

UNIT - I

ELECTRICAL CONDUCTANCE

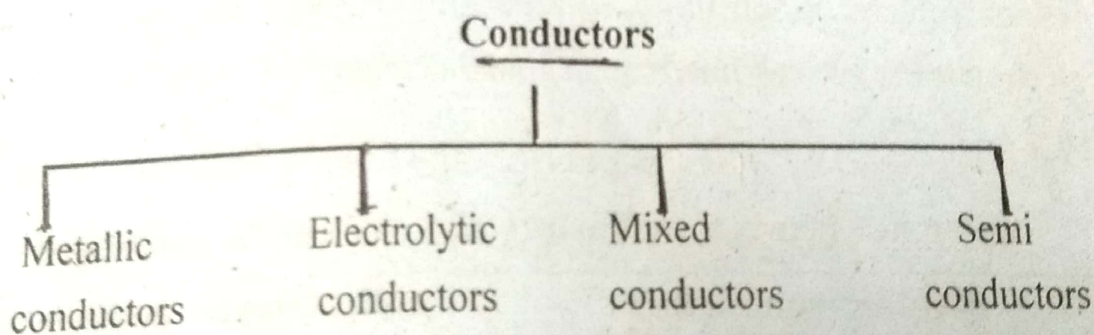
Conductors and Insulators:

All substances are classified into types based on their ability to allow current to pass through them. Those substances which allow electric current to pass through them are known as conductors. Examples of conductors are metals, their alloys and electrovalent compounds.

Those substances which do not allow current to pass through them are called as non-conductors (or insulators). Examples of insulators are glass, rubber and organic compounds such as benzene and carbon tetrachloride.)

Types of conductors:

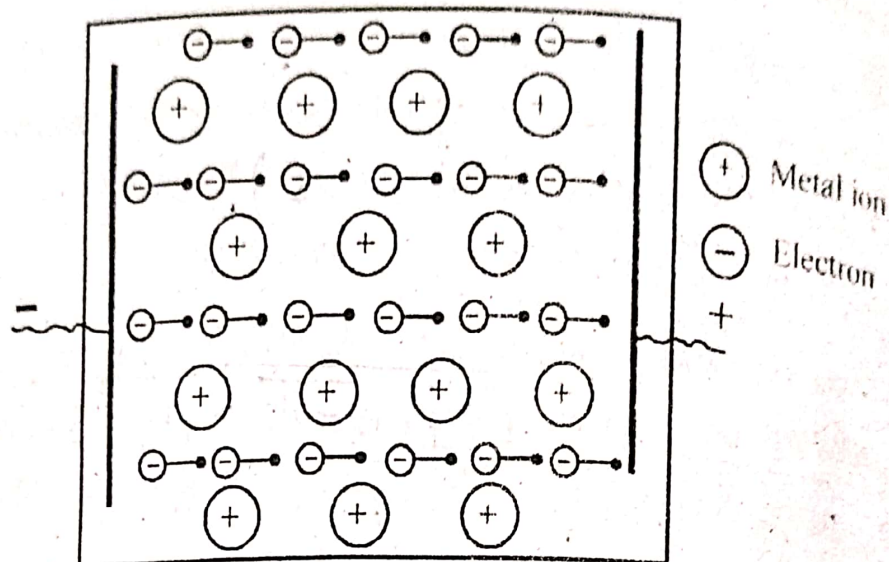
Conductors of electricity are further classified into four types depending on their mode of conducting current and the effects of current produced in them.



1. Metallic conductors.

These are metals and their alloys which conduct current due to presence of mobile electrons. Metallic conduction is not accompanied by any chemical transformations. In metals, there are free electrons.

surrounding each atom and the flow of electric current is due to movement of these electrons from one atom to another, Ex.. All metals & graphite.



2. Electrolytic conductors:

These are ionic compounds which conduct current either in solution or in fused state. They consist of charge particles called ions. These ions migrate in the presence of an applied electric field. This mobility of ions is responsible for electrolytic conduction. Passage of current through electrolytes is accompanied by chemical changes. Ex. NaCl, KCl, NaOH, HCl.

① Remark

Difference between conductors and electrolytic conductors.

No	Metallic conductors	Electrolytic conductors
1.	These are metallic elements and their solid solutions (alloys) which conduct current.	These are ionic compounds which conduct current either in solution or in molten state.
2.	Free electrons are responsible for electrical conductance in metals.	Ion conduct current in electrolytes.

3. There is no chemical change when current is passed through metals, though there may be physical change.	Electrolysis occurs when current is passed through electrolytes.
4. There is only flow of energy but there is no transfer of matter	Passage of electric current through electrolytes results in the actual transfer of matter.
5. The conductivity of metal decreases with increase in temperature. This is due to the enhanced vibration of metal ions which disrupts the flow of electrons	The conductivity of electrolytes increases with increase in temperature. This is due to increase in the ionic mobility.

3. Mixed conductors.

Those substances which conduct electric current partly electronically and partly ionically are called mixed conductors. Certain solids like ZnO and Cu_2O exhibit mixed conductivity due to crystal defects.

Similar mixed conductivity is also seen in solutions of alkali and alkaline earth metals in liquid ammonia.

4. Semiconductors.

These consist of covalent crystals which are poor conductors in pure state and at normal temperatures, but they become good conductors either at high temperature or in the presence of small quantity of impurities. Ex., Silicon, Germanium.

OHM'S LAW

"The strength of the current (I) flowing through a conductor is directly proportional to the potential difference (E) applied across the conductor

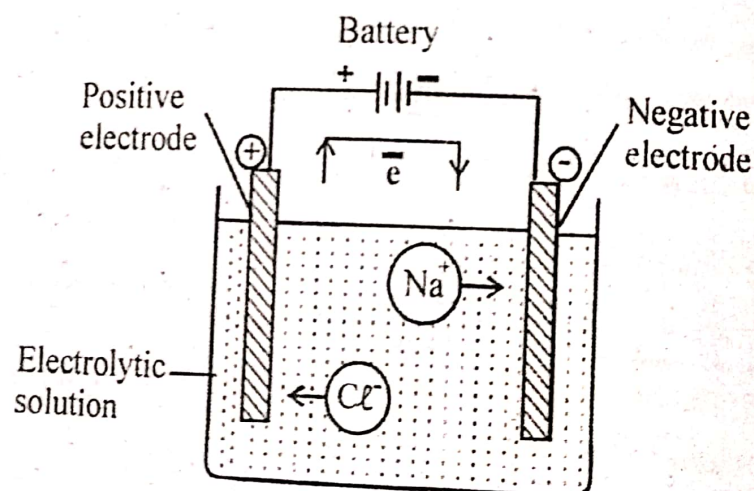
and is inversely proportional to the resistance (R) of the conductor.
It can be mathematically expressed as

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

I is the current strength in amperes, E -- is the potential difference in volts between the two ends of the conductor and R -- is the resistance of the conductor in ohms.

Mechanism of electrolytic conduction

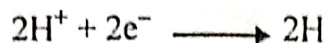
The mechanism by which an electric current passes through a solution can be understood by taking example, Let us consider a cell (fig) consisting of two platinum electrodes which are connected to the source S . The electrodes are dipping in an aqueous solution of sodium chloride. The electrode 'C' connected to the negative side of the battery is called the cathode. This is the electrode through which electrons flow from the battery into the solution. The electrode 'A' connected to the positive side of the battery is called the anode. This is the electrode through which electrons leave the solution and reach the battery.



Electrolytic solution

When the circuit is closed and a current passes through the solution, it is found that chlorine gas escapes at the anode and hydrogen gas at the

cathode. Sodium hydroxide is formed near the cathode. It may be explained as follows. Electrons enter the solution at the cathode C. The electrons combines with hydrogen ions (H^+) (of water) to form hydrogen atoms.



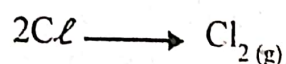
Two atoms of hydrogen combine to give a molecule of hydrogen which escape at the cathode.



The chloride ions go to the anode and leave electrons and become chloride atoms.



Two atoms of chlorine combine to give a molecule of chlorine which escape at the anode.



Thus we find that two electrons are removed from the cathode and are given upto the anode. In this manner the electrons flow from cathode to anode in an electrolyte.

