

UNIT - II

ELECTROCHEMICAL SENSORS

2.1 INTRODUCTION

Electrode: An electrode is a metal whose surface serves as the location where oxidation-reduction equilibrium is established between the metal and what is in the solution. The electrode can either be an anode or a cathode.

Types of Electrodes

Electrode is parts of an electrochemical setup where an element is in contact with its own ions at which oxidation or reduction takes place.

1. Metal/Metal ion electrode (M/M^{n+})

When a metal is immersed in its own salt solution, a type of electrode called metal/metal ion electrode is formed. Eg: Zn/Zn^{2+} , Cu/Cu^{2+} .

In general M/M^{n+}

The electrode reaction is $M^{n+} + ne^- \rightarrow M$

2. Gas Electrode

The gas is bubbled around an inert metal like platinum which is immersed in a solution containing ions of the same gas. Eg: Hydrogen electrode or SHE, chlorine electrode.

Electrode potential depends on the logarithmic concentration of the ion and the pressure at which the gas is bubbled.

3. Metal insoluble metal salt/ common ion electrode

The metal (M) is covered with an insoluble metal salt (MX) in contact with a solution containing anions of the insoluble metal salt(X). Eg: Calomel electrode ($Hg/Hg_2Cl_2/Cl^-$), silver-silver chloride electrode ($Ag/AgCl/Cl^-$).

Electrode potential is the logarithmic concentration of the common ion (Cl^-).

4. Redox electrode

In this electrode, an inert metal is immersed in a solution containing ions of the same metal having two different oxidation states. Eg: $Pt/Fe^{2+}/Fe^{3+}$.

Reaction: $Fe^{2+} \rightarrow Fe^{3+} + e^-$.

Electrode potential is the Ratio of logarithmic concentration of all ionic species involved in the redox reaction.

5. Ion selective electrode

In this type, the sensing part of the electrode is usually made of an ion-specific membrane. The membrane can be glass membrane, crystalline membrane and ion-exchange resin membrane. Eg: Glass electrode.

2.2 REFERENCE ELECTRODES

A reference electrode is an electrode which has a stable electrode potential. These electrodes are used to find out the potential of other electrodes.

Reference electrodes are of two types.

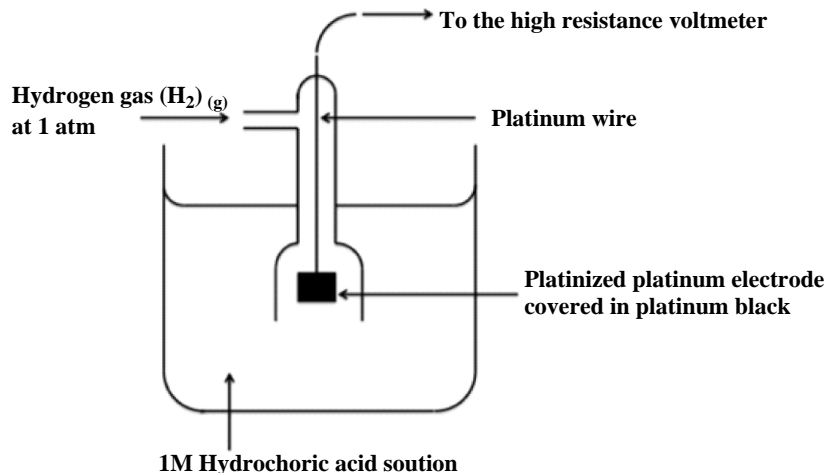
- (i) Primary reference electrode - Standard Hydrogen Electrode (SHE)
- (ii) Secondary reference electrode - Calomel electrode, glass electrode, quinhydrone electrode

2.2.1 PRIMARY REFERENCE ELECTRODE: SATURATED HYDROGEN ELECTRODE (SHE)

The standard hydrogen electrode is a gas electrode, used as the primary reference electrode. The electrode can be represented as $\text{Pt}/\text{H}_2(\text{g})\ 1\ \text{atm}, \text{H}^+(1\text{M})$.

