- **F.Y.B.Sc. CBCS COURSE IN CHEMISTRY CH: 101 Physical and Inorganic Chemistry -I (Section A) Core Course-A-1(Semester I)**
- **Chapter 1: Electrolytic conductance. (L: 10, M: 13)**

- **A POWERPOINT PRESENTATION FOR F. Y. B. Sc. CBCS COURSE IN CHEMISTRY ON THE TOPIC**
- **ENTITLED**

“Electrolytic Conductance”

BY

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Dondaicha. Dist- Dhule. **(M. S.)**

----- October 2020 -----

PHYSICAL CHEMISTRY

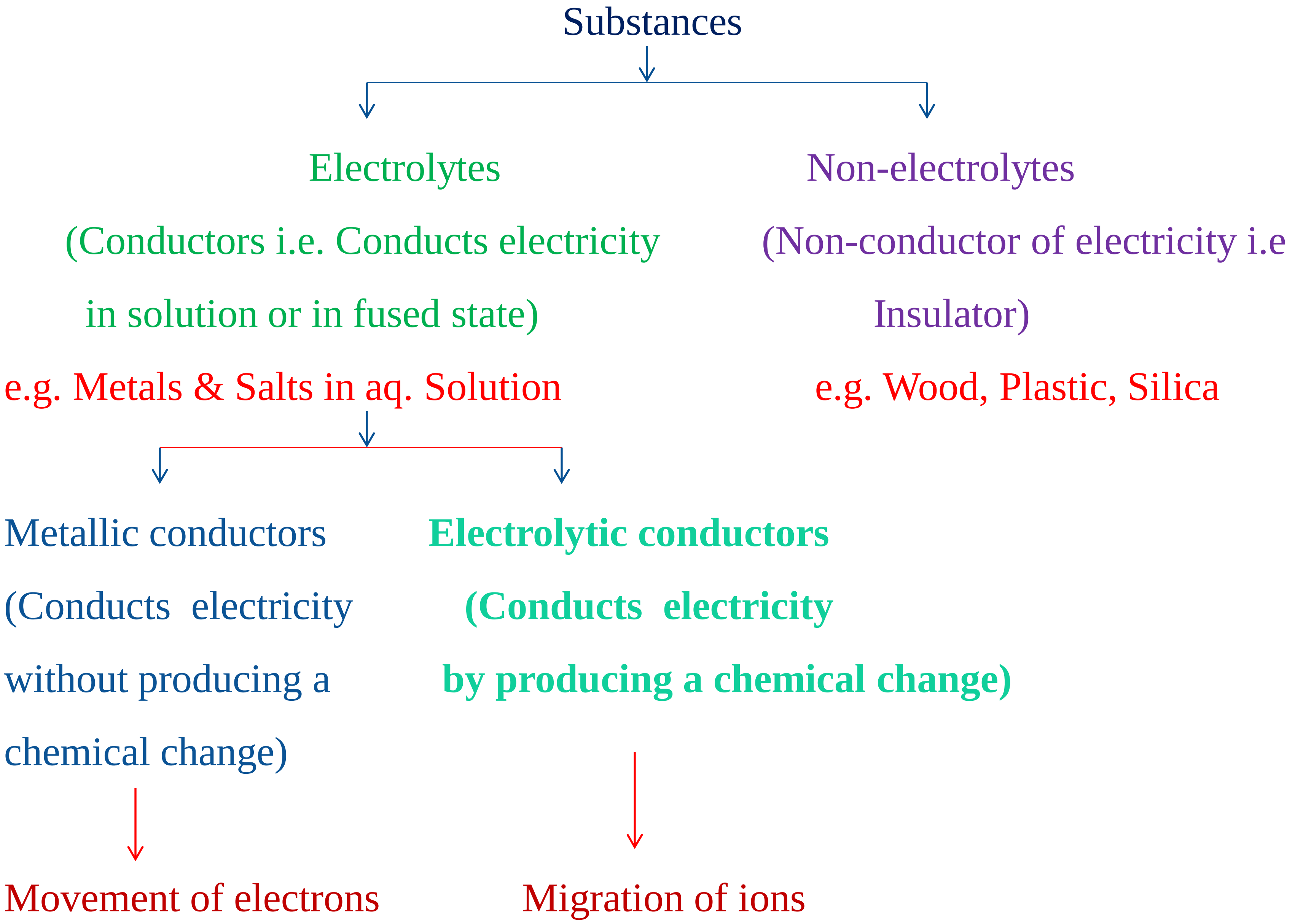
ONLINE LECTURE NO. 1

TOPIC: - ELECTROLYTIC CONDUCTANCE

DATE: -23, OCTOBER, 2020

TIME: 3.00 P.M.

“Electrolytic Conductance ”



Substances

Electrolytes

(Conductors i.e. Conducts electricity in solution or in fused state)

e.g. Metals & Salts in aq. Solution

Non-electrolytes

(Non-conductor of electricity i.e Insulator)

e.g. Wood, Plastic, Silica

Metallic conductors

(Conducts electricity without producing a chemical change)

Movement of electrons

Electrolytic conductors

(Conducts electricity by producing a chemical change)

Migration of ions

Substances can be classified as electrolytes and non-electrolytes, depending upon their ability to conduct the electricity. If the substance conducts electricity either in solution or in fused state then it is called as an electrolyte, and if the substance is a non-conductor of electricity then it is called as an insulator or non-electrolyte.

Substances such as metals and common salts in their aqueous solution allow an electric current to flow through them and hence are called as conductors.

Conductors are of two types: -

Metallic conductors: - Those substances which conducts the electricity without producing a chemical change are called as Metallic conductors. The movement of electrons is responsible for their conduction.

Electrolytic conductors: - Those substances which conducts the electricity by producing a chemical change are called as Electrolytic conductors. The migration of ions is responsible for their conduction.

All conductors obey Ohm’s law.

Ohm’s law: - “The strength of current (I) flowing through any conductor is directly proportional to the applied emf (E) across the conductor and inversely proportional to the resistance (R) of the conductor.

$$\text{i.e. } I \propto \frac{E}{R}$$

If emf (E) is constant, then $I = \frac{1}{R}$

Where, R is the resistance which is defined as the “Obstruction or oppose present in the system to the flow of current.” The unit of resistance is Ohm (Ω).

Conductance (L): - The reciprocal of resistance is called as Conductance.

$$\text{i.e. Conductance} = \frac{1}{\text{Resistance}}$$

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

Unit of conductance = or Ohm^{-1} or mho (Ω^{-1} or ℧).

Specific Resistance(ρ): - The resistance (R) of any material is directly proportional to its length (*l*) and inversely proportional to its area of cross-section (A).

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

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

Where ρ is the specific resistance or specific resistivity (Proportionality constant).

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

The specific resistance is the resistance of the material having area of cross-section A cm^2 and length *l* cm.

If $l = 1$ cm, and $A = 1\ cm^2$, then

$$\rho = R$$

Definition of Specific resistance: - "Sp. Resistance is the resistance offered by the × conductor having one cm length and one cm^2 area of cross-section."

or The specific resistance is the resistance of a cubic material of unit length.

Unit of sp. Resistance = $\rho = R\,\frac{A}{l}$

$= \text{Ohm.} \times \frac{\text{cm}^2}{\text{cm}} = \text{Ohm. cm}$

Specific Conductance (L_s): - "It is the reciprocal of specific resistance."

Specific Conductance = $\frac{1}{\text{Specific resistance}}$

$L_s = \frac{1}{\rho} = \frac{1}{R\frac{A}{l}} = \frac{1}{R} \times \frac{l}{A}$

But, $\frac{1}{R}$ = Conductance = L

$Ls = L \times \frac{l}{A}$

The specific conductance is the conductance of the material having area of cross section A cm^2 and length l cm.

If $l = 1$ cm, and $A = 1\ cm^2$, then $L_s = L$

Definition of Specific conductance: - “Sp. conductance is the conductance of the conductor having one cm length and one cm^2 area of cross-section.”

or The specific conductance is the conductance of a cubic material of unit length.

Unit of specific Conductance: - $Ls = L \times \frac{l}{A}$

$$= mho.\times \frac{cm}{cm^2} = mho.cm^{-1}$$

Equivalent Conductance (Λ): - It is defined as “The conductance of a volume of solution containing one gm equivalent of dissolved substance when placed between two large parallel electrodes one cm apart”.

Eq. conductance never be determined directly, but it is calculated from the specific conductance as follows:

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 2

TOPIC: - ELECTROLYTIC CONDUCTANCE

DATE: -24, OCTOBER, 2020

TIME: 9.00 A.M.

Equivalent Conductance (ʌ): - It is defined as “The conductance of a volume of solution containing one gm equivalent of dissolved substance when placed between two large parallel electrodes one cm apart”.

Eq. conductance never be determined directly, but it is calculated from the specific conductance as follows:

Eq. conductance = $\Lambda = \boxed{\dfrac{1000 \times \text{Sp. conductance}}{C}}$

Where, C is concentration of solution

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

$\Lambda = 1000 \times \text{Sp. Conductance} \times V$

Where, V is in litres.

If volume is expressed in ml, then

$\Lambda = \text{Sp. Conductance} \times V$

Unit of equivalent conductance: - $\Lambda = \text{Sp. Conductance} \times V$

= mho.$\text{cm}^{-1} \times \text{cm}^{3}.\text{equivalent}^{-1} = \text{mhos.cm}^{2}.\text{equivalent}^{-1}$

