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INORGANIC AND PHYSICAL CHEMISTRY

PAPER - I

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ELECTROLYSIS AND ELECTRICAL CONDUCTANCE
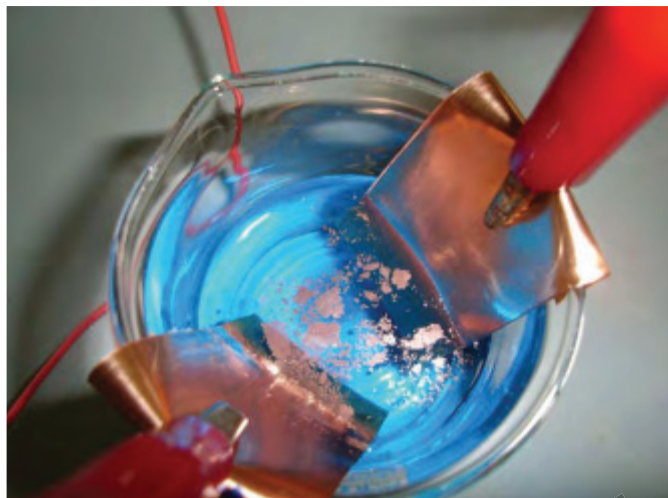
Water-soluble substances are distinguished as electrolytes or nonelectrolytes.

Electrolytes are electrovalent substances that form ions in solution which conduct an electric current. Sodium chloride, copper (II) sulphate and potassium nitrate are examples of electrolytes.

Nonelectrolytes, on the other hand, are covalent substances which furnish neutral molecules in solution. Their water-solutions do not conduct an electric current. Sugar, alcohol and glycerol are typical nonelectrolytes.

An electrolyte invariably undergoes chemical decomposition as a result of the passage of electric current through its solution.

The phenomenon of decomposition of an electrolyte by passing electric current through its solution is termed Electrolysis (Iyo = breaking).

The process of electrolysis is carried in an apparatus called the **Electrolytic cell**. The cell contains water-solution of an electrolyte in which two metallic rods (electrodes) are dipped. These rods are connected to the two terminals of a battery (source of electricity). The electrode connected to the positive terminal of the battery attracts the negative ions (anions) and is called anode. The other electrode connected to the negative end of the battery attracts the positive ions (cations) and is called cathode.

MECHANISM OF ELECTROLYSIS

How the electrolysis actually takes place, is illustrated in Fig 24.1. The cations migrate to the cathode and form a neutral atom by accepting electrons from it. The anions migrate to the anode and yield a neutral particle by transfer of electrons to it. As a result of the loss of electrons by anions and gain of electrons by cations at their respective electrodes chemical reaction takes place.

Example. Let us consider the electrolysis of hydrochloric acid as an example. In solution, HCl is ionised,

$$HCl \rightarrow H^+ + Cl^-$$
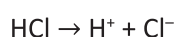
In the electrolytic cell Cl^- ions will move toward the anode and H^+ ions will move toward the cathode. At the electrodes, the following reactions will take place.

At cathode :

$$H^+ + e^- \rightarrow H \qquad\qquad\qquad\qquad\qquad\qquad (Reduction)$$

As you see, each hydrogen ion picks up an electron from the cathode to become a hydrogen atom. Pairs of hydrogen atoms then unite to form molecules of hydrogen gas, H_2.
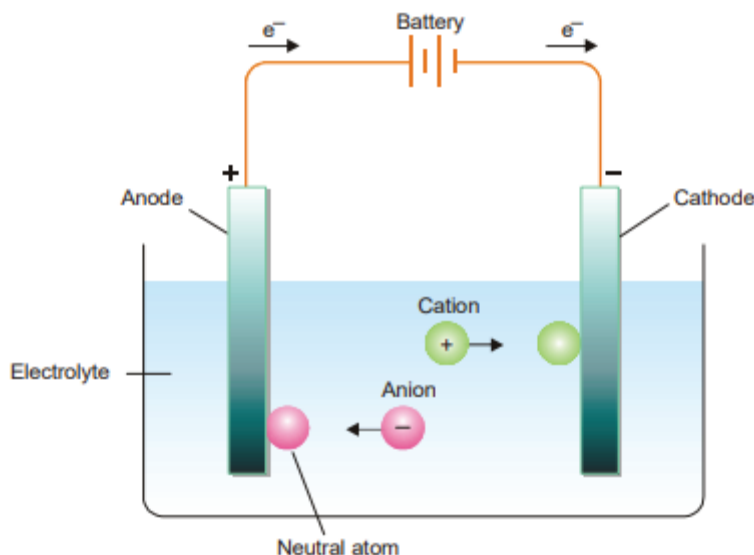
Figure 24.1 The mechanism of electrolysis.

At Anode :

$$Cl^- \rightarrow Cl + e^- \qquad\qquad \text{(Oxidation)}$$

After the chloride ion loses its electron to the anode, pair of chlorine atoms unite to form chlorine gas, Cl_2.

The net effect of the process is the decomposition of HCl into hydrogen and chlorine gases. The overall reaction is :

$$2HCl \rightarrow H_2 + Cl_2 \qquad\qquad \text{(Decomposition)}$$

ELECTRICAL UNITS

There are a few electrical units which we should understand before taking up the study of quantitative aspects of electrolysis. These are :

Coulomb

A coulomb is a unit quantity of electricity. It is the amount of electricity which will deposit 0.001118 gram of silver from a 15 per cent solution of silver nitrate in a coulometer.

Ampere

An ampere is a unit rate of flow of electricity. It is that current which will deposit 0.001118 gram of silver in one second. In other words, an ampere is a current of one coulomb per second.

Ohm

An ohm is a unit of electrical resistance. It is the resistance offered at 0ºC to a current by a column of mercury 106.3 cm long of about 1 sq mm cross-sectional area and weighing 14.4521 grams.

Volt

A volt is a unit of electromotive force. It is the difference in electrical potential required to send a current of one ampere through a resistance of one ohm.

FARADAY'S LAWS OF ELECTROLYSIS

Michael Faraday studied the quantitative aspect of electrolysis. He discovered that there exists a definite relationship between the amounts of products liberated at the electrodes and the quantity of electricity used in the process. In 1834, he formulated two laws which are known as Faraday's Laws of Electrolysis. These are :

First Law

The amount of a given product liberated at an electrode during electrolysis is directly proportional to the quantity of electricity which passes through the electrolyte solution.

Second Law

When the same quantity of electricity passes through solutions of different electrolytes, the amounts of the substances liberated at the electrodes are directly proportional to their chemical equivalents.

Definition of Electrochemical equivalent in light of First Law

If m is the mass of substance (in grams) deposited on electrode by passing Q coulombs of electricity, then

$$m \propto Q \qquad \text{(First Law)}$$

We know that $\qquad Q = I \times t$

where I is the strength of current in amperes and t is the time in second for which the current has been passed.

Therefore, $\qquad m \propto I \times t$

or $\qquad m = Z \times I \times t$

where Z is the constant known as the Electrochemical equivalent of the substance (electrolyte).

If $I = 1$ ampere and t = 1 second, then

$$m = Z$$

Thus, the electrochemical equivalent is the amount of a substance deposited by 1 ampere current passing for 1 second (i.e., one coulomb).

The Electrical unit Faraday

It has been found experimentally that the quantity of electricity required to liberate one gram-equivalent of a substance is 96,500 coulombs. This quantity of electricity is known as Faraday and is denoted by the symbol F.

It is obvious that the quantity of electricity needed to deposit 1 mole of the substance is given by the expression.

Quantity of electricity = n × F

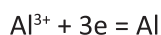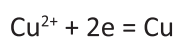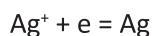where n is the valency of its ion. Thus the quantity of electricity required to discharge :

one mole of Ag^+ = 1 × F = 1F

one mole of Cu^{2+} = 2 × F = 2F

one mole of Al^{3+} = 3 × F = 3F

We can represent the reactions on the cathode as :

$Ag^+ + e = Ag$

$Cu^{2+} + 2e = Cu$

$Al^{3+} + 3e = Al$

It is clear that the moles of electrons required to discharge one mole of ions Ag^+, Cu^{2+} and Al^{3+} is one, two and three respectively. Therefore it means that the quantity of electricity in one Faraday is one mole of electrons. Now we can say that.

1 Faraday = 96,500 coulombs = 1 Mole electrons

Importance of the First law of Electrolysis

With the help of the first law of electrolysis we are able to calculate :

(1) the value of electrochemical equivalents of different substances; and

(2) the masses of different substances produced by passing a known quantity of electricity through their solutions.

Verification of the Second law of Electrolysis

According to this law when the same quantity of electricity is passed through different electrolyte solutions, the masses of the substances deposited on the electrodes are proportional to their chemical equivalents.
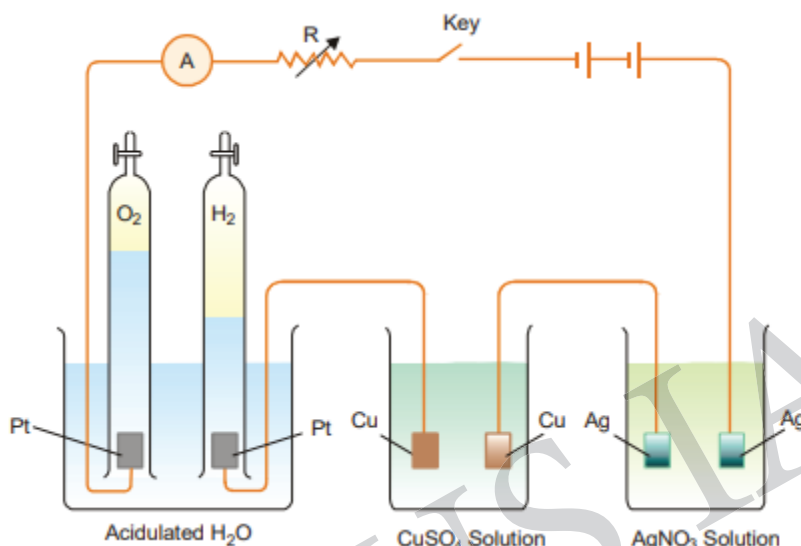

Figure 24.2 Illustrating Faraday's Second Law of Electrolysis.

To verify the law, let us take an arrangement of the type shown in Fig. 24.2. Pass the same quantity of electricity through the three coulometers (the term 'coulometer' is now in practicereplaced by the older term 'voltameter') containing solution of dilute H_2SO_4, $CuSO_4$ and $AgNO_3$ respectively. These coulometers are fitted with platinum, copper and silver electrodes as shown in Fig. 24.2. The masses of hydrogen, copper and silver liberated/deposited at the respective cathodes are in the ratio of their equivalent weights. That is,

$$\frac{\text{mass of hyrogen liberated}}{\text{mass of copper deposited}} = \frac{\text{Eq. Wt. of hydrogen}}{\text{Eq. Wt. of copper}}$$

and

$$\frac{\text{mass of copper deposited}}{\text{mass of silver deposited}} = \frac{\text{Eq. Wt. of copper}}{\text{Eq. Wt. of silver}}$$

From this experiment, we can calculate the mass of hydrogen, copper and silver liberated at their respective cathodes by one coulomb of electricity. We find these are always :

Hydrogen = 0.00001036 g

Copper = 31.78 × 0.00001036 = 0.0003292 g

Silver = 107.88 × 0.00001036 = 0.001118 g

Since the equivalent weights of hydrogen, copper and silver are 1, 31.78 and 107.88 respectively, it follows that the chemical equivalents are proportional to the chemical equivalents (or equivalent weights).

