

UNIT-II: Instrumental methods of analysis

Electrochemistry is the branch of chemistry which deals with the relationship between electrical energy and chemical energy and inter-conversion of one form into another.

Electrochemical cells are devices that can produce electrical energy from chemical energy and chemical energy from electrical energy.

The two types of electrochemical cells are:

1. Galvanic cells: It is a device in which a redox reaction is used to convert chemical energy to electrical energy.
2. Electrolytic cells: It is a device in which electrolysis is carried out using electricity to convert electrical to chemical energy.

Key differences between electrolytic cells and Galvanic cells

The cell reactions of electrolytic cells are non-spontaneous whereas the cell reactions of Galvanic cells are spontaneous. Galvanic cells generate electrical energy from chemical reactions whereas electrolytic cells generate non-spontaneous redox reactions by using electrical energy.

Primary components of electrolytic cells

The three main components of electrolytic cells include the **cathode, the anode, and the electrolyte**. In electrolytic cells **oxidation occurs at the anode and reduction occurs at the cathode**.

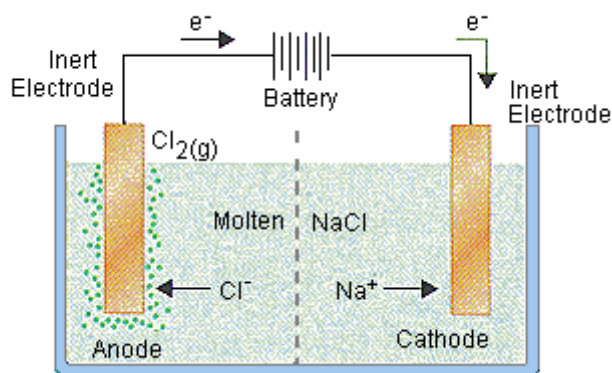


Diagram and Working of an Electrolytic Cell

Principle of Electrolytic Cell

In the above electrolytic cells molten **sodium chloride (NaCl) undergo electrolysis**. Here, two inert electrodes are dipped into molten sodium chloride. When an electric current is passed into the circuit, the cathode becomes rich in electrons and develops a negative charge. The positively charged sodium cations are now attracted towards the negatively charged cathode. This results in the formation of metallic sodium at the cathode.

Simultaneously, the chlorine atoms are attracted to the positively charged anode. This results in the formation of chlorine gas (Cl₂) at the anode.

- **Reaction at Cathode:** $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
- **Reaction at Anode:** $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
- **Cell Reaction:** $2\text{NaCl} \rightarrow 2\text{Na} + \text{Cl}_2$

Thus, molten sodium chloride can be subjected to electrolysis in an electrolytic cell to generate metallic sodium and chlorine gas as the products.

Applications of Electrolytic Cells

- The primary application of electrolytic cells is for the **production of oxygen gas and hydrogen gas from water**.
- They are also used for the **extraction of aluminium from bauxite**.

- Another notable application of electrolytic cells is in **electroplating**, which is the process of forming a thin protective layer of a specific metal on the surface of another metal.
- The **electrorefining** of many non-ferrous metals is done with the help of electrolytic cells.
- It can be noted that the industrial production of high-purity copper, high-purity zinc, and **high-purity aluminium** is almost always done through electrolytic cells.

Galvanic Cell - An electrochemical cell that converts the chemical energy of spontaneous redox reactions into electrical energy is known as a galvanic cell or a voltaic cell. It makes use of chemical reactions to generate electrical energy.

Let us understand how a voltaic or galvanic cell is created.

Example of Galvanic Cell

Daniel's cell is an example of a galvanic cell that converts chemical energy into electrical energy. In Daniel's cell, copper ions are reduced at the cathode while zinc is oxidized at the anode.

