

Module-4: Electrode System and Electrochemical Sensors

Electrode System: Introduction, types of electrodes, overview of Nernst equation, reference electrode-construction, working and applications of calomel electrode. Ion selective electrode-definition, construction, working of glass electrode, determination of pH using glass electrode. Construction and working of concentration cell and numerical.

Sensing Methods: Introduction, principle and instrumentation of colorimetric sensors; its application in the estimation of copper in PCBs. Principle and instrumentation of potentiometric sensors and its application in the estimation of iron in steel, conductometric sensors; its application in the estimation of acid mixture in the sample.

ELECTRODE SYSTEM

INTRODUCTION

Electrochemistry is a branch of chemistry that deals with the relationship between chemical energy and electrical energy and their inter conversions by means of redox reaction.

Some basic concepts of electrochemistry

1. **Electrochemical cell:** An electrochemical cell is a device that uses chemical reactions to either produce electricity from chemical energy or use electrical energy to drive chemical reactions. It consists of at least two electrodes (anode and cathode) in an electrolyte solution, facilitating redox (reduction-oxidation) reactions, and can be broadly classified into galvanic cells (which produce electricity) and electrolytic cells (which use electricity to cause reactions).
2. **Electrode:** Electrodes can be defined as conductors that are used to make electrical contact with a non-metallic part of the circuit (an electrolyte).
3. **Anode:** An anode is an electrode in electrical equipment that conducts electricity and it is where oxidation reactions occur. In galvanic cell anode is positively charged.
4. **Cathode:** Cathode is an electrode in electrical equipment that conducts electricity and it is where reduction reactions occur. In galvanic cell cathode is negatively charged.
5. **Oxidation:** The process by which a species loses electrons.

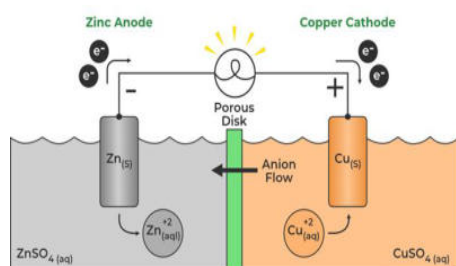
7. **Reduction:** The process by which a species gains electrons.
8. **Electrode potential:** The tendency of a metal to get oxidized or reduced when it is placed in a solution of its salt. When a metal [M] is placed in a solution containing its own ions [M^{n+}], then the metal may undergo either oxidation or reduction.
9. If the metal undergoes oxidation, then the positive metal ions may pass into the solution.



10. If the metal undergoes reduction, then the negative ions may get deposited over the metal.



11. **Electrolyte:** This is the material which provides ionic conductivity between positive and negative electrodes of the cell.
12. **Cell potential:** Cell Potential is the difference in electrical potential between an electrochemical cell's two electrodes.



$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

where,

E_{cell} is the Overall Potential of the Electrochemical Cell,
 E_{cathode} is the Reduction Potential of the Cathode Half-Cell
 (Half-Cell Where Reduction Occurs)
 E_{anode} is the Oxidation Potential of the Anode Half-Cell
 (Half-Cell Where Oxidation Occurs)

Overview of Nernst equation

The Nernst equation is used in electrochemistry to calculate the electrode potential of a half-cell or an electrochemical cell under non-standard conditions (that is, when concentration, pressure, or temperature are not at standard values). It shows how the voltage (potential) of a cell changes with concentration of ions involved in the reaction. General form Nernst equation is

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

Where: E = electrode potential under given conditions

E° = standard electrode potential

n = number of electrons transferred

R = gas constant

T = temperature (K)

F= Faraday constant

n= electrons transferred

Q= reaction quotient

Different forms of Nernst equation are

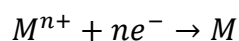
1. Logarithmic form at 298 K

At 25°C (298 K), the equation becomes:

$$E = E^{\circ} - \frac{0.0591}{n} \log Q$$

2. Metal–metal ion electrode form

For a metal electrode:

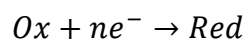


$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

Example: Zn | Zn²⁺

3. Redox electrode form

For a redox couple:



$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[Red]}{[Ox]}$$

Example: Fe³⁺ / Fe²⁺ electrode

5. Cell potential form

For a complete electrochemical cell:

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{n} \log Q$$

Types of electrodes

Electrodes are broadly classified into two types:

1. Reference electrode

Reference electrodes provide a stable and known electrode potential.