Importance of the Second law of Electrolysis

The second law of electrolysis helps to calculate :

(1) the equivalent weights of metals

(2) the unit of electric charge

(3) the Avogadro's number

CONDUCTANCE OF ELECTROLYTES

We have seen that electrolyte solutions conduct electric currents through them by movement of the ions to the electrodes. The power of electrolytes to conduct electric currents is termed conductivity or conductance. Like metallic conductors, electrolytes obey Ohm's law. According to this law, the current I flowing through a metallic conductor is given by the relation.

$$I = \frac{E}{R}$$

where E is the potential difference at two ends (in volts); and R is the resistance measured in ohms (or Ω). The resistance R of a conductor is directly proportional to its length, l, and inversely proportional to the area of its cross-section, A. That is,

$$R \propto \frac{l}{A}$$

or $\qquad R = \rho \times \frac{l}{A}$ (1)

where ρ "rho" is a constant of proportionality and is called resistivity or specific resistance. Its value depends upon the material of the conductor. From (1) we can write

$$\rho = R \times \frac{A}{l}$$

If l = 1 cm and A = 1 sq cm, then

ρ = R

Thus it follows that the Specific resistance of a conductor is the resistance in ohms which one centimetre cube of it offers to the passage of electricity.

Specific Conductance

It is evident that a substance which offers very little resistance to the flow of current allows more current to pass through it. Thus the power of a substance to conduct electricity or conductivity is the converse of resistance. The reciprocal of specific resistance is termed Specific conductance or Specific conductivity.
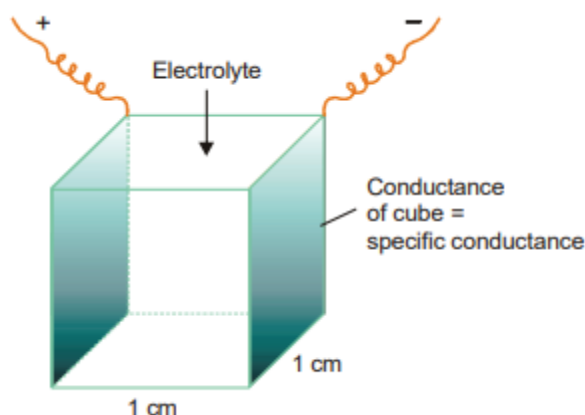
Figure 24.3 Diagrammatic illustration of definition of specific conductance.

It is defined as : **the conductance of one centimetre cube (cc) of a solution of an electrolyte.** The specific conductance is denoted by the symbol κ (kappa). Thus,

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{1}{A}$$

Units of Specific conductance Specific conductance is generally expressed in reciprocal ohms (r.o) or mhos or ohm^{-1}. Its unit can be derived as follows :

$$\kappa = \frac{1}{A} \times \frac{1}{R} = \frac{1}{ohm} \times \frac{cm}{cm^2}$$

= ohm^{-1}cm^{-1}

The internationally recommended unit for ohm^{-1} (or mho) is Siemens, S. When S is used, the conductance is expressed as S cm^{-1}. It may be noted that Siemens is not a plural, the unit is named after Sir William Siemens–a noted electrical engineer.

The specific conductance increases with : (i) ionic concentration, and (ii) speeds of the ions concerned.

In measuring the specific conductance of the aqueous solution of an electrolyte, the volume of water in which a certain amount of the electrolyte is dissolved is always measured in cubic centimeters (cc) and this is known as dilution. If the volume of a solution is V_{cc}, the specific conductance of the solution is written as κ.

Equivalent Conductance

It is defined as the conductance of an electrolyte obtained by dissolving one gram-equivalent of it in V cc of water.
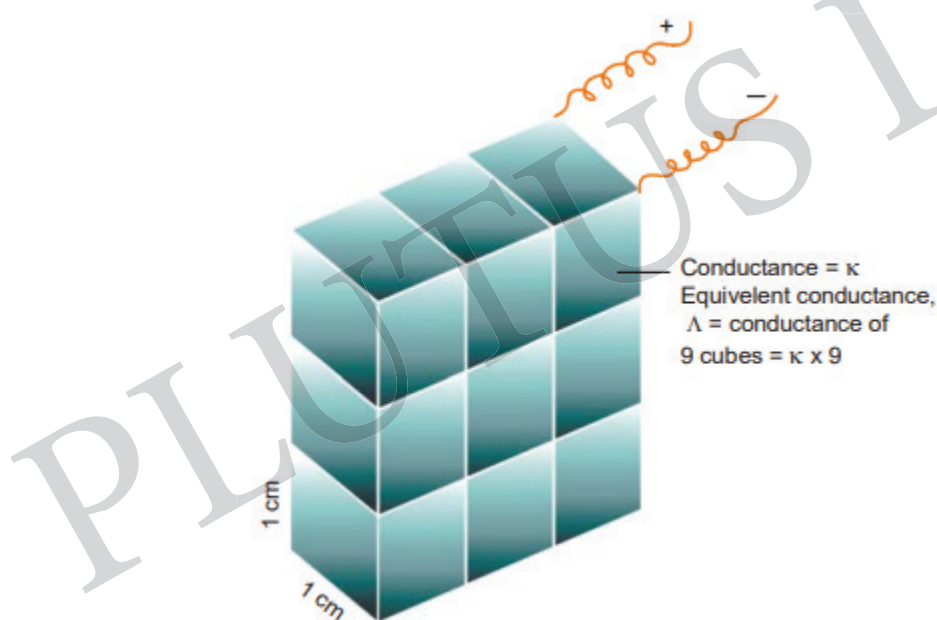

Figure 24.4 Solution of 1 g-eqvt. dissolved in 9 cc water between electrode plates 1 cm apart has L = κ x 9.

The equivalent conductance is denoted by Λ. It is equal to the product of the specific conductance, κ and the volume V in cc containing one gram-equivalent of the electrolyte at the dilution V.

Thus,

$$\Lambda = \kappa \times V$$

This is illustrated in Fig. 24.4. A solution having one gram-equivalent of the electrolyte dissolved in, say, 9cc water be placed between two electrodes 1 cm apart. The solution could be considered as consisting of nine cubes, each of which has a conductance k (specific conductance). Thus the total conductance of the solution will be 9 × κ. Similarly, Vcc of solution will form V cubes and the total conductance will be κ × V.

In general, if an electrolyte solution contains N gram-equivalents in 1000 cc of the solution, the volume of the solution containing 1 gram-equivalent will be 1000/N. Thus,

$$\Lambda = \frac{\kappa \times 1000}{N}$$

Unit of Equivalent conductance

The unit of equivalent conductance may be deduced as follows :

$$\Lambda = \kappa \times V$$

$$= \frac{1}{R} \times \frac{I}{A} \times V$$

$$= \frac{1}{ohm} \times \frac{cm}{cm^2} \times \frac{cm^3}{eqvt}$$

$$= ohm^{-1} \, cm^2 \, eqvt^{-1}$$

Variation of Equivalent conductance with Concentration (or Dilution)

The equivalent conductance of a solution does not vary linearly with concentration. The effect of concentration on equivalent conductance can be studied by plotting Λ values against the square root of the concentration. It has been found that variation of equivalent conductance with $\sqrt{C}$ depends upon the nature of electrolyte. Fig. 24.5 shows the behaviour of strong and weak electrolytes with change of concentration.
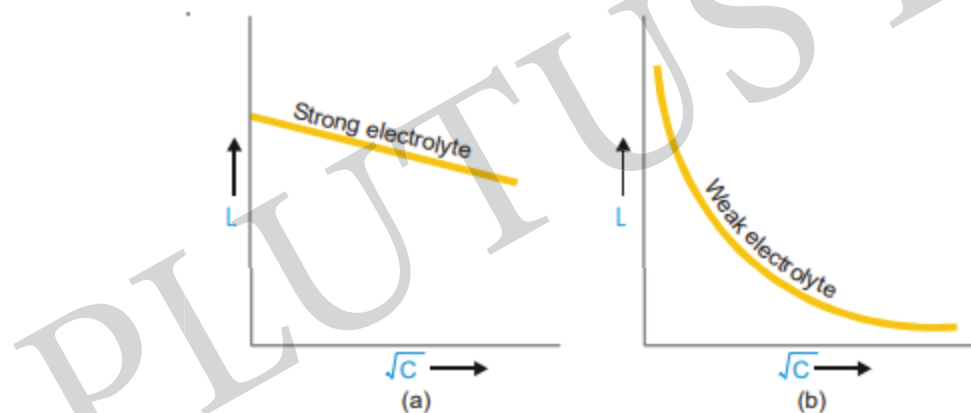

Figure 24.5 Variation of equivalent conductivity, L with $\sqrt{C}$: (a) for strong electrolyte; (b) for weak electrolyte.

Strong electrolytes are completely ionised at all concentrations (or dilutions). The increase in equivalent conductance is not due to the increase in the number of current carrying species. This is, in fact, due to the decrease in forces of attraction between the ions of opposite charges with the decrease in concentration (or increase in dilution). At higher concentration, the forces of attraction between the opposite ions increase (F $\propto$ q$_1$q$_2$ /r^2). Consequently, it affects the speed of the ions with which they move towards oppositely charged electrodes. This phenomenon is called ionic interference. As the solution becomes more and more dilute, the equivalent conductance increases, till it reaches a limitary value. This value is known as equivalent conductance at infinite dilution (zero concentration) and is denoted by A.

Weak electrolytes have low ionic concentrations and hence interionic forces are negligible. Ionic speeds are not affected with decrease in concentration (or increase in dilution). The increase in equivalent conductance with increasing dilution is due to the increase in the number of currentcarrier species. In other words, the degree of ionisation (α) increases. Thus **increase in equivalent conductance (Λ) in case of a weak electrolyte is due to the increase in the number of ions.**

In case of a weak electrolyte Λ_∞ is the equivalent conductance when ionisation is complete. So, the conductance ratio Λ/Λ_∞ is the degree of ionisation. That is,

$$\alpha = \frac{\Lambda}{\Lambda_\infty}$$

Molar Concentration

It is another quantity which helps in comparing the conductivities of electrolytes. It is defined as : **the conductance of all ions produced by one mole (one gram-molecular weight) of an electrolyte when dissolved in a certain volume V cc.**

Molar conductance is denoted by µ. Its value is obtained by multiplying the specific conductance, κ, by the volume in cc containing one mole of the electrolyte.

Thus,

Molar conductance, µ = k × V where V is the volume of the solution in cc containing one mole of the electrolyte.

Units of Molar Concentration

Since

$$\kappa = \frac{1}{R} \times \frac{I}{A}$$

$$\mu = \frac{1}{R} \times \frac{I}{A} \times V$$

$$= \frac{1}{ohm} \times \frac{cm}{cm^2} \times \frac{cm^3}{mol}$$

= ohm^{-1} cm^2 mol^{-1}

Calculation of Molar conductance

Molar conductance can be calculated by using the relation :

$$\mu = \frac{\kappa \times 1000}{M}$$

Where M is the number of moles of the electrolyte present in 1000 cc of solution.

Upon dilution specific conductance decreases, while Equivalent conductance and Molar conductance increases.

It is important to not that specific conductance decrease with dilution. It is the conductance of one cc of the solution. Upon diluting the solution, the concentration of ions per cc decreases. Hence the specific conductance falls. On the other hand, the equivalent and molar conductance show an increase as these are the products of specific conductance and the volume of the solution containing one gram-equivalent or one mole of the electrolyte respectively. With dilution, the first factor decreases, while the other increases. The increase in the second factor is much more than the decrease in the first factor. The specific and molar conductance of NaCl solution at 18ºC are shown in Table 24.1.

