UNIT-I: ELECTROCHEMISTRY (11)

Reference books:

1. Engineering chemistry by PC Jain & M Jain

2. Engineering chemistry by Sashi Chawla

3. Engineering chemistry by OG Palanna

Introduction, conductance, types of conductance- specific, equivalent, molar conductance and their interrelationship- numericals.

Principle and applications of conductometric titrations-

strong acid *vs* strong base,

weak acid *vs* strong base and

mixture of acids *vs* strong base.

UNIT-I: ELECTROCHEMISTRY.

Electrochemistry is a branch of physical chemistry which mainly deals with the relation between electrical energy and chemical energy or vice versa.

Conductance: it is the ability or capacity of a substance to allow the current.

Based on the conductance property substances can be classified as

1. Conductors   2. Insulators   3. Semiconductors 4. Superconductors.

Types of conductors:

Conductors can be further classified in to two types based on physical state and charge carriers they are

| Electronic conductors	Electrolytic conductors
1. These are solids	1. These are liquids or solutions
2. charge carriers are valance electrons	2. Charge carriers are mobile ions
3. There is no chemical change	3. There is chemical change
4. as the temperature increases conductance decreases	4. As the temperature increases conductance increases and viscosity decreases

<u>**Types of conductance:**</u>

Specific conductance:

Definition: Conductance offered by 1 c.c of an electrolyte solution.

Units: **Seimen per centimeter (S / c.m.)**

Resistance R, is proportional to the distance between the electrodes l, and is inversely proportional to the cross-sectional area of the electrodes A
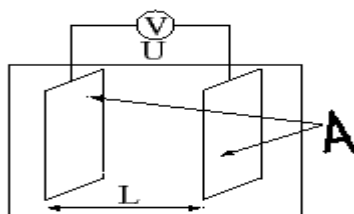
$$R = \frac{l}{A}\rho.$$

The specific conductance, κ (kappa) is the reciprocal of the specific resistance. (ρ (rho) for the specific resistance (or resistivity)

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

Conductivity is also temperature-dependent. The ratio of l and A is known as the cell constant, denoted as G^*, and conductance is denoted as G. Then the specific conductance κ (kappa), can be more conveniently written as

$$\kappa = G^* \times G$$

Molar conductance:

The specific conductance of a solution containing one electrolyte depends on the concentration of the electrolyte. Therefore, the specific conductance devided by concentration. This quotient, termed molar conductivity, is denoted by Λ_m

The molar conductance is the product of specific conductivity and the volume V of the solution containing one mole of the electrolyte. or

The conductance of a solution containing 1 gm molecular weight of the electrolyte when placed between two sufficiently large electrodes one unit apart.

$$\lambda_m = \frac{k \times 1000}{M}$$

Where k is in S cm^{-1} and molarity in mol/L

In SI units: Λ_m (S m^2 mol^{-1}) = k (S m^{-1})/C (mole/m^{-3})

When Concentration is taken in mol/L: Λ_m (S m^2 mol^{-1}) = k (S m^{-1})/1000 M (mol/L)

Molar conductivity SI unit: **S m^2 mol^{-1}.** Older publications use the unit Ω^{-1} cm^2 mol^{-1}.

Equivalent conductance: when quantity of electrolyte is taken as gram equivalents then concentration is expressed as gram equivalent per unit volume.

The conductance offered by all the ions produced by one gram equivalent of an electrolyte is known as Equivalent conductance.

$$\Lambda_{eq} = kV \qquad \text{or} \qquad \lambda_{eq} = \frac{k \times 1000}{N}$$

Thus equivalent conductivity is the product of specific conductivity and the volume V of the solution containing 1 gram, equivalent of the electrolyte.

or

The conductance of solution containing 1 gm equivalent of an electrolyte when placed between two sufficiently large electrodes which are 1 unit, apart

$$A_{eq} = k \ (S \ cm - 1) \ X \ V \ (cm^3)$$

The unit of Λ_{eq} is **Ohm⁻¹ cm² equivalent⁻¹ or S Cm² equivalent⁻¹ or Sm² equivalent⁻¹.**

Numericals:

1. The conductivity of a solution is 0.02 siemen cm⁻¹. Calculate the equivalent and Molecular conductance of N/10 solution of $CuSO_4$. If the electrodes are 8 cm apart and 5.4 cm² in area of cross section.