They are classified into:

- Primary reference electrode
- Secondary reference electrode (Metal–Insoluble Salt Electrodes)

e.g., SHE, Calomel, Ag-AgCl

2. Working electrode

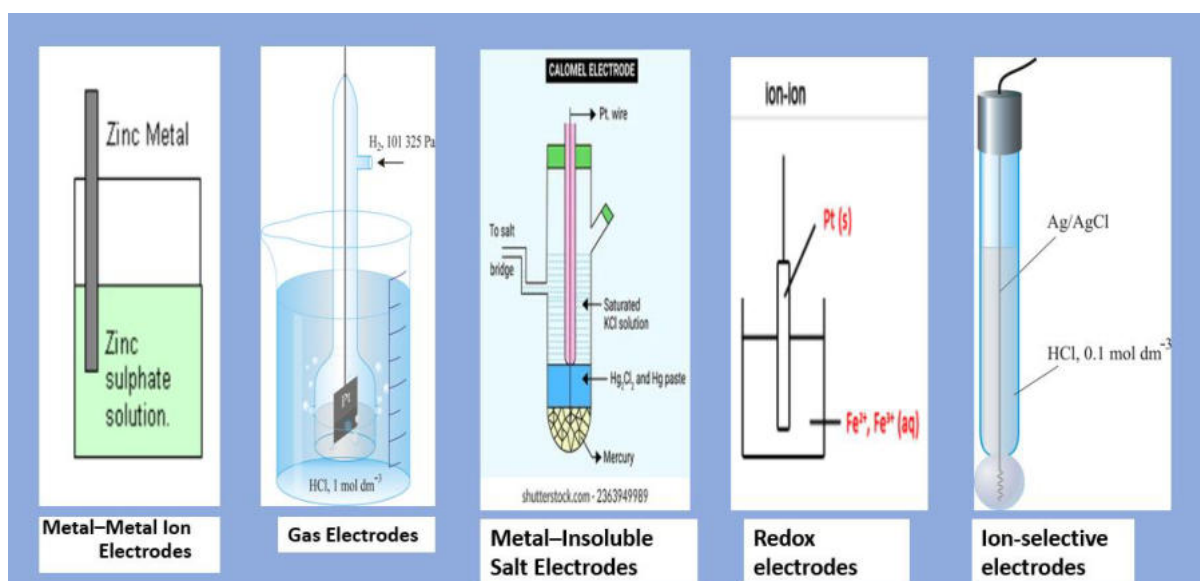
Working electrodes respond to the analyte in an electrochemical system.

Types of working electrodes include:

- Metal–metal ion electrodes
- Gas electrodes
- Redox electrodes
- Ion-selective electrodes (ISEs)

e.g., Platinum, Gold

Type of Electrode	Definition	Reaction	Example
Metal–Metal Ion Electrodes	A metal dipped in a solution containing its own ions.	$M \rightleftharpoons M^{n+} + ne^{-}$	$Cu Cu^{2+} ; Zn Zn^{2+}$ (Indicator electrode)
Gas Electrodes	A gas in contact with a solution containing its ions, with an inert conductor (like platinum) as electrode.	$H_2 \rightleftharpoons 2H^{+} + 2e^{-}$	Standard Hydrogen Electrode (SHE): $Pt H_2 \text{ (gas, 1 atm)} H^{+} \text{ (1 M)}$
Metal–Insoluble Salt Electrodes	A metal coated with a sparingly soluble salt, dipped in a solution containing the anion of the salt.	$Hg_2Cl_2 + 2e^{-} \rightleftharpoons 2Hg + 2Cl^{-}$	Calomel electrode: $Hg Hg_2Cl_2 Cl^{-}$
Redox Electrodes	An inert metal electrode in contact with a solution containing ions of a redox couple.	$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$	$Pt Fe^{2+}, Fe^{3+}$
Ion-selective Electrodes	Special electrodes that respond selectively to the activity (effective concentration) of a specific ion in solution.	$H^{+}(\text{solution}) + Na^{+}(\text{glass}) \rightleftharpoons H^{+}(\text{glass}) + Na^{+}(\text{solution})$	Glass membrane electrode (Glass pH electrode)



Types of reference Electrode

Primary reference electrodes: The electrodes whose potential is arbitrarily taken as zero, for example Hydrogen electrode. It is used to measure potential of all other electrodes.

e.g., Standard Hydrogen Electrode

Secondary reference electrodes: The electrodes whose potential is known w.r.t SHE and it is used to measure potential of other electrodes.

- It is simple to construct.
- The cell potential is reproducible and constant for long period.
- The cell potential does not vary with temperature.

e.g., Calomel, Ag-AgCl electrode etc.

CALOMEL ELECTRODE

Calomel electrode is a type of half-cell in which the electrode is mercury coated with calomel (Hg_2Cl_2) and the electrolyte is a solution of potassium chloride and saturated calomel.

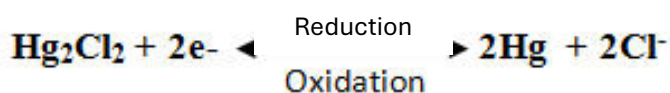
Construction

- Calomel Electrode is a Secondary Reference electrode.
- It consists of a drop of mercury at the bottom, over which a paste of mercury-mercurous chloride is placed.
- A solution of Sat/Std potassium chloride is then filled.
- A platinum wire sealed in a glass tube helps in making the electrical contact.
- The electrode is connected with the help of electrical connection to make a complete cell.