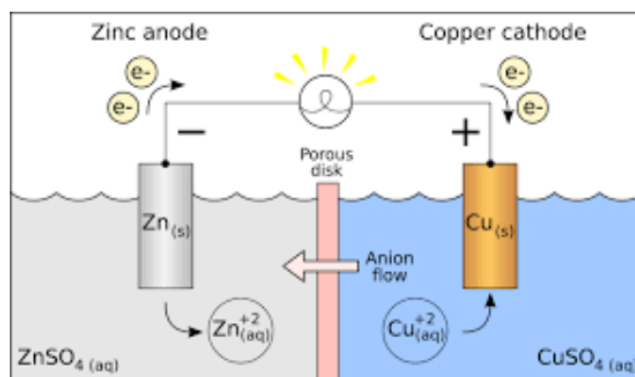
Reactions of Daniel cell at cathode and anode are:

At cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

At anode: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

Principle of Galvanic (Voltaic) Cell

The basic cell or voltaic cell is made up of two electrodes, one of copper and the other of zinc dipped in a glass vessel solution of dilute sulfuric acid. The current flows from copper to zinc outside the cell and from zinc to copper inside the cell when the two electrodes are connected externally with a piece of wire.



Galvanic Cell (Voltaic Cell) Diagram

REPRESENTATION OF CELL:-

Let us illustrate the convention taking the example of Daniel cell.

- Anodic half-cell is written on left and cathodic half-cell on right hand side. $\text{Zn(s)} \mid \text{ZnSO}_4(\text{sol}) \parallel \text{CuSO}_4(\text{sol}) \mid \text{Cu(s)}$
- Two half cells are separated by double vertical lines: Double vertical lines indicate salt bridge or any type of porous partition.
 $\text{Zn} \mid \text{ZnSO}_4(\text{aq.}) \parallel \text{CuSO}_4(\text{aq.}) \mid \text{Cu}$
- Single vertical lines indicate the phase separation between electrode and electrolyte solution.
 $\text{Zn} \mid \text{Zn}^{2+} \parallel \text{Cu}^{2+} \mid \text{Cu}$

Parts of Galvanic Cell

- **Anode** – Oxidation occurs at this electrode.
- **Cathode** – Reduction occurs at this electrode.
- **Salt bridge** – Contains electrolytes which are required to complete the circuit in a galvanic cell.

- **Half-cells** – reduction and oxidation reactions are separated into compartments.
- **External circuit** – Conducts the flow of electrons between electrodes

Applications of Galvanic cell

In torches, electrical appliances such as cell phones (long-life alkaline batteries), digital cameras (lithium batteries), hearing aids (silver-oxide batteries), digital watches (mercury/silver-oxide batteries), military applications (thermal batteries)

EMF of a Galvanic or Electrochemical cell

The difference in potentials of the two half cells is known as electromotive force (emf) of the cell or cell potential. The emf of the cell or cell potential can be calculated from the values of electrode potential of the two half-cells constituting the cell.

The following are the three methods,

1) $E^0_{\text{cell}} = \text{Oxidation potential of anode} + \text{Reduction potential}$

$$\text{of cathode } E^0_{\text{cell}} = E^0_{\text{ox. (anode)}} + E^0_{\text{red. (cathode)}}$$

2) $E^0_{\text{cell}} = \{\text{Standard reduction potential of cathode}\} - \{\text{Standard reduction}$

$$\text{potential of anode}\} E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

3) $E^0_{\text{cell}} = \text{Oxidation potential of anode} + \text{oxidation potential of cathode}$

$$E^0_{\text{cell}} = E^0_{\text{ox. (anode)}} + E^0_{\text{ox. (cathode)}}$$

Nernst Equation for Single Electrode Potential

$$E = E^0 - \frac{2.303RT}{nF} \log_{10} \left[M^{n+}_{(\text{aq})} \right]$$

Application of Nernst equation in electrochemistry:-

1. The potential of an electrode and EMF of a cell can be calculated at any temperature and concentration.
2. If potential of an electrode is known, the concentration of the reactant can be calculated.
3. The concentration of a solution in the galvanic cell can be determined.
4. The pH of a solution can be calculated by measuring the EMF.

Types of Electrodes:-

- 1 Reference electrodes
- 2 Indicator electrode

Reference electrodes are the electrode whose standard potential is exactly known or strength is known. Ideal reference electrodes are:

- 1) It is reversible and obeys the Nernst's equation.
- 2) It exhibits a potential that is constant with time.
- 3) It returns to its original potential after being subjected to small currents.