TABLE 24.1. SPECIFIC AND MOLAR CONDUCTANCE OF NACL SOLUTION AT 18ºC		
Volume, V in cc containing 1 g mol	Specific conductance, ohm^{-1} cm^2 eqvt^{-1}	Molar conductance ohm^{-1} cm^2 mol^{-1}
1,000	0.0744	74.4
5,000	0.01760	88.2
20,000	0.0479	95.9
500,000	0.000213	106.7
1,000,000	0.0001078	107.3
2,000,000	0.0000542	108.5
5,000,000	0.0000218	109.2
10,000,000	0.00001097	109.7

The equivalent conductance of some common electrolytes at 18ºC is given in Table 24.2

TABLE 24.2. EQUIVALENT CONDUCTANCE OF SOME COMMON ELECTROLYTES AT 18ºC					
Volume, containing 1 g equivalent	V in cc Equivalent conductance Λ, ohm^{-1} cm^2 eqvt^{-1}				
	NaOH	KCl	HCl	CH$_3$COOH	CH$_3$COONa
1,000	160	98.3	301	1.32	41.2
2,000	172	120.4	327	2.01	49.4
10,000	183	112.0	351	4.60	61.1
20,000	190	115.9	360	6.48	64.2
100,000	200	122.4	370	14.3	70.2
200,000	203	124.4	372	20.0	72.4
500,000	206	126.3	376	30.2	74.3
	210	127.3	377	41.0	75.2

Summary of Electrochemical Quantities

A summary of the electrochemical terms, their symbols and units in which they are expressed are listed in Table 24.3 for reference.

TABLE 24.3. THE ELECTROCHEMICAL QUANTITIES, THEIR SYMBOLS AND UNITS		
Quantity	Symbol	Unit
Resistance	R	ohm or Ω
Resistivity or Specific resistance	ρ (rho)	ohm cm
Conductance	1/R	ohm^{-1} or Siemens
Specific conductance	κ (kappa)	ohm^{-1} cm^{-1}
Dilution	V	Cc
Equivalent conductance	Λ	ohm^{-1} cm^2 eqvt^{-1}
Molar conductance	μ	ohm^{-1} cm^2 mol^{-1}

Variation of Conductance with Temperature

The conductance of a solution of an electrolyte generally increases with rise in temperature. It has been found by experiment that the conductance of a given solution increases by 2-3 per cent for one degree rise in temperature. For example, the conductances of 0.1 M KCl at two different temperatures are

1.12×10^{-2} ohm^{-1} cm^{-1} at 18ºC

1.29×10^{-2} ohm^{-1} cm^{-1} at 25ºC

The conductance of a given electrolyte depends on two factors :

(1) The number of ions present in unit volume of solution

(2) The speed at which ions move towards the electrodes

At a given temperature, the first factor remains the same for a particular electrolyte. Thus the increase in conductance with rise in temperature is due to the influence of factor (2). With rise in temperature the viscosity of the solvent (water) decreases which makes the ions to move freely toward the electrodes.

For weak electrolytes, the influence of temperature on conductance depends upon the value of ΔH accompanying the process of ionisation. If the ionisation is exothermic (–ΔH), the degree of ionisation is less at higher temperature (Le Chatelier's principle) and conductance decreases. Conversely, if the ionisation is endothermic (+ΔH), the degree of ionisation is more at higher temperature and conductance increases.

STRONG AND WEAK ELECTROLYTES

Electrolytes may be divided into two classes :

(a) Strong electrolytes

(b) Weak electrolytes

Strong Electrolytes

A strong electrolyte is a substance that gives a solution in which almost all the molecules are ionised. The solution itself is called a strong electrolytic solution. Such solutions are good conductors of electricity and have a high value of equivalent conductance even at low concentrations. The strong electrolytes are :

(1) The strong acids e.g., HCl, H_2SO_4, HNO_3, $HClO_4$, HBr and HI.

(2) The strong bases e.g., NaOH, KOH, Ca $(OH)_2$, Mg $(OH)_2$, etc.

(3) The salts. Practically all salts (NaCl, KCl, etc) are strong electrolytes.

Weak Electrolytes

A weak electrolyte is a substance that gives a solution in which only a small proportion of the solute molecules are ionised. Such a solution is called a weak electrolytic solution, that has low value of equivalent conductance. The weak electrolytes are :

(1) The weak acids : All organic acids such as acetic acid, oxalic acid, sulphurous acid (H_2SO_3) are examples of weak electrolytes.

(2) The weak bases : Most organic bases e.g., alkyl amines ($C_2H_5NH_2$) are weak electrolytes.

(3) Salts. A few salts such as mercury (II) chloride and lead (II) acetate are weak electrolytes.

Measurement of Electrolytic conductance

We know that conductance is the reciprocal of resistance. Therefore it can be determined by measuring the resistance of the electrolytic solution. This can be done in the laboratory with the help of a Wheatstone bridge.

The solution whose conductance is to be determined is placed in a special type of cell known as the conductance cell.

A simple type of conductance cell used in the laboratory is shown in Fig. 24.6. The electrodes fitted in the cell are made of platinum plates coated with platinum black. These are welded to platinum wires fused in two thin glass tubes. The contact with copper wires of the circuit is made by dipping them in mercury contained in the tubes.
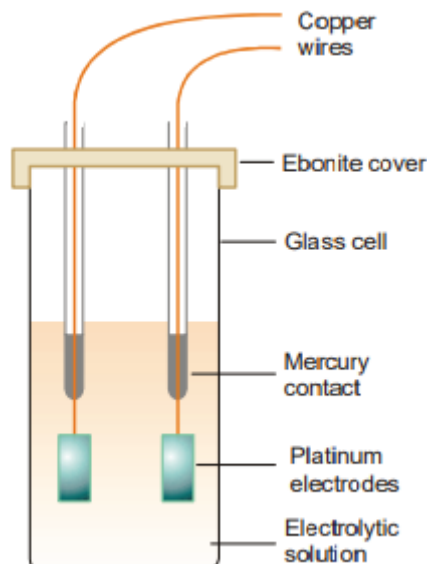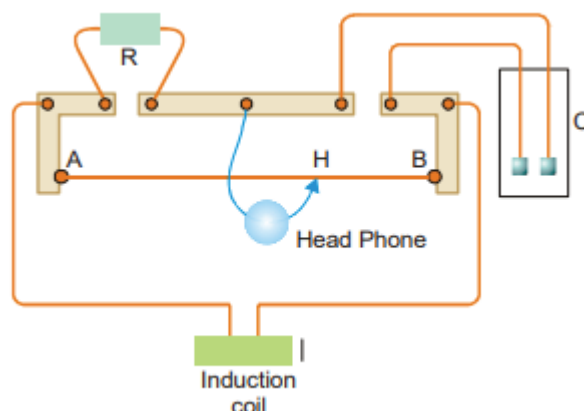

Figure 24.6 A Conductance cell.

The arrangement commonly used for the measurement of resistance of the conductance cell is shown in Fig. 24.7. It may be noted that a head-phone is used in place of a galvanometer. AB is a manganin wire tightly stretched over a meter rule graduated in milli-meters. A sliding contact H (shown by arrow-head) moves along this wire. R is a

resistance box. C is the conductance cell containing electrolytic solution. I is the induction coil from which alternating current is led as shown in the diagram. When the current is flowing, any resistance is unplugged in the resistance box R. The sliding contact H is moved until the sound in the headphone is minimum. When this occurs, we have

$$\frac{\text{resistance of } C}{\text{resistance of } R} = \frac{\text{resistance BH}}{\text{resistance AH}} = \frac{\text{length BH}}{\text{length AH}}$$

Or

$$\text{resistance of } C = \frac{\text{length BH}}{\text{length AH}} \times \text{resistance R}$$

The resistance of a solution in the conductance cell as measured above can be converted to specific conductance by using the equation

$$\kappa = \frac{1}{R} \times \frac{I}{A} \qquad \qquad \dots (1)$$

or

$$\kappa = \frac{1}{R} \times x \qquad \qquad \dots (2)$$

The ratio l/A has been put equal to x. That is,

$$\frac{\text{distance between electrodes}}{\text{area of electrode}} = x\left(\text{cell constant}\right)$$

The value of x is the same for a given cell and is called the cell constant.

After determining the specific conductance, k, the equivalent conductance, Λ, and the molar conductance of the solution can be calculated by using the expressions.

$$\Lambda = \frac{\kappa \times 1000}{N}$$

$$\mu = \frac{\kappa \times 1000}{M}$$

where N is the gram-equivalent and M is the gram-mole of the electrolyte.

Determination of the Cell constant

The exact value of the cell constant (I/A) can be determined by measuring the distance between the electrodes (I) and their area of cross sections (A). Actual measurement of these dimensions is very difficult. Therefore an indirect method is employed to determine the value of cell constant.

We know that :

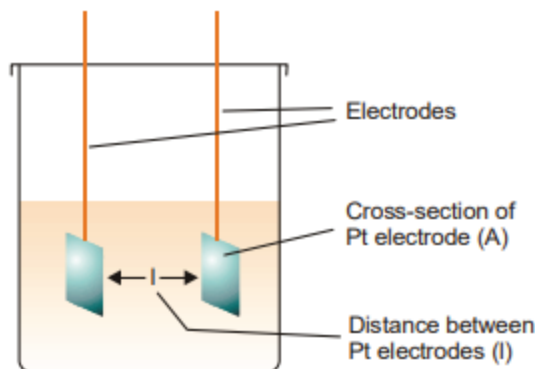$$\text{specific conductance } \kappa = \frac{1}{R} \times \frac{I}{A}$$

Figure 24.8 Dimensions of a Conductance cell.

or $\qquad \kappa$ = observed conductance × cell constant

$\therefore \qquad$ cell constant, x = $\dfrac{\text{specific conduc} \tan \text{ce}}{\text{observed conduc} \tan \text{ce}}$

To determine the cell constant, a standard solution of KCl whose specific conductance at a given temperature is known, is used. Then a solution of KCl of the same strength is prepared and its conductance determined experimentally at the same temperature. Substituting the two values in the above expression, the cell constant can be calculated.

For example, according to Kohlrausch the specific conductance of N/50 solution at 25ºC is 0.002765 mho. Now, an N/50 solution of KCl is prepared by dissolving 0.372 g pure KCl in 250 cc 'extra-pure' water (conductance water) and its conductance determined at 25ºC. The cell constant is then calculated by substituting the observed conductance in the expression

$$\text{cell cons} \tan \text{t} = \frac{0.002765}{\text{observed conduc} \tan \text{ce}}$$

Theory of Electrolytic Dissociation
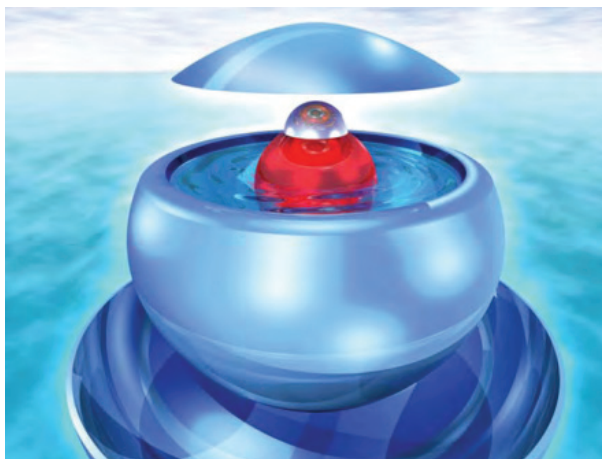
ARRHENIUS THEORY OF IONISATION

Savante Arrhenius studied the conduction of current through water solutions of electrolytes. He came to believe that the conductivity of solutions was due to the presence of ions. In 1884, Arrhenius put forward his theory of ionisation. Arrhenius theory of ionisation may be stated as :

(1) When dissolved in water, neutral electrolyte molecules are split up into two types of charged particles. These particles were called ions and the process was termed ionisation. The positively charged particles were called cations and those having negative charge were called anions.

In its modern form, the theory assumes that the ions are already present in the solid electrolyte and these are held together by electrostatic force. When placed in water, these neutral molecules dissociate to form separate anions and cations. Thus,

$$AB \rightarrow A^+ + B \qquad\qquad \text{(Old view)}$$

$$A^+ B^- \rightarrow A^+ + B \qquad\qquad \text{(Modern view)}$$

For that reason, this theory may be referred to as the theory of electrolytic dissociations.