Working: It is a reversible electrode. It undergoes both oxidation and reduction depending upon the other electrode (Half-cell) in contact. If it acts as anode, undergoes oxidation and vice versa.

It is represented as $\text{KCl(satd)} \mid \text{Hg}_2\text{Cl}_2(\text{satd}) \mid \text{Hg}$
Half-cell for Calomel Electrode:

The net reaction involving both anode and cathode is,



$$E = E_{\text{Hg}_2\text{Cl}_2/\text{Hg}}^\circ + 0.0591 \log[\text{Cl}^-]$$

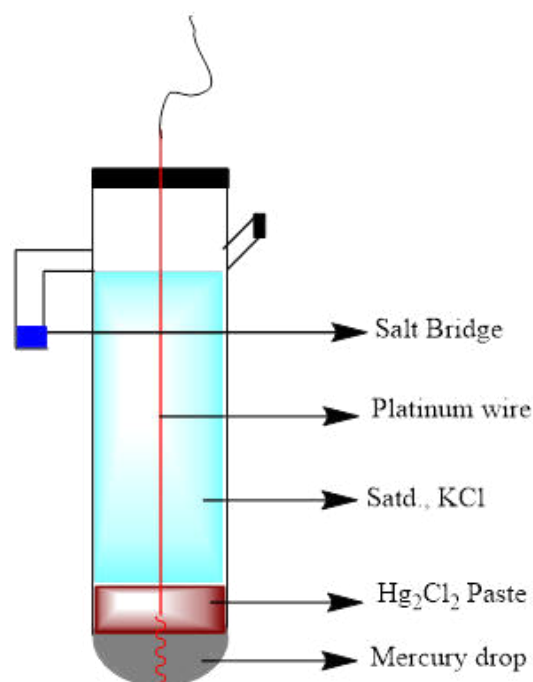


Figure Standard Calomel Electrode

The potential of the calomel electrode depends upon the concentration of the potassium chloride solution. The reduction potentials of the calomel electrodes on hydrogen scale at 298K are as follows:

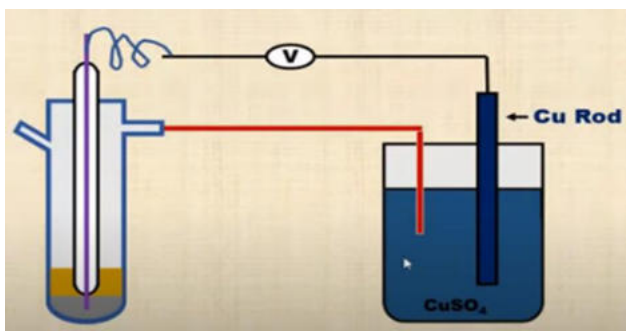
Saturated KCl 0.2415 V, 1.0 N KCl 0.2800 V & 0.1N KCl 0.3338 V.

Advantages:

- Simple to Construct.
- Electrode potential is reproducible and constant for long period.
- Used as reference electrode to measure pH.

Application of calomel electrode in the determination of electrode potential of copper electrode

1. Electrode potential of copper electrode can be determined by combining it with calomel electrode which has known and stable potential.
2. Calomel electrode is taken as anode and copper electrode is taken as cathode and both are connected to voltmeter.
3. According to Nernst equation we know that $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$.
4. As E_{cell} and E_{anode} are known E_{cathode} or potential of copper electrode can be determined.



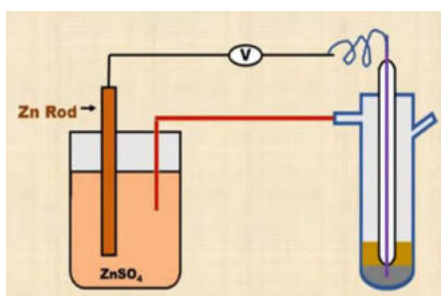
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_{\text{Cu}} - E_{\text{calomel}}$$

$$E_{\text{Cu}} = E_{\text{cell}} + E_{\text{calomel}}$$

Application of calomel electrode in the determination of electrode potential of zinc electrode

1. Electrode potential of copper electrode can be determined by combining it with calomel electrode which has known and stable potential.
2. Calomel electrode is taken as anode and copper electrode is taken as anode and both are connected to voltmeter.
3. According to Nernst equation we know that $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$.
4. As E_{cell} and E_{anode} are known E_{cathode} or potential of copper electrode can be determined.



$$E_{\text{Cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= E_{\text{Calomel}} - E_{\text{Zn}}$$