The formation of sodium hydroxide may be explained as follows. Since hydrogen ions are removed from the solution, hydroxide ions are left in excess. Since they have no existence, they combine with positive sodium ions. The positive sodium ions are found near the cathode and so sodium hydroxide is formed near the cathode.

From the above discussion, the mechanism of electrolytic conduction may be summerised as follows:

1. Electron enter and leave the solution through chemical changes at the electrons.

2. Electrons pass through the solution by migration of ions. The evidence for this statement follows from Faraday's laws of electrolysis.

Faraday's law of electrolysis:

First law: "The amount of a substance deposited or evolved at the electrodes is proportional to the quantity of electricity passed through the solution."

It can be mathematically expressed as

$$W \propto Q \quad (\text{or}) \quad W \propto It$$

$$\text{i.e., } W = ZIt$$

where W = Weight of the substance

I = Current strength ; t = Time of passage of current and

Z = Electrochemical equivalent

Second law: "The amount of different substances deposited or evolved at the electrodes by the same quantity of electricity are proportional to their chemical equivalent".

One equivalent of a substance is liberated by the passage of one faraday of electricity. One faraday = 96,500 coulombs. The second law may be expressed by the equation.

$$\frac{\text{Equivalent weight of A}}{\text{Equivalent weight of B}} = \frac{\text{Weight of A deposited}}{\text{Weight of B deposited}}$$

SPECIFIC CONDUCTANCE AND EQUIVALENT CONDUCTANCE

Ohm's law is applicable to metallic as well electrolytic conductors.

According to Ohm's law $I = \frac{E}{R}$. Here R refers to the resistance of the conductor.

Specific Resistance (ρ)

The resistance of a conductor is directly proportional to its length (l) and inversely proportional to its area of cross-section (a). It can be mathematically expressed as

$$R \propto \frac{l}{a}; R = \rho \frac{l}{a}$$

Where ρ is the proportionality constant. It is called the specific resistance.

$$\therefore \rho = \frac{Ra}{l}$$

Specific resistance is the resistance of a conductor of unit length and unit area of cross-section. The unit specific resistance is ohm.cm.

Conductance (C)

The reciprocal of resistance is called conductance or conductivity.

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

The unit for conductance is mho or Ohm^{-1} .

Specific conductance (κ)

The reciprocal of specific resistance is called specific conductance or specific ductantivity.

$$\kappa = \frac{1}{\rho}; \kappa = \frac{l}{Ra}; \kappa = \frac{1}{R} \frac{l}{a}$$

In the case of metallic conductors the length ' l ' and the area of cross-section ' a ' of the conductor can be directly measured and substituted in

the equation to get the value of κ . But in the case of conductivity cells the shape of electrolytic column may not be regular. In such cases the value of ℓ

is determined indirectly by measuring the resistance of a solution with known conductivity. Usually potassium chloride is used for this purpose. This ℓ

is called the cell constant since it is constant for a given cell. Therefore now, the specific conductance can be calculated as,

$$\kappa = \frac{1}{R} \cdot \frac{\ell}{a} = \text{Conductance} \times \text{Cell constant},$$

The unit for specific conductance is $\text{ohm}^{-1} \cdot \text{cm}^{-1}$.

Equivalent conductivity : (Λ)

2 mark Equivalent conductance is defined as the specific conductance multiplied by the volume in cc of the solution containing one gram equivalent of the electrolyte. In other words equivalent conductivity is the conductivity if one equivalent of the electrolyte were present in every cubic centimeter of the electrolyte.

$$\Lambda = \kappa V$$

Where V is the volume in cc containing one gram equivalent of the electrolyte

$$\text{Further } \Lambda = \kappa \cdot \frac{1000}{C}$$

where C is the normality of the solution.

Molar conductance of molecular conductance (μ)

Molar conductance is defined as the specific conductance multiplied by volume in cc of the solution containing one gram mole of the electrolyte.

$$\mu = \kappa V = \kappa \cdot \frac{1000}{M}$$

Where M is the molarity of the solution.

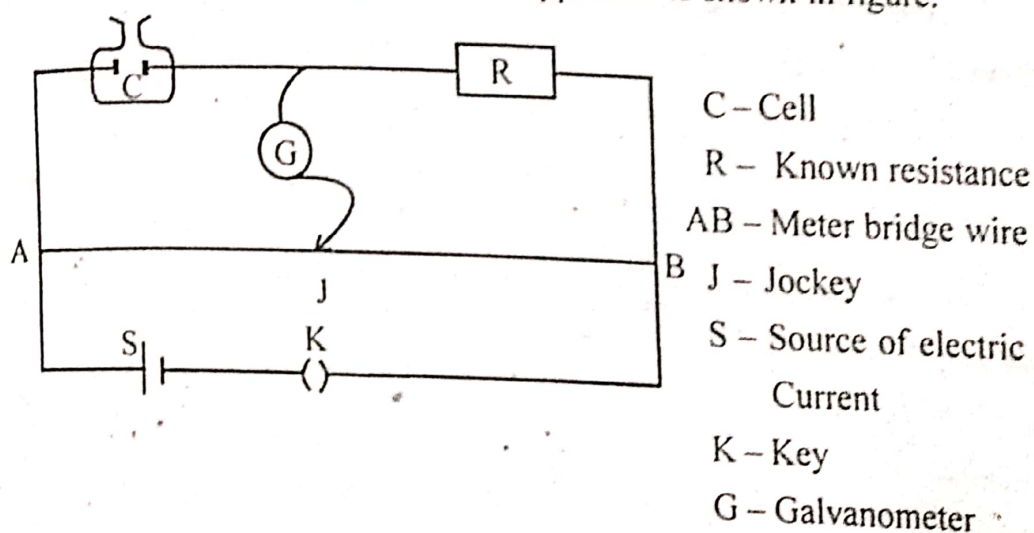
MEASUREMENT OF EQUIVALENT CONDUCTANCE USING KOHLRAUSCH BRIDGE

The Wheatstone bridge method is generally employed for the determination of conductance. A meter bridge, also called Kohlrausch bridge, is used as described in the experiment. The experiment is carried out in two stages; 1. the determination of cell constant 2. the determination of conductance.

Experiment:

1. Determination of cell constant:

A schematic diagram of the apparatus is shown in figure.



Connections are given as shown in figure. A solution of known specific conductance is taken in the cell C. Usually potassium chloride solution is taken. A known resistance R is introduced in the circuit. The jockey is touched at the end A. The deflection in the galvanometer will be in one direction. The jockey is touched at the other end B. Now the deflection in the galvanometer will be in the opposite direction. The jockey is moved along the wire AB until no deflection is noticed in the galvanometer. The length of the wire AJ and JB are measured.

$$\text{Now } \frac{R_{\text{KCl}}}{R} = \frac{AJ}{JB};$$

$$\therefore R_{KCl} = R \frac{AJ}{JB}$$

Thus the resistance of KCl solution is determined. We know the specific conductance of KCl.

$$\text{So } \kappa \frac{1}{R} \times \text{cell constant}$$

$$(\text{or}) \text{ cell constant} = \kappa \cdot R$$

Thus the cell constant is determined.

2. Determination of conductance

The cell is washed and then filled with the solution whose conductance is to be determined. The above experiment is repeated and a new balancing point J' is determined.

$$\text{Now } \frac{R_{\text{soin}}}{R} = \frac{AJ'}{J'B}; \therefore R_{\text{soin}} = R \times \frac{AJ'}{J'B}$$

Thus the resistance of the solution is calculated. Knowing the cell constant, the specific is calculated as

$$\kappa \frac{1}{R} \times \text{cell constant}$$

From the value of specific conductance and knowing the concentration of the solution, the equivalent conductance can be calculated.

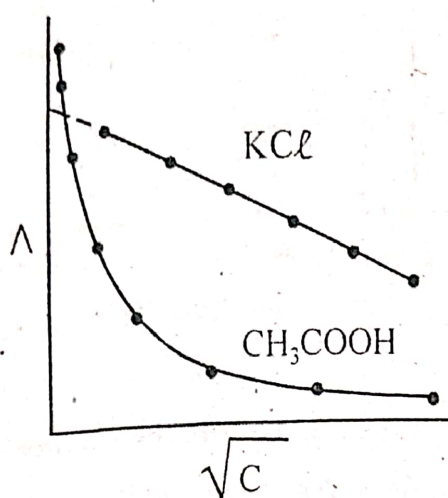
$$V = \kappa \frac{1000}{C}$$

VARIATION OF EQUIVALENT CONDUCTANCE WITH CONCENTRATION

Kohlrausch found that the equivalent conductance depends on the concentration of the electrolyte and conductance increase as dilution increases. It may be represented as

$$\Lambda = \Lambda^\circ - b \sqrt{c}$$

where Λ is the conductance at the concentration c and b is a constant. The plot of equivalent conductance of strong and weak electrolytes against the square root of concentration is shown in figure.