2. A conductivity cell is filled with 0.2 M solution of KCl at 25 0 C Shows a resistance of 125 ohms. The specific conductance of a solution is 2.77 x10⁻³ s/cm. The same cell containing 0.01M NaCl solution gives a resistance of 388 ohms. Calculate equivalent and Molecular conductance of NaCl.

Principle and applications of conductometric titrations- strong acid *vs* strong base, weak acid *vs* strong base and mixture of acids *vs* strong base.

Conductometer is an instrument used for measuring the conductance of solution. Conductance is the ability of a substance to pass the current through it. And it is reciprocal of resistance.

Conductance of a solution depends on various factors such as

1) nature of electrolyte 2) concentration 3) temperature, etc.

For a specific electrolyte the conductance depends on

1) no. of ions produced (degree of dissociation) 2) mobility of the ions and 3) temperature.

The conductance of one cubic centimeter of the solution is called specific conductance (κ) or conductivity.

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

To measure the conductance of a solution, a conductivity cell is used. It consists of two electrodes i.e. platinum disc or plate coated with finely divided platinum black which increases the surface area of electrode. The electrodes are welded to a platinum wire that is fused to a glass tube so that the distance between the electrodes would not change during the experiment. The cell is open at one end. This cell is dipped in a beaker containing electrolytic solution and the other end is connected to the conductivity-meter.

Cell constant = Distance between the electrodes / cross sectional area of electrodes

Cell constant $= \dfrac{l}{A}$

→ Pt Electrode

Conductivity Cell
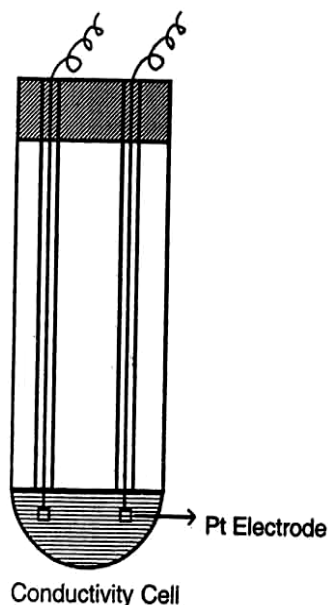
conductometric titrations carriedout at a constatnt temperature. Generally at 25°C.
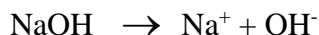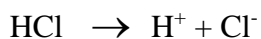
CONDUCTOMETRIC ACID-BASE TITRATION:
1. strong acid *vs* strong base (HCl *vs.* NaOH)
PRINCIPLE :

HCl is completely ionized. The major share of conductance is due to highly mobile H^+ ions and minor share is due to slow moving Cl^- ions. As NaOH is added to HCl, the fast   moving H^+ ions are replaced by slow moving Na^+ ions (since OH^- Ions of the base to form poorly dissociated H_2O with H^+ ions) hence, as the titration proceeds, the conductance of the solution decreases gradually till the equivalence point (HCl is completely neutralized) is reached.

 At equivalence point the conductance will be minimum (not zero) due to the presence of relatively slow moving Na^+ and Cl^- ions only.

Addition of the base beyond the equivalence point results in a steep increase of conductance due to increase in the no. of ions including highly mobile free OH^- ions.

$$HCl \rightarrow H^+ + Cl^-$$
$$NaOH \rightarrow Na^+ + OH^-$$
$$H^+ + Cl^- + Na^+ + OH^- \rightarrow H_2O + NaCl$$
$$H_3O^+ + OH^- \rightarrow 2 H_2O \quad or \quad H^+ + OH^- \rightarrow H_2O$$

**Determination of concentration of given HCl using standardized NaOH solution.**

1. Take 40 mL of the acid in a 100 mL beaker. Place the conductivity cell in solution and measure the initial conductance.
2. NaOH is added from the burette in small lots of 0.5 mL. After each addition of NaOH, the solution is mixed gently with a glass rod and conductance is recorded.
3. At neutralization point the conductance reaches minimum and after that the conductance value increases.
4. After equivalence point, 5 or more readings of conductance should be recorded.

Step III: Determination of strength of given HCl using standardized NaOH solution.