Determination of Conductance: -

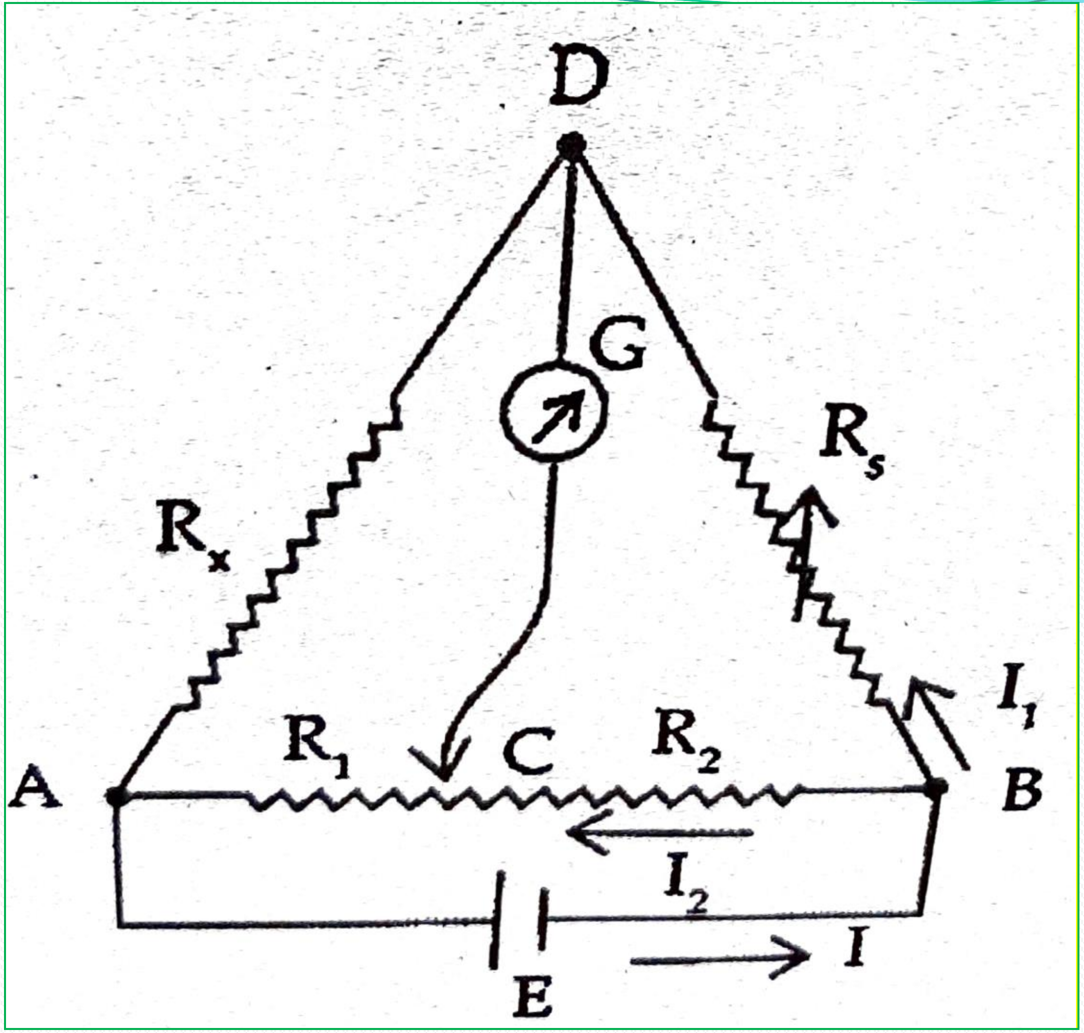


Figure 1: Wheatstone bridge for measurement of conductance

Determination of Conductance: -

Conductance of the solution cannot be measured directly. First, the resistance is determined and the reciprocal of measured resistance gives the conductance. The measurement of resistance is based upon the Wheatstone bridge principle.

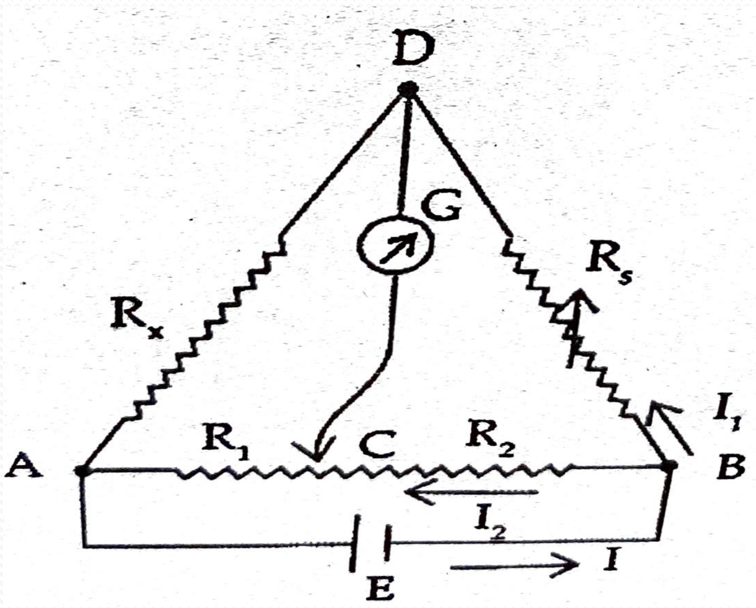


Figure 1: Wheatstone bridge for measurement of conductance

AB is the metal wire of uniform thickness having some resistance, which is stretched over a meter rule and a sliding contact C moves across the wire. E is the source of alternating current. R_x is the unknown resistance which is to be determined. It is placed in one arm of the bridge, while variable known resistance R_s is placed at another arm. When current is flowing a known resistance R_s is introduced. To balance the current of the bridge, the sliding contact is moved along the wire till no current flows through the galvanometer G.

When current I is supplied from the battery E and reaches to point B , it devides into two parallel paths with current I_1 and I_2.

Due to the flow of these currents I_1 and I_2 through the resistance R_s and R_2 respectively, there is potential drops across these resistances.

The purpose of balancing the bridge is to find a point C along the wire AB, such that the potential drop from B to C is exactly equal (balance) to that from B to D. When such a condition is obtained, then D and C are at the same potential.

At null point, $R_s I_1 = R_2 I_2$-------------(1)

and similarly, $R_x I_1 = R_1 I_2$-------------(2)

Deviding equation (2) by (1),

$$\frac{RxI1}{RsI1} = \frac{R1I2}{R2I2}$$

$$\frac{Rx}{Rs} = \frac{R1}{R2}$$

$$R_x = R_s \times \frac{R1}{R2}$$

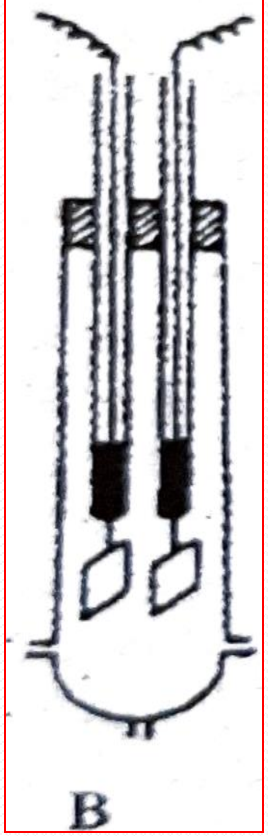
Where, R_1 →Resistance from A to C = Length of wire AC

and R_2 →Resistance from C to B = Length of wire BC.

However, instead of alternating current, if direct current is used, then following complications arises:

Direct current may cause electrolysis, which alters the resistance of the solution.

Due to electrolysis, the conc. Of the solution changes at the electrode.



Conductivity Cell: - Conductance of an electrolyte solution is measured by using a special type of cell called as conductivity cell.

Conductivity cell consists of two identical electrodes made up of either Pt or gold. These electrodes are fitted in a outer glass jacket. These electrodes are coated with Pt black. The Pt black coating is obtained electrolytically from a solution of Chloroplatinic acid. During such electroplating, a thin layer of finely divided Pt is get deposited on electrodes.

Advantages of Pt black coating are:

1) It overcomes imperfections in current and other effects (polarization) at the electrodes.

2) Cell can be used in presence of strong inorganic acids, bases, oxidising and reducing agents.

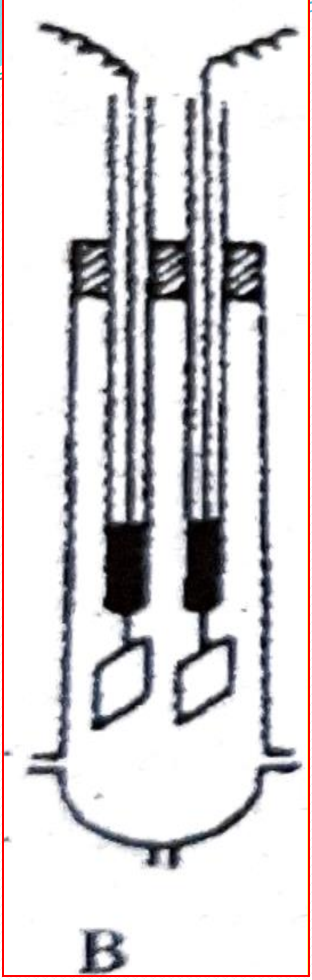
PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 3

TOPIC: - ELECTROLYTIC CONDUCTANCE

DATE: -31, OCTOBER, 2020

TIME: 9.00 A.M.



Conductivity Cell

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Conductivity cell consists of two identical electrodes made up of either Pt or gold. These electrodes are fitted in a outer glass jacket. These electrodes are coated with Pt black. The Pt black coating is obtained electrolytically from a solution of Chloroplatinic acid. During such electroplating, a thin layer of finely divided Pt is get deposited on electrodes.

Advantages of Pt black coating are:

1) It overcomes imperfections in current and other effects (polarization) at the electrodes.

2) Cell can be used in presence of strong inorganic acids, bases, oxidising and reducing agents.

Cell constant and its determination: -

We know, specific Conductance: - $Ls = L \times \frac{l}{A}$

To obtain specific conductance, the measured conductance will have to be multiplied by a certain factor depending upon the area of cross-section and the distance between two electrodes. This factor is called as a cell constant.

It is defined as the ratio of distance between two electrodes and the area of cross-section of one of the electrode.

$$\text{Cell constant} = \boxed{\frac{\text{Distance between two electrodes}}{\text{Area of cross} - \text{section of one of the electrode}}}$$

$$\text{Cell constant} = k = \frac{l}{A}$$

Unit of cell constant: -

$$\text{Cell constant} = \frac{l}{A} = \frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}$$

Cell constant is characteristic of the cell, and it is always constant. It has nothing to do with any solution. It cannot be determined directly, because it is difficult to measure the distance *l* and area A.

For its determination, the aqueous solution of KCl of known conc. and known sp. Conductance is used. The conductance of this solution is measured and from which the cell constant is determined as,

Sp. Conductance = conductance × Cell constant

Ls = L × Cell constant

$$\text{Cell constant} = \frac{\text{Sp. conductance of KCl solution}}{\text{Conductance of KCl solution}} = \frac{Ls}{L}$$

Or Cell constant = Sp. Conductance of KCl solution × Resistance of KCl

Problem: 1) 0.5N solution of an electrolyte between two Pt electrodes 2.2.cm apart and 3.78 cm^2 in area was found to offer a resistance of 45 Ohm. Calculate equivalence conductance of the solution?

Answer: - Given: Conc. = C = 0.5N

Distance between two electrodes = l = 2.2 cm.

Area of cross-section = A = 3.78 cm^2.

Resistance = R = 45 Ohms

Equi. Conductance = Λ =?

we know, Cell constant = k = $\frac{l}{A} = \frac{2.2}{3.78} = 0.5820\ cm^{-1}$

Now, sp. Conductance = Conductance × Cell constant

Or Sp. Conductance = $\frac{\text{Cell constant}}{\text{Resistance}} = \frac{0.5820}{45} = 0.01293\ Ohm^{-1}.cm^{-1}$.