From the graph we understand that the equivalent conductance of weak electrolytes decrease much rapidly with increasing concentration. But the equivalent conductance of strong electrolytes does not change much with concentration.

From such a graph, it is possible to find the equivalent conductance at infinite dilution Λ° for strong electrolytes by the extrapolation of the curve. Further it is not possible to find the Λ° for weak electrolytes from the graph because the extrapolation of the curve does not cut the axis.

MIGRATION OF IONS AND KOHLRAUSH'S LAW

Examination of equivalent conductance at infinite dilution of solutions of two salts having an ion in common reveals certain regularities. For example, in the case of pairs of potassium and sodium salts with a common ion, a constant difference of 21.1 in the conductance is noted, More example are also given in table.

Table

Electrolyte	Λ°	Difference
KCl ₃	130.0	
NaCl	108.9	21.1
KNO ₃	126.3	
NaNO ₃	105.2	21.1
NaBr	110.9	

NaCl	108.9	2.0
Kbr	132.0	
KCl	130.0	2.0

Therefore the difference in the equivalent conductances of potassium and sodium ions or bromide and chloride ions are independent of the nature of the other ion. This was observed by Kohlrausch and a law was stated which read as follows: "At infinite dilution, each ion contributes a definite amount to the total conductance of the electrolyte, irrespective of the nature of the other ion". This law is also known as the law of independent migration of ions. It may be represented as,

$$\Lambda^\infty = \lambda_+^\infty + \lambda_-^\infty$$

It is strictly correct only if the electrolyte is at infinite dilution λ_+^∞ and λ_-^∞ are the equivalent ionic conductances at infinite dilution of the cation and anion respectively.]

APPLICATIONS OF KOHLRAUSCH'S LAW:

1. The absolute of sparingly of ions can be determined.
2. The solubility of sparingly soluble salts can be determined.
3. Ionic product of water can be calculated.

4. An important use of Kohlrausch's law is to determine the equivalent conductance at infinite dilution of weak electrolytes. The Λ^∞ of the weak electrolytes cannot be evaluated from direct experimental data. The extrapolation to infinite dilution of the graph obtained by plotting the equivalent conductivities and the concentrations of the solution is not possible for a weak electrolyte. But it can be evaluated using Kohlrausch's law. For instance, the equivalent conductance of acetic acid at infinite dilution can be obtained from the knowledge of equivalent conductances at infinite dilution of hydrochloric acid sodium acetate and sodium chloride.

It can be computed as

$$\Lambda_{\text{HAc}}^{\circ} = \Lambda_{\text{NaAc}}^{\circ} + \Lambda_{\text{HCl}}^{\circ} - \Lambda_{\text{NaCl}}^{\circ}$$

It is because

$$\begin{aligned} \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Ac}^-}^{\circ} + \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ} - \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ} \\ = \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{Ac}^-}^{\circ} \\ = \Lambda_{\text{HAc}}^{\circ} \end{aligned}$$

Ionic Conductances:

The individual ions of an electrolyte contribute to the total equivalent conductance.

According to Kohlrausch law the equivalent conductance of an electrolyte is the sum of the ionic conductances and that the contribution of an ion is independent of the other ion of the electrolyte.

Therefore at infinite dilution.

$$\Lambda^{\circ} = \lambda_{+}^{\circ} + \lambda_{-}^{\circ}$$

Where λ_{+}° and λ_{-}° are the equivalent ionic conductances at infinite dilution. Since the transport number is the fraction of the total current carried by each ion, we can write.

$$\lambda_{+}^{\circ} = t_{+}^{\circ} \Lambda^{\circ} \text{ and } \lambda_{-}^{\circ} = t_{-}^{\circ} \Lambda^{\circ}$$

Where t_{+}° and t_{-}° are the transport number at infinite dilution.

One can use the values of equivalent conductance and the transport numbers at concentrations other than that infinite dilution to obtain values λ_{+} and λ_{-} of at these higher concentrations. However at these concentrations the law of independent migration of ions fails. Therefore the concept of ionic conductances is valuable only at infinite dilution.

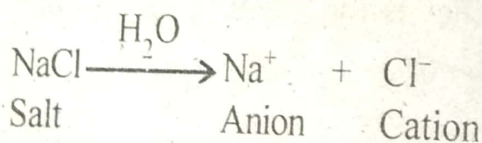
ARRHENIUS THEORY OF ELECTROLYTIC DISSOCIATION

Need for the theory

Though Faraday was able to give the most important laws of electrolysis, he could not explain the mechanism of conduction. The origin of charge was also not explained. Van't Hoff found that electrolytic solutions show much deviation from ideal behaviour. They have high values of osmotic pressure elevation of boiling point, depression of freezing point etc. This indicates that they have abnormally large number of solute particles. The molecules of an electrolyte must have been split into large number of solute particles. The molecules of an electrolyte must have been split into large number of smaller particles. These observations could be explained only by Arrhenius theory.

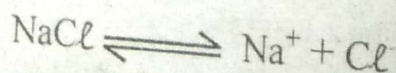
POSTULATES OF ARRHENIUS THEORY:

1. When an acid, or base or a salt is dissolved in water, it splits or dissociates into charged particles is called ions. The positively charged ions are called cations (as they move towards the cathode) and the negatively charged ions are called anions (as they move towards the anode).



2. The total number of positive charges is equal to the total number of negative charges. It means that an electrolyte is electrically neutral.

3. An equilibrium is established between the dissociated ions and undissociated molecules. Thus when sodium chloride is dissolved in water it dissociates into sodium ions and chloride ions. Thus



4. Electricity is conducted by free ions.

5. When an electric potential is applied, the positive ions move towards the negative electrode, namely, cathode and the negative ions move towards the positive electrode, namely, anode.
6. At the electrodes the ions lose their charge and become neutral atoms or molecules.
7. The electrolyte may not be completely ionised. The ratio of the dissociated molecules to the total number of molecules is called the degree of dissociation. The degree of dissociation increases with dilution of the solution. It tends to unity at infinite dilution.

Evidences of Arrhenius Theory

1. The Arrhenius theory explains not only the mechanism of conduction but also Faraday's laws of electrolysis.
2. This theory explains the observed deviation in osmotic pressure, elevation of boiling point, depression of freezing point etc., in the case of solutions of electrolytes.

3. The variation of equivalent conductance with dilution is also explained.

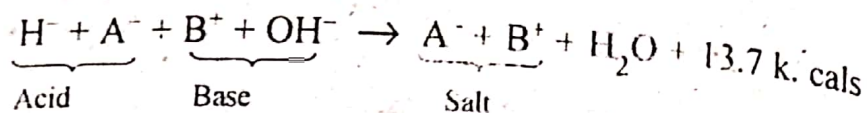
We have seen that there is an equilibrium between the dissociated ions in the undissociated molecules. The ratio of the dissociated molecules to the total number of molecules is called the degree of dissociation (α). The degree of dissociation increases with dilution. Therefore the number of ions increases with dilution. This is the reason why the equivalent conductance increases with dilution.

4. The degree of dissociation can be calculated from the conductance measurements. The degree of dissociation,

$$\alpha = \frac{\Lambda}{\Lambda^{\circ}}$$

5. The observed value of heat of neutralisation is explained by the Arrhenius theory.

We know that the heat of neutralisation of strong acids and strong bases is about 13.7 k.cals. This fact can also be explained on the basis of electrolytic dissociation. As strong acids and bases are completely ionised, neutralisation can be represented as,



Thus the heat of neutralisation is simply the heat of formation of water from its ions. This reaction is involved in all neutralisation processes. Therefore the heat evolved is always the same.