S. No.	Volume of NaOH (mL)	Conductance (mS)
1		
2		
3		
4		

5		
6		

Plot a graph by taking conductance on Y-axis and volume of NaOH on X-axis. Select the straight lines which passes through maximum number of points.The point of intersection of the two lines is the equivalence point of the titration. i.e. exact volume of NaOH consumed for neutralization of HCl taken

E.P. = Equivalence point

$NaOH + HCl \rightarrow NaCl + H_2O$
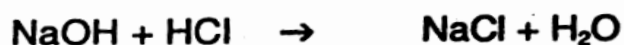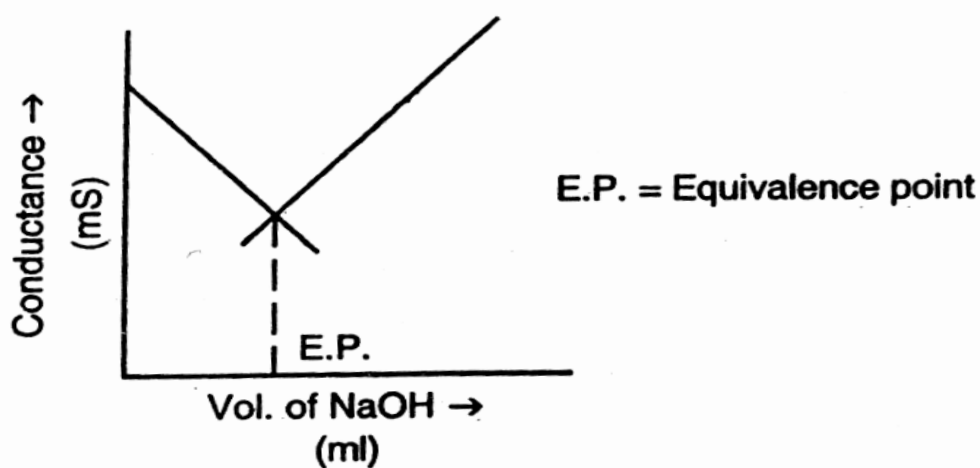
N_2 = Normality of NaOH =   N (from Step-II); N_3 = Normality of HCl =?

V_2 = Volume of NaOH [E.P.] =   mL (from graph) V_3= Volume of HCl = 40 mL

$$N_2 V_2 = N_3 V_3$$

$$N_3 = \frac{N_2 \times V_2}{V_3}$$

N_3 (Test HCl) =

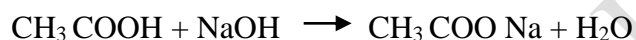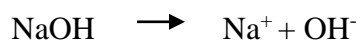N_3 X eq.wt of HCl = Weight of HCl in g/L

Principle and applications of conductometric titration:

2.weak acid *vs* strong base. (CH₃COOH *vs.* NaOH)

PRINCIPLE: The initial conductance of an aqueous solution of acetic acid will be low, due to low degree of dissociation. i.e. due to less number of CH_3COO^- & H^+ ions. As NaOH added, the conductance will increase gradually up to the equivalent point, due to

> a) Increase in dissociation of acetic acid (according to Le Chatelier's principle)

> b) Formation of highly ionized sodium acetate,

After the equivalence point, any further addition of NaOH will produce a more rapid increase in the conductance due to increase in the no. of ions including highly mobile free OH^- ions. The point of intersection of the lines, in the plot of the conductance against the volume of the alkali added is the equivalence point.

$$CH_3\,COOH \rightleftharpoons CH_3\,COO^- + H^+$$

$$NaOH \longrightarrow Na^+ + OH^-$$

$$CH_3\,COOH + NaOH \longrightarrow CH_3\,COO\,Na + H_2O$$

## Determination of concentration of given CH₃COOH using standardized NaOH solution.

1. Take 40 mL of the acid in a 100 mL beaker. Place the conductivity cell in solution and the conductance is measured. Note down the initial conductance.

2. NaOH is added from the burette in small lots of 0.5 mL. After each addition of NaOH, the solution is mixed gently with a glass rod and conductance is recorded.

3. As the addition of NaOH continues the conductance increase gradually till the neutralization is completed. Further addition of NaOH results in rapid increase in conductance. When rapid increase is noticed take 4-5 readings.

4. By plotting the graph between conductance and volume of NaOH, equivalence point is obtained.

Determination of concentration of given CH₃COOH using standardized NaOH solution.