Now eq. conductance = $\Lambda = \dfrac{1000 \times \text{Sp. conductance}}{C}$

$$= \frac{1000 \times 0.01293}{0.5}$$

$= 25.86$ mhos.cm^2.equi^{-1}.

2) Sp. Conductance of 0.02M KCl solution at 25^0c is 0.002765 $Ohm^{-1}.cm^{-1}$. If the resistance of the cell containing this solution is 200 Ohms, then calculate cell constant?

Answer: - Cell constant = Sp. Conductance of KCl × Resistance of KCl

= 0.002765 × 200 = 0.5530 cm^{-1}.

3) Conductance of o.5N solution of a salt surrounding two Pt electrodes 2.10 cm apart and 4.2 cm2 in area was found to be 0.04 mhos. Calculate a) Resistance of the solution b) Eq. conductance of the solution.

Ans: - Cell constant = k = $\frac{l}{A}$ = $\frac{2.10}{4.2}$ = 0.5 cm^{-1}.

a) Conductance of 0.5 N soln. of a salt = 0.04mhos

Resistance = $\frac{1}{Conductance}$ = $\frac{1}{0.04}$ = 25 Ohm.

b) Eq. conductance = $\Lambda = \dfrac{1000 \times \text{Sp. conductance}}{C}$

But, Sp. Conductance = $\dfrac{\text{Cell constant}}{\text{Resistance}} = \dfrac{0.5}{25}$ = 0.02 Ohm^{-1}. cm^{-1}.

Now, eq. conductance = $\dfrac{1000 \times \text{Sp. conductance}}{C} = \dfrac{1000 \times 0.02}{0.5}$ = 40 $\text{mhos.cm}^2\text{.equi}^{-1}$.

Problem (4): - A particular cell measure resistance of 150 Ohms at 25°c of 0.01M soln. of KCl.

While, HCl of the same conc. gave resistance of 51.40 Ohms at the same temperature.

Calculate cell constant, sp. Conductance and eq. conductance of HCl. (Given: Sp. Conductance

at 25°c of 0.01M soln. of KCl = 0.001408).

Ans: - Given: Resistance of 0.01M KCl = 150 Ohms.

Ls of 0.01M KCl = 0.001408

Resistance of 0.01M HCl = 51.40 Ohms

Cell constant = Sp. Conductance of KCl × Resistance of KCl i.e. k = Ls × R = 0.001408 ×150 = 0.2112 cm^{-1}.

Now, to calculate Sp. Conductance of HCl, we know that

Cell constant = Sp. Conductance of HCl × Resistance of HCl

i.e. Sp. Conductance of HCl = $\frac{\text{Cell constant}}{\text{Resistance of HCl}} = \frac{0.2112}{51.40}$ = 0.004108 $\text{Ohm}^{-1}.\text{cm}^{-1}$.

Now, Eq. conductance = $\frac{1000 \times \text{Sp. conductance}}{\text{C}} = \frac{1000 \times 0.004108}{0.01}$

= 410.8 $\text{mhos.cm}^{2}.\text{equi}^{-1}$.

Problem 5): - The resistance of a cell containing 0.1N KCl and 0.1N $AgNO_3$ was 307.62 and 362.65 Ohm resply at 25^0c. The sp. Conductance of 0.1N KCl is 0.01286 $Ohm^{-1}.cm^{-1}$ at 25^0c. Calculate a) Cell constant, b) Eq. conductivity of $AgNO_3$.

Ans: - Given: Resistance of KCl solution = 307.62 Ohm

Resistance of $AgNO_3$ solution = 362.65 Ohm

Sp. Conductance of KCl = 0.01286 $Ohm^{-1}.cm^{-1}$. Conc. = C = 0.1N

Cell constant = ?

Eq. conductivity of $AgNO_3$ =?

a) We know, Cell constant = Sp. Conductance of KCl solution × Resistance of KCl

$$= 0.01286 \times 307.62 = 3.9559\ cm^{-1}.$$

b) Now, Sp. Conductance of $AgNO_3$ = $\frac{\text{Cell constant}}{\text{Resistance}} = \frac{3.9559}{362.65} = 0.01090\ Ohm^{-1}.cm^{-1}$.

We know, the Eq. conductance of $AgNO_3$ = $\frac{1000 \times \text{Sp. conductance}}{C} = \frac{1000 \times 0.01090}{0.1}$

= 109.086 $Ohm^{-1}.cm^{2}.equi.^{-1}$.

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 4

TOPIC: - ELECTROLYTIC CONDUCTANCE

DATE: -6, NOVEMBER, 2020

TIME: 3.00 P.M.

Variation of conductance with concentration:-

(Effect of dilution on conductance): -

As dilution of solution increases, conc. decreases. Hence, both the specific conductance and equivalent conductance of a solution changes with change in its conc.

- **Effect of Conc. on sp. Conductance:** -

The sp. Conductance depends on the number of ions per unit volume of the solution. When the conc. of the solution increases, the number of ions per unit volume increases and hence, sp. Conductance increases.

In case of strong electrolytes, the sp. Conductance increases sharply (rapidly) with increase in conc. because, strong electrolyte undergoes complete ionization and hence the number of ions per unit volume increases in proportion with conc. (i.e. directly proportional).

In weak electrolytes, the sp. Conductance has initially a low value due to its incomplete ionization. But, as its conc. increases, the sp. Conductance increases gradually (slowly) because, increase in conc., increases the number of ions per unit volume but this increase cannot be quite so large.

Thus, in both cases (for strong and weak electrolytes) the sp. Conductance increases with increase in conc. At higher conc. the increase in sp. Conductance becomes relatively less due to electrostatic and viscosity effects.

Solute + Solvent = Solution

10gm + 100ml = 10% (Definite concentration)

10gm + 1000ml = 1% (Increase in solvent quantity, Conc. decreases i.e. soln. is diluted

20gm + 100ml = 20% (Increase in solute quantity, Conc. increases)

As dilution increases, concentration decreases. i.e. Conc. & Volume of solution are Inversely proportional.

i.e. $C = \frac{1}{\text{Volume}}$

Variation of conductance with concentration:-

(Effect of dilution on conductance): - Both the specific conductance and equivalent conductance of a solution changes with change in its conc.

Effect of Conc. on sp. Conductance: - Concentration α No. of ions per unit volume

Conductance α No. of ions per unit volume

& Sp. Conductance α Conductance

(Since, sp. Conductance = Cond.× Cell constant)

When the conc. of the solution increases, the number of ions per unit volume increases and hence, sp. Conductance increases.

Electrolytes

Strong electrolytes	Weak electrolytes
Complete ionization	Partial ionization
Produces large no. of ions	Produces less no. of ions
Sp. Conductance increases sharply (rapidly) with increase in conc.	sp. Conductance increases gradually (slowly)

In case of strong electrolytes, the sp. Conductance increases sharply (rapidly) with increase in conc. because, strong electrolyte undergoes complete ionization and hence the number of ions per unit volume increases in proportion with conc. (i.e. directly proportional).

In weak electrolytes, the sp. Conductance has initially a low value due to its incomplete ionization. But, as its conc. increases, the sp. Conductance increases gradually (slowly) because, increase in conc., increases the number of ions per unit volume but this increase cannot be quite so large.

Thus, in both cases (for strong and weak electrolytes) the sp. Conductance increases with increase in conc. At higher conc. the increase in sp. Conductance becomes relatively less due to electrostatic and viscosity effects.

2) Effect of conc. on Eq. conductance: -The eq. conductance of both strong and weak electrolytes increases by decreasing the conc. or by increasing the volume of solution (i.e. on dilution).

On dilution, number of ions per unit volume decreases and hence sp. Conductance decreases. But, the decrease in sp. Conductance is more than compensated by an increase in 1/C factor. i.e. On dilution, the same amount of an electrolyte is capable to provide large number of ions. (i.e. On dilution, more and more of the electrolyte ionizes). The increase in eq. conductance with dilution is due to the increase in the degree of ionization of the electrolyte. But, the increase in number of ions is less as compared to the increase in volume of the solution.

For strong electrolytes, on dilution the eq. conductance increases slowly while, for weak electrolytes it increases rapidly.

2) Effect of conc. on Eq. conductance: - We know,

Eq. conductance $= \Lambda = \frac{1000 \times \text{Sp. conductance}}{C} = 1000 \times \text{Sp. Coductance} \times V$

The eq. conductance of both strong and weak electrolytes increases by decreasing the conc. or by increasing the volume of solution (i.e. on dilution).

On dilution, number of ions per unit volume decreases and hence sp. Conductance decreases. But, the decrease in sp. Conductance is not more and it is compensated by an increase in 1/C factor. i.e. On dilution, the same amount of an electrolyte is capable to provide large number of ions. (i.e. On dilution, more and more of the electrolyte ionizes). The increase in eq. conductance with dilution is due to the increase in the degree of ionization of the electrolyte. But, the increase in number of ions is less as compared to the increase in volume of the solution.

For strong electrolytes, on dilution the eq. conductance increases slowly while, for weak electrolytes it increases rapidly.

Suppose no. of ions = Conc. = 20

and conductance = 10,

with cell constant = 1

Sp. Conductance = 10 × 1 = 10

Eq. conductance = $\dfrac{1000 \times \text{Sp. conductance}}{C}$

No. of ions = Conc. = 10

and conductance = 5,

with cell constant = 1

Sp. Conductance = 5 × 1 = 5

Eq. conductance = $\dfrac{1000 \times \text{Sp. conductance}}{C}$

Hence, sp. Conductance decreases from 10 to 5 = $\frac{1}{2}$ = 0.5

While, $\frac{1}{C}$ factor is,

$\frac{1}{C} = \frac{1}{20} = 0.05$

$\frac{1}{C}$ factor is

$\frac{1}{C} = \frac{1}{10} = 0.1$

i.e. $\frac{1}{C}$ Increased from 0.05 to 0.1 (i.e. Twice = 2)

Net increase in eq. conductance = 2-0.5 = 1.5

Equivalent Conductance at infinite dilution (Λ_∞ or Λ_0): -

For strong electrolytes, the equivalent conductance increases slowly and finally shows a tendency to approach a limiting value when the concentration approaches to zero. This quantity is called the equivalent conductance at infinite dilution or at zero concentration.

The equivalent conductance at infinite dilution means a solution is so dilute that further dilution has no effect on the value of equivalent conductance.