Limitations

1. Arrhenius theory fails when applied to strong electrolytes.
2. The degree of dissociation (α) calculated from conductivity measurements as was found to be different from the calculated value based on the colligative properties.
3. The values of equilibrium constants of strong electrolytes were found to vary with concentration of the electrolyte. This raised the fundamental question whether ionic equilibrium assumed by Arrhenius existed or not in these solutions.
4. When solution of different electrolytes are mixed, heat changes occur. This cannot be explained with the Arrhenius theory.
5. Arrhenius theory could not explain the variation of transport number with concentration.
6. Bragg showed that NaCl exists as ions (Na^+ and Cl^-) even in the solid state. So Arrhenius statement that there is an equilibrium between ionised and unionised molecules in an electrolyte is ambiguous.

7. We know that equivalent conductance of electrolytes increases with dilution. This increase is understandable in the case of weak electrolytes because the degree of strong electrolytes which are fully ionised even in the solid state, this increase in equivalent conductance on dilution cannot be obtained.

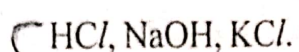
WEAK AND STRONG ELECTROLYTES

Strong electrolytes

Strong electrolytes are substances which at ordinary temperature and concentration.

1. ionise completely.
2. have high conductance values.
3. have no association.
4. have the degree of dissociation (degree of ionisation) as unity.
5. do not show considerably increase in equivalent conductance due to dilution. (However there is some increase in conductance during dilution in the case of strong electrolytes also).

The following are some examples for strong electrolytes



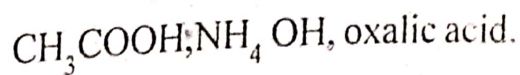
Weak electrolytes

Weak electrolytes are substances which at ordinary temperature and concentration.

1. do not ionise completely. There exists an equilibrium between ions and unionised molecules.
2. have low conductance values.
3. have association in some cases.

4. have the degree of dissociation less than unity.
5. show an increase in equivalent conductance due to dilution.

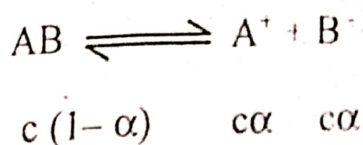
The following are some example for weak electrolytes:



OSTWALD'S DILUTION LAW

According to Arrhenius theory of electrolytic dissociation there is dynamic equilibrium between ions and unionised molecules. Ostwald applied the law of mass action to such systems.

Consider an electrolyte AB. Let "c" moles of the electrolyte be dissolved in 1 litre and " α " be the degree of dissociation. The equilibrium condition is



The equilibrium constant K, is given by the formula.

$$K = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} = \frac{c\alpha \times c\alpha}{c(1-\alpha)} = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

$$K = c\alpha^2 \quad (1-\alpha \text{ is negligible in comparison with } 1)$$

$$(\text{or}) \quad \alpha^2 = \frac{K}{c}; \quad \alpha = \sqrt{\frac{K}{c}}$$

$$\alpha \text{ is proportional to } \frac{1}{\sqrt{c}}$$

$$\alpha \propto \frac{1}{\sqrt{c}}$$

This is the Ostwald dilution law. "As the concentration of the electrolyte decreases or the dilution increases, the degree of dissociation increases."

This law is applicable to weak electrolytes only.

Applications of Ostwald's dilution law

Determinations of the dissociation constant K of Acid.

We have seen that Ostwald's dilution law relates V , the volume of the electrolyte, and α , the degree dissociation as

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

The equilibrium constant K , for a dissociation equilibrium such as $AB \rightleftharpoons A^+ + B^-$ is called dissociation constant or dissociation constant.

With the help of the above equation, the dissociation constant of an electrolyte can be determined provided α is known. The value of α can be known from conductance measurements. The degree of dissociation

$\alpha = \frac{\Lambda^\circ}{\Lambda_\infty}$ where Λ is the conductance at the required concentration and Λ_∞ is the conductance at infinite dilution. The determination of K on the basis of Ostwald's dilution law was found to hold good in the case of weak electrolytes such as acetic acid ammonium hydroxide.

Limitations

This law fails when applied to strong electrolytes. This is because for, strong electrolytes $\alpha = 1$. There is no possibility of the existence of an equilibrium between the ionised and unionised molecules in their solutions, since their molecules are completely ionised in solutions.

DEBYE HUCKEL - ONSAGER CONCEPT OF STRONG ELECTROLYTES

Need for the Debye - Huckel Theory

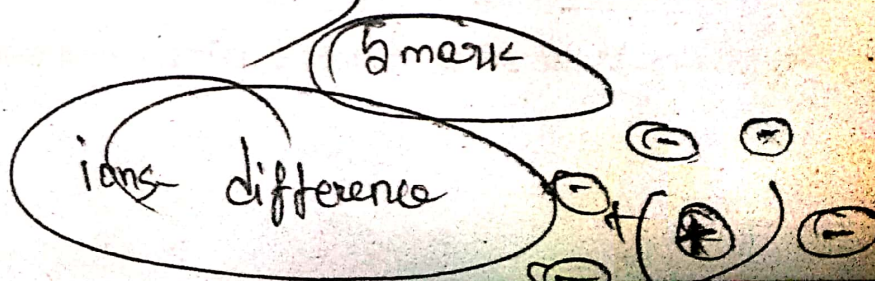
The conductance of a given electrolyte solution depend upon two factors namely.

1. The speed of ions and ✓
2. The number of ions. In the Arrhenius theory, it is assumed that the

speed of the ions does not vary with concentration, and the change in equivalent conductance is due to the difference in the degree of ionisation only. The Arrhenius theory fails in the case of strong electrolytes as explained earlier. So to explain the behaviour of strong electrolytes the Debye Huckel theory and equation were proposed.

5 mark Postulates of Debye - Huckel Theory

1. ✓ Every strong electrolyte is completely ionised at all dilutions.
2. ✓ Two forces act on mobile ions. They are (i) electrical force and (ii) resistance force due to the viscosity of the medium.
3. ✓ The forces acting between the ions are electrostatic forces governed by Coulomb's law.
4. ✓ The change in the speed of the ions is the reason for variation in equivalent conductance with dilution. The attraction between oppositely charged ions, called the interionic forces, depends upon various factors like dielectric constant and concentration of the solution. If the dielectric constant of the solvent is more, the interionic forces will be less. On the other hand if the dielectric constant of the solvent, is less, the interionic, force will be more. If the concentration of the solution is high the interionic force will be more. Under these conditions some of the ions will not separate out completely from one another and then remain in pairs such as $A^+ B^-$. These are known as ionic doubles or ion pairs.
5. ✓ Each ion is surrounded by a number of oppositely charged ions. Such an atmosphere is known as ionic atmosphere. The ionic atmosphere plays an important role in the conductance of the electrolyte and it leads to the following effects (1) Relaxation effect and (2) Electrophoretic effect.



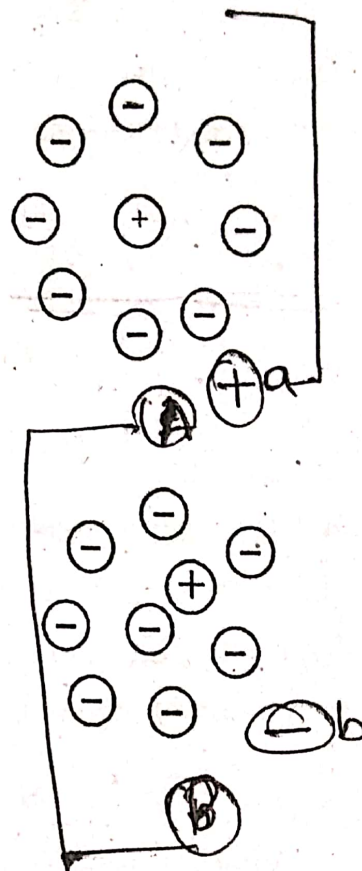
Asymmetry effect or Relaxation effect

2 mark

Consider a cation surrounded by an ionic atmosphere of anions as shown in figure – a.

Under the influence of electric field the cation will move towards the cathode, leaving behind the ionic atmosphere of anions. As the cation moves, a new ionic atmosphere will be formed. But the new ionic atmosphere is not formed at the same rates as the old atmosphere decays. This time lag is known as relaxation time. Due to this time lag there will always be an excess of negative ions on the left of the cation and they will exert a retarding effect on the movement of the central cation Figure – b. This retarding effect is called asymmetry effect or relaxation effect.

2 mark



The asymmetry effect can also be explained by taking an anion as the central ion and cations as ionic atmosphere. In anycase the speed of the ions is decreased by the relaxation effect. When the solution is diluted the relaxation effect becomes less and less significant with the result that conductivity increase with dilution in the case of strong electrolytes also.