In general, there are two types of reference electrodes

1. Reference electrode - e.g. Hydrogen electrode
2. Secondary reference electrode – e.g. Calomel electrode, silver-silver chloride electrode, mercury-mercury

sulphate electrode, mercuric oxide electrode, glass electrode, quinhydrone electrode.

Hydrogen electrode- As by using standard hydrogen electrode many difficulties arises such as, Platinum used in it, gets poisoned by absorption of impurities from the solution and the gas, hence it does not behave reversible for longer period.

Because of presence of oxidizing agent, unsaturated organic compounds, alkaloids etc. in solution alters the potential.

1. It cannot be used in presence of Cu, Ag, Au etc.
2. It is difficult to prepare and maintain.

Because of above disadvantages, secondary reference electrode is used which is convenient to handle.

★ Secondary Reference Electrode: Calomel Electrode

Principle:

The potential of the calomel electrode depends upon the concentration of KCl. If KCl solution is saturated, then its potential is 0.2415V and such electrode is called saturated calomel electrode(SCE). If KCl solution is 1N, then its potential is 0.280V and such electrode is called normal calomel electrode(NCE). If KCl solution is 0.1N, then its potential is 0.3338V.

Construction: It consists of an outer glass tube, inside this glass tube there is another tube having mercury at the bottom over which a paste of mercury-mercurous chloride is placed. A solution of potassium chloride (KCl) is then placed over the paste. A platinum wire sealed in the glass tube helps in making electrical contact.

Representation of calomel electrode: - $\text{Hg}|\text{Hg}_2\text{Cl}_2.\text{KCl}(x\text{M})$

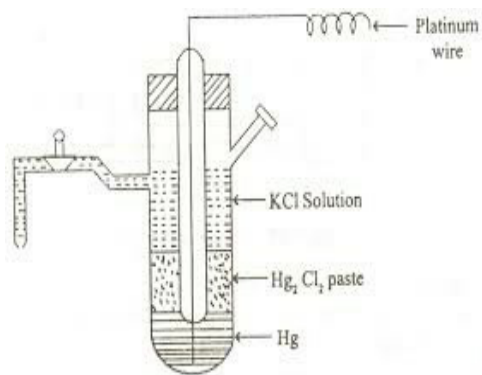


Fig: Calomel

electrode Reactions:- At Anode :- $2\text{Hg} \rightarrow 2\text{Hg}^+ + 2\text{e}^-$

At cathode: - $2\text{Hg}^+ + 2\text{Cl}^- + 2\text{e}^- \rightarrow \text{Hg}_2\text{Cl}_2$



Advantages of Calomel electrode:-

- It is very handy, compact and easy to transport.
- Its potential can remain constant and it can easily be reproduced.
- It is easy to construct and maintain.

It operated at very low temperature i.e. below 800C, because it is disproportionate at very high temperature into mercury and mercuric chloride. The calomel electrode contains mercury, which poses much greater health hazards

Indicator Electrode (Glass Electrode):-

Construction : The glass electrode consists of a very thin walled glass bulb, made from a low melting glass having high electrical conductivity, blown at the end of a glass tube as shown in figure. The bulb contains 1M HCl solution sealed into glass tube is a silver wire coated with silver chloride at its lower end. The lower end of the silver wire dips into the HCl, forming silver-silver chloride electrode.

Working : When glass electrode is placed in a solution the potential develops across the glass membrane as a result of a concentration difference of H^+ ions on the two side of the membrane. The potential of a glass electrode is determined using standard calomel electrode as shown in fig (a) & (b).

