *A* and *B* (Fig. 54), is so influenced by an electromagnet, *E*, fixed perpendicularly to the plane in which *A* and *B* lie, that a pointed, highly deflected arc, *L*, is formed. The point of this arc is directed against the substance *S*, which is contained in the fire-proof furnace *U*. This principle has been used by Lejeune and Ducretet in the furnace constructed by them (Fig. 55). In this furnace any gas may be introduced

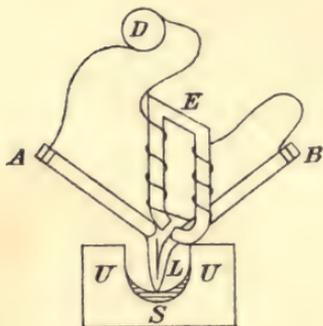


FIG. 54.

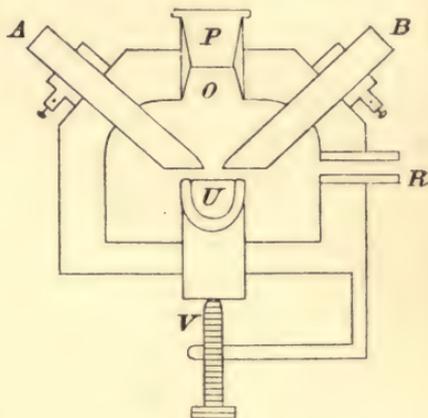


FIG. 55.

through the side tube *R*; it is provided on two sides with mica windows, so that the process taking place inside may be observed. The crucible is filled through the opening *O*, which can be closed by the plug *P*. The crucible *U*, containing the reaction mixture, can be moved up or down by means of the screw *V*. The arc formed between *A* and *B* is directed by the aid of an electromagnet placed outside.

Moissan's furnace (15) differs from the one just described, inasmuch as the carbon electrodes are placed horizontally, and the charge can be introduced through a slightly bent carbon tube, which is fixed on the side of the furnace, whose walls are made of lime.

Zerener's electrical blowpipe was originally constructed for soldering and welding, but in recent times it, as well as

the other two furnaces mentioned, has been an important piece of apparatus in the laboratory. In this connection we need only recall Moissan's comprehensive investigations, in which he has succeeded for the first time in producing several metals and carbides in a pure state.

**Production of Calcium Carbide.**—Within the last few years calcium carbide, used in the preparation of acetylene, has obtained an ever-increasing economic importance. The calcium carbide industry has, no doubt, a great future before it, especially in countries where water-power is easy to obtain.

Calcium carbide is produced by heating a mixture of 56 parts of lime and 36 parts of coal to a temperature of about 2000°. The reaction takes place according to the equation—



Instead of lime, an equivalent quantity of limestone ( $\text{CaCO}_3$ ) may be used, since at the high temperature this is dissociated into lime and carbon dioxide. If an insufficiency of coal be taken, metallic calcium is formed, and this, dissolving in the carbide, gives rise to certain difficulties. On the other hand, an excess of coal contaminates the carbide and hinders its proper fusion. Furthermore, the lime used should be almost free from sulphates and phosphates, otherwise sulphides and phosphides are formed, which render the acetylene prepared from the carbide impure, and must be removed. The presence of magnesia in the lime also interferes with the fusion of the carbide. If the furnace used is first coated with coal, this is partially attacked, and 10 per cent. less coal is introduced into the charge; the charge is put into the furnace in the form of small lumps of coal and lime about the size of a hazel-nut.

Calcium carbide is comparatively easy to prepare, and a number of types of furnace for its production have been invented, amongst which is the resistance furnace of Borchers mentioned above. The furnace constructed by Rathenau (16) consists of a containing vessel,  $UU$  (Fig. 56), provided

with carbon plates,  $A$ ; a thick carbon rod,  $K$ , stands upright in the middle, and is surrounded by the carbon plates  $B$  and  $B_1$ . The charge  $S$  is introduced between  $K$  and  $B$ , and it gradually sinks as it is transformed into a liquid mass,  $T$ , by

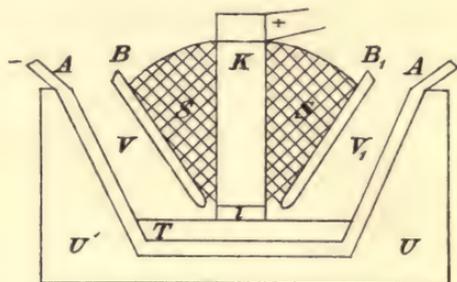


FIG. 56.

the action of the arc light  $l$ . The large quantity of gas evolved escapes through the channels  $V$  and  $V_1$  between  $A$  and  $BB_1$ .