Electrophoretic effect:

2 mark

Each ion is associated with some molecules of the solvent. That is, the central ion is solvated. Under the influence of the electric field, the ions move towards the oppositely charged electrodes. When the solvated central ion moves in one direction, the oppositely charged ions which are also solvated move in opposite direction. Suppose that the central ion is an anion. The anion is solvated and the solvated anion moves towards the anode. Similarly (positive ions) cations which are also solvated have to

migrate through molecules of solvents carried by anion in the opposite direction. These counter currents make it more difficult for the ion to move through the solution. Thus the velocity of the ion decrease. This effect is known as electrophoretic effect. This effect also decrease with dilution and so conductance increases with dilution even in the case of strong electrolytes.

DEBYE - HUCKEL - ONSAGER EQUATION

Debye and Huckel showed that the relaxation effect and electrophoretic effect on an ion produce a decrease in equivalent conductance. As dilution increases these effects become less and less and so conductance increases. A mathematical treatment was later extended by Onsager including the above two effects and also the Brownian movement of ions. The electrical force acting on an ion is ZeE where Ze is the charge and E the potential. If the motion of the ion is given by Stoke's law,

$$f = 6 \pi \eta r v$$

Where η is the viscosity of the medium and v the velocity of the ion. When the frictional force is equal to the electrical force

$$ZeE = 6 \pi \eta r v$$

The mobility of the ion

$$I = \frac{v}{E} = \frac{Ze}{6\pi\eta r}$$

The equivalent conductance of an electrolyte is given by the equation]

$$\Lambda^\circ = F(I_+ + I_-)$$

$$\Lambda^\circ = F \left[\frac{Z^+ e}{6\pi\eta r^+} + \frac{Z^- e}{6\pi\eta r^-} \right]$$

$$\Lambda^\circ = \frac{Fe}{6\pi\eta} \left[\frac{Z^+}{r^+} + \frac{Z^-}{r^-} \right]$$

$$(or) \Lambda^\circ \eta = \text{constant}$$

So the Λ° of an electrolyte depends on the viscosity of the medium. Taking into consideration the asymmetric effect, electrophoretic effect and Brownian movement, the Onsager equation is arrived at and the equation is given below

$$\Lambda = \Lambda^\circ - (A + B \Lambda^\circ) \sqrt{c}$$

A and B are constants and c is the concentration of the electrolyte.

Significance of Debye- Huckel Onsager equation:

Λ is always less than Λ° . This is partly due to electrophoretic effect and partly due to asymmetric effect. The first term 'A' is a measure of electrophoretic effect and the second term 'B Λ° ' is a measure of the asymmetric effect. The values of A and B for water at 25° C are 60.2 and 0.229 respectively.

If this equation is correct, by plotting equivalent conductance Λ against the square roots of concentrations, \sqrt{c} a straight line of slope $60.22 + 0.229 \Lambda^\circ$ should be obtained. This has been found to be correct in the case of uni-valent electrolytes.

The conductance at high fields and high frequencies

The concept of the ion atmosphere is further substantiated by the Wien effect and Debye- Falkenhagen effect. In every high field $E > 10^5 \text{ v/cm}$, an increase in conductivity is observed. This is known as Wein effect. We know that a finite time (namely the relaxation time) is required for the formation of an ionic atmosphere. When very high fields are applied the ion moves so quickly that it loses its atmosphere and does not have time to form a new atmosphere. So the ion cannot be slowed down. The asymmetry effect disappears and the conductance increases.

Similarly the conductivity increases at high frequencies (3×10^6 cycles / second). This is called Debye- Falkenhagen effect. The ion changes its direction so quickly that its atmosphere cannot adjust and

follow the motion of the ion. The ion moves as if it had no atmosphere and so the conductivity increases. At high frequencies both asymmetry and electrophoretic effect are absent.

TRANSPORT NUMBER 2016 April

It has been shown that the different ions of an electrolyte do not have the same speed. Therefore it is evident that the quantities of electricity carried by cations are not the same. The quantity of electricity carried by the different ions is studied under transference number.

Definition 2 mark

"The fraction of the total current carried by each kind of ion is called its transport number or transference number".

Explanation

The quantity of positive electricity carried by the cation must be proportional to the speed of the cations and their concentration in equivalents. Similarly the quantity of negative electricity carried by the anions must be proportional to the speed of the anions and their concentration in equivalents.

Let c_+ and c_- be the concentration of cations and anions respectively. Let u_+ and u_- be their speeds. Then the transport number of ions are

$$\text{transport number of cation} = t_+ = \frac{c_+ u_+}{c_+ u_+ + c_- u_-}$$

$$\text{transport number of anion} = t_- = \frac{c_- u_-}{c_+ u_+ + c_- u_-}$$

In the case of electrolytes of the type KCl , ZnSO_4 , Al_2BO_4 , etc., the concentration (in equivalents) of cations and anions are the same. So in such cases

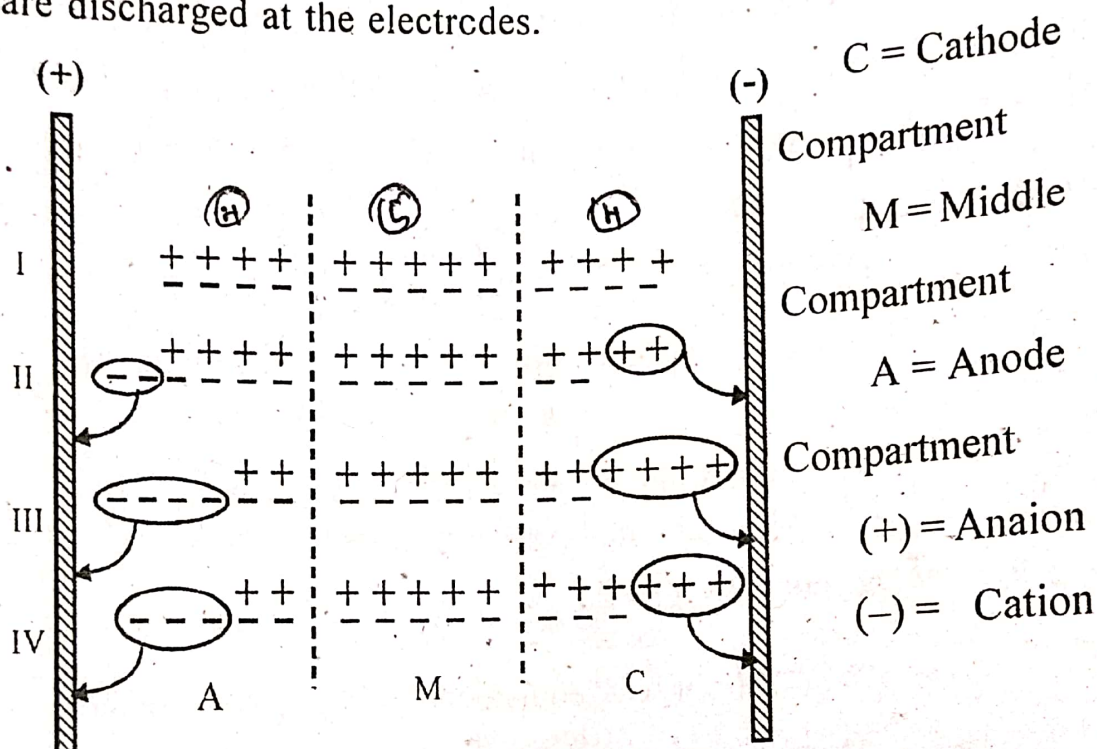
$$t_+ = \frac{u_+}{u_+ + u_-} \text{ and } t_- = \frac{u_-}{u_+ + u_-}$$

HITTORF'S RULE

(As a result of passage of current through a solution, concentration changes occur near the electrodes. The concentration change is directly proportional to the velocities of ions. This is called Hittorf's rule) It is explained with the following illustration.

Let an electrolyte be contained in a vessel divided into three imaginary compartments as shown in figure.

By passing a current through the electrolyte the positive ions are attracted towards the cathode and negative ions towards the anode and are discharged at the electrodes.



So concentration changes take place at the cathode and anode compartments. If the electrolysis is not carried out for a long time, no change takes place in the middle compartment.