(2) The ions present in solution constantly reunite to form neutral molecules. Thus there is a state of equilibrium between the undissociated molecules and the ions.

AB $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $A^+ + B^-$

Applying the Law of Mass Action to the ionic equilibrium we have,

$$\frac{\left[A^+ \right]\left[B^+ \right]}{\left[AB \right]} = K$$

where K is called the **Dissociation constant.**

(3) The charged ions are free to move through the solution to the oppositely charged electrode. This movement of the ions constitutes the electric current through electrolytes. This explains the conductivity of electrolytes as well as the phenomenon of electrolysis.

(4) The electrical conductivity of an electrolyte solution depends on the number of ions present in solution. Thus the degree of dissociation of an electrolyte determines whether it is a strong electrolyte or a weak electrolyte.

MIGRATION OF IONS

We know that electrolytes dissociate in solution to form positive ions (cations) and negative ions (anions).

$$AgNO_3 \longrightarrow Ag^+ + NO_3^-$$
$$CuSO_4 \longrightarrow CU^{2+} + SO_4^{2-}$$
$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$
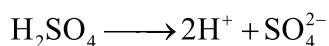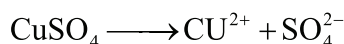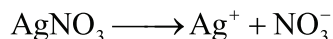
As the current is passed between the electrodes of the electrolytic cell, the ions migrate to the opposite electrodes. Thus in the

electrolytic solution of AgNO$_3$, the cations (Ag$^+$) will move to the cathode and anions (NO_3^-) will move to the anode. Usually different ions move with different rates. The migration of ions through the electrolytic solution can be demonstrated by the following experiments.
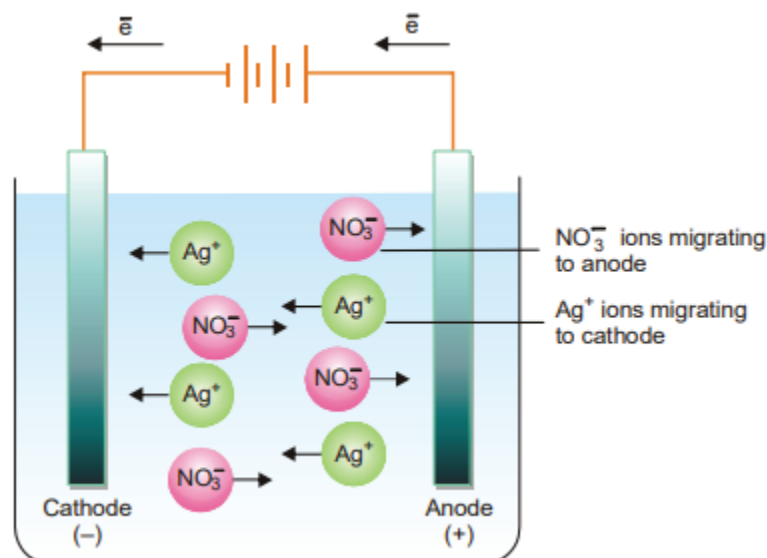
Figure 25.1 Migration of ions through electrolytic solution to opposite electrodes.

(1) Lodge's moving boundary experiment

The apparatus used consists of a U-tube which has a long horizontal portion. It is fitted with electrodes in the side limbs. The horizontal portion is filled with a jelly of agar-agar treated with a trace of alkali. This is then made red by addition of a few drops of phenolphthalein. When the jelly is set, dilute sulphuric acid is added in the anodic limb of the tube. Sodium sulphate solution is added in the cathodic limb. On passing the current, H^+ ions in the left limb solution eventually move into the agar-agar jelly. Their passage is marked by the gradual discharge of the red colour due to the neutralisation of the alkali by H^+ ions. The movement of the red boundary through the agar-agar jelly shows that H^+ ions migrate to the cathode limb.
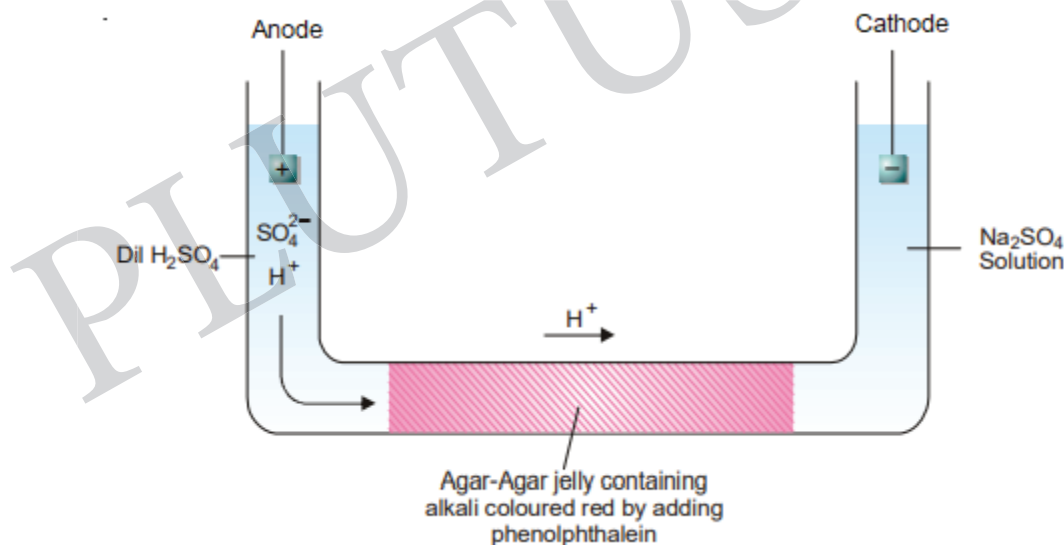

Figure 25.2 Experiment showing the migration of H ions as indicated by the movement of the red boundary through the agar-agar jelly.
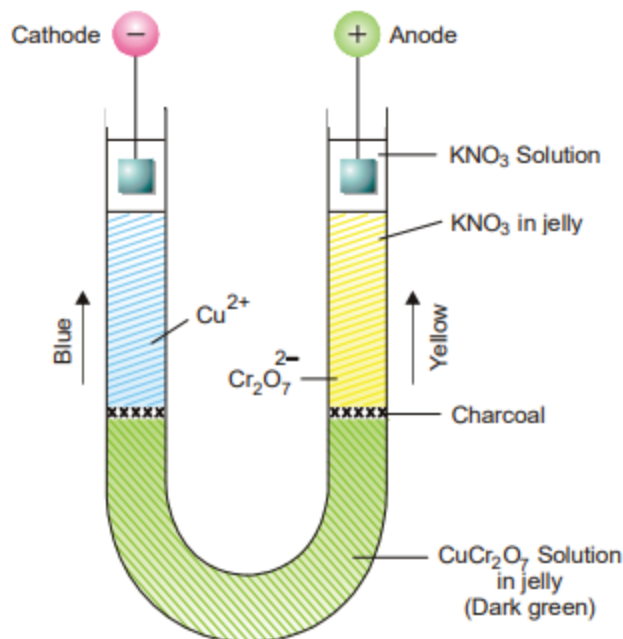
Figure 25.3 Apparatus for demonstrating the migration CU^{2+} and $Cr_2O_7^{2-}$ ions.

(2) Movement of coloured ions

The lower part of a U-tube is filled with a 5 percent water-solution of agar-agar with a small amount of copper dichromate ($CuSO_4$ + $K_2Cr_2O_7$). The dark green colour sets to a jelly. The surface of the green solution in the two limbs of the U-tube is marked by a small amount of charcoal. In both the limbs is then placed a layer of solution of potassium nitrate and agar-agar. This is also allowed to set. Over this second layer is placed some solution of pot. nitrate in pure water and the two electrodes are inserted in it. As the current is turned on, the blue colour of Cu^{2+} ions rises into the jelly under the cathode. The reddish yellow dichromate ions ($Cr_2O_7^{2-}$)move up under the anode. After some time the two types of ions are seen rising with well-defined boundaries. The use of jelly in this experiment prevents the mixing of the solutions by diffusion.

RELATIVE SPEED OF IONS

We have already considered that ions move to the oppositely charged electrodes under the influence of the electric current. But the speeds of cations migrating towards the cathode and those of anions migrating towards the anode are not necessarily the same. However, the speed of a cation moving away from the anode will be proportional to the fall of concentration of these ions at the anode. Similarly, the speed of an anion moving away from the cathode will be proportional to the fall of concentration of anions around the cathode. Hittorf studied such changes experimentally and gave a general rule known as the Hittorf's Rule. It states that : the loss of concentration around any electrode is proportional to the speed of the ion moving away from it. Hittorf's Rule may be illustrated by the following scheme.

In Fig. 25.4, A is anode and C is cathode. AA' and BB' are two imaginary planes which divide the cell into three compartments, the anode compartment, the middle compartment and the cathode compartment. The sign (+) represents a cation while the sign (–) represents an anion.
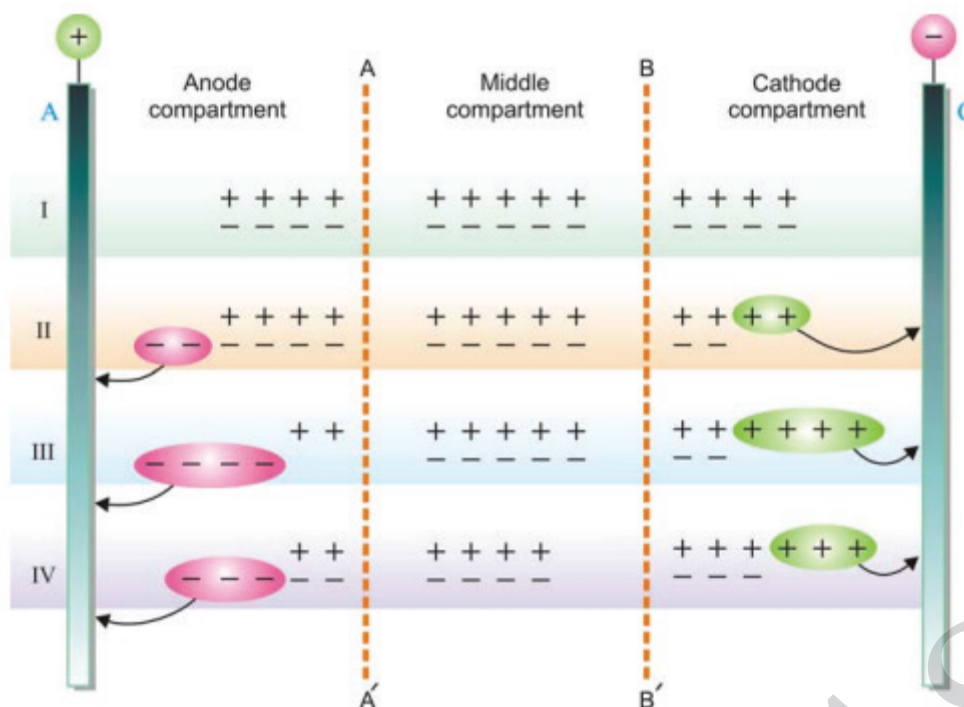
Figure 25.4 Scheme showing that the loss of concentration around any electrode is proportional to the speed of the ion moving away from it.

Before electrolysis, let there be 13 ion-pairs in the cell. The number of ion-pairs in the two outer compartments is 4 each and there are 5 ion-pairs in the middle compartment (Position I). Now let us consider the following cases:

(i) Let the anions alone be capable of movement

When, say, two anions have moved towards the anode, we get the position as shown in II. The cations have not moved at all. But inspite of that the number of discharged anions and cations is the same viz., 2. The concentration in the anode compartment, however, has not altered while in the cathode compartment it has fallen by two ion-pairs.