S. No.	Volume of NaOH (mL)	Conductance (mS)
1		
2		
3		
4		
5		
6		
7		

8		
9		
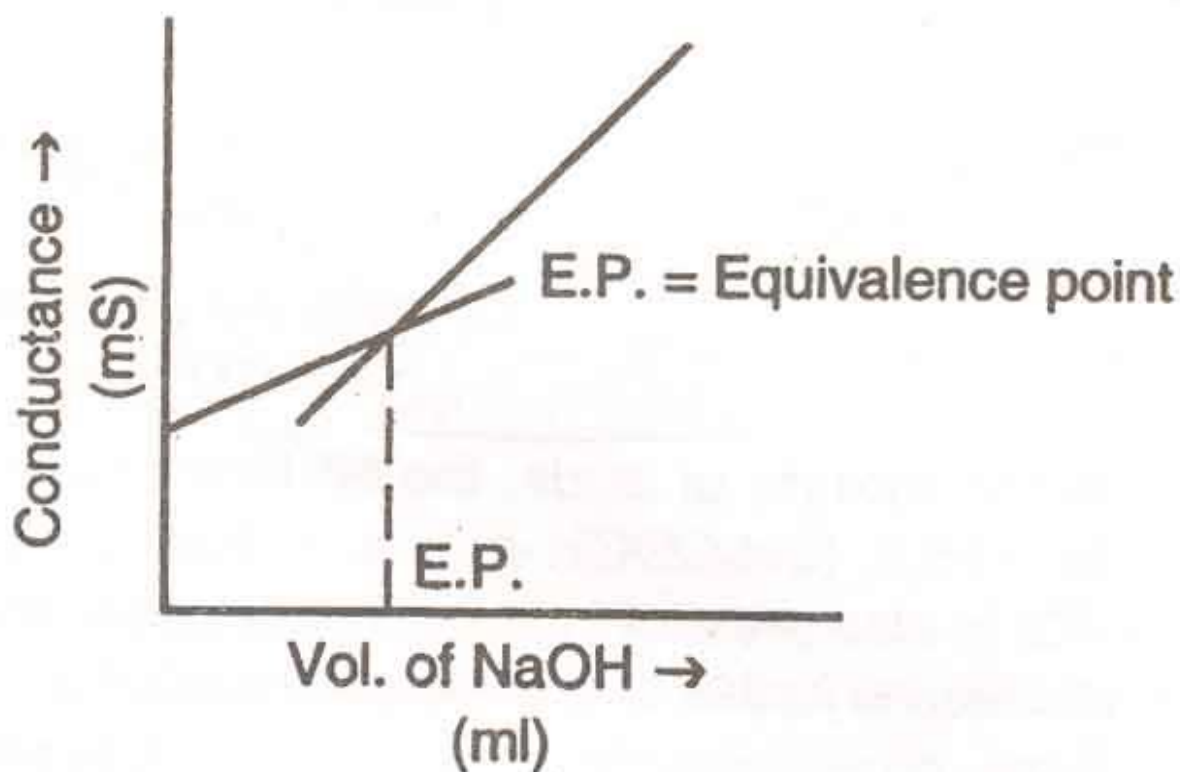
Plot a graph by taking conductance on Y-axis and volume of NaOH on X-axis. Two straight lines are selected, which passes through maximum number of points. The point of intersection of the two lines is the equivalence point of the titration. i.e. exact volume of NaOH required for neutralization of acetic acid taken.

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

N_2 = Normality of NaOH =   (from Step-II) N_3 = Normality of HCl =?

V_2 = Volume of NaOH [E.P.] =   mL (from graph) V_3 = Volume of HCl = 40 mL

$$N_2 V_2 = N_3 V_3$$

$$N_3 = \frac{N_2 \times V_2}{V_3}$$

$$N_3 (CH_3 COOH) =$$

N_3 X eq.wt of **CH₃ COOH** = Weight of **CH₃ COOH** in g/L

Principle and applications of conductometric titration: 3.mixture of acids *vs* strong base.(HCl + CH₃COOH *vs*. NaOH)

PRINCIPLE: In the mixture of acids the initial conductance is almost due to ionized HCl, the H^+ ions concentration is exclusively from HCl. (CH_3COOH itself is a weak acid, i.e. ionizes very less. When HCl is present in the solution, the dissociation of CH_3COOH suppressed further due to the common ion effect and it is almost in unionized form). When the base is added, HCl will react first as indicated by a gradual decrease in conductance. When all the HCl is neutralized, CH_3COOH starts forming salt sodium acetate. Hence the conductance of solution then gradually increases. Beyond the equivalence point with the addition of excess NaOH, conductance will shoot up.