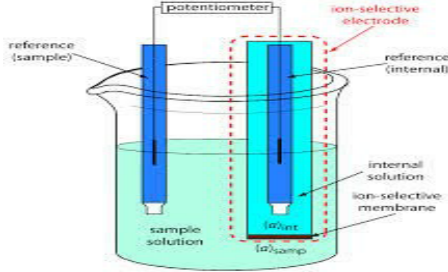


Fig (a): Indicator electrode

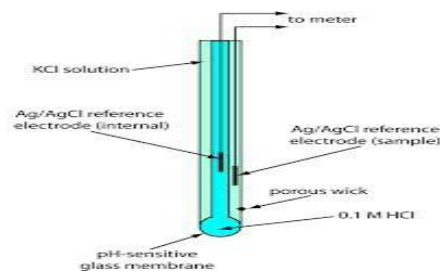


Fig (b): Glass electrode connect calomel electrode

Representation of glass electrode:- $Ag, AgCl | 1M HCl | H^+ (Test Solution)$

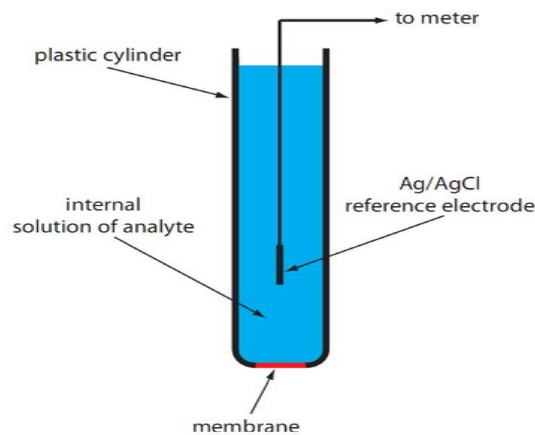
Advantages of glass electrode:-

- 2) It is portable and compact.
- 3) Equilibrium is easily attained.
- 4) It can be used in the presence of biological fluids.
- 5) It is used for determining pH of the solution and estimate H^+ ions in presence of other type of ions.
- 6) It is not used in strongly acidic and alkaline solutions.

Ion selective electrodes

An ion selective electrode measures the potential of a specific ion in solution. It gives potential difference in response to specific ion in solution. The most important feature of an ion selective electrode is the selective membrane that it is made up of.

Principle of I.S.E.- An ideal I.S.E. consists of a thin membrane across which only the intended ion can be transported. • The transport of ions from a high conc. to a low one through a selective binding with some sites within the membrane creates a potential difference.



Construction :

- Made from an ion-conducting membrane (ion-exchange material that allows ions of one electrical charge to pass through)
- Internal Reference electrode
- Internal solution (solution inside electrode) contains ion of interest with constant activity
- Ion of interest is usually mixed with membrane material
- Membrane is nonporous and water insoluble

Types of I.S.E.

1. Glass membrane (i.e. H^+ electrode)
2. Solid-state electrode (e.g. F^- electrode uses a Eu^{2+} -doped LaF_3 crystal)
3. Liquid-based electrode (e.g. Ca^{2+} electrode uses a liquid chelator)

- 4. Compound electro

Advantages and limitations of I.S.E.

Advantages: -

1. Non-contaminating.
2. Short response time: in sec. or min.
3. Useful in industrial applications.
4. Unaffected by color or turbidity.

Limitations:

1. Precision is rarely better than 1%.
2. Electrodes can be disturbed by proteins or other organic solutes.
3. Electrodes are fragile and have limited shelf life.
4. Electrodes respond to the activity of uncomplexed ion.

TYPES OF ION SELECTIVE ELECTRODE (ISE)

• Glass Membrane Electrode • Solid State Electrode • Liquid Membrane Electrode • Gas Sensing Electrode

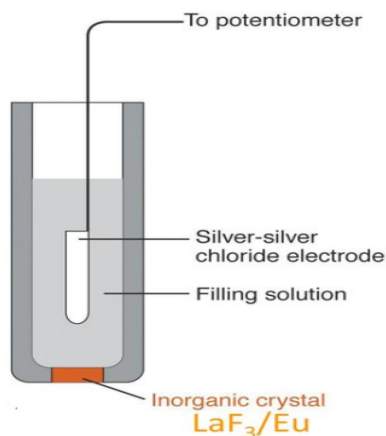
GLASS MEMBRANE ELECTRODE - Glass electrode are responsive to univalent cations (H^+ , Na^+). The selectivity for these cations is by varying the composition of a thin ion sensitive glass membrane. • Example: pH electrode - used for pH measurement –

SOLID STATE ELECTRODE - Solid state electrode are selective to anions. • The membrane is made up of ionic compound (Single Crystal) or homogeneous mixture of ionic compounds (polycrystalline).