(ii) Let the anions and cations move at the same rate

When two ions of each type have crossed over towards the opposite electrodes, we get the condition as shown in III. The number of discharged anions and cations is the same viz., 4. The concentration of both the anode compartment and the cathode compartment has fallen to the same extent viz, by two ion-pairs.

(iii) Let the cations move at twice the speed of the anions

In this case, when cations have moved to the cathode compartment, one anion passes into the anode compartment. The state of affairs is shown in IV. The total number of discharged anions and cations is again the same viz., 3. Although the concentration in the cathode compartment has fallen by one ion-pair, the concentration in the anode compartment decreases by two ion-pairs.

It is evident from the above considerations that ions are always discharged in equivalent amounts on the opposite electrodes. It is really due to the difference in the speeds of anions and cations that the changes in concentration around electrodes are caused. We also conclude that the loss in concentration around any electrode is proportional to the speed of the ion moving away from it.

This is Hittorf's Rule. We can write the expression :

$$\frac{\text{Fall around anode}}{\text{Fall around cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}} = \frac{v_+}{v_-}$$

where v_+ and v_- is the speed of cations and anions respectively.

In deriving the above relation, an important assumption has been made, namely, the discharged ions do not react with the material of the electrodes. However, in many cases they combine with the material of the electrodes rather than depositing on it. This results in an increase in concentration around such an electrode instead of a decrease.

Migration Speed of Ag$^+$ and NO$_3^-$ ions

Let us study the electrolysis of a solution of silver nitrate in a cell of the type described above but using silver electrodes. We find that instead of a fall in concentration of silver nitrate around the anode, it increases. This is due to the fact that every NO$_3^-$ ion that arrives at the anode dissolves from it one Ag$^+$ ion to form AgNO$_3$. If the electrodes were of platinum, the state of affairs would be as shown in Fig. 25.4 III when ions moved at the same rate. That is, there should have taken place a fall in concentration by 2 ion-pairs in each compartment. With silver electrodes, however, we have the condition shown in Fig. 25.5.

Figure 25.5 With silver electrodes, concentration around the cathode falls while it increases around the anode.

It is clear that the concentration around the cathode has fallen from 4 to 2 ion-pairs but around the anode it has increased from 4 to 6 ion-pairs. It is very easy to calculate the speed ratio of ions in this case as well by putting a silver coulometer in the circuit. This would give us the total current passed or increase in concentration around the anode as if no silver ions had migrated towards the cathode. The difference of the total increase and the actual increase around the anode would give the fall in concentration around the anode due to the migration of silver ions.

WHAT IS TRANSPORT NUMBER ?

During electrolysis the current is carried by the anions and the cations. The fraction of the total current carried by the cation or the anion is termed its Transport number or Hittorf's number. If v$_+$ represents the speed of migration of the cation and v$_-$ that of the anion,

the transport number of cation = $\dfrac{v_+}{v_+ + v_-}$

the transport number of anion = $\dfrac{v_-}{v_+ + v_-}$

The transport number of the cation is represented by t and that of the anion by t$_-$.

Thus $\qquad t_+ = \dfrac{v_+}{v_+ + v_-}$ $\qquad$ and $\qquad t_- = \dfrac{v_-}{v_+ + v_-}$

Or $\qquad \dfrac{t_+}{t_-} = \dfrac{v_+}{v_-}$ $\qquad$ and $\qquad t_+ + t_- = 1$

If the speed ratio v$_+$/v$_-$ be denoted by r, we have,

$$r = \frac{t_+}{t_-} = \frac{t_+}{1 - t_+}$$

and $$t_- = \frac{1}{1 + r}$$

DETERMINATION OF TRANSPORT NUMBER

There are two methods for determination of the transport number of an ion :

(1) Hittorf's method

(2) Moving Boundary method

Hittorf's Method

This method of determining transport number is based on Hittorf's Rule. According to this rule, the loss of concentration around any electrode is proportional to the speed of the ion moving away from that electrode. The transport number of an ion is calculated from the changes in concentration found experimentally around the electrodes. The apparatus used in this method consists of two vertical glass tubes joined together through a U-tube in the middle. All the three tubes are provided with stopcocks at the bottom. The U-tube is also provided with stopcocks at the tops of the two limbs. By closing these stopcocks, the communication between the solutions in the cathode and anode limbs can be stopped. The silver anode is sealed in a glass-tube and the cathode is a piece of freshly silvered foil. The apparatus is filled with a solution of silver nitrate and a steady current of about 0.01 ampere is passed for two to three hours. It is an important precaution that the current is passed only for a short time so that too large a change in concentrating does not take place. The apparatus is connected with a silver or copper coulometer as shown in Fig. 25.6, which shows the circuit for the experiment.
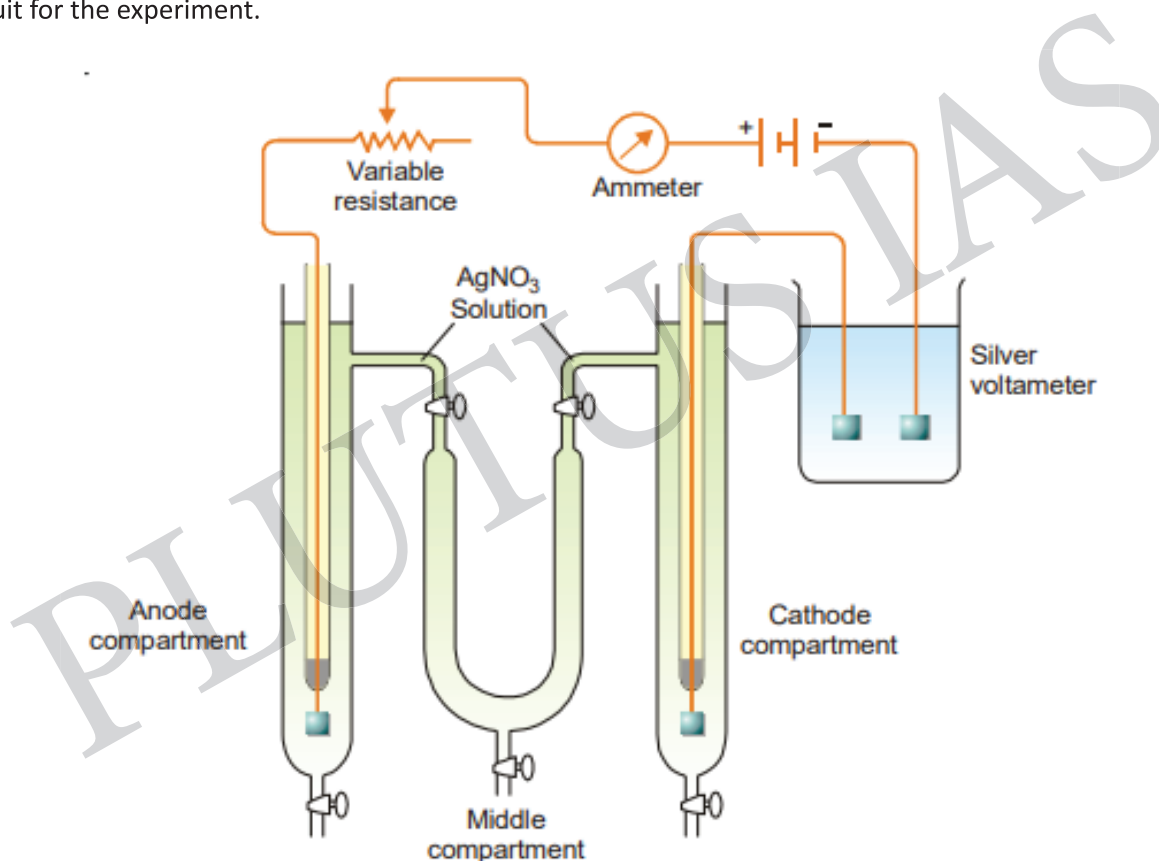

Figure 25.6 Hittorf's apparatus for determining Transport numbers.

When the current has been passed for about three hours, the stopcocks at the top of the U-tube are closed. The whole of the liquid in the anode compartment is carefully drained into a weighed flask and its weight determined. Its silver content is determined by titrating against a standard solution of potassium thiocyanate. The weight of silver deposited in the silver coulometer is also noted. If a copper coulometer is used in place of silver coulometer, the weight of silver equivalent to the copper deposited is calculated by multiplying it with 108/31.5. There should be no change in the concentration of the solution in the U-tube if the experiment has been successfully performed.

If the above experiment has been performed by using silver electrodes, in this case nitrate ions attack the silver anode. Consequently, there is an increase in concentration of Ag^+ ions rather than decrease. The same experiment can also be performed by using platinum electrodes to avoid the attack of anions on the anode.

Calculations :

Two different cases may arise :

Case 1. When electrodes are unattackable (Pt electrodes are used).

After passing electric current :

Let the weight of anodic solution taken out = a g

weight of AgNO3 present in it by titration = b g

weight of water = (a − b) g

Before passing electric current :

Let weight of $AgNO_3$ in (a − b) g of water before passing electric current be = c g

∴ Fall in concentration

$$= \left(c - b\right) g \text{ of } AgNO_3 = \frac{\left(c - b\right)}{170} g \text{ eqvt of } AgNO_3$$

$$= \frac{\left(c - b\right)}{170} g \text{ eqvt of } Ag = d\left(say\right)$$

Let the weight of silver deposited in silver coulometer be

$$= w_1 g$$

$$= \frac{w_1}{108} g \text{ eqvt of } Ag$$

$$= W(Say) \text{ g eqvt of } Ag$$

Transport number of $Ag^+ \left(t_{Ag^+}\right) = \dfrac{\text{Fall in concentration around anode in g eqvt}}{\text{Amt. of Ag deposited in g eqvt}} = \dfrac{d}{W}$

and Transport number of NO_3^- ion $\left(t_{NO_3^-}\right) = 1 - \dfrac{d}{W}$

Case 2. When electrodes are attackable (Ag electrodes are used).

Increase in conc. of anodic solution = (b − c) g of $AgNO_3$

$$= \frac{\left(b - c\right)}{170} \times 108 \text{ g of } Ag$$

$$= \frac{\left(b - c\right)}{170} g \text{ eqvt of } Ag$$

= e (say)

If no Ag⁺ ions had migrated from the anode, the increase in concentration of Ag⁺ ions would have been equal to W.

∴ Fall in concentration due to migration of Ag⁺ ion = W − e

Hence, transport number of Ag⁺ ion $\left(t_{Ag^+}\right) = \dfrac{W - e}{W}$

and transport number of NO_3^- ion $\left(t_{NO_3^-}\right) = 1 - \dfrac{W-e}{W}$

Moving Boundary Method

The moving boundary method is based on the direct observation of migration of ions under the influence of applied potential. This method is very accurate and has been used in recent years for precision measurements.

The apparatus used consists of a long vertical tube fitted with two electrodes at the two ends (Fig. 25.7). The tube is filled with a solution of cadmium chloride ($CdCl_2$) at the lower end and hydrochloric acid at the upper end in a way that there is a sharp boundary between the two (due to difference in their refractive indices).

The platinum cathode dipped in HCl solution is inserted at the top and the anode (cadmium stick) is introduced at the bottom.
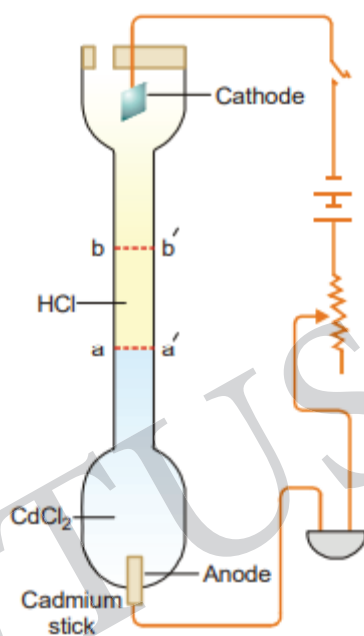

Figure 25.7 Determination of transport number by moving boundary method.