If the fused carbide is not run off at a tap-hole, the molten mass must be allowed to cool after some time, and the process thus becomes discontinuous. As the melting point of the carbide is high, and its heat conductivity is small, it is extremely difficult to prevent stopping up of the tap-hole.

Furnaces have been constructed which can be continuously worked, although they theoretically functionate discontinuously. King's furnace is of this type; in it the hearth consists of an iron box, covered inside with plates of carbon, and mounted on wheels which run on rails. A receiver of this sort forms one of the poles, and it is run in under the other pole consisting of a bundle of carbon rods, which are then lowered so as to form an arc. The charge is introduced through channels into the carriage, and is gradually transformed into carbide. When the carriage is full it is removed, and its place taken by a fresh one. The whole apparatus is set in a large furnace built of fire-proof, bad-conducting material, and provided with an

opening for the receiver to pass through. This process is carried on with success in the works at Niagara.

Another type of furnace worthy of attention is that devised by Memmo (17). The space in which the fusion takes place consists of a prismatic iron receiver, *A*, covered inside with plates of carbon, and closed at the bottom by a plate of graphite, *B*, resting on an iron plate; the bottom can be raised or lowered by means of a toothed-wheel arrangement. Two electrodes, *CC* (with a three-phase current three electrodes are used), are so placed in the walls of the iron receiver *A* that an arc light is formed between them immediately above the plate *B*. The charge is put into a chimney arrangement, *D*, above *A*, and is lowered into the receiver as required by a scoop-shaped feeder. In the path of the arc some carbide is formed, and this flows over the graphite plate and gradually solidifies as *B* is lowered. A fresh charge is then introduced, and in this way there is an almost continuous production of carbide between the electrodes *CC*. A solid column of carbide is formed, the upper level of which is kept at a constant height. When the bottom plate *B* has been lowered to a certain depth, the top part of the column is supported by a plate introduced from the side, and the lower portion is then cut out. When this lower portion has been removed, the plate *B* is pushed up, the side support withdrawn, and the process continued.

The carbon monoxide which is evolved, and the air which is heated by the hot carbide, are each led up through a tube into *D*, and thus the charge is preliminarily heated before being introduced into the furnace. The same gases may also be used for heating the space *A*, in which the fusion takes place.

**Silent Electrical Discharges.**—If the conductor of a Holtz electrical machine be connected to a point, the electricity flows out through this, and a so-called *electrical wind* is formed.

In a dark room a small ball of light can be seen at the

point, which may assume the form of a brush (*aigret*) if there be a sufficient outflow of positive electricity. The discharge is discontinuous, as can easily be proved by making use of a rotating mirror; the hissing noise also indicates that the discharge is discontinuous. When the discharge takes place in the air a smell of ozone becomes perceptible; many other chemical actions are also brought about by this action of points. For instance, in the air some oxidation products of nitrogen are formed as well as ozone; in acetylene, benzene is formed; in an atmosphere of carbon monoxide and water vapour combination takes place, and formic acid is produced, if carbon dioxide is used oxygen is evolved (this reaction corresponds with the process of vegetation); nitrogen and hydrogen give ammonia, which is again partially decomposed; sulphur dioxide and oxygen give sulphur trioxide; cyanogen and hydrogen give hydrocyanic acid; and nitrogen and oxygen, in presence of water, give ammonium nitrate, a compound whose presence has also been detected after lightning.

The same reactions can also be brought about by a spark discharge, which only differs from the "silent" or "dark" discharge in its greater intensity. A gas may be brought to the glowing point when it is enclosed between two condenser plates separated by an insulator (*e.g.* glass), when these are connected with the poles of a high tension alternating current machine. In this case there is formed a comparatively large quantity of ozone, as in the discharge from the poles of a Tesla alternating current machine.

The most remarkable method of bringing about chemical actions by the silent discharge is that found by Berthelot (18). The apparatus devised by him is shown in Fig. 57. Two thin-walled glass tubes, *a* and *b*, are arranged concentrically one within the other. The outer tube *b* is furnished at its upper end with side tubes, *c* and *d*, and immediately above these it is sealed on to *a*. The tube *a* is filled with sulphuric acid, and *b* is immersed in a cylinder filled with the same liquid. When solid substances are to

be investigated they are introduced into *c* (between *a* and *b*); gases are introduced through *c* or *d*. (A later construction, in which *d* is continued into the apparatus and ends near *e*, is evidently more suitable when gases are used.) The inner and outer layers (sulphuric acid) of this Leyden jar are connected each with one pole of a galvanic battery. After introducing the substance to be investigated, *c* and *d* are closed.