Since the solution must always be electrically neutral. The cations and anions must always be equal in number. This is the condition at the beginning of electrolysis as shown in the figure.

Suppose that the cations only are able to move under the influence of the applied potential and that two of these ions move from right to left as shown in II, at each electrode the two unpaired ions are discharged. That is, two electrons are given up at the anode and two electrons are taken up at the cathode. Thus a change in the concentration of the electrolyte equivalent to two is noted in the anode compartment.

In a similar manner the anion alone may be assumed to be moving. Suppose that three of the anions move from left to right as shown in III. There will be concentration change in the cathode compartment.

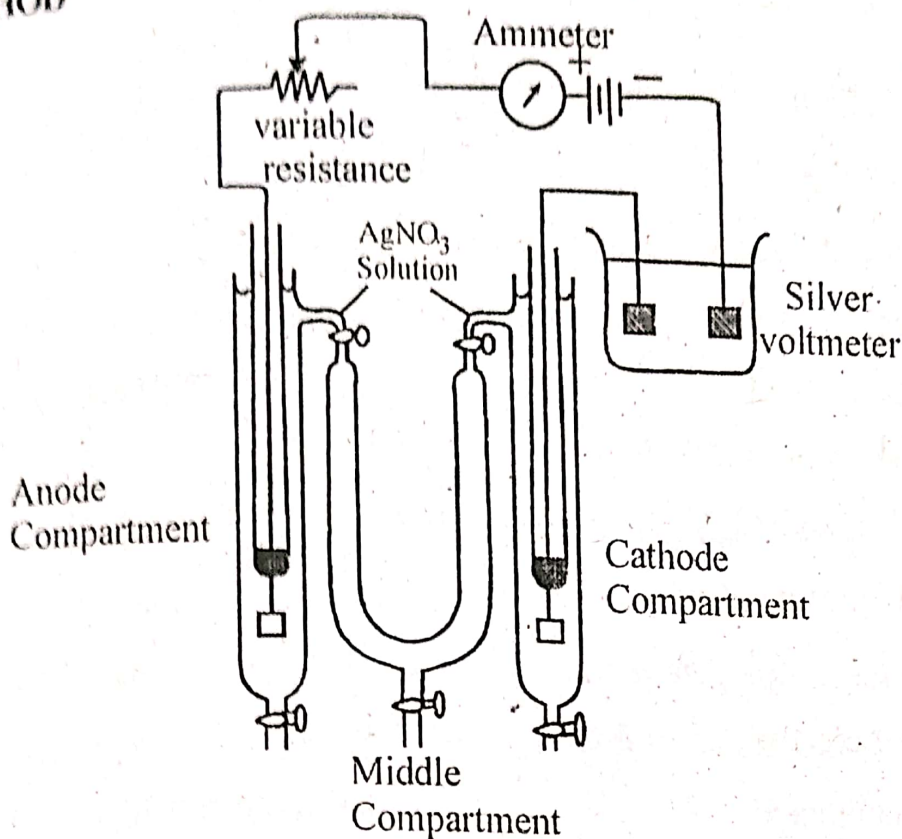
If we consider that both ions are moving as shown in IV, there will be concentration change at both the compartments. The change in the anode compartment (equal to two) is proportional to the speed of the cation. Similarly the change in cathode compartment (equal to three) is proportional to the speed of the anions. The total is equal to the sum of the changes in the two compartments. So the transport number of the cation,

$$t_+ = \frac{\text{No. of gm. equivalents of the electrolyte lost from anode compartment}}{\text{Total no. of gm. equivalents lost from both compartments}}$$

Similarly the transport number of anion

$$t_- = \frac{\text{No. of gm. equivalents of the electrolyte lost from cathode compartment}}{\text{Total no. of gm. equivalents lost from both compartments}}$$

1. DETERMINATION OF TRANSPORT NUMBER BY HITTORF METHOD



The Hittorf apparatus is shown in figure . It consists of two vertical glass tubes connected together through a U tube in the middle. The end tubes contain anode and cathode and constitute anodic and cathodic compartments. The U tube constitutes the middle compartment.

To find the transport number of silver and nitrate ions in a solution of AgNO_3 (about 50 to 70 volts) is applied to the silver electrodes dipping in the solution to send a steady current of about 10 milli amperes through the cell. Higher strengths of current are avoided in order to prevent heating up of electrolyte and a subsequent setting up of concentration currents. After passing the current for about 2 hours, the major bulk of the solutions in the anode and cathode compartments are separately collected and weighed.

partments.

$$\text{initially} = p$$

$$\text{finally} = q$$

Number of gram equivalents of Ag deposited at the cathode = r .

When r gram equivalents of Ag^+ is deposited at the cathode, r gram equivalents of NO_3^- will attack the anode and r gram equivalents of AgNO_3 will be produced. So if there is no transport, the number of gram equivalents of AgNO_3 that will be present at the anode = $p + r$.

$$\text{But actually present after electrolysis} = q$$

$$\text{So, loss in the anode compartments} = (p + r) - q$$

$$\text{Total loss of electrolyte from both compartments} = r$$

$$\begin{aligned} \text{Transport number of cation, } \text{Ag}^+ &= t_+ = \frac{\text{Loss in the anode compartment}}{\text{Loss in both compartments}} \\ t_+ &= \frac{(p + r) - q}{r} \end{aligned}$$

$$\text{Transport number of anion } \text{NO}_3^- = t_- = 1 - t_+ \quad (\text{since } t_+ + t_- = 1)$$

Limitations

Although the Hittorf method is simple, accurate result are difficult to obtain especially with dilute solutions. The small concentration changes can not be measured accurately.

2. DETERMINATION OF TRANSPORT NUMBER BY MOVING BOUNDARY METHOD PRINCIPLE

By measuring the absolute speed of ions the transport number can be determined accurately. The absolute velocity of ions may be observed by the moving boundary method.

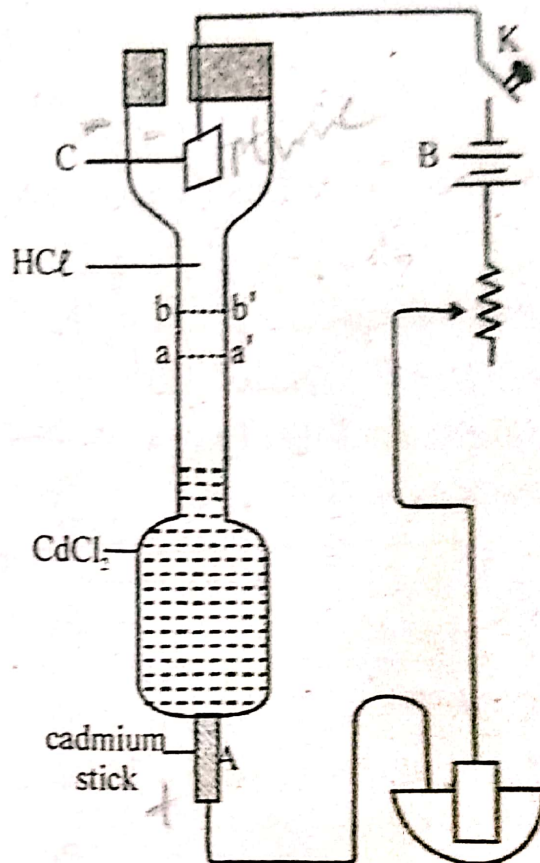
Experiment



The arrangements used for the moving boundary method is shown in figure .

The transport number of H^+ and Cl^- can be determined as follows: The cell, which is a tube, is mounted vertically and filled with cadmium chloride solution and HCl solution is such a way that there is definite (sharp) boundary visible at the junction of the two solutions (a, a'). The cathode 'C' is a platinum wire while the anode 'A' is a cadmium rod.

As the current is passed, cadmium dissolves at the anode as Cd^{2+} ions. The H^+ ions migrate towards the cathode through the cell. Their place is taken by Cd^{2+} ions.