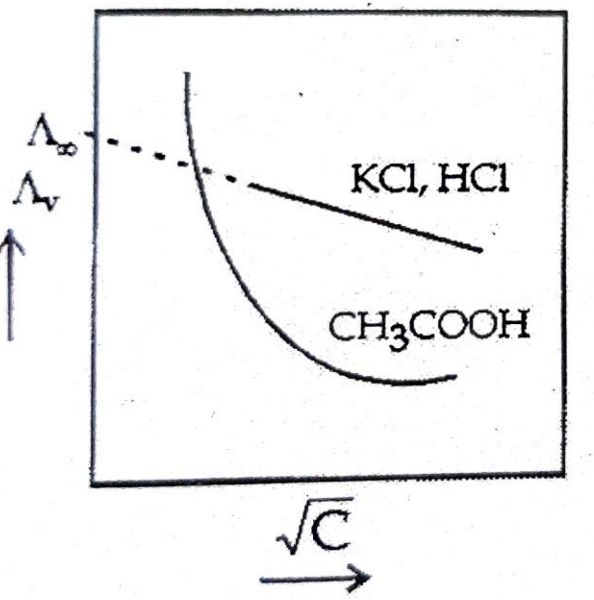

Figure 2: Variation of Equi. cond. with Conc.

Kohlrausch has pointed out that the equivalent conductance for strong electrolytes is related with the conc. by the equation,

$$\Lambda = \Lambda_0 - b\sqrt{C}$$

Where, Λ = Equivalent conductance at Conc. C

Λ_0 = Equivalent conductance at zero Conc.(i.e. Infinite dilution)

b is constant and C is concentration

To obtain Λ_0 for strong electrolytes, the straight line is extrapolated to **= 0.**

This method of obtaining Λ_0 cannot be used in case of weak electrolytes. Because,

- The graph of weak electrolyte is not linear and extrapolation to zero conc. is not possible.
- Practically it is not possible to measure the equivalent conductance at infinite dilution below 10^{-4} N conc. Because at this stage, the equivalent conductance of H_2O becomes appreciable.

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 5

TOPIC: - ELECTROLYTIC CONDUCTANCE

DATE: -7, NOVEMBER, 2020

TIME: 9.00 A.M.

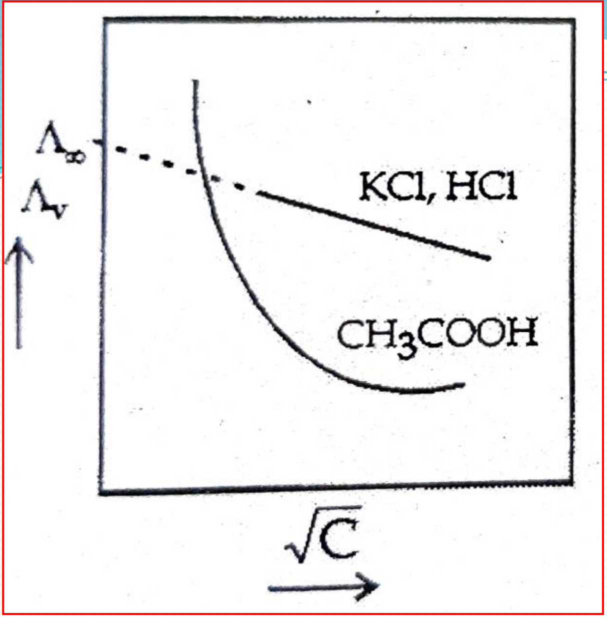

Figure 2: Variation of Equi. cond. with Conc.

Kohlrausch has pointed out that the equivalent conductance for strong electrolytes is related with the conc. by the equation,

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Where, $\mathbf{\Lambda}$ = Equivalent conductance at Conc. C

$\mathbf{\Lambda_0}$ = Equivalent conductance at zero Conc.(i.e. Infinite dilution)

b is constant and C is concentration

To obtain $\mathbf{\Lambda_0}$ for strong electrolytes, the straight line is extrapolated to **= 0.**

This method of obtaining Λ_0 cannot be used in case of weak electrolytes. Because,

- The graph of weak electrolyte is not linear and extrapolation to zero conc. is not possible.
- Practically it is not possible to measure the equivalent conductance at infinite dilution below 10^{-4} N conc. Because at this stage, the equivalent conductance of H_2O becomes appreciable.

Kohlrausch's law of independent migration of Ions:-

"At infinitely dilute solution, where dissociation of all the electrolyte is complete and all the inter ionic effects disappear, then each ion migrates independently of its co-ion and makes a definite contribution to the total equivalent conductance which depends only on its nature and does not depend on the ion with which it is associated."

According to this law, difference between Λ_0 of electrolytes containing a common ion is constant. This difference is equal to difference between the equivalent conductances of ions that are not common.

Electrolyte	Λ_0 at 25^0c	Difference	Electrolyte	Λ_0 at 25^0c	Difference
KCl	149.8	34.8	HCl	426.1	4.8
LiCl	115.0		HNO_3	421.3	
KNO_3	145.0	34.8	KCl	149.8	4.8
$LiNO_3$	110.2		KNO_3	145.0	
KOH	271.5	34.8	LiCl	115.0	4.8
LiOH	236.7		$LiNO_3$	110.2	

The replacement of K^+ ion by Li^+ ion in any of the electrolyte always gives the same difference of 34.8.

Hence, irrespective of nature of the co-ion, the difference between the conductance of K^+ and Li^+ is constant. It is true for Cl^- and NO_3^- ions.

Hence, the total equivalent conductance at infinite dilution of an electrolyte is the sum of equivalent conductances of the ions comprising it.

$$\boxed{\Lambda_0 = l_0^{+} + l_0^{-}}$$

Where, l_0^{+} → Eq. ionic conductance of cation at infinite dilution

And l_0^{-} → Eq. ionic conductance of anion at infinite dilution

Applications of Kohlrausch’s laws: - 1) Calculation of Λ_0 for weak electrolytes: -

On the basis of Kohlrausch’s law, by direct addition and subtraction of l_0 values of suitable salts, we are able to determine $\mathbf{\Lambda_0}$ for weak electrolytes.

e.g. $\mathbf{\Lambda_0}$ (CH_3COOH) = ?

If we know, $\mathbf{\Lambda_0}$ (HCl), $\mathbf{\Lambda_0}$ (NaCl) and $\mathbf{\Lambda_0}$ (CH_3COONa) then, from Kohlrausch’s law,

$\mathbf{\Lambda_0}$ (CH_3COOH) = l_0 CH_3COO^- + l_0 H^+

$\mathbf{\Lambda_0}$ (HCl) = l_0 H^+ + l_0 Cl^-

$\mathbf{\Lambda_0}$ (NaCl) = l_0 Na^+ + l_0 Cl^-

$\mathbf{\Lambda_0}$ (CH_3COONa) = l_0 CH_3COO^- + l_0 Na^+

Now, $\mathbf{\Lambda_0}$ (CH_3COONa) + $\mathbf{\Lambda_0}$ (HCl) - $\mathbf{\Lambda_0}$ (NaCl)

= l_0 CH_3COO^- + l_0 Na^+ + l_0 H^+ + l_0 Cl^- - l_0 Na^+ - l_0 Cl^-

= l_0 CH_3COO^- + l_0 H^+

= $\mathbf{\Lambda_0}$ (CH_3COOH)

2)To calculate Λ_0 for strong electrolytes:-

e.g. Λ_0 HNO_3 =?

If Λ_0 HCl, Λ_0 KNO_3 and Λ_0 KCl are known, then

$\Lambda_0 \, HNO_3 = \Lambda_0 \, HCl + \Lambda_0 \, KNO_3 - \Lambda_0 \, KCl$

$= l_0 \, H^+ + l_0 \, Cl^- + l_0 \, K^+ + l_0 \, NO_3^- - l_0 \, K^+ - l_0 \, Cl^-$

$= l_0 \, H^+ + l_0 \, NO_3^- = \Lambda_0 \, HNO_3$

3) Determination of Transport number:-

“Transport number of an ion is the fraction of the total current carried by that ion.”

i.e. Transport number of cation = $t_0^+ = \frac{l_0^+}{\Lambda 0}$

Similarly, Transport number of anion = $t_0^- = \frac{l_0^-}{\Lambda 0}$

Hence, $l_0^+ = t_0^+ \, . \, \Lambda_0$ and $l_0^- = t_0^- \, . \, \Lambda_0$

Where, t_0^+ and t_0^- are tranference number of cation and anion respectively at infinite dilution.

Similarly, $t_0^+ + t_0^- = 1$

Problem:- 1) The equivalent conductance of CH_3COONa, HCl and NaCl at infinite dilution are 91.0, 426.16 and 126.45 mhos respectively at 25^0c. Calculate the equivalent conductance at infinite dilution for CH_3COOH?

Ans:- Given: $\mathbf{\Lambda_0}$ $(CH_3COONa) = l_0\, CH_3COO^- + l_0\, Na^+ = 91.0$ mhos

$\mathbf{\Lambda_0}$ $(HCl) = l_0\, H^+ + l_0\, Cl^- = 426.16$ mhos

$\mathbf{\Lambda_0}$ $(NaCl) = l_0\, Na^+ + l_0\, Cl^- = 126.45$ mhos

$\mathbf{\Lambda_0}$ $(CH_3COOH) = ?$

With the help of Kohlrausch's law,

$$\mathbf{\Lambda_0}\,(CH_3COOH) = l_0\, CH_3COO^- + l_0\, H^+$$

$$= \mathbf{\Lambda_0}\,(CH_3COONa) + \mathbf{\Lambda_0}\,(HCl) - \mathbf{\Lambda_0}\,(NaCl)$$

$$= l_0\, CH_3COO^- + l_0\, Na^+ + l_0\, H^+ + l_0\, Cl^- - l_0\, Na^+ - l_0\, Cl^-$$

$$l_0\, CH_3COO^- + l_0\, H^+ = 91.0 + 426.16 – 126.45$$

$$= 390.71 \text{ mhos.}$$

2) The equivalent conductance of NH_4Cl at infinite dilution is 149.7 mhos and ionic conductance of OH^- and Cl^- ions are 198 and 76.3 mhos respectively. Calculate the equivalent conductance of NH_4OH at infinite dilution?

Ans: - Given: $\mathbf{\Lambda_0}\ NH_4Cl = 149.7$ mhos

$l_0\ OH^- = 198$ mhos and $l_0\ Cl^- = 76.3$ mhos

$\Lambda_0\ NH_4OH =?$

From Kohlrausch's law, $\mathbf{\Lambda_0}\ NH_4Cl = l_0\ NH_4^+ + l_0\ Cl^- = 149.7$

$l_0\ NH_4^+ = \mathbf{\Lambda_0}\ NH_4Cl - l_0\ Cl^- = 149.7 - 76.3 = 73.4$ mhos.

Now, $\mathbf{\Lambda_0}\ NH_4OH = l_0\ NH_4^+ + l_0\ OH^- = 73.4 + 198 = 271.4$ mhos.

3) At 15^0c, the Λ_0 of HCl and CH_3COONa are 380 and 80 mhos respectively. The transport number of H^+ and CH_3COO^- ions in these electrolytes are 0.83 and 0.56 resply. Calculate the equivalent conductance of CH_3COOH at infinite dilution?