Or, $E_{\text{Zn}} = E_{\text{Calomel}} - E_{\text{Cell}}$

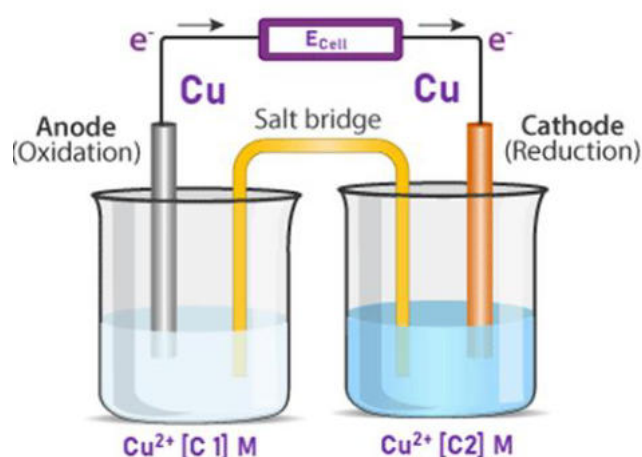
CONCENTRATION CELLS

“Concentration cells are the electrochemical devices in which both the electrodes are made up of same metal and are in contact with their own electrolyte, but of different concentrations”.

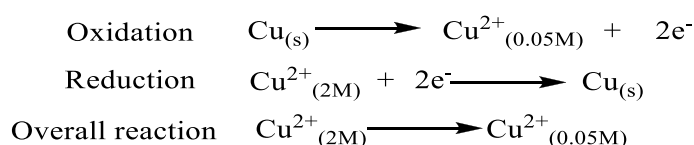
Electrolyte concentration cell (Difference in the concentration of electrolyte):

Example: An electrochemical cell, where two copper electrodes are submerged in two copper (II) sulfate solutions, whose concentrations are C_1 and C_2 , ($C_2 > C_1$) connected through a salt bridge. Le Chatelier's principle indicates that the reaction is more favorable to reduction as the concentration of Cu^{2+} ions increases. Reduction take place in the cell's compartment where concentration is higher and oxidation occur on the more dilute side.

The following cell diagram describes the cell mentioned above:



Where the half-cell reactions for oxidation and reduction are:



Where the cell's emf is calculated through Nernst equation as follows:

$$\begin{aligned} E_{\text{cell}} &= E^0_{\text{cathode}} - E^0_{\text{anode}} \\ E_{\text{cell}} &= \left[E^0_{\frac{\text{Cu}^{n+}}{\text{Cu}}} + \frac{0.0591}{2} \log (C_2) \right] - \left[E^0_{\frac{\text{Cu}^{n+}}{\text{Cu}}} + \frac{0.0591}{2} \log (C_1) \right] \\ E_{\text{cell}} &= \left[\frac{0.0591}{2} \right] [\log (C_2) - \log (C_1)] \end{aligned}$$

E^0 's value of concentration cell is zero, as electrodes and ions are the same.

$$\text{Generally, } E = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Where $C_2 > C_1$

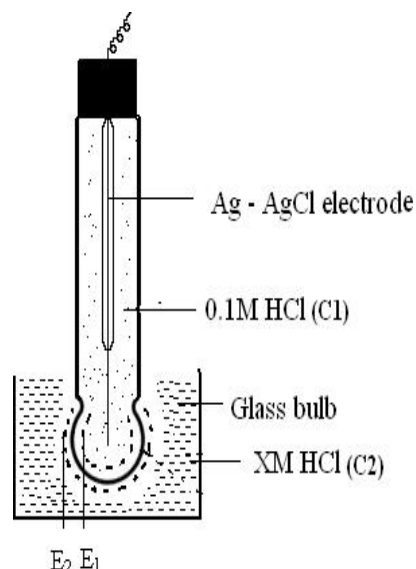
Ion selective electrode (Glass electrode)

1. The electrode which responds to a specific ion in a mixture by ignoring other ions are called as ion selective electrodes.
2. They consist of a thin membrane in contact with ion solution.
3. Potential of that electrode is a function of those ions in the solution.
Example, glass electrode
4. Glass electrode is an ion selective electrode which is sensitive to H^+ ions in the solution and it is used to determine pH of the solutions.

5. Magnitude of potential depends upon difference in pH between two solutions.
6. If pH of one of the solutions is kept constant then glass electrode's potential is a linear function of pH of second solution.

Construction

1. It consists of a long glass tube with a thin-walled glass bulb containing 0.1 M HCl [C_1].
2. The bulb contains 0.1 M HCl and Ag/AgCl electrode (internal reference electrode) is placed in the solution and connected by a platinum wire for external contact.
3. The glass electrode is dipped in unknown solution of concentration C_2 .
4. The potential developed across the membrane due to difference in concentration of H^+ ions across the membrane is known as the boundary potential E_b ($E_2 - E_1$).
5. Even when $C_1 = C_2$, $E \neq 0$ a small potential is developed across the membrane, it is called as asymmetric potential (Easy).
6. The composition of the glass bulb used in glass electrode is Na_2O -22%, CaO -6% and SiO_2 -72%.