C = Cathode
A = Anode
B = Battery
K = Key

Hence the boundary between the two solutions moves upwards to bb' . By determining the volume 'V' swept out by the moving boundary the transport number H^+ ion is calculated from the formula

$$t_+ = \frac{V \times C}{1000 \times Q}$$

Formula

V = Volume
C = Concentration
Q = Quantity

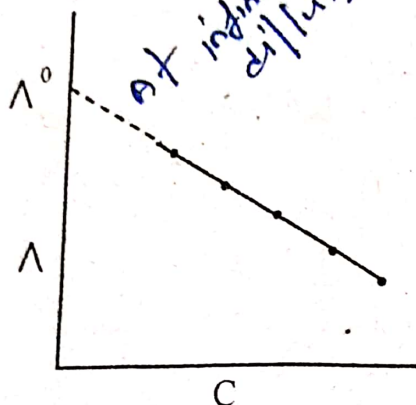
V - is the volume between aa' and bb' . Q is the quantity of electricity passed in faradays. c is the concentration in gram equivalents per litre.

10 Mark

APPLICATIONS OF CONDUCTANCE MEASUREMENTS

1. Determination of Λ° of a strong electrolyte

As described under heating measurement of conductance, in page number 7 the specific conductance of the given strong electrolyte is determined.



- Λ = Equivalent conductance
 Λ° = Equivalent conductance at infinite dilution
 C = Concentration

The same experiment is repeated for different concentrations of the strong electrolyte. From the specific conductance values the equivalent conductance for the various concentrations of the strong electrolyte is calculated using the formula

$$\Lambda = \kappa \frac{1000}{C}$$

A graph is plotted between concentration of the electrolyte and equivalent conductance.

The shape of the curve obtained is shown in figure. Extrapolation of the curve meets the axis at Λ° , which gives the value of the equivalent conductance at infinite dilution of the electrolyte.

2. Determination of dissociation constant K_a of Acids

To determine the dissociation constant of an organic acid we have to first find the degree of dissociation of the weak organic acid. From the degree of dissociation we can calculate the dissociation constant.

$$K = \alpha^2 C$$

i) To find the degree of dissociation (α) **Application.**

The equivalent conductivity (Λ) of the solution of weak organic acid is determined at a given concentration. Using the wheatstone bridge the resistance is measured and from that the equivalent conductance is computed as explained earlier. The equivalent conductance infinite dilution (Λ°) of the organic acid cannot be found by the extrapolation of the graph since it is a weak electrolyte. The Λ is calculated from ionic conductances as described under Kohlrausch's law. Knowing Λ and Λ° values, the degree of dissociation.

α is calculated using the relation $\alpha = \frac{\Lambda}{\Lambda^\circ}$

ii) To find the dissociation constant K_a

Let HA be organic acid which dissociates as H^+ and A^-



If c moles per litre of HA are taken and if μ is the degree of dissociation then the active masses of the different species at equilibrium will be

$$[HA] = c(1 - \alpha)$$

$$[H^+] = c\alpha$$

$$[A^-] = c\alpha$$

So the equilibrium constant $K_a = \frac{[H^+][A^-]}{[HA]}$

$$K_a = \frac{c\alpha \times c\alpha}{c(1 - \alpha)} ; \quad K = \frac{c^2\alpha^2}{c(1 - \alpha)}$$

This equilibrium constant is called the dissociation constant of the weak organic acid. Knowing value of α , the value of K_a can be calculated.

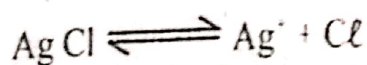
3. Determination of Solubility Product of a Sparingly Soluble Salt
 Substance like BaSO_4 , AgCl , PbSO_4 , AgI , PbI_2 , Ag_2CrO_4 are examples for sparingly soluble salts. Since they are sparingly (slightly) soluble their solutions may be considered as solutions at infinite dilution. The equivalent conductance measured for this solution may be taken as equivalent conductance at infinite dilution.

A Saturated solution of the sparingly soluble salt in water is prepared and its equivalent conductance measured. Now

$$\boxed{\Lambda = \kappa V} \quad \text{Formula}$$

Where κ is the specific conductance and V is the volume in cc containing 1 gram equivalent of the electrolyte. Knowing Λ and κ , the volume containing one gram equivalent V is calculated. From V the amount of the solute present in one litre can be calculated. This gives the solubility of the substance.

From the solubility (S) of the sparingly soluble substance, the solubility product (K_{sp}) may be calculated. Suppose we consider AgCl as the sparingly soluble salt, it ionises as



and the equilibrium constant

$$K = \frac{a_{\text{Ag}^+} a_{\text{Cl}^-}}{a_{\text{AgCl}}}$$

Since the salt is sparingly soluble a_{AgCl} may be taken as 1.

$$\text{Then, } K_{sp} = a_{\text{Ag}^+} a_{\text{Cl}^-}$$

Since the solution is dilute the concentration of the ions may be considered instead of activity.

$$\text{Then, } K_{sp} = C_{Ag^+} \times C_{Cl^-} = SS = S^2$$

CONDUCTOMETRIC TITRATIONS

V.V.I

Significance of conductometric titration ✓

10 Mark

These titrations have the following advantages:

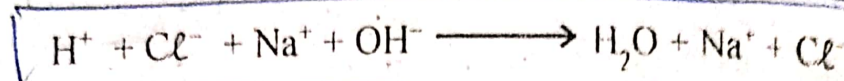
1. The titrations which cannot be carried out by ordinary methods can be carried out successfully under conductometric method.
2. Even titrations with turbid and coloured solutions where indicators cannot be used can be done.
3. Reactions in which precipitates are formed can also be titrated.
4. A weak acid can be titrated against a weak base.
5. Very dilute solutions can also be titrated.

Procedure:

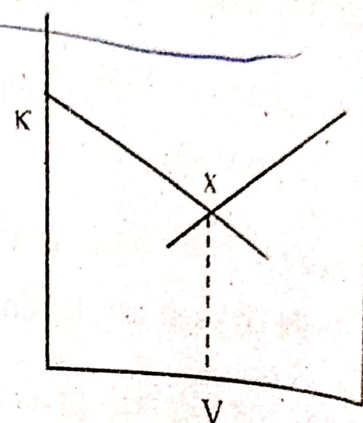
In the conductometric titrations, the variation of electrical conductivity of a solution during the course of the titration is measured. It is necessary to measure the actual specific conductivity; and quantity proportional to conductivity can be measured and used. An electrolyte is taken in a small beaker and a conductivity cell is immersed in the electrolyte. The titrant is added from the burette and the corresponding conductance reading is taken. The conductance readings are plotted against the volume of titrant added. The break in the curve gives the end point. The titrant should be at least 10 times stronger than the solution being titrated in order to keep the volume change small (negligible).

1. Strong acid against strong base:

The titration of HCl against NaOH can be taken as an example (usual) the acid is taken in the beaker and the base is added from the burette. To start with we take a strong acid namely HCl in the beaker. It will have high value of conductance. During the titration the following reaction takes place. We find that H^+ ions are replaced.



by Na^+ ions during the titration. The speed of the Na^+ ions is less than that of H^+ ions. Therefore conductance decreases when more and more of NaOH is added. When all of H^+ ions are replaced by Na^+ ions the conductance reaches a minimum value. At this point namely the end point we have Na^+ and Cl^- ions only.

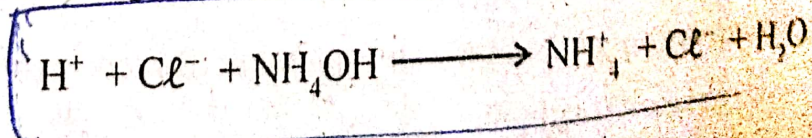


κ = specific conductance
 V = volume of NaOH
 x = End point

If we add any more amount of NaOH the conductance increases rapidly. It is because NaOH is a strong electrolyte and the addition of it causes an increase of Na^+ and OH^- ions. The OH^- ions have high mobility and so conductance increases rapidly. The curve obtained in a titration is shown in figure. The break in the curve gives the neutralisation (end) point.

2. Strong acid against weak base

The titration of HCl against NH_4OH can be taken as an example. To start with we taken strong acid HCl in the beaker. It will have a high value of conductance. During the titration the following reaction takes place.

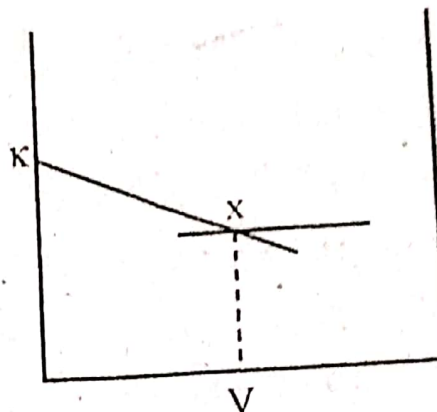


We find the H^+ ions are replaced by NH_4^+ ions during the titration. The speed of the NH_4^+ ions is less than H^+ ions. Therefore conductance decreases when more and more of NH_4OH is added.