Ans: - Given: Λ_0 HCl = 380 mhos and Λ_0 CH_3COONa = 80 mhos.

$t_0 H^+ = 0.83$ and $t_0 CH_3COO^- = 0.56$

$\Lambda_0 CH_3COOH = ?$

From Kohlrausch's law, $\Lambda_0 CH_3COOH = l_0 CH_3COO^- + l_0 H^+$ -------- eq^n. (1)

We know, $t_0^+ = \frac{l_0^+}{\Lambda 0}$ i.e. $t_0 H+ = \frac{l_{0H^+}}{\Lambda 0}$

$l_{0H^+} = t_0 H+.\Lambda 0 = 0.83 \times 380 = 315.4$ mhos

Similarly, $l_{0CH3COO-} = \cdot t_o CH_3COO^- \Lambda 0 = 0.56 \times 80 = 44.8$ mhos

Substitute in eq^n. (1), $\Lambda_o CH_3COOH = l_o CH_3COO^- + l_o H^+$

$= 44.8 + 315.4 = 360.2$ mhos

4) The equivalent conductivity of a very dilute solution of $NaNO_3$ at18^0c is 105.2 mhos. cm^2. Ionic conductance of NO_3^- ions in the same solution at 18^0c is 61.7 mhos cm^2. Calculate the transport number of Na^+ ions?

Ans: - Given: Λ_0 $NaNO_3$ = 105.2 mhos.cm^2

l_o NO_3^- = 61.7 mhos cm^2

t_o Na^+ = ?

We know, $t_0^{NO3-} = \frac{l_0^{NO3-}}{\Lambda 0} = \frac{61.70}{105.2} = 0.5865$

We know, t_0 Na^+ + t_0 NO_3^- = 1

t_0 Na^+ = 1- t_0 NO_3^- =1- 0.5865 = 0.4135.

Applications of conductance measurement:-

Solubility of sparingly soluble salts:- Salts like AgCl, BaSO4, PbSO4 are sparingly soluble in water. Their solubility is very low and hence cannat be measured directly. But by measurement of conductance it is easily determined.

To determine the solubility, a saturated solution of sparingly soluble salt is prepared by using water of known specific conductance. Then, the specific conductance of a saturated solution is measured, which is the sum of specific conductance of water and specific conductance of dissolved salt (Solute).

i.e. L_s(Sat'd soln.) = L_s (Salt) + L_s (H_2O)

L_s (Salt) = L_s(Sat'd soln.) - L_s (H_2O)

3) Conductometric Titrations: - Definition: “The determination of the equivalence point of titration by measurement of conductance is called as conductometric titration.”

These titrations are based on the principle that, the conductance of a solution depends upon number of ions present and their velocity. In such titrations, either the number of ions in the solution changes or one of the ion is replaced by another ion having different velocity. Hence, the conductance of a solution changes before and after the end point.

A) Titration of a strong acid with strong base: -

Consider, the titration between HCl and NaOH.

$HCl + NaOH \rightarrow NaCl + H_2O$

Initially, before without addition of any base, the titration flask contains only acid, which possess fast moving H+ ions. Therefore, the conductance of solution initially is very high. But, when NaOH is added, the highly conducting fast moving H+ ions are replaced by slow moving Na+ ions, which have low conductance. Therefore, the conductance of the solution decreases. This process is continued till the acid is completely neutralized. After complete neutralization of acid, further addition of base introduce an excess of fast moving OH- ions, due to which conductance increases.

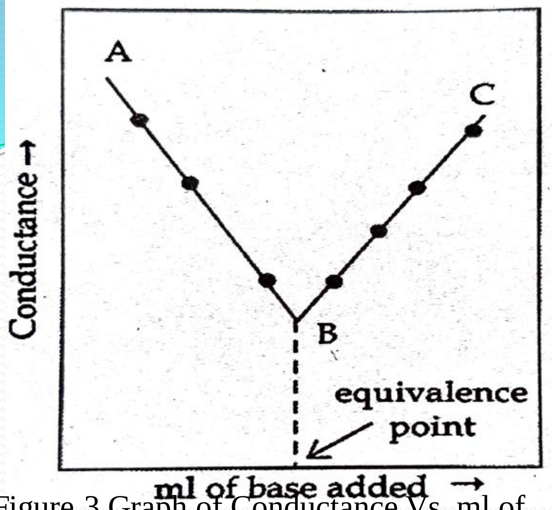

Figure 3 Graph of Conductance Vs. ml of NaOH added

If the graph of conductance against volume of NaOH added is plotted, then the lines AB and BC are obtained. Along the line AB, the conductance of mixture of acid and salt is shown while, along the line BC, the conductance of mixture of salt and excess base is shown. But, at point B, there are neither excess of H+ ions nor OH- ions and hence, it is an equivalence point of the titration.

B) Titration of weak acid with strong base: - Consider the titration between CH_3COOH with NaOH.

$CH_3COOH + NaOH \rightarrow CH_3COONa + H2O$

Initally, when base is not added, the titration flask contains weak acid(CH_3COOH) whose conductance is low. But, when NaOH is added, there is formation of highly ionized CH_3COONa salt and thus conductance gradually (slowly) increases. When the acid is completely neutralized, then further addition of base introduces excess of fast moving OH- ions and hence, conductance increases more sharply (rapidly) than before.

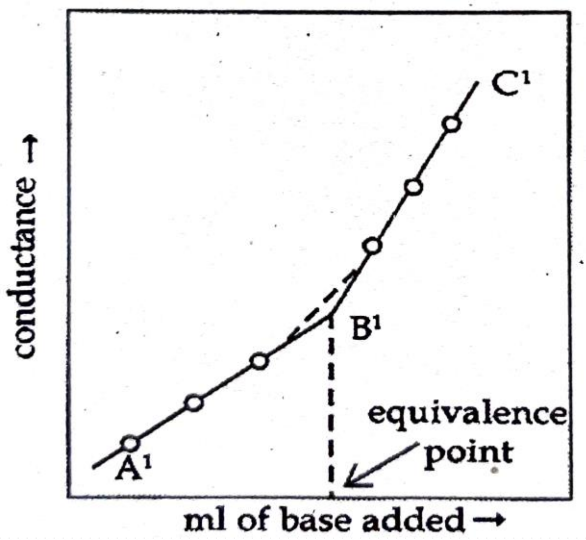

Figure 4.Graph of conductance Vs. ml of NaOH added

If the graph of conductance against ml of NaOH added is plotted then the point of intersection between two lines gives the equivalence point of the titration.

Problem:-1) Equivalence conductance of 1M solution of NaCl is 98.2 at 25^0c, calculate the degree of ionization of NaCl at this dilution. (Given: Equi. conductance at infinite dilution of NaCl at 25^0c is 131).

Ans:- Given:- Eq. Conductance = Λ = 98.2

And Eq. Conductance at infinite dilution = $\mathbf{\Lambda_0}$ = 131

Advantages of conductometric titrations: -

1) Coloured solutions can not be titrated volumetrically, but they can be carried out conductometrically.

2) The titration between very weak acids and bases are not possible volumetrically, because, there is no suitable indicator available. But, it is carried out conductometrically.

3) Mixture of strong and weak acids can be readily titrated by this technique, which is very difficult by usual methods.

4) Conductometric titrations are useful in case of very dilute solutions.

5) Accurate results are obtained graphically.

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 6

TOPIC: - ELECTROLYTIC CONDUCTANCE

DATE: -20, NOVEMBER, 2020

TIME: 3.00 P.M.

Problem:- 1) The equivalent conductance of CH_3COONa, HCl and NaCl at infinite dilution are 91.0, 426.16 and 126.45 mhos respectively at 25^0c. Calculate the equivalent conductance at infinite dilution for CH_3COOH?

Ans:- Given: $\mathbf{\Lambda_0}$ $(CH_3COONa) = l_0\, CH_3COO^- + l_0\, Na^+ = 91.0$ mhos

$\mathbf{\Lambda_0}$ $(HCl) = l_0\, H^+ + l_0\, Cl^- = 426.16$ mhos

$\mathbf{\Lambda_0}$ $(NaCl) = l_0\, Na^+ + l_0\, Cl^- = 126.45$ mhos

$\mathbf{\Lambda_0}$ $(CH_3COOH) = ?$

With the help of Kohlrausch’s law,

$\mathbf{\Lambda_0}$ $(CH_3COOH) = l_0\, CH_3COO^- + l_0\, H^+$

$= \mathbf{\Lambda_0}\, (CH_3COONa) + \mathbf{\Lambda_0}\, (HCl) - \mathbf{\Lambda_0}\, (NaCl)$

$= l_0\, CH_3COO^- + l_0\, Na^+ + l_0\, H^+ + l_0\, Cl^- - l_0\, Na^+ - l_0\, Cl^-$

$l_0\, CH_3COO^- + l_0\, H^+ = 91.0 + 426.16 – 126.45$

$= 390.71$ mhos.

2) The equivalent conductance of NH_4Cl at infinite dilution is 149.7 mhos and ionic conductance of OH^- and Cl^- ions are 198 and 76.3 mhos respectively. Calculate the equivalent conductance of NH_4OH at infinite dilution?

Ans: - Given: $\mathbf{\Lambda_0}\ NH_4Cl = 149.7$ mhos

$l_0\ OH^- = 198$ mhos and $l_0\ Cl^- = 76.3$ mhos

$\Lambda_0\ NH_4OH = ?$

From Kohlrausch's law, $\mathbf{\Lambda_0}\ NH_4Cl = l_0\ NH_4^+ + l_0\ Cl^- = 149.7$

$l_0\ NH_4^+ = \mathbf{\Lambda_0}\ NH_4Cl - l_0\ Cl^- = 149.7 – 76.3 = 73.4$ mhos.

Now, $\mathbf{\Lambda_0}\ NH_4OH = l_0\ NH_4^+ + l_0\ OH^- = 73.4 + 198 = 271.4$ mhos.

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 7

TOPIC: - ELECTROLYTIC CONDUCTANCE

DATE: -21, NOVEMBER, 2020

TIME: 9.00 A.M.

3) At 15^0c, the Λ_0 of HCl and CH_3COONa are 380 and 80 mhos respectively. The transport number of H^+ and CH_3COO^- ions in these electrolytes are 0.83 and 0.56 resply. Calculate the equivalent conductance of CH_3COOH at infinite dilution?

Ans: - Given: Λ_0 HCl = 380 mhos and Λ_0 CH_3COONa = 80 mhos.

$t_0 H^+ = 0.83$ and $t_0 CH_3COO^- = 0.56$

$\Lambda_0 CH_3COOH$ =?