On passing electric current through the apparatus, hydrogen gas is evolved at the cathode and H$^+$ ions move toward the anode. The H$^+$ ions are replaced by Cd^{2+} ions and hence the boundary line moves in the upward direction. By noting the length through which the boundary moves and the quantity of electricity passed through the cell, the transport number of H$^+$ ion can be calculated.

In general, if the transport number of a cation A$^+$ is to be determined, the electrolyte AX solution is taken in the upper part of the apparatus and a layer of another electrolyte BX having the common ion X$^-$ is introduced in the lower part of the apparatus. The electrolyte BX is selected so that the velocity of B$^+$ ion is less than that of A$^+$ ion. In such a case, the situation is described in Fig. 25.8.
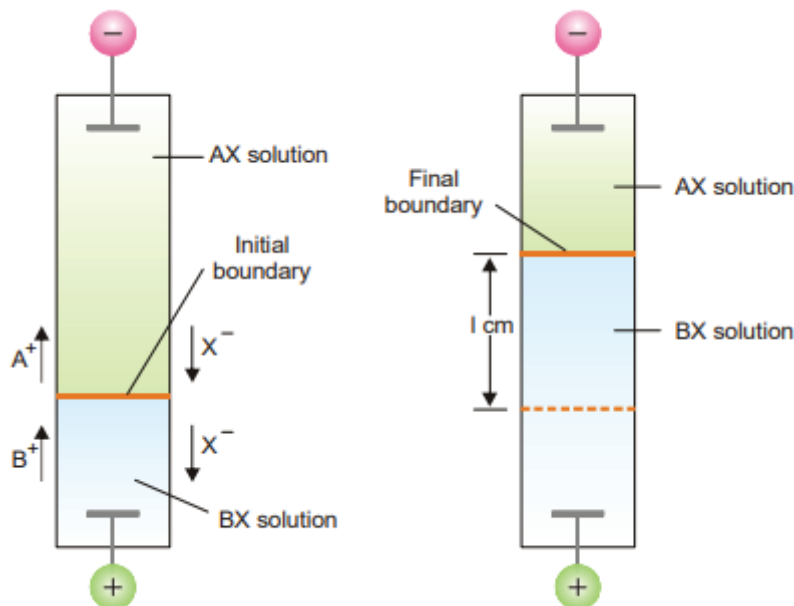
Figure 25.8 Moving boundary experiment for determining the transport number of A^+ ion.

Calculations :

Let c be the original concentration of A^+ ions in gram-equivalents per ml of the solution.

If the distance through which boundary moves = l cm, and the area of cross-section of the tube = s sq cm.

Then the number of equivalents of A^+ moving upward = $s \times l \times c$

Let the number of Faradays of current passed = n

The fraction of current carried by A^+ ions = $n \times t_{A^+}$

Hence
$$n \times t_{A^+} = s \times l \times c$$

and
$$t_{A^+} = \frac{s \times l \times c}{n} \qquad \qquad \text{... (1)}$$

where n = Q/F. Q being the quantity of current passed and F stands for Faraday (= 96, 500 coulombs).

The above expression can now be written as

$$t_{A^+} = \frac{s \times l \times F \times c}{Q} \qquad \qquad \text{... (2)}$$

With the help of the expressions (1) and (2), the value of t_{A^+} (transport number of A^+), can be found from the experimental values of s, l, c and n.

KOHLRAUSCH'S LAW

From a study of the equivalent conductances of different electrolytes at infinite dilution ($\lambda\infty$), Kohlrausch discovered that each ion contributes to the conductance of the solution. In 1875, he enunciated a generalisation which is called the Kohlrausch's Law. It states that : the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductances of the component ions.

The law may be expressed mathematically as :

$$\lambda_\infty = \lambda_a + \lambda_c$$

where λ_a is the equivalent conductance of the anion and λ_c that of the cation.

For example, the equivalent conductance of NaCl at infinite dilution at 25°C is found to be 126.45. The equivalent conductance of Na⁺ and Cl⁻ ion is 50.11 ohm⁻¹ and 76.34 ohm⁻¹ respectively. Thus,

$$\lambda_\infty \left(NaCl \right) = \lambda_{Cl^-} + \lambda_{Na^+}$$

or   126.45 = 50.11 + 76.34

This is in conformity with the Kohlrausch's Law.

Applications of Kohlrausch's Law

Each ion has the same constant ionic conductance at a fixed temperature, no matter of which electrolyte it forms a part. It is expressed in ohm⁻¹ cm² and is directly proportional to the speeds of the ions.

$$\lambda_a \propto v_- \text{ or } \lambda_a = k \times v_-$$

$$\lambda_c \propto v_+ \text{ or } \lambda_c = k \times v_+$$

where k is the proportionality constant.

Also $\lambda_\infty \propto (\lambda_a + \lambda_c) = k (v_- + v_+)$

$\therefore$ $$\frac{\lambda_a}{\lambda_\infty} = \frac{kv_-}{k\left(v_- + v_+\right)} = \frac{v_-}{v_- + v_+} = t_-$$ ... (1)

and $$\frac{\lambda_c}{\lambda_\infty} = \frac{kv_+}{k\left(v_- + v_+\right)} = \frac{v_+}{v_- + v_+} = t_+ = 1 - t_-$$ ... (2)

Dividing (1) by (2), we have

$$\frac{\lambda_a}{\lambda_c} = \frac{t_-}{1 - t_-}$$

... (3)

With the help of the expression (3), we can determine ionic conductances from the experimental values of the transport number of the ions.

(1) Calculation of λ_∞ for Weak electrolytes

Weak electrolytes do not ionise to a sufficient extent in solution and are far from being completely ionised even at very great dilution. The practical determination of λ_∞ in such cases is, therefore, not possible. However, it can be calculated with the help of Kohlrausch's law.

$$\frac{\lambda_a}{\lambda_c} = \frac{t_-}{1 - t_-}$$

$$\lambda_a - t_- \lambda_a = t_- \lambda_c$$

$$\lambda_a - t_- \left(\lambda_a + \lambda_c\right)$$

$$= t_- \lambda_\infty$$

Thus the ionic conductance of an ion is obtained by multiplying the equivalent conductance at infinite dilution of any strong electrolyte containing that ion by its transport number.

In this manner, the ionic mobilities of the two ions present in the weak electrolyte can be calculated. Thus we can get the equivalent conductance of the electrolyte at infinite dilution by adding up these two values.

(2) Calculation of Absolute Ionic mobilities

The absolute ionic mobility of an ion is defined as **the velocity of an ion in centimetres per second under a potential gradient of one volt per centimetre.** (Potential gradient = applied EMF/ distance between (the electrodes). It is expressed in cm sec^{-1}.

For example, let the velocity of the ion at infinite dilution be U cm per second when the distance between the electrodes is 20 cm and the voltage 100 V. Then the potential difference is 100/20 i.e., 5 volts per cm and the ionic mobility is U/5 cm sec^{-1}.

It has been found that the ionic conductance is directly proportional to the ionic mobility i.e.,

$$\lambda_a \propto U_a \qquad \text{and} \qquad \lambda_c \propto U_c$$

or
$$\lambda_a = k\,U_a \qquad \text{and} \qquad \lambda_c = k\,U_c$$

where k is the proportionality constant. Its value is equal to the charge on one gram-equivalent of the ion under the potential gradient of 1 volt per cm i.e., k = 96,500 coulomb (1 Faraday). Therefore, the ionic mobility is obtained by dividing the ionic conductance by 96,500 coulombs.

$$U_{\neq} = \frac{\lambda_{\neq}}{96,500}$$

or
$$\lambda_{\neq} = FU_{\neq}$$

(3) Calculation of the solubility of sparingly soluble salts

Substance like AgCl or $PbSO_4$ which are ordinarily called insoluble do possess a definite value of solubility in water. This can be determined from conductance measurements of their saturated solutions (Chapter 24). Since a very small amount of solute is present it must be completely dissociated into ions even in a saturated solution so that the equivalent conductance κV is equal to equivalent conductance at infinite dilution. This according to Kohlrausch's Law is the sum of the ionic mobilities.

i.e., $\qquad \kappa V = \lambda_{\infty} = \lambda_a + \lambda_c$

knowing κ and λ_{∞}, V can be found out which is the volume in ml containing 1 g-eqvt of the electrolyte.

(4) Calculation of the Degree of Dissociation or Conductance Ratio

The apparent degree of dissociation, α, of an electrolyte at the dilution V is given by $\alpha = \lambda_v / \lambda_{\infty}$, where λ_v is the equivalent conductance of the electrolyte at the dilution V and λ_{∞} is its equivalent conductance at infinite dilution. This according to Kohlrausch's Law is the sum of λ_a and λ_c.

(5) Calculation of the Ionic product for Water

The observed specific conductance of the purest water at 25°C is 5.54×10^{-8} mhos. The conductance of one litre of water containing 1 gram eqvt of it would be :

$$\lambda_{H_2O} = 5.54 \times 10^{-8} \times 1000 = 5.54 \times 10^{-5} \text{ mhos}$$

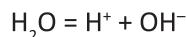At the same temperature the conductance of H$^+$ ions and OH$^-$ ions are :

$$\lambda_{H^+} = 349.8 \text{ mhos}$$

$$\lambda_{OH^-} = 198.5 \text{ mhos}$$

According to Kohlrausch's Law

$$\lambda_{H_2O} = \lambda_{H^+} + \lambda_{OH^-}$$

$$= 349.8 + 198.5 = 548.3 \text{ mhos}$$

One molecule of water gives one H^+ ion and one OH^- ion

$$H_2O = H^+ + OH^-$$

Assuming that ionic concentration is proportional to conductance, we have

$$\left[H^+\right] = \left[OH^-\right] = \frac{5.5 \times 10^{-5}}{548.3} = 1.01 \times 10^{-7} \text{ g ion litre}^{-1}$$

The ionic product of water is then

$$K_w = [H^+][OH^-] = 1.02 \times 10^{-14} \text{ at } 25°C$$

For most purposes, the value of K_w is taken to be 10^{-14}

CONDUCTOMETRIC TITRATIONS

Titrations in which conductance measurements are made use of in determining the end-point of acid-alkali reactions, some displacement reactions or precipitation reactions are called Conductometric titrations. In these titrations, advantage is taken of the fact that the conductance of a solution at a constant temperature depends upon the number of ions present in it and their mobility. For this purpose, the titrant is added from a burette into a measured volume of the solution to be titrated which is taken in a conductance cell and the conductance readings corresponding to the various additions are plotted against the volume of the titrant. In this way two linear curves are obtained, the point of intersection of which is the end-point. Several phenomena like hydrolysis of reactants or products or partial solubility of a precipitated product give rise, however to a curvature in the curves. The shapes of curves obtained in certain types of titration are discussed below :

(1) Titration of a Strong acid against a Strong base

Consider the reaction in which hydrochloric acid solution is titrated against a solution of sodium hydroxide. Take 20 ml of the acid solution in the conductance cell placed in a thermostat and determine its conductance. Now add 1 ml sodium hydroxide solution from the burette at a time. After each addition, determine the conductance of the solution after through mixing and plot the conductance of the solution against the volume of the alkali added. It will be observed that the points lie on two lines which are almost straight. The point of intersection of the interpolated lines will be the end point and the volume of alkali corresponding to this point is the volume of alkali required to neutralise 20 ml of the acid (Fig. 25.9). The reason for this is that before the addition of alkali, the conductance of the solution is due to presence of H^+ and Cl^- ions. Since hydrogen ions possess the greatest mobility of any ion, the greater part of the conductance is due to it. As alkali solution is added, the hydrogen ions are removed by combination with the hydroxyl ions forming feebly ionised water molecules and their place is taken up by comparatively slow moving Na^+ ions.