Determination of strengths of given HCl & CH₃COOH using standardized NaOH solution.

1. Take 40 mL of the acid mixture in a 100 mL beaker. Place the conductivity cell in Solution. Note down the initial conductance.

2. NaOH is added from the burette in small lots of 0.5mL. After each addition of NaOH, the solution is mixed gently with a glass rod and conductance is recorded.

3. The conductance decreases and reaches a minimum value at first equivalence point (a). At this point HCl is completely neutralized. Then continue the addition of NaOH, the conductance increases gradually till CH_3COOH is neutralized (b). On further addition of NaOH, conductance increases rapidly.

4. After equivalence point, 5 or more readings of conductance should be recorded.

5. Two equivalence points are noted by plotting the graph between conductance and volume of NaOH.

Determination of strengths of given HCl & CH₃COOH using standardized NaOH solution

S. No.	Volume of NaOH (mL)	Conductance (mS)
1		
2		
3		
4		
5		
6		
7		
8		
9		
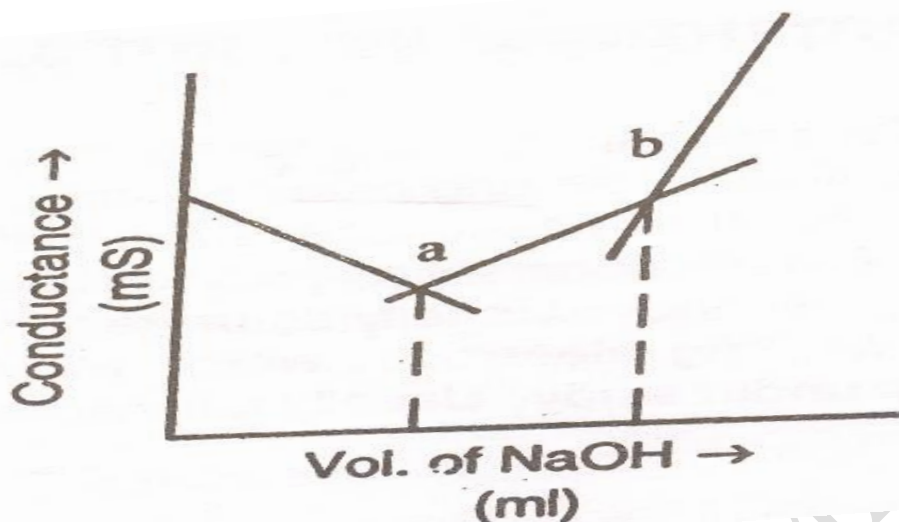
Conductance is plotted against the volume of the alkali added. Two equivalence points are obtained. E.P. a is volume of NaOH consumed for neutralization of HCl only, b is volume of NaOH consumed for neutralization of HCl & CH_3COOH.

E.P. b – a is volume of NaOH consumed for neutralization of CH_3COOH only.

A). **Calculation of HCl conc.:**

$$NaOH + HCl \rightarrow NaCl + H_2O$$

Standardized NaOH   **HCl**

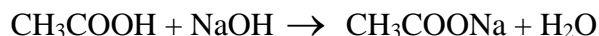N_2 = Normality of NaOH = (from step-II) N_3 = Normality of HCl in the given mixture = ?

V_2 = Volume of NaOH (a) =   mL (from graph) V_3 = Volume of mixture = 40 mL

$$N_2 V_2 = N_3 V_3$$

$$N_3 = \frac{N_2 \ x \ V_2}{V_3}$$

$$\mathbf{N_3 \ (HCl)} \quad =$$

B). **CALCULATION OF CH_3 COOH CONC.:**

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

Standardized NaOH   **CH_3 COOH**

N_2 = Normality of NaOH = (from step-II) N_4 = Normality of CH_3 COOH in the given mixture =?

V_2 = Volume of NaOH (b – a) =   mL (from graph) V_4 = Volume of mixture = 40 mL

$$N_2 V_2 = N_4 V_4$$

$$N_4 = \frac{N_2 \ x \ V_2}{V_4}$$

$$\mathbf{N_4 \ (CH_3 \ COOH)} \quad =$$