Berthelot succeeded in bringing about quite remarkable actions with a potential difference between the two acids of only 8 volts, although a single experiment required several months. The apparatus was afterwards used by others, but much higher potential differences or high-tension alternating currents were invariably employed.

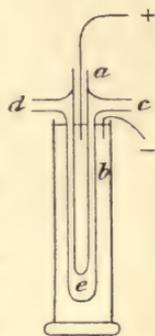


FIG. 57.

**Electrothermic and Electrochemical Actions.**—All the conditions of experiment mentioned—except those applied by Berthelot, the actions of which have not yet been explained—agree in this respect, that for an exceedingly short time a gas is heated to the glowing point and then cools. Judging from the spectra of gases glowing under the influence of action of points, sparks, or electrical oscillations, the temperature at certain times is much higher than that of the arc light. This is concluded from the fact that the spark spectrum excels the arc spectrum in number of lines and brilliancy just as the arc spectrum excels that obtained with a Bunsen burner. Of course, quantitative differences exist between the phenomena of the action of points, spark discharge, and vibrations in the ether, in so far as the heat effect is concerned, according to the greater or smaller quantity of energy possessed by the discharge; but all must, as the spectra prove, produce, during a very short time, a higher temperature than the arc light.

At these high temperatures chemical reactions proceed in quite a different direction from that taken at the ordinary

temperature, and the velocity is also much greater. During the extremely short time of heating, the gas pressure cannot come into equilibrium with that of the surrounding atmosphere, and it is assumed that the pressure of the gas stands in about the same ratio to that of the surrounding atmosphere as the corresponding absolute temperatures do to each other, *i.e.* about 20 : 1. After the short heating a *sudden* cooling takes place, so that the products of the reaction are prevented from passing back into the original condition during the cooling interval. The conditions striven after by Sainte Claire-Deville and his pupils by other methods [“the hot and cold tube”] (19), are in these cases fulfilled to a large extent, namely, heating the substance to a very high degree, and suddenly cooling, so that further reaction with total decomposition is prevented.

Besides the electrothermic process, others of a truly electrochemical character take place. In 1849, Perrot showed that a series of sparks from an induction machine can electrolyse water vapour so that oxygen collects at the anode and hydrogen at the cathode, and indeed in the proportions required by Faraday's law. This observation has been recently confirmed by Lüdeking (20) and by J. J. Thomson (21). An electrothermic decomposition also takes place so that electrolytic gas (a mixture of hydrogen and oxygen) is produced at both poles. The electrothermic evolution of electrolytic gas is often much greater than the electrolytic, and can, of course, be distinguished from this.

I (22) have shown that gases are often electrolytically dissociated, as in the case of the vapours produced from alkali salts in a Bunsen burner. All salts of the same metal conduct equally well; probably on account of the large amount of water vapour present the salts are as good as completely converted into hydroxides. With respect to conductivity, the series is: thallium, lithium, sodium, potassium, rubidium, and caesium, of which the last is the best conductor. The rubidium and caesium (hydroxide) vapours are so strongly dissociated that their conductivity at extreme dilution can

be calculated; these compounds follow exactly Ostwald's dilution law. This is also the case for the other salts whose conductivity is, therefore, proportional to the square root of the concentration. Two metal poles (of nickel, copper, iron, or platinum) placed in a flame containing such a vapour showed a potential difference which approximated to that which would be obtained in an aqueous solution. No polarisation could be observed, which is probably due to the strong "polarisation current;" quite the same observation is made with fused electrolytes and glowing oxides. For small electromotive forces (up to 0.5 volt) the current strength is nearly proportional to this force, but it afterwards increases much more slowly, probably on account of an insufficiency of gaseous ions. Besides the electrolytic conduction, there is also a so-called *convective conduction* through the particles which become charged at one electrode and are discharged at the other. In the case of the salts of the alkaline earth metals this convective current is much greater than the electrolytic, and with other salts the electrolytic conduction in the Bunsen flame cannot be detected.