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O \qquad \text{(feebly ionised)}$$

As a result of this, the conductance of the solution decreases and continues to fall with every subsequent addition of alkali till the end-point is reached. After the equivalence point, the further addition of sodium hydroxide solution results in an increase of conductance since the hydroxyl ions are no longer removed in the chemical reaction in the form of feebly ionised water. The point of minimum conductance, therefore, coincides with the end-point of the titration.

In order to get accurate results, the volume change during titration should be as little as possible. The titrant should, therefore, be about 10 times as strong as the acid solution in the conductance cell in order to keep the volume change small. If this is not so, a correction to the readings has to be applied viz,

$$\text{actual conductance} = \left(\frac{v+V}{V}\right) \times \text{observed conductance}$$

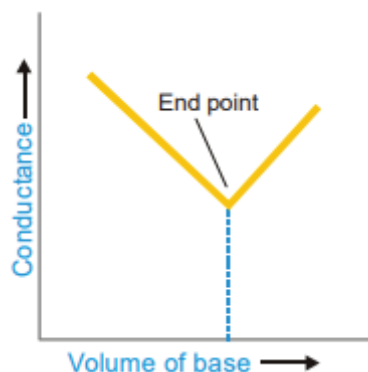where v is the volume of the titrant and V is the original volume of the solution to be titrated

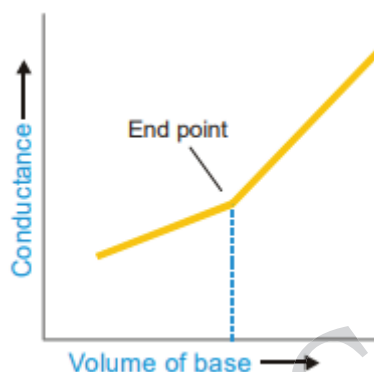Figure 25.9 Conductometric titration curve for strong acid and strong base.

Figure 25.10 Curve for titration of a weak acid against a strong base.

(2) Titration of a Weak acid against a Strong alkali

When a weak acid like acetic acid is titrated against a strong alkali like sodium hydroxide, we get a curve of the type shown in Fig. 25.10. The initial conductance of the solution is low because of the poor dissociation of the weak acid. On adding alkali, highly ionised sodium acetate is formed. The acetate ions at first tend to suppress the ionisation of acetic acid still further due to Common Ion Effect but after a while the conductance begins to increase because the conducting power of highly ionised salt exceeds that of the weak acid.

$$CH_3COOH + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + H_2O \qquad \text{(feebly ionised)}$$
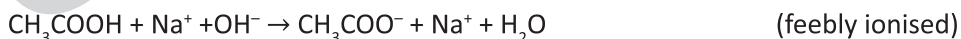
Immediately after the end point, further addition of sodium hydroxide introduces the fast moving hydroxyl ions. Thus, the conductance value shows a sharp increase. The point of intersection of the two curves, gives the end-point.

$$H^+ + Cl^- + NH_4OH \rightarrow NH_4^+ + Cl^- + H_2O \qquad \text{(feebly ionized)}$$

After the end-point has been reached, the addition of ammonium hydroxide will not cause any appreciable change in conductance value as it is a weak electrolyte and its conductance is very small compared with that of the acid or its salt. The shape of this part of the curve will, therefore, be as shown in the figure.

(3) Titration of a Strong acid against a Weak base

The curve obtained for the titration of a strong acid against a weak base is shown in Fig. 25.11. In this case, the conductance of the solution will first decrease due to the fixing up of the fast moving H^+ ions and their replacement by slow moving NH_4^+ ions.

(4) Titration of a Weak acid against a Weak base

The conductometric method is particularly suitable as such titrations do not give a sharp end-point with indicators. Consider the titration of acetic acid with ammonium hydroxide. The complete titration curve is shown in Fig. 25.12. The initial conductance of the solution in this case is also low due to the poor dissociation of the weak acid. But it starts increasing as the salt CH_3COONH_4 is formed. After the equivalence point, the conductivity remains almost constant because the free base NH_4OH is a weak electrolyte. The end-point is quite sharp.
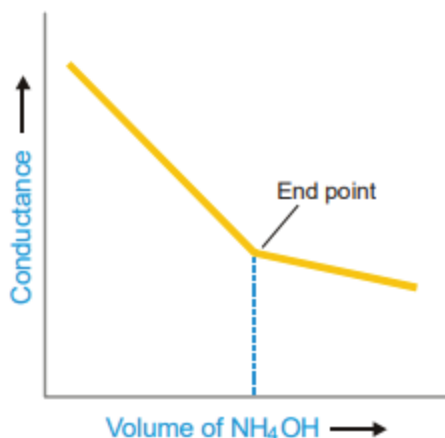
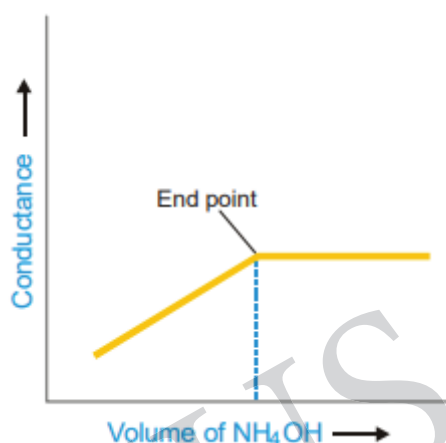Figure 25.11 Curve for titration of a strong acid against a weak base.

Figure 25.12 Curve for titration of acetic acid against ammonium hydroxide.

(5) Precipitation reactions

The end-point in precipitation reactions can be accurately determined by conductometric titration. The accuracy is further increased by working with fairly dilute solutions and addition of alcohol which reduces the solubility of the precipitate and prevents adsorption. In the titration of potassium chloride against silver nitrate, for example, the change in conductance on the addition of silver nitrate is not much since the mobility of the potassium ion and the silver ion is of the same order. Thus the curve is nearly horizontal.

$$Ag^+ + NO_3^- + K^+ + Cl^- \longrightarrow K^+ + NO_3^- + AgCl\left(ppt\right)$$

After the end-point, there is a sharp increase in conductance due to an increase in the number of free ions in solution.
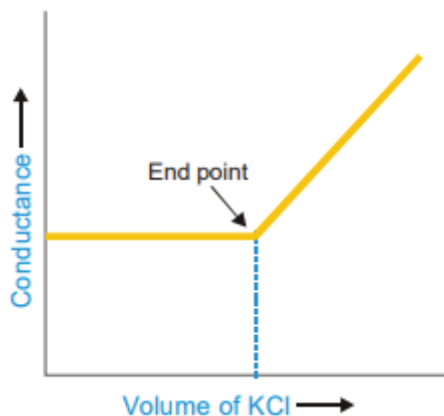

Figure 25.13 Titration of potassium chloride against silver nitrate.

Advantage of Conductometric Titrations

(1) Coloured solutions where no indicator is found to work satisfactorily can be successfully titrated by this method.

(2) This method is useful for the titration of weak acids against weak bases which do not give a sharp change of colour with indicators in ordinary volumetric analysis.

(3) More accurate results are obtained because the end -point is determined graphically.

Precautions. (i) It is necessary to keep the temperature constant throughout the experiment. (ii) In acid-alkali titrations, the titrant should be about 10 times stronger than the solution to be titrated so that the volume change is as little as possible.

DIFFERENCES BETWEEN CONDUCTOMETRIC AND VOLUMETRIC TITRATIONS

Conductometric Titrations

1. Conductance measurements are done to check end points.

2. Titrations can be carried out even with coloured solution.

3. Accurate results are obtained.

4. End point is determined graphically.

5. In case of polybasic acids conductometric titrations can be used.

6. These are successful even in weak acids and strong bases.

Volumetric Titrations

1. Volume measurements are done to check end points.

2. These titrations fail in coloured solutions as suitable indicators are not available some times.

3. Results are not so accurate.

4. End point is determined by change in colour of indicator.

5. In case of polybasic acids volumetric titrations do not give correct end points.

6. These are not successful in weak acids and strong bases.

Ionic Equilibria Solubility Product

OSTWALD'S DILUTION LAW

According to the Arrhenius Theory of dissociation, an electrolyte dissociates into ions in water solutions. These ions are in a state of equilibrium with the undissociated molecules. This equilibrium is called the Ionic equilibrium. Ostwald noted that the Law of Mass Action can be applied to the ionic equilibrium as in the case of chemical equilibria.

Let us consider a binary electrolyte AB which dissociates in solution to form the ions A^+ and B^-.

$$AB \rightleftharpoons A^+ + B^-$$
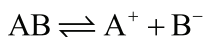
Let C moles per litre be the concentration of the electrolyte and α (alpha) its degree of dissociation. The concentration terms at equilibrium may be written as :

$[AB] = C(1 - \alpha)$ mol litre^{-1}

$[A^+] = C\alpha$ mol litre^{-1}

$[B^-] = C\alpha$ mol litre^{-1}

Applying the Law of Mass Action :

Rate of dissociation = $k_1 \times C(1 - \alpha)$

Rate of combination = $k_2 \times C\alpha \times C\alpha$

At equilibrium :

$$k_1 \times C(1 - \alpha) = k_2 \times C\alpha \times C\alpha$$

or
$$\frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{k_1}{k_2} = K_c$$

or
$$K_c = \frac{\alpha^2 C}{(1-\alpha)} \text{ mol litre}^{-1} \qquad \qquad \ldots (1)$$

The equilibrium constant K_c is called the Dissociation constant or Ionization constant. It has a constant value at a constant temperature.

If one mole of an electrolyte be dissolved in V litre of the solution, then

$$C = \frac{1}{V}$$

V is known as the Dilution or the solution. Thus the expression (1) becomes

$$K_c = \frac{\alpha^2}{(1-\alpha)V} \qquad \qquad \ldots (2)$$

This expression which correlates the variation of the degree of dissociation of an electrolyte with dilution, is known as **Ostwald's Dilution Law**

For Weak Electrolytes

For weak electrolytes, the value of α is very small as compared to 1, so that in most of the calculation we can take $1 - \alpha \simeq 1$. Thus the Ostwald's Dilution Law expression becomes

$$K_c = \frac{\alpha^2}{V}$$

It implies that the degree of dissociation of a weak electrolyte is proportional to the square root of the dilution i.e.,

$$\alpha \propto \sqrt{K_c V}$$

or

$$\alpha = K' \sqrt{V}$$

For Strong Electrolytes

For strong electrolytes, the value of α is large and it cannot be neglected in comparison with 1. Thus we have to use the original expression (2). That is,

$$K_c = \frac{\alpha^2}{(1-\alpha)V} \qquad \text{or} \qquad \alpha^2 = K_c V - \alpha K_c V$$

which gives a quadratic equation

$$\alpha^2 + \alpha\, K_c\, V - K_c\, V = 0$$

from this equation the value of α can be evaluated.

Experimental Verification of Ostwald's Law

The Ostwald's Dilution law can be verified if the values of α, the degree of dissociation, at different dilutions are known. The values of α are determined experimentally by using the relation.

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

where λ_v and λ_∞ are the equivalent conductances at dilution V and infinite dilution respectively. Their values are found by conductance measurements and Kohlrausch's law. The value of α at various dilutions thus determined are inserted in the expression :

$$K_c = \frac{\alpha^2}{(1-\alpha)V}$$

If the values of K_c come out to be constant, the Ostwald's law stands verified.

Limitation of Ostwald's Law

Ostwald's Dilution law holds good only for weak electrolytes and fails completely when applied to strong electrolytes. For strong electrolytes, which are highly ionised in solution, the value of the dissociation constant K, far from remaining constant, rapidly falls with dilution. In Table 26.1, the values of K at different dilutions illustrate the point.