FLUORIDE ION SELECTIVE ELECTRODE –

A fluoride ion selective electrode is a type of ion selective electrode sensitive to the concentration of the fluoride ion. The electrode is highly specific to fluoride.

Construction- In the lanthanum fluoride electrode, the sensing element is a crystal of lanthanum fluoride LaF_3 , doped with europium fluoride EuF_2 . Such a crystal is an ionic conductor of fluoride ions. An electrochemical cell may be constructed using such a crystal as a membrane separating two fluoride solutions.

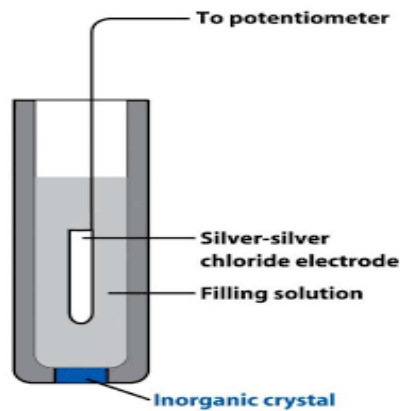


At membrane-solution interface, the following equilibrium takes place:



Formation of LaF^{+2} creates a charge at the surface. The equilibrium will be shifted to the right for the solution with a smaller F^- concentration, and the potential will become more positive relative to the other side of the membrane. It is this potential difference across the LaF_3 crystal membrane that is measured and related to F^- ion concentration. The fluoride electrode is extremely selective for F^- ion.

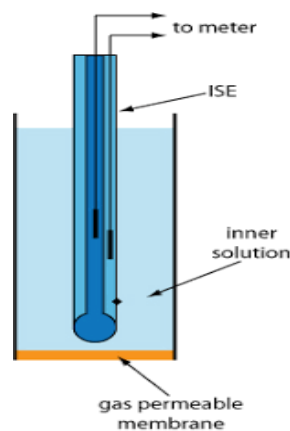
CHLORIDE ELECTRODE



Pellets of Ag_2S and AgCl is used. The electrode is made up of teflon and the pellet is attached using epoxy resin. When electrode membrane is in contact with solution containing chloride ions an electrode potential develops.

GAS SENSING ELECTRODE: It is a one of the type of Ion selective electrode.

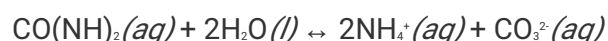
Construction- It has a gas permeable membrane and an internal buffer solution whose pH changes as the gas reacts with it, and this change is detected by a combination pH sensor within the electrode. There are special ISE designed to measure ammonia, carbon dioxide, nitrogen dioxide, and oxygen gases.



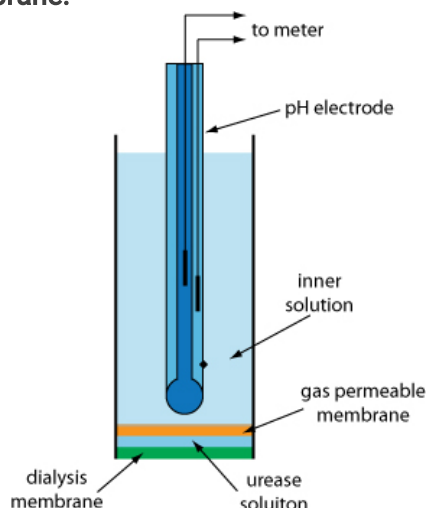
Application - Gas sensing electrode is used to measure gases dissolved in aqueous solution.

ENZYME BASED MEMBRANE ELECTRODES: A gas-sensing electrode can be modified to enzyme based membrane electrodes which can respond to biochemically important species, such as enzymes.

Construction One example of an enzyme electrode is the urea electrode, which is based on the catalytic hydrolysis of urea by urease.



The schematic diagram here shows one version of the urea electrode, which is a modified gas-sensing NH_3 electrode by adding a dialysis membrane that traps a pH 7.0 buffered solution of urease between the dialysis membrane and the gas permeable membrane.



Application – Enzyme based electrode is used to detect enzymes present in solution.

CONDUCTOMETRY

INTRODUCTION

The ability of any ion to transport charge depends on the mobility of the ion, mobility of ion is affected by factors like the charge on ion, size and mass of ion and extent of dilution.