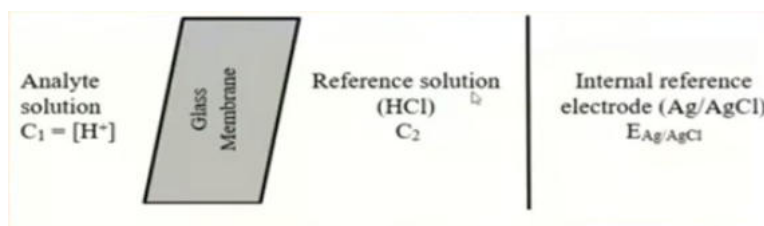


Cell representation: $Ag / AgCl / HCl (0.1M) / \text{unknown solution} / \text{Glass}$

Working of glass electrode

1. When a glass electrode is dipped in analyte solution, a potential develops across the membrane.
2. As the glass bulb filled with HCl having known concentration, pH inside the bulb is constant.

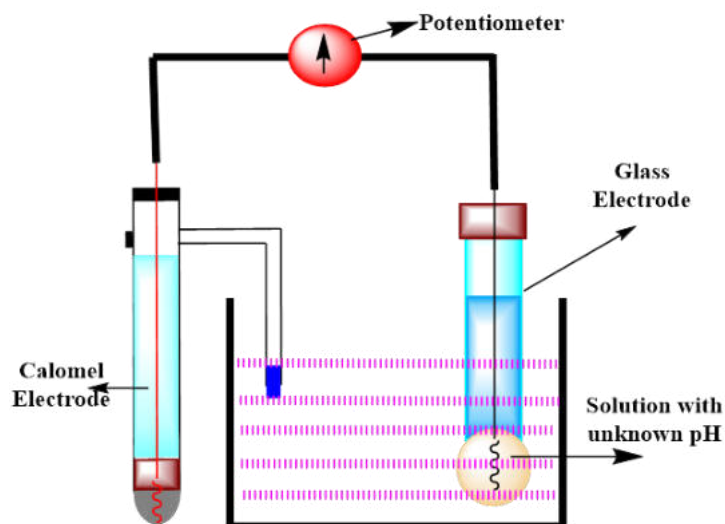
3. When glass electrode is dipped in a solution of unknown pH it can be represented as:



While immersing in analyte solution, the glass membrane exchanges ions with the solution.



Determination of pH of a solution by using glass electrode



The potential of a glass electrode depends on the concentration of H^+ ions. Hence, pH of a solution can be determined by using glass electrode and calomel electrode assembly. The cell assembly is represented as:



The Glass electrode potential is given by

$$E_G = E_b + E_{\text{Ag/AgCl}} + E_{\text{asy}}$$

Where E_b and E_{asy} are boundary potential and asymmetric potential of glass electrode respectively.

E_1 & E_2 is the potential developed at outer and inner membrane respectively. The boundary potential is,

$$E_b = E_2 - E_1$$

$$E_b = E^0 + \frac{0.0591}{n} \log [C2] - \left\{ E^0 + \frac{0.0591}{n} \log [C1] \right\}$$

$$E_b = \frac{0.0591}{n} \log [C2] - \frac{0.0591}{n} \log [C1]$$

$$E_b = \frac{0.0591}{n} \log [C2] + \frac{0.0591}{n} \log \frac{1}{[C1]}$$

Where,

$$L = \frac{0.0591}{n} \log \frac{1}{[C1]}$$

Therefore,

$$E_b = L + \frac{0.0591}{n} \log [C2]$$

Here $n = 1$, $[C2] = [H^+]$ ions in outer membrane. Then

$$E_b = L + 0.0591 \log [H^+]$$

$$E_b = L - 0.0591 \text{ pH} (\text{pH} = -\log [H^+])$$

The glass electrode potential is given by,

$$E_G = E_b + E_{Ag/AgCl} + E_{Asy}$$

Substitute the value of E_b

$$E_G = L - 0.0591 \text{ pH} + E_{Ag/AgCl} + E_{Asy}$$

Consider

$$L_1 = L + E_{Ag/AgCl} + E_{Asy}$$

Therefore,

$$E_G = L_1 - 0.0591 \text{ pH}$$

The emf of a cell is determined by using voltmeter.

E_{cell} is the difference between glass electrode potential E_G and the calomel electrode potential E_{SCE} .

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cell}} = E_G - E_{\text{SCE}}$$

$$E_{\text{cell}} = L_1 - 0.0591 \text{ pH} - E_{\text{SCE}}$$

$$\text{pH} = \frac{K - E_{\text{cell}}}{0.0591} \quad [K = L_1 - E_{\text{SCE}}]$$

Where K = Electrode assembly constant.