From Kohlrausch's law, $\Lambda_0 CH_3COOH = l_0 CH_3COO^- + l_0 H^+$ -------- eq^n. (1)

We know, $t_0^+ = \frac{l_0^+}{\Lambda 0}$ i.e. $t_0 H+ = \frac{l_{0H^+}}{\Lambda 0}$

$l_{0H^+} = t_0 H^+ . \Lambda 0 = 0.83 \times 380 = 315.4$ mhos

Similarly, $l_{0CH3COO-} = \cdot t_o CH_3COO^- \Lambda 0 = 0.56 \times 80 = 44.8$ mhos

Substitute in eq^n. (1), $\Lambda_o CH_3COOH = l_o CH_3COO^- + l_o H^+$

= 44.8 + 315.4 = 360.2 mhos

4) The equivalent conductivity of a very dilute solution of $NaNO_3$ at18^0c is 105.2 mhos. cm^2. Ionic conductance of NO_3^- ions in the same solution at 18^0c is 61.7 mhos cm^2. Calculate the transport number of Na^+ ions?

Ans: - Given: $\mathbf{\Lambda_0}$ $NaNO_3$ = 105.2 mhos.cm^2

l_0 NO_3^- = 61.7 mhos cm^2

t_0 Na^+ = ?

We know, $t_0^{NO3-} = \frac{l_0^{NO3-}}{\Lambda 0} = \frac{61.70}{105.2} = 0.5865$

We know, t_0 Na^+ + t_0 NO_3^- = 1

t_0 Na^+ = 1- t_0 NO_3^- =1- 0.5865 = 0.4135.

Applications of conductance measurement:-

Solubility of sparingly soluble salts:- Salts like AgCl, $BaSO_4$, $PbSO_4$ are sparingly soluble in water. Their solubility is very low and hence cannot be measured directly. But by measurement of conductance it is easily determined.

To determine the solubility, a saturated solution of sparingly soluble salt is prepared by using water of known specific conductance. Then, the specific conductance of a saturated solution is measured, which is the sum of specific conductance of water and specific conductance of dissolved salt (Solute).

i.e. L_s(Sat'd soln.) = L_s (Salt) + L_s (H_2O)

L_s (Salt) = L_s(Sat'd soln.) - L_s (H_2O)

We know, Equi. Conductance = $\Lambda = \dfrac{1000 \times \text{sp.conductance of salt}}{\text{Conc.}}$

$$C = \frac{1000 \times Ls(\text{salt})}{\Lambda}$$

Where C is the conc. of salt in gm equivalent per litre and hence it is called as the solubility (S). i.e. C = S

$$S = \frac{1000 \times Ls(\text{salt})}{\Lambda}$$

As the sparingly soluble salt solutions are very very dilute, their equivalent conductance is called as equivalent conductance at infinite dilution (**Λ_0**).

$$S = \boxed{\frac{1000 \times Ls(\text{salt})}{\Lambda_0}}$$

2) Determination of degree of Ionization (α): -

The degree of ionization ‘α’ is given by the equation

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

Where, $\Lambda \longrightarrow$ is eq.cond. at any dilution

$\Lambda_0 \longrightarrow$ is eq. cond. At infinite dilution.

3) Conductometric Titrations: - Definition:- “The determination of the equivalence point of titration by measurement of conductance is called as conductometric titration.”

These titrations are based on the principle that, the conductance of a solution depends upon number of ions present and their velocity. In such titrations, either the number of ions in the solution changes or one of the ion is replaced by another ion having different velocity. Hence, the conductance of a solution changes before and after the end point.

A) Titration of a strong acid with strong base: -

Consider, the titration between HCl and NaOH.

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Initially, before without addition of any base, the titration flask contains only acid, which Possess fast moving H+ ions. Therefore, the conductance of solution initially is very high. But, when NaOH is added, the highly conducting fast moving H+ ions are replaced by slow moving Na+ ions, which have low conductance.

Therefore, the conductance of the solution decreases. This process is continued till the acid is completely neutralized. After complete neutralization of acid, further addition of base introduce an excess of fast moving OH- ions, due to which conductance increases.

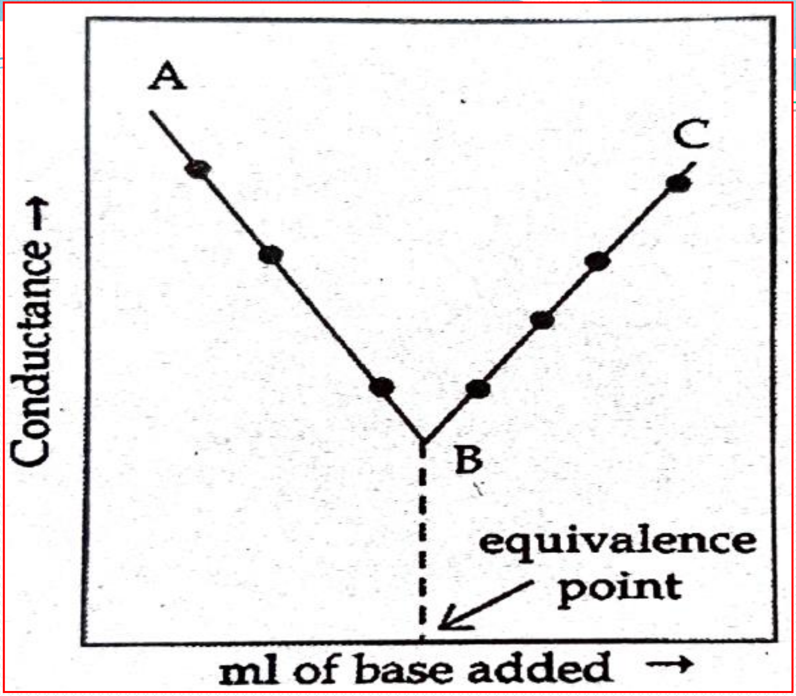

Figure 3 Graph of Conductance Vs. ml of NaOH added

If the graph of conductance against volume of NaOH added is plotted, then the lines AB and BC are obtained. Along the line AB, the conductance of mixture of acid and salt is shown while, along the line BC, the conductance of mixture of salt and excess base is shown. But, at point B, there are neither excess of H+ ions nor OH- ions and hence, it is an equivalence point of the titration.

B) Titration of weak acid with strong base: - Consider the titration between CH_3COOH with NaOH.

$CH_3COOH + NaOH \rightarrow CH_3COONa + H2O$

Initally, when base is not added, the titration flask contains weak acid(CH_3COOH) whose conductance is low. But, when NaOH is added, there is formation of highly ionized CH_3COONa salt and thus conductance gradually (slowly) increases. When the acid is completely neutralized, then further addition of base introduces excess of fast moving OH- ions and hence, conductance increases more sharply (rapidly) than before.

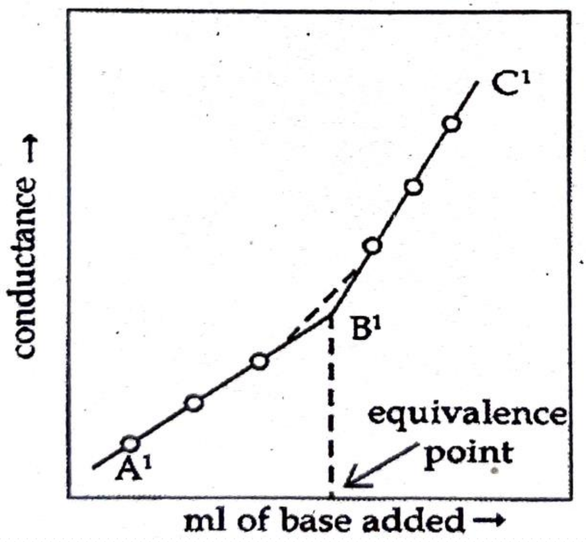

Figure 4.Graph of conductance Vs. ml of NaOH added

If the graph of conductance against ml of NaOH added is plotted then the point of intersection between two lines gives the equivalence point of the titration.

Problem:-1) Equivalence conductance of 1M solution of NaCl is 98.2 at 25^0c, calculate the degree of ionization of NaCl at this dilution. (Given: Equi. conductance at infinite dilution of NaCl at 25^0c is 131).

Ans:- Given:- Eq. Conductance = Λ = 98.2

And Eq. Conductance at infinite dilution = $\mathbf{\Lambda_0}$ = 131

Advantages of conductometric titrations: -

1) Coloured solutions can not be titrated volumetrically, but they can be carried out conductometrically.
2) The titration between very weak acids and bases are not possible volumetrically, because, there is no suitable indicator available. But, it is carried out conductometrically.
3) Mixture of strong and weak acids can be readily titrated by this technique, which is very difficult by usual methods.
4) Conductometric titrations are useful in case of very dilute solutions.
5) Accurate results are obtained graphically.

Problem:-1) Equivalence conductance of 1M solution of NaCl is 98.2 at 25^0c, calculate the degree of ionization of NaCl at this dilution. (Given: Equi. conductance at infinite dilution of NaCl at 25^0c is 131).

Ans:- Given:- Eq. Conductance = Λ = 98.2

And Eq. Conductance at infinite dilution = Λ_0 = 131

We know, the degree of ionization = $\alpha = \dfrac{\Lambda}{\Lambda_0}$

$$= \frac{98.2}{131} = 0.749.$$

Hence, in 1M solution, NaCl ionized = 74.9%

2) For a saturated solution of AgCl at 25^0c, sp. conductance was 3.41×10^{-6} ohm^{-1}.cm^{-1}, the sp. conductance of water used to prepare the solution was 1.60×10^{-6} ohm^{-1}.cm^{-1}. Determine solubility of AgCl in water in moles/lit. at 25^0c. (Given: Λ_0 for AgCl =

= 138.3 ohm^{-1}.cm^{-1}).

Ans:- Given: L_s AgCl (Sat'd soln.) = 3.41×10^{-6} ohm^{-1}.cm^{-1}

L_s (H_2O) = 1.60×10^{-6} ohm^{-1}.cm^{-1}

Solubility = S = Conc. = C

L_s AgCl (Salt) = L_s AgCl (Sat'd soln.) - L_s (H_2O)

$= 3.41\times10^{-6} - 1.60\text{X}10^{-6}$

$= 1.81\times10^{-6}$ohm^{-1}.cm^{-1}.

Now, we know, Equi. Conductance = Λ = $\dfrac{1000 \times \text{sp. conductance of AgCl salt}}{\text{Conc.}}$

$$C = \frac{1000 \times Ls(\text{AgCl salt})}{\Lambda}$$

$$S = \frac{1000 \times Ls(\text{AgCl salt})}{\Lambda_0} = \frac{1000 \times 1.81 \times 10^{-6}}{138.3}$$

$= 1.308 \times 10^{-5}$ moles/lit.

3) At 18^0c, the equi. conductance at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 $ohm^{-1}.cm^2$. Calculate equi. conductance at infinite dilution of NH_4OH. If equi. conductance of 0.01 N solution of NH_4OH at 18^0c is 9.33, then calculate the degree of ionization of NH_4OH at this conc.?