What is a conductive solution? Conductivity is typically measured in aqueous solutions of electrolytes. Electrolytes are substances containing ions, i.e. solutions of ionic salts or of compounds that ionise in solution. The ions formed in solution are responsible for carrying the electric current. Electrolytes include acids, bases and salts and can be either strong or weak.

Strong electrolytes Strong electrolytes are substances that are fully ionised in solution. They include ionic solids and strong acids, for example HCl. Solutions of strong electrolytes conduct electricity because the positive and negative ions can migrate largely independently under the influence of an electric field. **Weak electrolytes** Weak electrolytes are substances that are not fully ionised in solution. For example, acetic acid partially dissociates into acetate ions and hydrogen ions, so that an acetic acid solution contains both molecules and ions. A solution of a weak electrolyte can conduct electricity, but not as strong electrolyte because there are fewer ions to carry the charge from one electrode to the other.

IMPORTANT LAWS, DEFINITIONS AND RELATIONS USED IN CONDUCTOMETRY

Ohm's Law:- "The current passing through a given solution is directly proportional to the potential difference between the two ends of the conductor through which the current is flowing".

$$I \propto E$$

$E = RI$ (Where I = current strength, E =potential difference)

R =Proportionality constant called resistance

i.e. $R = E/I$, Unit of resistance (R)=Volts/ampere, therefore its unit is Ω (ohm).

Conductance (c):- It is the reciprocal of resistance and it is written as,

$$C = 1/R,$$

Therefore the unit of conductance is reciprocal of ohm or mho (ohm^{-1})

Specific resistance (ρ): It is defined as a resistance offered by a cube of unit length of it to the passage of electricity through it.

Mathematically $R \propto l/a$ or $R = \rho \cdot l/a$, As $l = 1\text{cm}$ and $a = 1\text{cm}^2$ then, $R = \rho$

Therefore, $\rho = R \cdot a/l$

$\rho = \text{ohm.cm}^2/\text{cm} = \text{ohm.cm}$ Hence, unit of ρ is ohm.cm

Specific conductance (K): It is defined as the conductance of solution between two parallel electrodes which have cross sectional area 1 cm^2 and which are kept 1 cm apart.

$K = 1/\rho$, as we know $R = l/a$ -----(1)

Taking inverse of equation 1, we

get $1/R = 1/\rho \cdot 1/l/a$ ----- (2),

as $1/\rho = K$ substitute this value in equation 2

$1/R = K \cdot 1/l/a$ or $C = K/l/a$ where C is conductance

Therefore, $K = C \cdot l/a$ ----- (3)

The unit of specific conductance (K) will be

as,

$K = \text{mho} \times \text{cm}/\text{cm}^2 = \text{mho.cm}^{-1}$

Cell constant: - The ratio of (l/a) is called cell constant.

$K = C \cdot (l/a)$

i.e. Specific conductance = Measured conductance(C) x Cell constant (l/a) therefore

cell constant = Specific conductance / Measured conductance

The unit of cell constant is cm^{-1}

Equivalent conductance (λ_v): It is defined as the conductance of a solution containing one gram equivalent of an electrolyte at any particular concentration, when placed between two electrodes 1 cm apart.

Equivalent conductance (λ_v) = Specific conductance (K) x Volume in ml per gm equivalent of the electrolyte

i.e. $\lambda_v = K \times 1000/C$

Therefore unit of $\lambda_v = (\text{ohm}^{-1}.\text{cm}^{-1}) \times \text{cm}^3.\text{gm}^{-1}\text{equiv}^{-1}$

$\lambda_v = \text{ohm}^{-1}.\text{cm}^2.\text{gm}^{-1}\text{equiv}^{-1}$

$\lambda_v = \text{mho.cm}^2.\text{gm}^{-1}\text{equiv}^{-1}$

Molar conductance (μ): It is the conductivity of the solution containing 1 mole of the electrolyte, when placed between two large electrodes 1cm apart.