Table 26.1. Dissociation of KCl at 18°C λ_∞ = 129.9			
V	λ_v	$\alpha = \lambda_v / 129.9$	$K = \alpha^2 / (1 - \alpha)\, V$
1	98.27	0.565	2.350
2	102.41	0.7883	1.434
5	107.96	0.831	0.8154
20	115.75	0.891	0.3642
200	119.96	0.9234	0.2221
500	124.41	0.9577	0.1084

Factors that explain the failure of Ostwald's law in case of strong electrolytes

(1) The law is based on Arrhenius theory which assumes that only a fraction of the electrolyte is dissociated at ordinary dilutions

and complete dissociation occurs only at infinite dilution. However, this is true for weak electrolytes. Strong electrolytes are almost completely ionised at all dilutions and λ_v/λ_∞ does not give the accurate value of α.

(2) The Ostwald's law is derived on the assumption that the Law of Mass Action holds for the ionic equilibria as well. But when the concentration of ions is very high, the presence of charges affects the equilibrium. Thus the Law of Mass Action in its simple form cannot be applied.

(3) The ions obtained by dissociation may get hydrated and may affect the concentration terms. Better results are obtained by using activities instead of concentrations.

THEORY OF STRONG ELECTROLYTES

A number of theories have been put forward by different workers in order to explain the high conductance of strong electrolytes. Southerland (1906) held the view that ions in solution were surrounded by a large number of ions of opposite charge. Due to the weakening of interionic forces, the ionic velocities were accelerated. This resulted in the increase of conductance of the electrolyte solution. However, not much notice was taken of Southerland's view.

Ghosh's Formula

In 1918 J.C. Ghosh revived the above theory. He assumed that though the electrolyte is completely ionised, all the ions are not free to move owing to the influence of electric charges and it is only the mobile ions which contribute to the conductance of the solution. The value α represents the "active" proportion of the electrolyte and can be determined by purely electrical data, the Law of Mass Action playing no part whatsoever. His formula

$$\sqrt[3]{V} \log \alpha = K$$

was applicable to univalent strong electrolytes.

Debye-Huckel Theory

In 1923 Debye and Huckel and in 1926 Onsagar put forward the modern theory of strong electrolytes in which account is taken of the electrostatic forces between the ions. Without going into its mathematical details, a brief outline of the main ideas of the theory is given below :

(1) The strong electrolyte is completely ionised at all dilutions. The present position as it has emerged from the study of Raman spectra, X-ray analysis of crystals, Distribution coefficients and vapour pressures is that there is a very small amount of unionised substance also present and therefore instead of saying 'completely ionised' we should say 'almost completely ionised'.

(2) Since oppositely charged ions attract each other, it suggests that anions and cations are not uniformly distributed in the solution of an electrolyte but that the cations tend to be found in the vicinity of anions and vice-versa (Fig. 26.1). Though the solution is on the whole neutral, there is in the vicinity of any given ion a predominance of ions of opposite charge which we call as counter ions. The ions are all the time on the move in all directions but on the average, more counter ions than like ions pass by any given ion. This spherical haze of opposite charge is called **ionic atmosphere**.
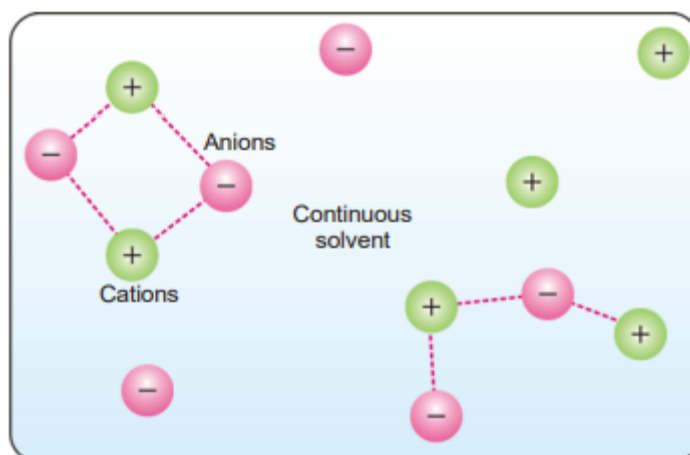

Figure 26.1 The ions of a particular charge are surrounded by more ions of the opposite charge and solvent molecules. Because of the large number of ions in concentrated solution,the ion activity is reduced due to hindered movement of the ions.

(3) Decrease in equivalent conductance with increase in concentration is due to fall in mobilities of the ions due to greater inter-ionic effect and vice-versa.

(4) The ratio $\lambda_\mathrm{v} / \lambda_\infty$ does not correctly give the degree of dissociation α for strong electrolytes but only the conductance or conductance coefficient f c .

(5) In spite of almost complete ionisation, λ_v is much less than λ_∞.

The observed deviations are due to the following reasons :

(1) Asymmetry or Relaxation Effect. Imagine a central negative ion. This is surrounded by a number of positively charged ions which form its 'ionic atmosphere.' This atmosphere is symmetrically situated in the absence of any electrical field and the force of attraction exerted by the atmosphere on the central ion is uniform in all directions. When an electric field is applied, the negative ion moves towards the anode and the positive ionic atmosphere towards the cathode. This leaves a large number of positive ions behind it than there are in front of the negative ion with the result that the symmetry of the atmosphere about the central negative ion is destroyed (Fig. 26.2) and it becomes distorted.

Whereas initially the force of attraction exerted by the atmosphere on the central ion was uniform it becomes greater now behind the ion than in front. As a result of this the negative ion experiences a force which tends to drag it backwards and this slows down its movement in the forward direction. This behavior is known as Asymmetry Effect. It may be said that the negative ion which leaves the ionic atmosphere of positive ions behind to die away would build a new ionic atmosphere and the asymmetry would be corrected. If this process of building up and dying away were instantaneous, there would be no cause for asymmetry and the atmosphere would always be symmetrically placed about the ion. But, as it is, the formation of the new ionic atmosphere does not take place at the same rate at which the old one decays and the latter lags behind or takes more time, known as 'relaxation time'. During this interval, there is a preponderance of positive ions to the left of the central negative ion which is under move and these tend to drag it back. For this reason asymmetry effect is also known as Relaxation Effect. Moreover, the central ion moves into a place where there is an excess of ions of its own sign and this has also a retarding effect.
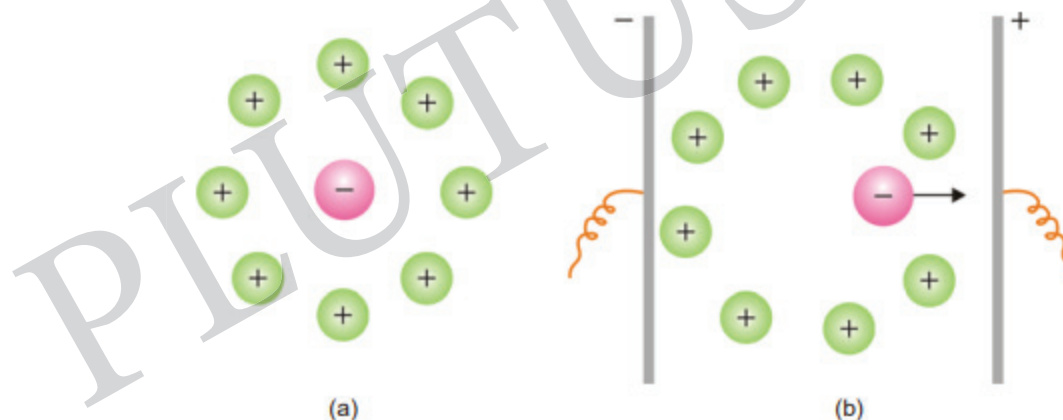

Figure 26.2 (a) Symmetrical ionic atmosphere at rest; (b) Asymmetrical ionic atmosphere under the influence of applied field.

(2) Electrophoretic Effect. Another factor which acts as a drag and tends to retard the motion of an ion in solution is the tendency of the applied field to move the ionic atmosphere (to which solvent molecules are also attached) in a direction opposite to that in which the central ion associated with solvent molecules is moving. Thus the central negative ion moving towards the anode has to make its way through the ionic atmosphere with its associated solvent molecules which is moving in the opposite direction i.e., towards the cathode. This causes a retarding influence on the movement of the ion the effect of which is equal to the increase in the viscous resistance of the solvent. By analogy to the resistance acting on the movement of a colloidal particle under an electrical field, this effect is called **Electrophoretic Effect.**

Both the above causes reduce the velocity of the ion and operate in solutions of strong electrolytes with the result that a value of equivalent conductance (λ_v) lower than the value at infinite dilution (λ_∞) is obtained. At infinite dilution since the electrical effects are practically absent, the two values tend to approach each other.

Debye-Huckel-Onsagar Conductance Equation takes these causes into account and for a univalent electrolyte supposed to be completely dissociated is written in the form

$$\lambda_v = \lambda_\infty - (A + B\lambda_\infty)\sqrt{C}$$

where A and B are constants and c is the concentration in gm-equivalents per litre. These constants depend only on the nature of the solvent and the temperature and are given by the relationships :

$$A = \frac{82.4}{(DT)^{1/2}\eta} \quad \text{and} \quad B = \frac{8.20 \times 10^5}{(DT)^{3/2}}$$

where D and η are the dielectric constant and coefficient of viscosity of the medium respectively at the absolute temperature T. The constant A is a measure of the electrophoretic effect while B is that of the asymmetry effect. For water at 25°C with D = 78.5 and η × 10³ = 8.95, the value of A is 60.20 and that of B is 0.229. On substituting these values in the above equation, we have

$$\lambda_v = \lambda_\infty - (60.20 + 0.229\lambda_\infty)\sqrt{C}$$

It follows, therefore, that if the above equation is correct, a straight line of slope equal to ($60.20 + 0.229\,\lambda_\infty$) should be obtained by plotting observed equivalent conductance (λ_0) against the square root of the corresponding concentration i.e., $\sqrt{C}$. The Onsager equation responds to this test favourably and for aqueous solutions of univalent electrolytes, it is closely obeyed at concentrations upto about 2×10^{-3} equivalents per litre (Fig. 26.3). Slight deviations at higher concentrations are attributed to certain approximations assumed in deriving the equation.
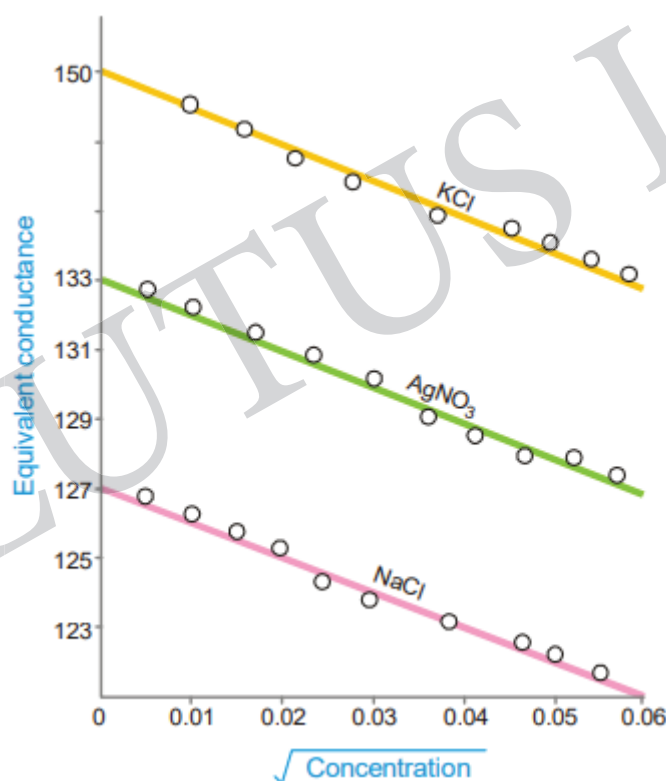
Figure 26.3 Testing of Onsagar equation. The circles represent the observed value l_n of whereas the dotted line stands for the theoretical values of the slopes expected from the Onsagar equation.