SENSING METHODS:

Introduction

Sensors are devices that detect and measure physical or chemical changes in their environment and convert them into electrical or other signals that can be analyzed or used to control a system. They can be classified into various categories based on their operating principles, including optical, thermal, magnetic, electrochemical, and mechanical sensors.

Components of a Sensor System

1. Receptor (Recognition Element)

Description & Function:

The part that selectively interacts with the analyte (the substance being measured). It undergoes a physical or chemical change.

e.g., Glass membrane in a pH electrode interacts with H^+ ions.

2. Transducer

Description & Function:

Converts the chemical or physical change at the receptor into an electrical signal (such as potential difference, current, or resistance).

e.g., Converts change in ion activity $\rightarrow$ voltage signal (as in glass or ion-selective electrodes).

3. Amplifier

Description & Function:

The electrical signal produced is often very weak. The amplifier increases signal strength without changing its nature.

e.g., Operational amplifier (op-amp) in pH meters or biosensors.

4. Processor (Signal Conditioner)

Description & Function:

The signal is then processed, filtered, and converted into a readable form (analog or digital).

e.g., Microcontroller in digital pH meter converts voltage $\rightarrow$ pH value.

5. Output (Display or Recorder)

Description & Function:

Displays or records the final measurement result.

Digital display shows pH, concentration, or potential.

Working Principle

Step 1: The analyte interacts with the recognition element.

Step 2: A chemical change occurs (e.g., ion exchange, redox reaction, adsorption).

Step 3: The transducer converts this change into an electrical signal.

Step 4: The signal is processed and displayed as a measurable output (voltage, current, resistance, etc.)

Optical sensors (Colorimetric sensors)

- The working principle of optical sensors is based on the interaction of light with matter. When light interacts with matter, it can be absorbed, reflected, or transmitted. Optical sensors use these interactions to detect changes in the environment.
- There are several types of optical sensors, including photodetectors, photodiodes, phototransistors, and photovoltaic cells.
- **Example:** Photovoltaic cells are devices that convert light energy into electrical energy.

Theory:

Colorimetry is a quantitative analytical technique used for measuring the transmittance and absorbance of light passing through a liquid sample. The most important idea in colorimetry is that colour intensity is proportional to the concentration.

There are two fundamental laws of absorption which are highly important in colorimetric estimation. These are Lambert's law and Beer's law.

When light falls on a homogenous medium of colored solution, a part of it is reflected, a part is absorbed and rest is transmitted as shown in figure. If I_0 , I_r , I_a and I_t are the intensities of light incident, reflected, absorbed and transmitted. Then,

$$I_0 = I_r + I_a + I_t$$

For air-liquid medium I_r is negligible

$$I_0 = I_a + I_t$$

Thus, Colorimeter is based on Beer-Lambert Law which states that “when a monochromatic light is passed through a colored solution, the absorbance is directly proportional to the concentration of the solution when the path length is kept constant.” which is given by

$$A = \epsilon Ct$$

Where A is absorbance, ϵ is molar absorption constant, C is concentration, t is path length. If the path length is kept constant, then A is proportional to C . The absorbance of the colored solution is measured at a particular wavelength ($\lambda_{\max}$).

Instrumentation:

The instrument is also called as photoelectric colorimeter and is as shown in the figure.

It consists of

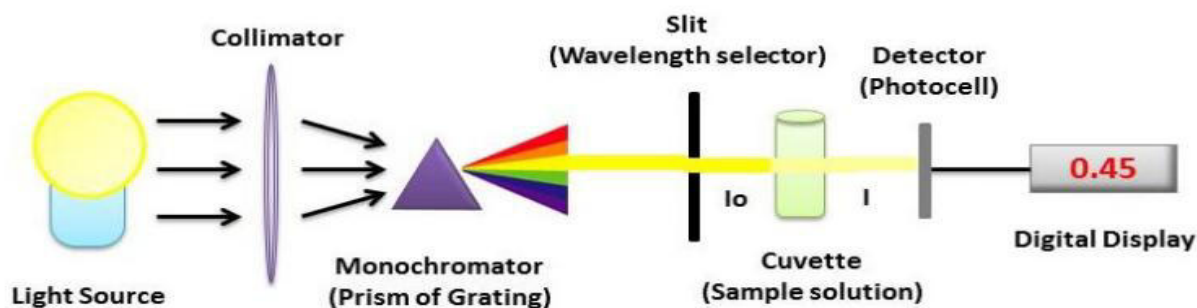
A source Light: Tungsten lamp in the range (400-750nm).

Monochromator: A filter or grating to obtain monochromatic light.

A Sample Cell: To keep sample in the path of light.

A Photo Cell Detector: To detect the light transmitted and converts it into an electrical signal.