$\mu = K \times V = K \times 1000/\text{Molarity}$

Therefore unit of $\mu = \text{ohm}^{-1}.\text{cm}^{-1}.\text{cm}^3\text{mol}^{-1}$

$\mu = \text{mho.cm}^2.\text{gmol}^{-1}$

Effect of dilution on conductivity:-

- (i) The conductivity of solution increases on dilution.
- (ii) The specific conductivity decreases on dilution (as number of ions decreases w.r.t. to volume).
- (iii) The equivalent and molar conductivities increase with dilution.
- (iv) The equivalent and molar conductivities tend to acquire maximum value with increasing dilution. [Maximum at dilution]

Effect of temperature on conductivity:-

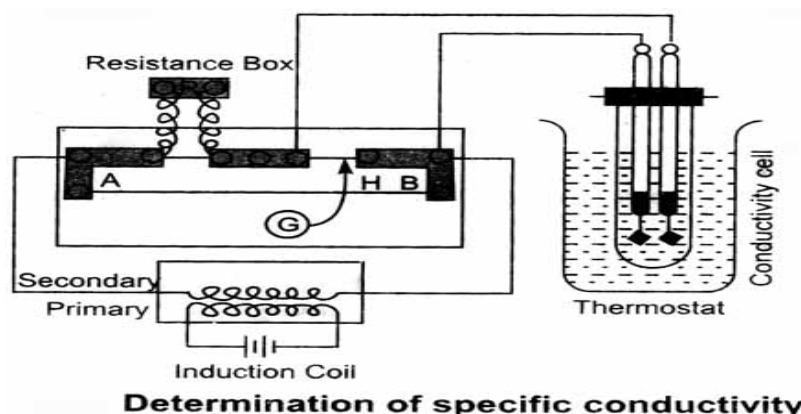
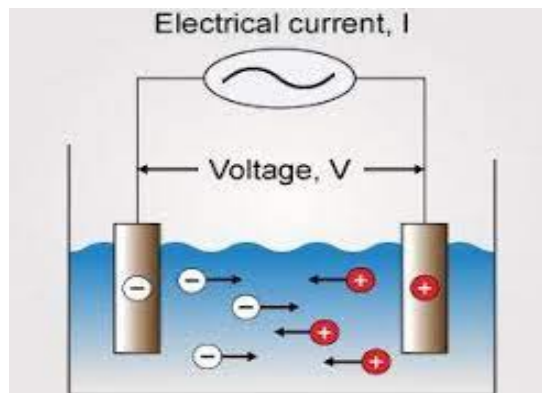
The conductance of the solution increases with increase in temperature due to

1. Increase in the velocity of ions.
2. Decrease in the viscosity of the medium.
3. Decrease in the interaction between the ions.

Determination of conductivity of the solution

Method:

Conductivity may be measured by applying an alternating electrical current (I) to two electrodes immersed in a solution and measuring the resulting voltage (V). During this process, the cations migrate to the negative electrode, the anions to the positive electrode and the solution acts as an electrical conductor.



Determination of specific conductivity:

The cell is connected to resistance box, R on one side and thin uniform wire AB of Meter Bridge. The meter bridge is connected to alternating current. The solution whose resistance is to be measured is placed in conductivity cell and is attached to Wheatstone's bridge. The observed conductivity of solution is then calculated by applying the following formula:

Determination of cell constant

$$\therefore \text{Specific Conductivity} = \frac{\text{Cell constant, } x}{\text{Resistance}}$$

$$\therefore \text{Cell constant, } x = \text{Sp. Conductivity} \times \text{resistance}$$

$$\text{or } x = 0.002765 \times \text{resistance}$$

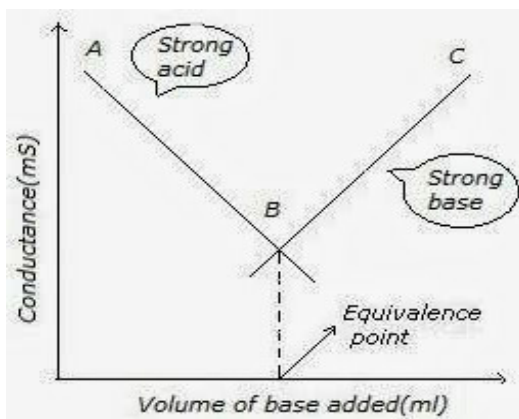
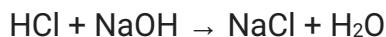
CONDUCTOMETRIC TITRATIONS

The principle involved is that electrical conductance depends upon number and mobility of ions in the solutions.