Construction

- It is a primary reference electrode.
- A small Pt plate coated with Pt black is connected to a Pt wire which is sealed in a glass jacket.
- Glass jacket having an inlet for Hydrogen gas at the top and a number of small holes at the bottom for the escape of Hydrogen gas.
- It is dipped in 1M HCl solution at 298 K.



Working

- SHE is a reversible electrode which can act as cathode or anode, depending on the potential of electrode to which it is coupled.
- The electrode potential of hydrogen electrode fixed as zero volt.
- At the cathode, $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_{2(\text{g})}$ (reduction).
- If the potential of a coupled electrode is less than zero (Eg: Zn, Mg).
- At the anode, $\text{H}_{2(\text{g})} \rightarrow 2\text{H}^+ + 2\text{e}^-$ (oxidation).

- If the potential of a coupled electrode is greater than zero (Eg:Cu, Ag).

Representation of electrode:

When acting as an anode, $\text{Pt} | \text{H}_{2(\text{g})} (1 \text{ atm.}) | \text{H}^+_{(\text{aq})} (1 \text{ M})$

When acting as cathode, $\text{H}^+_{(\text{aq})} (1 \text{ M}) | \text{H}_{2(\text{g})} (1 \text{ atm.}) | \text{Pt}$

Limitations

- Generally, impurities in hydrogen and HCl spoil ideal platinum electrodes and reduce the life of standard hydrogen electrodes.
- It cannot be used in presence of strong oxidizing and reducing agents.
- It is expensive due to Pt.
- The Pt surface must be specially prepared and maintained or it is difficult to maintain the Pt surface.

Applications

- Standard hydrogen electrode is used as a primary reference electrode to know the standard electrode potentials (relative) of elements and other electrodes.
- Used in the determination of pH.

2.2.2 SECONDARY REFERENCE ELECTRODE: SATURATED CALOMEL ELECTRODE (SCE)

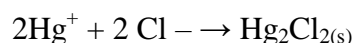
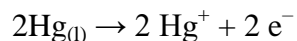
Saturated calomel electrode is a secondary reference electrode.

Construction and Working

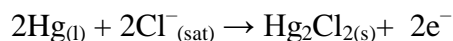
- The calomel electrode consists of a broad glass tube having a sidearm as shown in the figure.
- The sidearm is used for dipping any solution used for coupling the calomel electrode.
- At the bottom of the glass tube, there is pure mercury and a platinum wire is sealed into it at the bottom for electrical connections.
- The wire runs through a separator glass tube to the top of the tube for electrical contact. Above pure mercury, there is a paste of mercurous chloride (calomel) (Hg_2Cl_2) in mercury.
- The rest of the glass vessel and sidearm A is filled with a saturated KCl solution. KCl solutions of 0.1 M or of 1 M can also be used. Sidearm is plugged with glass wool. The glass tube is closed from the top.

Working:

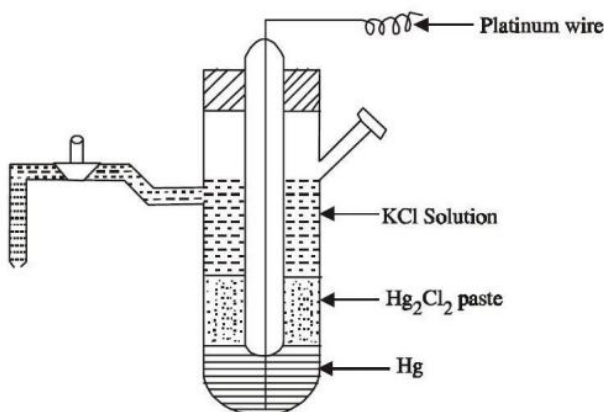
- Since the calomel electrode is reversible, two types of reactions are possible depending upon the nature of another electrode with which it is coupled.
- **When acting as negative electrode:**



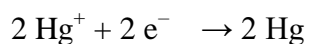
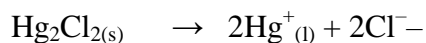
The net oxidation reaction is



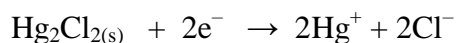
Thus oxidation takes place when it is coupled with other electrodes having lower oxidation potential.