Ans: - Given: Λ_0 $(NH_4Cl) = 129.8$, Λ_0 $(NaOH) = 217.4$, Λ_0 $= (NaCl) = 108.9$

Λ_0 $(NH_4OH) =?$ $\Lambda = 9.33$, $\alpha =?$

From Kohlrausch’s law,

$$\Lambda_0 (NH_4OH) = \Lambda_0 (NH_4Cl) + \Lambda_0 (NaOH) - \Lambda_0\ NaCl$$

$$= 129.8 + 217.4 - 108.9 = 238.3$$

Now, degree of ionization of NH_4OH = $= \alpha = \frac{\Lambda}{\Lambda_0} = \frac{9.33}{238.3} = 0.0322.$

4) The sp. Conductivities of a saturated solution of AgCl and water at 25^0c are 3.41×10^{-6} and 1.60×10^{-6} $ohm^{-1}.cm^{-1}$ respectively. If equivalent ionic conductances at infinite dilution of Ag^+ and Cl^- ions are 61.92 and 76.34 $ohm^{-1}.cm^2$ at 25^0c, calculate the solubility of AgCl.

Ans: - Given: L_s AgCl (Sat'd soln.) = 3.41×10^{-6} $ohm^{-1}.cm^{-1}$

L_s (H_2O) = 1.60×10^{-6} $ohm^{-1}.cm^{-1}$

l_0 Ag^+ = 61.92, l_0 Cl^- = 76.34 $ohm^{-1}.cm^2$

S =?

L_s AgCl (Salt) = L_s AgCl (Sat'd soln.) - L_s (H_2O)

$= 3.41\times10^{-6} - 1.60\times10^{-6}$

$= 1.81\times10^{-6}$ $ohm^{-1}.cm^{-1.}$

Now, calculate $\mathbf{\Lambda_0}$ AgCl = l_0 Ag^+ + l_0 Cl^-

$= 61.92 + 76.34 = 138.26$ $ohm^{-1}.cm^2$

To, calculate, Solubility, we know, C

$$C = \frac{1000 \times Ls(AgCl\ salt)}{\Lambda}$$

$$S = \frac{1000 \times Ls(AgCl\ salt)}{\Lambda_0} = \frac{1000 \times 1.81 \times 10^{-6}}{138.3} = 1.308 \times 10^{-5}\ \text{gmequi./lit.}$$

5) The sp. Conductance of saturated solution of AgBr and water are 4.1×10^{-6} and 1.60×10^{-6} mhos.cm^{-1} respectively at 25^0c. If the ionic conductivities of Ag^+ and Br^- ions are 56.90 and 68.90 mhos.cm^2.equi.$^{-1}$ resply then, calculate the solubility of AgBr in water.

Ans: - Given: L_s AgBr (Sat'd soln.) = 4.1×10^{-6} ohm^{-1}.cm^{-1}

L_s (H_2O) = 1.60×10^{-6} ohm^{-1}.cm^{-1}

l_0 Ag^+ = 56.90, l_0 Br^- = 68.90 ohm^{-1}.cm^2

S =?

L_s AgBr (Salt) = L_s AgBr (Sat'd soln.) - L_s (H_2O)

= 4.1×10^{-6} - 1.60×10^{-6}

= 2.5×10^{-6} ohm^{-1}.cm^{-1}.

Now, calculate $\mathbf{\Lambda_0}$ AgBr = l_0 Ag$^+$ + l_0 Br$^-$

$$= 56.90 + 68.90 = 125.80 \text{ ohm}^{-1}.\text{cm}^2$$

To, calculate, Solubility, we know, $C = \dfrac{1000 \times \text{Ls(AgBr salt)}}{\Lambda}$

$$S = \frac{1000 \times \text{Ls(AgBr salt)}}{\Lambda_0 \text{ of salt}}$$

$$= \frac{1000 \times 2.5 \times 10^{-6}}{125.80}$$

$$= 19.87 \times 10^{-6} \text{ gmequi./lit.}$$

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 8

TOPIC: - ELECTROLYTIC CONDUCTANCE

DATE: -27, NOVEMBER, 2020

TIME: 3.00 P.M.

Applications of conductance measurement:-

Solubility of sparingly soluble salts:- Salts like AgCl, $BaSO_4$, $PbSO_4$ are sparingly soluble in water. Their solubility is very low and hence cannot be measured directly. But by measurement of conductance it is easily determined.

To determine the solubility, a saturated solution of sparingly soluble salt is prepared by using water of known specific conductance. Then, the specific conductance of a saturated solution is measured, which is the sum of specific conductance of water and specific conductance of dissolved salt (Solute).

i.e. $L_s(\text{Sat'd soln.}) = L_s\,(\text{Salt}) + L_s\,(H_2O)$

$L_s\,(\text{Salt}) = L_s(\text{Sat'd soln.}) - L_s\,(H_2O)$

We know, Equi. Conductance = $\Lambda = \dfrac{1000 \times \text{sp.conductance of salt}}{\text{Conc.}}$

$$C = \frac{1000 \times Ls(salt)}{\Lambda}$$

Where C is the conc. of salt in gm equivalent per litre and hence it is called as the solubility (S). i.e. C = S

$$S = \frac{1000 \times Ls(salt)}{\Lambda}$$

As the sparingly soluble salt solutions are very very dilute, their equivalent conductance is called as equivalent conductance at infinite dilution (**Λ_0**).

$$S = \boxed{\frac{1000 \times Ls(salt)}{\Lambda_0}}$$

2) Determination of degree of Ionization (α): -

The degree of ionization ‘α’ is given by the equation

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

Where, Λ → is eq.cond. at any dilution

Λ_0 → is eq. cond. At infinite dilution.

3) Conductometric Titrations: - Definition:- "The determination of the equivalence point of titration by measurement of conductance is called as conductometric titration."

These titrations are based on the principle that, the conductance of a solution depends upon number of ions present and their velocity. In such titrations, either the number of ions in the solution changes or one of the ion is replaced by another ion having different velocity. Hence, the conductance of a solution changes before and after the end point.

A) Titration of a strong acid with strong base: -

Consider, the titration between HCl and NaOH.

$HCl + NaOH \rightarrow NaCl + H_2O$

Initially, before without addition of any base, the titration flask contains only acid, which Possess fast moving H^+ ions. Therefore, the conductance of solution initially is very high. But, when NaOH is added, the highly conducting fast moving H^+ ions are replaced by slow moving Na^+ ions, which have low conductance.

Therefore, the conductance of the solution decreases. This process is continued till the acid is completely neutralized. After complete neutralization of acid, further addition of base introduce an excess of fast moving OH^- ions, due to which conductance increases.

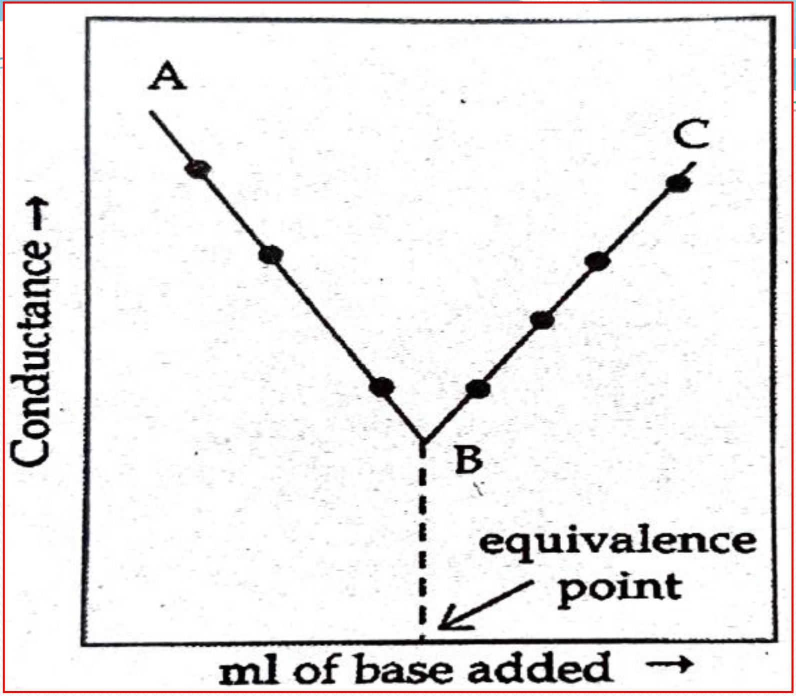

Figure 3 Graph of Conductance Vs. ml of NaOH added

If the graph of conductance against volume of NaOH added is plotted, then the lines AB and BC are obtained. Along the line AB, the conductance of mixture of acid and salt is shown while, along the line BC, the conductance of mixture of salt and excess base is shown. But, at point B, there are neither excess of H+ ions nor OH- ions and hence, it is an equivalence point of the titration.

PHYSICAL CHEMISTRY

ONLINE LECTURE NO. 9

TOPIC: - ELECTROLYTIC CONDUCTANCE

DATE: -11, DECEMBER, 2021

TIME: 12.30 P.M.

3) Conductometric Titrations: - Definition:- "The determination of the equivalence point of titration by measurement of conductance is called as conductometric titration."

These titrations are based on the principle that, the conductance of a solution depends upon number of ions present and their velocity. In such titrations, either the number of ions in the solution changes or one of the ion is replaced by another ion having different velocity. Hence, the conductance of a solution changes before and after the end point.

A) Titration of a strong acid with strong base: -

Consider, the titration between HCl and NaOH.

$HCl + NaOH \rightarrow NaCl + H_2O$

Initially, before without addition of any base, the titration flask contains only acid, which Possess fast moving H^+ ions. Therefore, the conductance of solution initially is very high. But, when NaOH is added, the highly conducting fast moving H^+ ions are replaced by slow moving Na^+ ions, which have low conductance.

Therefore, the conductance of the solution decreases. This process is continued till the acid is completely neutralized. After complete neutralization of acid, further addition of base introduce an excess of fast moving OH^- ions, due to which conductance increases.