When all the H^+ ions are replaced by NH_4^+ ions the conductance reaches a minimum value. If we add any more amount of NH_4OH there is no considerable change in the conductance.

It is because NH_4OH is a weak electrolyte. It ionises to a very small extent.

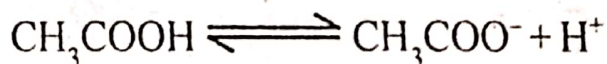
So addition of NH_4OH does not cause addition of any more ions. Thus the conductance remains almost constant.



The curve obtained in such a titration is shown in figure . The break in the curve 'X' gives the neutralisation point.

3. Weak acid against strong base:

The titration of CH_3COOH against $NaOH$ can be taken as an example. To start with, we take the weak acid namely CH_3COOH in the beaker. The weak acid has a low ionisation.



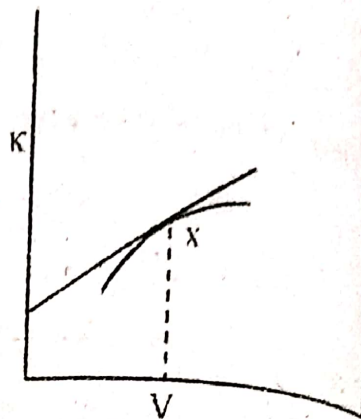
So it will have a low conductance. During the titration the following reaction take place.



Addition of $NaOH$ produces sodium acetate salt which totally ionises to give Na^+ and CH_3COO^- ions. So during the course of the reaction more of Na^+ and CH_3COO^- are produced and hence conductance increases.

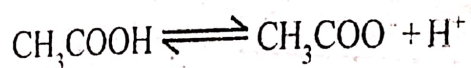
At the end point, the conductance is due to Na^+ and CH_3COO^- ions only. If we add any more amount of NaOH the conductance increases rapidly.

It is because NaOH is a strong electrolyte and the addition of it causes an increase of Na^+ and OH^- ions. The OH^- ions have high mobility and so conductance increases rapidly. The curve obtained in such a titration is shown in figure. The break in the curve 'X' is the neutralisation point.

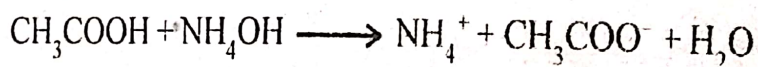


4. Weak acid against weak base:

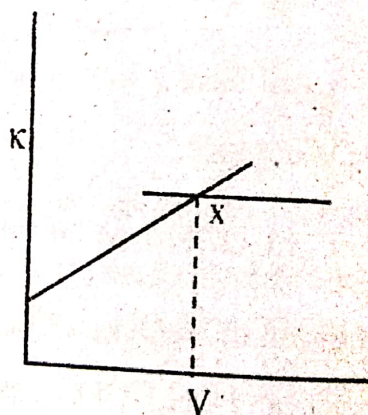
The titration of CH_3COOH against NH_4OH can be taken as an example. To start with we take the weak acid namely CH_3COOH in the beaker. The weak acid has low ionisation.



So it will have a low conductance. During the titration the following reaction takes place.



Addition of NH_4OH produces ammonium acetate salt which totally ionises to give NH_4^+ and CH_3COO^- ions. So during the course of the reaction more and more of NH_4^+ and CH_3COO^- are produced and hence conductance increases.

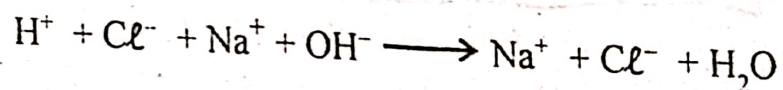


At the end point the conductance is due to NH_4^+ and CH_3COO^- ions only. If we add any more amount of NH_4OH there is no considerable change

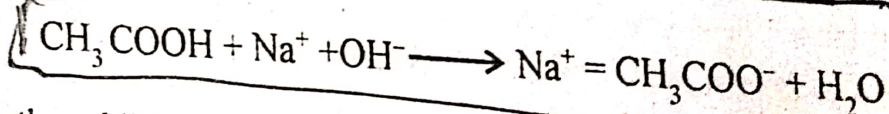
in the conductance. It is because NH_4OH is a weak electrolyte. It ionises to a very low extent. So addition of NH_4OH does not cause addition of any more ions. Thus the conductance remain almost constant. The curve obtained in such a titration is shown in figure .

5. Mixture of strong acid and weak acid against strong base:

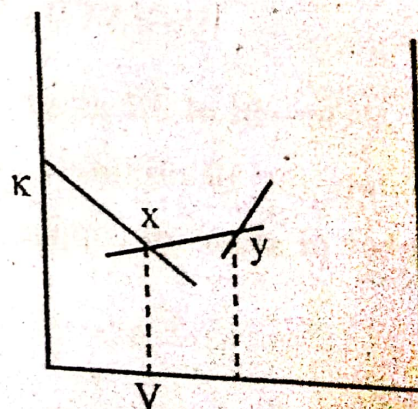
The titration of a mixture of HCl and CH_3COOH against NaOH can be taken as an example. In the beaker we take the mixture of acids. The strong acid namely HCl ionises totally to give H^+ and Cl^- ions. So it will have high value of conductance. During the titration the strong acid (HCl) first reacts with NaOH . The following reaction takes place.



H^+ ions are replaced by Na^+ ions. The speed of Na^+ ions is less than H^+ ions. Therefore conductance decrease when more and more of NaOH is added. When the strong acid has completely reached we have Na^+ and Cl^- ions and CH_3COOH . This point is the end point for strong acid noted as X in figure. If we added NaOH reacts with the weak acid (CH_3COOH) and produces sodium acetate salt which totally ionises to give Na^+ and CH_3COO^- ions.



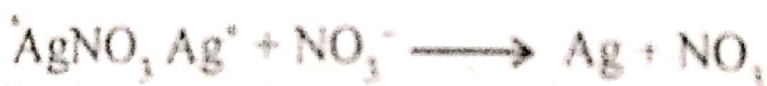
So during the addition of NaOH more and more of Na^+ and CH_3COO^- are produced and hence conductance increases. At the end point 'Y' the conductance is due to Na^+ + Cl^- and CH_3COO^- ions only. The end point 'Y' gives the volume of alkali required by both acids.



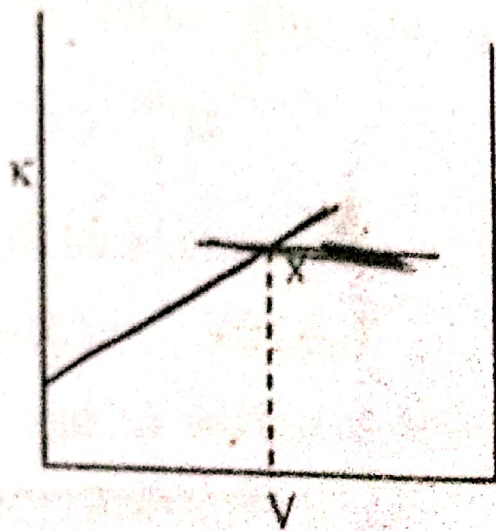
Knowing X the volume, of alkali required by weak acid alone ($Y - X$) can be found. After the end point Y if we add any more amount of NaOH the conductance increase rapidly. It is because NaOH is a strong electrolyte and addition of it causes an increase of Na^+ and OH^- ions. This curve obtained in such a titration is shown in figure.

6. Precipitation titrations:

The titration of AgNO_3 against NaCl can be taken as an example. If we take AgNO_3 solution in the cell, it totally ionises as Ag^+ and NO_3^- .



The less mobile Ag^+ ions are replaced by more mobile Na^+ ions. When more and more of NaCl is added more Na^+ is introduced and so the conductance increases regularly. At the end point we have Na^+ and NO_3^- only. If we add any more amount of NaCl the conductance increases rapidly.



It is because NaCl is a strong electrolyte and the addition of it causes an increase of Na^+ and Cl^- ions. The curve obtained in such a titration is similar to the curve as shown in figure. The break in the curve 'X' gives the end point.