When acting as positive electrode:



The net reduction reaction is



Thus reduction takes place when it is coupled with other electrodes having greater oxidation potential.

Representation of Electrode:

When acting as anode: $\text{Pt} | \text{Hg}_{(l)} | \text{Hg}_2\text{Cl}_{2(s)} | \text{KCl}_{(\text{sat})}$

When acting as cathode: $\text{KCl}_{(\text{sat})} | \text{Hg}_2\text{Cl}_{2(s)} | \text{Hg}_{(l)} | \text{Pt}$

Oxidation Potential of Calomel Electrode:

The oxidation potential of the calomel electrode depends upon the concentration of KCl solution used. The negative potentials indicate that when combined with SHE reduction takes place at the calomel electrode.

Concentration of KCl	Oxidation potential at 298 K
0.1 M or 0.1N	-0.3338 V
1 M or 1N	-0.2800 V
Saturated	-0.2415 V

Advantages of calomel electrode:

- It is easy to set up and easily reproducible.
- It is convenient and easy to transport.
- It is very compact and smaller in size and requires little space.

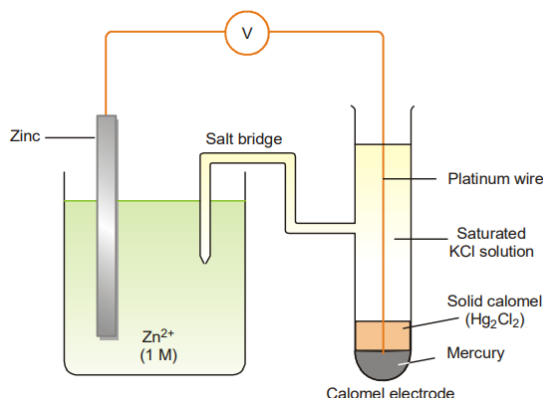
- No separate salt bridge is required as it already has a side tube containing KCl solution.
- Potential does not change appreciably with time and a slight change in temperature.

Disadvantages of Calomel Electrode:

- When half-cell potentials are to be measured, compensation for potential is necessary.
- The calomel electrode cannot be used in the measurement of potentials of the cell where K^+ and Cl^- ions interfere in the electrochemical reactions of the cell.
- The oxidation potential of the electrode depends on the concentration of KCl. If the concentration of KCl changes, the oxidation potential of the electrode changes.
- Calomel electrodes should not be used above $50^\circ C$ because the mercurous chloride breaks down yielding unstable readings.
- Recently, calomel has been disfavored because of its toxicity.

2.3 DETERMINATION OF SINGLE ELECTRODE POTENTIAL (E^0) OF Zn USING CALOMEL ELECTRODE

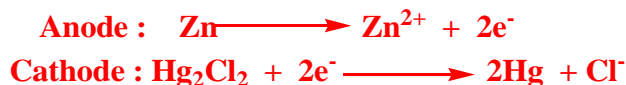
To determine the cell potential of Zn/Zn^{2+} electrode, a cell made of a Zn electrode immersed in 1M $ZnSO_4$ is coupled with a saturated calomel electrode. The E.M.F. of the above cell is 1.0022 V at $25^\circ C$. The direction of flow of current indicates that oxidation takes place at the Zn electrode. Thus the Zn electrode is anode and the calomel electrode is cathode.



The cell may be represented as:



The Zn electrode is coupled with a calomel electrode. Since, the reduction potential of the Zn electrode is less than the E_{cal} ; calomel electrode will act as cathode and the reaction.



$$E_{cell} = E_{right}^0 - E_{left}^0 ; E_{cell} = E_{cal}^0 - E_{Zn}^0$$

$$E_{Zn}^0 = E_{cal}^0 - E_{cell} = +0.2422 - 1.0025 = -0.7603V$$

Thus, the standard electrode potential of Zn is -0.76 V. The reduction reaction is not feasible w.r.t. SCE and hence the electrode acts as anode while SCE acts as cathode.

2.4 ION-SELECTIVE ELECTRODES (ISE)

Ion-selective electrodes are the electrodes having the ability to respond only to particular ions, and develop potential, ignoring the other ions in a mixture totally. The potential developed by an ion-selective electrode depends only on the concentration of particular ions.