At the ordinary temperature gases assume an electrolytic conductivity under the influence of ultraviolet, Röntgen, or Becquerel rays. So far as the investigations on this subject go, it has been found that here, too, the laws of electromotive effect between two metals, Ostwald's dilution law, etc., apply just as well as for electrolytes in solution. The electrolytic conductivity of gases is not yet of any practical interest.

**Production of Ozone.**—The production of ozone by the silent electrical discharge is of practical importance. This substance is frequently found at the anode of an electrolytic bath. Thus, McLeod (23) found that by working with an extremely high current density he obtained an anode gas containing up to 17.4 per cent. of ozone; the anode consisted of a so-called Wollaston point, *i.e.* a fine platinum wire fused into a glass tube so that only the end remained free. Traces of ozone are found in the arc light in which a number of gas

reactions can be realised which are characteristic of the silent electrical discharge.

The ozoniser devised by von Babo (24) has the form shown in Fig. 58. Metal wires are inserted into glass tubes sealed at one end, and they are alternately connected with the poles of an induction coil. When the coil is in action, electrical oscillations arise in the capillary spaces between the glass tubes, and these ozonise the air. A current of air passed through a tube containing the wires is therefore ozonised. From a large number of experiments with ozonisers of this type it has been found that the presence of a

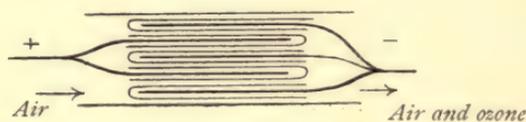


FIG. 58.

small quantity of water vapour favours the production of ozone, whilst a large quantity (or carbon dioxide) has a disturbing effect. The air to be ozonised is, therefore, dried with some not too hygroscopic substance (sulphuric acid at the ordinary temperature, or calcium chloride at temperatures below  $0^{\circ}$ ). Low temperature favours the formation of ozone because the amount formed is not then so easily decomposed as at higher temperatures. The air should be free from dust, as the ozone in oxidising this is destroyed. The yield of ozone diminishes with decreasing pressure; since ozone occupies  $\frac{2}{3}$  of the volume of the oxygen from which it is formed, increase of pressure must favour its formation (see p. 99).

Working at the pressures and temperatures given in the table, Hautefeuille and Chappuis (25) obtained the following percentages by weight of ozone :—

Pressure of the oxygen. mm. Hg.	Temperature.			
	-23°.	0°.	20°.	100°.
760	21·4	14·9	10·6	—
380	20·4	15·2	12·5	1·17
300	20·1	15·2	11·2	—
225	19·1	15·3	10·4	1·18
180	18·1	13·7	8·9	—

The presence of chlorine or oxidation products of nitrogen hinders the formation of ozone. Presence of hydrogen promotes the yield, if formation of water be rigidly avoided (*i.e.* if the tension is not too high). Silicon fluoride greatly aids the formation. If an induction apparatus be used, the current must not be made and broken too many times per second, otherwise it is not possible to keep the air sufficiently cool. Shenstone (26) recommends 16 breaks per second; but, of course, if the air be changed rapidly this number may be increased.

The Siemens and Halske ozoniser consists of two concentric tubes, coated inside and outside, separated by a thin mica plate placed close to the inside of the outer tube, and by a narrow space through which the air to be ozonised must pass. The apparatus is very similar to the Berthelot tube. It works with an alternating current of 6500 volts; the yield, *i.e.* the quantity of heat consumed in the ozone formation (36,000 cal. for 48 grams) corresponds with only 2·2 per cent. of the electrical energy spent. The yield is, however, nine times as great as that calculated on the assumption that the process is an electrolytic one which follows Faraday's law. The inner tube of the ozoniser is kept cold by a current of water.

Andreoli (27) has recently described an ozoniser which is said to give a yield of ozone about five times as great as the apparatus of Siemens and Halske, namely, up to 120 grams of ozone per kilowatt-hour. The apparatus consists of a number of square aluminium plates of about 70 cm. length

of side. Alternate plates are smooth, and the others are in the form of a grid, made up of 80 pieces of notched aluminium strips, each of which possesses 111 points. The smooth and grid plates are separated by thin plates of glass. Five pairs of these are combined to one system. A combination of eight such systems, when actuated by an induction coil whose primary current was 5.9 amperes at a tension of 85 volts—*i.e.* absorbed 500 watts—and whose secondary current was at a tension of 3000 volts, gave 60 grams of ozone per hour. The air is blown through the various systems; on account of the small amount of energy transformed, no particular cooling apparatus is said to be required.

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