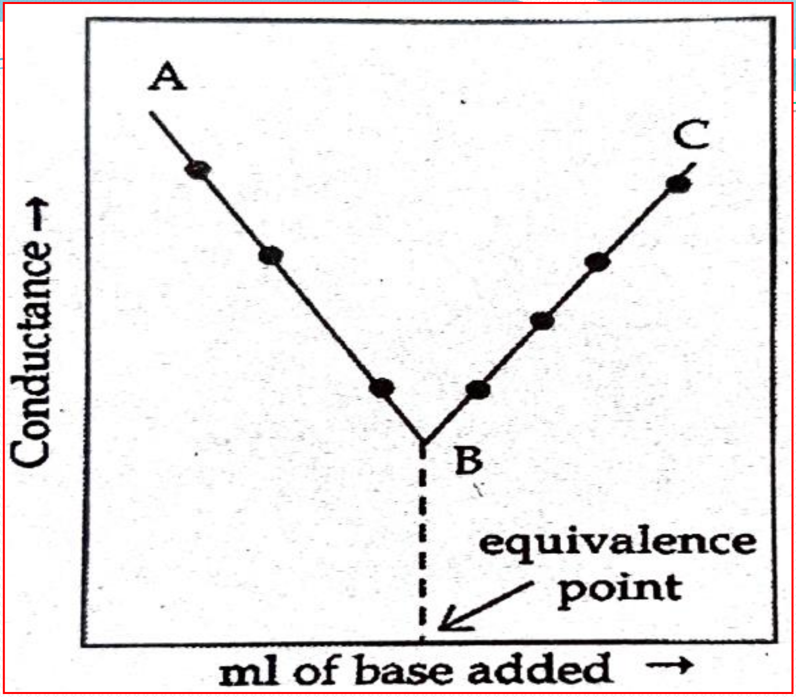

Figure 3 Graph of Conductance Vs. ml of NaOH added

If the graph of conductance against volume of NaOH added is plotted, then the lines AB and BC are obtained. Along the line AB, the conductance of mixture of acid and salt is shown while, along the line BC, the conductance of mixture of salt and excess base is shown. But, at point B, there are neither excess of H+ ions nor OH- ions and hence, it is an equivalence point of the titration.

B) Titration of weak acid with strong base: - Consider the titration between CH_3COOH with NaOH.

$CH_3COOH + NaOH \rightarrow CH_3COONa + H2O$

Initially, when base is not added, the titration flask contains weak acid(CH_3COOH) whose conductance is low. But, when NaOH is added, there is formation of highly ionized CH_3COONa salt and thus conductance gradually (slowly) increases. When the acid is completely neutralized, then further addition of base introduces excess of fast moving OH^- ions and hence, conductance increases more sharply (rapidly) than before.

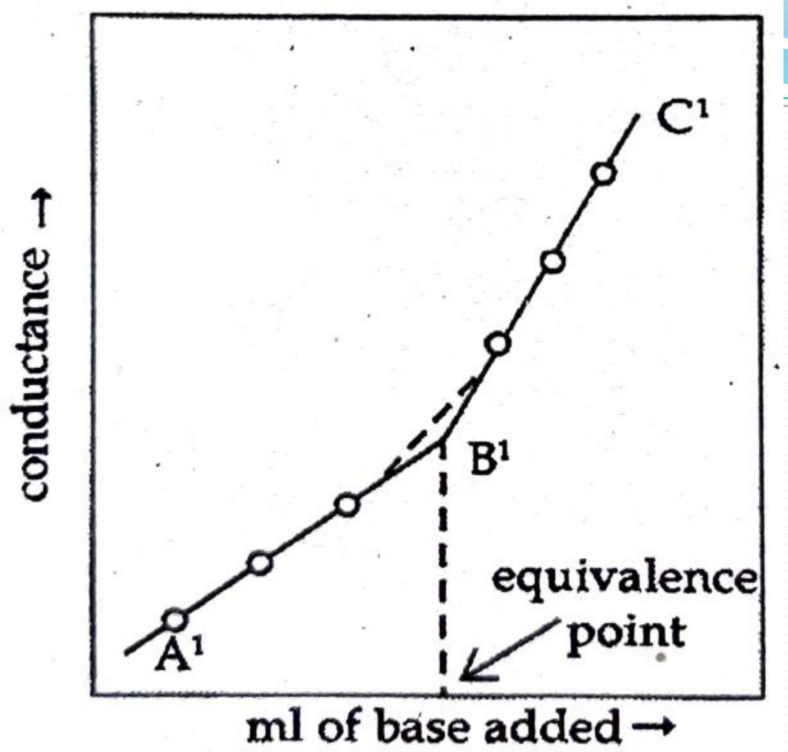

Figure 4.Graph of conductance Vs. ml of NaOH added

If the graph of conductance against ml of NaOH added is plotted then the point of intersection between two lines gives the equivalence point of the titration.

Advantages of conductometric titrations: -

1) Coloured solutions can not be titrated volumetrically, but they can be carried out conductometrically.
2) The titration between very weak acids and bases are not possible volumetrically, because, there is no suitable indicator available. But, it is carried out conductometrically.
3) Mixture of strong and weak acids can be readily titrated by this technique, which is very difficult by usual methods.
4) Conductometric titrations are useful in case of very dilute solutions.
5) Accurate results are obtained graphically.

Problem:-1) Equivalence conductance of 1M solution of NaCl is 98.2 at 25^0c, calculate the degree of ionization of NaCl at this dilution. (Given: Equi. conductance at infinite dilution of NaCl at 25^0c is 131).

Ans:- Given:- Eq. Conductance = Λ = 98.2

And Eq. Conductance at infinite dilution = Λ_0 = 131

We know, the degree of ionization = $\alpha = \dfrac{\Lambda}{\Lambda_0}$

$$= \frac{98.2}{131} = 0.749.$$

Hence, in 1M solution, NaCl ionized = 74.9%

2) For a saturated solution of AgCl at 25^0c, sp. conductance was 3.41×10^{-6} $ohm^{-1}.cm^{-1}$, the sp. conductance of water used to prepare the solution was 1.60×10^{-6} $ohm^{-1}.cm^{-1}$. Determine solubility of AgCl in water in moles/lit. at 25^0c. (Given: Λ_0 for AgCl =

= 138.3 $ohm^{-1}.cm^{-1}$).

Ans:- Given: L_s AgCl (Sat'd soln.) = 3.41×10^{-6} $ohm^{-1}.cm^{-1}$

L_s (H_2O) = 1.60×10^{-6} $ohm^{-1}.cm^{-1}$

Solubility = S = Conc. = C

L_s AgCl (Salt) = L_s AgCl (Sat'd soln.) - L_s (H_2O)

= $3.41\times10^{-6} - 1.60X10^{-6}$

= $1.81\times10^{-6} ohm^{-1}.cm^{-1}$.

Now, we know, Equi. Conductance = Λ = $\frac{1000 \times \text{sp. conductance of AgCl salt}}{\text{Conc.}}$

$$C = \frac{1000 \times Ls(\text{AgCl salt})}{\Lambda}$$

$$S = \frac{1000 \times Ls(AgCl\ salt)}{\Lambda_0} = \frac{1000 \times 1.81 \times 10^{-6}}{138.3}$$

$= 1.308 \times 10^{-5}$ moles/lit.

3) At 18^0c, the equi. conductance at infinite dilution of NH_4Cl, NaOH and NaCl are 129.8, 217.4 and 108.9 $ohm^{-1}.cm^2$. Calculate equi. conductance at infinite dilution of NH_4OH. If equi. conductance of 0.01 N solution of NH_4OH at 18^0c is 9.33, then calculate the degree of ionization of NH_4OH at this conc.?

Ans: - Given: $\Lambda_0 (NH_4Cl) = 129.8$, $\Lambda_0 (NaOH) = 217.4$, $\Lambda_0 = (NaCl) = 108.9$

$\Lambda_0 (NH_4OH) =?$ $\Lambda = 9.33$, $\alpha =?$

From Kohlrausch’s law,

$$\Lambda_0 (NH_4OH) = \Lambda_0 (NH_4Cl) + \Lambda_0 (NaOH) - \Lambda_0\ NaCl$$

$$= 129.8 + 217.4 – 108.9 = 238.3$$

Now, degree of ionization of NH_4OH = $= \alpha = \frac{\Lambda}{\Lambda_0} = \frac{9.33}{238.3} = 0.0322.$

4) The sp. Conductivities of a saturated solution of AgCl and water at 25^0c are 3.41×10^{-6} and 1.60×10^{-6} $ohm^{-1}.cm^{-1}$ respectively. If equivalent ionic conductances at infinite dilution of Ag^+ and Cl^- ions are 61.92 and 76.34 $ohm^{-1}.cm^2$ at 25^0c, calculate the solubility of AgCl.

Ans: - Given: L_s AgCl (Sat'd soln.) = 3.41×10^{-6} $ohm^{-1}.cm^{-1}$

L_s (H_2O) = 1.60×10^{-6} $ohm^{-1}.cm^{-1}$

l_0 Ag^+ = 61.92, l_0 Cl^- = 76.34 $ohm^{-1}.cm^2$

S =?

L_s AgCl (Salt) = L_s AgCl (Sat'd soln.) - L_s (H_2O)

$= 3.41\times10^{-6} - 1.60\times10^{-6}$

$= 1.81\times10^{-6}$ $ohm^{-1}.cm^{-1.}$

Now, calculate $\mathbf{\Lambda_0}$ AgCl = $l_0\,Ag^+ + l_0\,Cl^-$

$= 61.92 + 76.34 = 138.26$ $ohm^{-1}.cm^2$

To, calculate, Solubility, we know, C

$$C = \frac{1000 \times Ls(\text{AgCl salt})}{\Lambda}$$

$$S = \frac{1000 \times Ls(\text{AgCl salt})}{\Lambda_0} = \frac{1000 \times 1.81 \times 10^{-6}}{138.3} = 1.308 \times 10^{-5} \text{ gmequi./lit.}$$

5) The sp. Conductance of saturated solution of AgBr and water are 4.1×10^{-6} and 1.60×10^{-6} mhos.cm^{-1} respectively at 25^0c. If the ionic conductivities of Ag^+ and Br^- ions are 56.90 and 68.90 mhos.cm^2.equi.$^{-1}$ resply then, calculate the solubility of AgBr in water.

Ans: - Given: L_s AgBr (Sat'd soln.) = 4.1×10^{-6} ohm^{-1}.cm^{-1}

L_s (H_2O) = 1.60×10^{-6} ohm^{-1}.cm^{-1}

l_0 Ag^+ = 56.90, l_0 Br^- = 68.90 ohm^{-1}.cm^2

S =?

L_s AgBr (Salt) = L_s AgBr (Sat'd soln.) - L_s (H_2O)

$= 4.1 \times 10^{-6} - 1.60 \times 10^{-6}$

$= 2.5 \times 10^{-6}$ ohm^{-1}.cm$^{-1.}$

Now, calculate Λ_0 AgBr = l_0 Ag$^+$ + l_0 Br$^-$

$$= 56.90 + 68.90 = 125.80 \text{ ohm}^{-1}.\text{cm}^2$$

To, calculate, Solubility, we know, $C = \dfrac{1000 \times Ls(\text{AgBr salt})}{\Lambda}$

$$S = \frac{1000 \times Ls(\text{AgBr salt})}{\Lambda_0 \text{ of salt}}$$

$$= \frac{1000 \times 2.5 \times 10^{-6}}{125.80}$$

$$= 19.87 \times 10^{-6} \text{ gmequi./lit.}$$

Thank You.