A Meter: To read the electrical signal directly as absorbance or transmittance.



Basic Instrumentation of a Spectrophotometer

Working: Light from a tungsten lamp is passed through the monochromator to obtain the radiations of desired wavelength ($\lambda_{\max}$). This monochromatic light is allowed to pass through the colored solution (Analyte) taken in the sample cell, certain amount of light gets absorbed by the chemical species and remaining gets transmitted. The transmitted light is detected by photo cell and converted into electrical signal as absorbance or transmittance.

Application

- Most of the elements in the periodic table can be determined using this technique.
- This method is widely used in industries like Pharmaceutical, Dye etc.

Colorimetric Determination of Copper

Extraction of copper from E-waste

Mechanical Pre-treatment: Shred and separate PCBs to obtain copper-rich fractions.

Leaching: Dissolve copper using acid or alkaline chelating solutions.

Solution Conditioning: Filter and adjust the leachate for metal recovery.

Procedure for determination of Copper

Draw out 10, 15, 20 and 25ml of copper sulphate solution into 5 separate 100ml volumetric flasks. Add 5ml of ammonia solution to each of them and also in to another 100ml volumetric flask containing the test solution of unknown concentration. Dilute the flasks up to the mark and mix well.

Measure the absorbance at 620nm ($\lambda_{\max}$) of each of these solutions against blank solution (only ammonia and water). Plot a graph of volume of copper sulphate and determine the concentration of copper in the test solution.

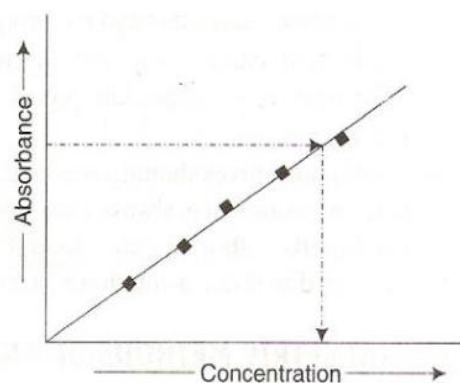


Fig. Calibration curve

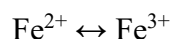
POTENTIOMETRIC SENSORS

Theory:

The principle involved in the potentiometer is when the pair of electrodes is placed in the sample solution it shows the potential difference by the addition of the titrant or by the change in the concentration of the ions. The potential developed depends upon the concentration of the ions, given by Nernst's equation,

$$E = E^0 + \frac{RT}{nF} \ln [M^{n+}]$$

For example, in the redox reaction



The Nernst's equation is given by $E = E^0 + \frac{RT}{nF} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$

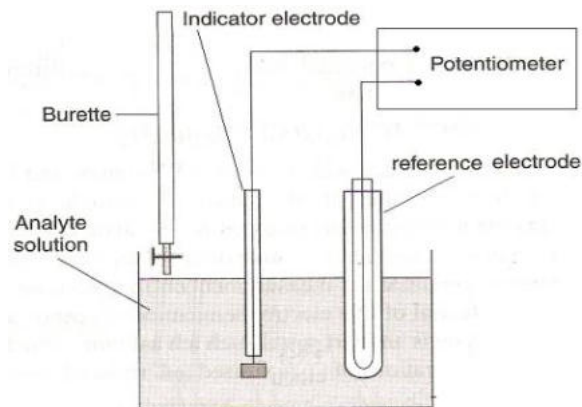
The equivalence point can be determined by using characteristic graph.

Instrumentation:

The basic components of potentiometer are

1. An indicator electrode
2. A reference electrode
3. A salt bridge if necessary
4. A potentiometer to measure the variation of potential.

A typical electrochemical cell for potentiometric studies is constructed by coupling two half cells, one is a reference electrode and the other is indicator electrode. The potential of the analyte solution is observed with the variation of concentration of ions during titration. The variation of concentration of ions can be controlled by adding titrant. Generally saturated calomel electrode is coupled with inert platinum electrode during titration.



Applications

- Determine thermodynamic constants like K_a , K_b etc
- Determine the accurate end point of a titration.
- Measure of pH of a solution.
- Determine Fluoride concentration in a solution or underground water.

Potentiometric Determination of FAS

Procedure: Pipette out 50ml of FAS solution into a 100ml beaker. Add 1 test tube of dilute H_2SO_4 . Immerse calomel electrode and platinum electrode assembly of the potentiometer and measure the potential.

Add potassium dichromate solution from the micro burette in increments of 0.5ml and measure the potential after each addition. Plot a graph of $\Delta E/\Delta V$ against volume of $K_2Cr_2O_7$ as shown in the figure. And calculate the number of FAS in the solution.