Types of Conductometric Titrations:

1. Titration of strong acid (HCl) with strong base (NaOH):

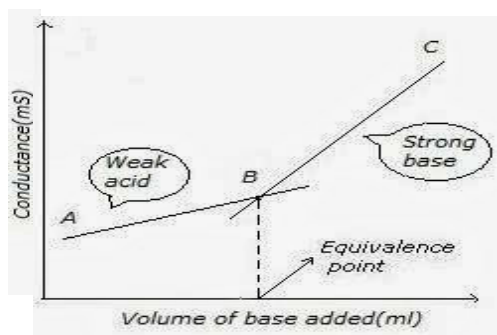
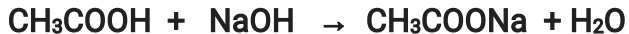
- The conductivity cell is placed in the acid solution HCl taken in the beaker and the alkali NaOH in the burette.
- Initially the conductivity of acid solution is high due to the presence of strong electrolyte due to highly mobile H^+ ions. This is represented by point A on the curve. On gradual addition of NaOH from the burette, highly mobile H^+ ions are removed by the added OH^- ions to form nearly non-conducting water molecules.



- Hence the conductivity of the solution decreases progressively, till the point B is reached. Point B corresponds to the equivalence point where there is no excess of either acid or base and hence.
- On further addition of NaOH, the conductivity of the solution will rise along the curve of BC, due to the addition of strong electrolyte due to highly mobile OH^- ions to the solution.

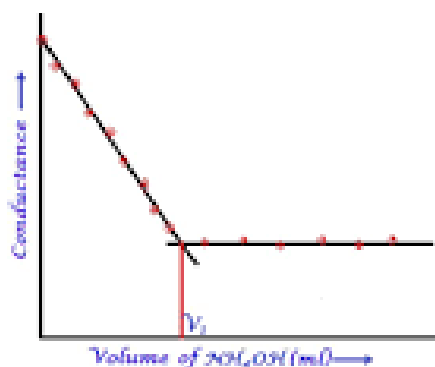
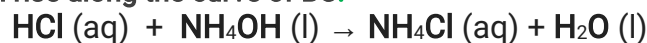
2. Titration of a weak acid (CH_3COOH) with strong base (NaOH) :

- The conductivity cell is placed in the acid solution (CH_3COOH) taken in the beaker and the alkali NaOH in the burette.
- Initially the conductivity of acid solution is low due to the presence of weak electrolyte. This is represented by point A on the curve. Acetic acid is a weak electrolyte has low conductivity. Point B corresponds to the equivalence point.
- On gradual addition of NaOH strong electrolyte from the burette, acid gets neutralized and the poorly conducting acid is converted into highly ionized salt, CH_3COONa and gradually the conductivity will rise along the curve of BC.



3. Titration of strong acid with a weak base, e.g. HCl Vs NH₄OH

- The conductivity cell is placed in the acid solution HCl taken in the beaker and the alkali NH₄OH in the burette.
- Initially the conductivity of acid solution is high due to the presence of strong electrolyte due to highly mobile H⁺ ions. This is represented by point A on the curve.
- Initially the conductance is high and then it decreases due to the replacement of hydrogen ions. But after the endpoint has been reached the graph gradually decreases and becomes almost horizontal due to the presence of unionized salt of ammonium chloride
- On gradual addition of NH₄OH weak electrolyte from the burette, acid gets neutralized and the poorly conducting acid is converted into highly ionized salt, CH₃COONa and gradually the conductivity will rise along the curve of BC.



Q - Explain titration weak acid with a weak base.

Advantage of conductometric titrations:-

- This method can be used with very diluted solutions
- This method can be used with colored or turbid solutions in which end point cannot be visible.
- This method can be used in which there is no suitable indicator is found to work satisfactorily can be successfully titrated by this method.
- It has many applications, i.e. it can be used for weak acid and weak bases, redox, precipitation, or complex titrations.
- More accurate results are obtained because the end point is determined graphically.