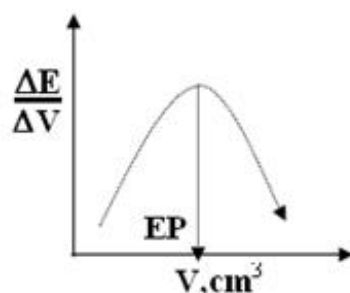


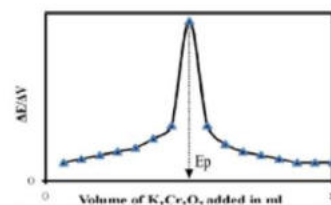
Figure: First Derivative Curve

1.4. Experimental observation

Date: _____

1.6. Demo Graph

Volume of $K_2Cr_2O_7$ solution		Potential		$\frac{\Delta E}{\Delta V}$	Volume of $K_2Cr_2O_7$ solution		Potential		$\frac{\Delta E}{\Delta V}$
Total V	Increment ΔV (cm³)	E (mV)	ΔE (mV)		Total V	Increment ΔV (cm³)	E (mV)	ΔE (mV)	
0	0		---	---	5.5	0.5			
0.5	0.5				6.0	0.5			
1	0.5				6.5	0.5			
1.5	0.5				7.0	0.5			
2.0	0.5				7.5	0.5			
2.5	0.5				8.0	0.5			
3.0	0.5				8.5	0.5			
3.5	0.5				9.0	0.5			
4.0	0.5				9.5	0.5			
4.5	0.5				10.0	0.5			
5.0	0.5				10.5	0.5			



1.5. Experimental calculation

Normality of standard $K_2Cr_2O_7$ solution $N_2 =$ (given)

Vol. of $K_2Cr_2O_7$, $V_2 =$ cm³ (from graph)

Volume of FAS solution taken, $V_1 = 50$ cm³

Normality of FAS solution $N_1 = \frac{N_2 \times V_2}{V_1}$

Weight of FAS per dm³ of diluted FAS solution $= N_1 \times \text{Eq. wt. of FAS}$

$= \dots \times 392 = \dots$ (w)

Weight of FAS in 50 cm³ $= \frac{w \times 50}{1000} = \dots$ g

CONDUCTOMETRIC SENSORS

Theory:

Conductometry deals with the measurement of conductance in a solution. The conductivity of an electrolyte solution depends upon,

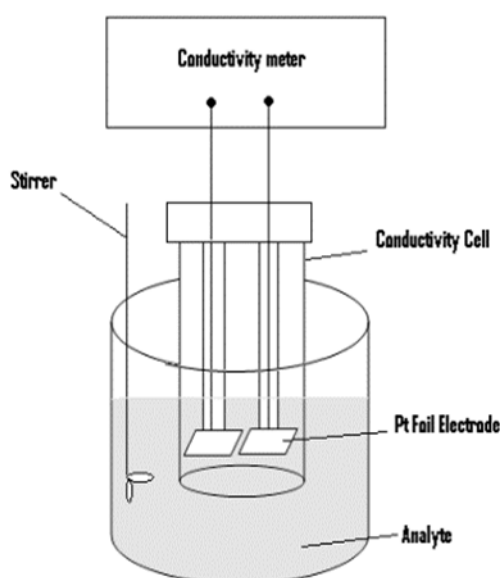
1. Distance b/n the electrodes. (Greater the distance conductivity is lesser)

Number of ions present in the solution. (Higher the concentration high is the conductivity)

2. The mobility of the ions. (Smaller the ion greater is the mobility and hence conductivity).
3. The temperature of the solution. (Higher the temperature, increases the mobility and hence conductivity increases)

Principle: Conductivity of an electrolytic solution depends on the concentration of the ions present when the distance between the electrodes and temperature is kept constant. The conductivity of ionic solutions can be measured by using a conductometer. H^+ ions' being the smallest ions shows the highest conductivity. For the given solution at a given temperature the conductance is directly proportional to the number of ions or concentration of the solution.

Instrumentation: It consists of Conductivity cell which contains two platinized foils placed at 1cm apart is immersed in the sample solution at constant temperature and is connected to a conductivity meter. The conductivity is varied by the addition of titrants.



Application:

- a. Colored solution can be titrated
- b. Accuracy is high compared to conventional method.

- c. It can be used for very weak acids and bases.
- d. Example: Mixture of strong acid and a weak acid with a strong base (HCl+CH₃COOH)

In the titration of acid mixture containing strong and weak acid, the strong acid gets completely neutralized first and then the weak acid neutralization starts. The initial conductivity will be very high due to the presence of small H⁺ ions. On addition of NaOH the conductivity decreases due to the formation of H₂O and NaCl. This decrease in conductance is observed till all the acid is completely neutralized (First equivalence point A). Thereafter the conductivity slowly increases till equivalence point due to the presence of Sodium acetate which is a strong electrolyte (Second Equivalence point B). After the 2nd equivalence point, the NaOH added adds more Na⁺ ions to the solution thereby increasing the conductance rapidly.