An **ion-selective electrode (ISE)**, also known as a **specific ion electrode (SIE)**, is a transducer (or sensor) that converts the change in the concentration of a specific ion dissolved in a solution into an electrical potential.

Ion selective electrode types

The essential part of an ISE is the ion-selective membrane which is commonly placed between the sample and inner solutions that contain an analyte ion. The membrane used in ISE may be a glass, a crystalline solid, or a liquid. Ion selective electrodes are mainly four types according to the nature of membrane material. These are,

- Glass electrodes
- Crystalline electrodes
- Ion exchange electrodes
- Enzyme electrodes

Applications of Ion Selective Electrodes (ISE's)

The ISE can be used in a wide variety of experiments, including the following:

Water hardness (Calcium ISE)

Calcium is very useful as an indicator to detect the hardness of water in fresh water samples. Water hardness is also due to other ions (Mg^{2+} and Fe^{3+}), because calcium normally predominates hardness as Ca^{2+} ion, which is a reliable indicator of water hardness.

Nitrate monitoring (Nitrate ISE)

This ISE can be used to quantitatively determine the concentration of the nitrate ion (NO_3^-) in fresh water samples. This ion may appear in samples due to waste or fertilizer runoff. Increased levels of nitrate may also be present in water samples in waste from plant and animal decay.

Salinity and chloride monitoring in sea water (Chloride ISE)

This ISE can be used to quantitatively determine the concentration of chloride ions (Cl^-) or salinity levels in seawater samples. The wide range of this electrode allows it to measure salinity or chloride concentration of seawater.

Monitoring streams of ammonium (ammonium ISE)

Ammonium (NH_4^+) is often present as a result of water runoff from fertilizer fields. ISE is also used to monitoring the ammonia levels in source waters for intake protection for drinking water treatment plants.

Calcium in milk (Calcium ISE)

This ISE can be used to determine calcium levels in skim milk.

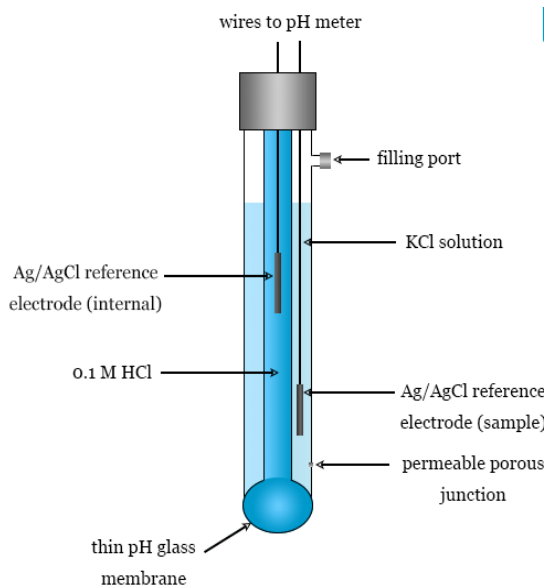
2.4.1. HOW AN ION SELECTIVE ELECTRODE WORKS

- Ion selective electrodes are a membrane-based electrode that measures a specific ion (e.g. Na^+ , Ca^{2+}) in aqueous solutions.
- When the membrane of the electrode is in contact with a solution containing the specific ion, a voltage, dependent on the level of that ion in solution, develops at the membrane.
- All ISEs measure the specific ion concentration directly. Samples need to be aqueous to avoid contaminating or dissolving the membrane.
- The voltage developed between the sensing and the reference electrode is a measure of the concentration of the reactive ion being measured. As the concentration of the reacting ion at the sensing electrode varies, so does the voltage measured between two electrodes.

2.4.2. GLASS ELECTRODE (INTERNAL REFERENCE ELECTRODE)

Construction

- A glass electrode consists of thin-walled glass bulb (the glass is a special type having low melting point and high electrical conductivity) containing a Pt wire in 0.1M HCl.
- The glass electrode is represented as, Pt, 0.1 M HCl / Glass



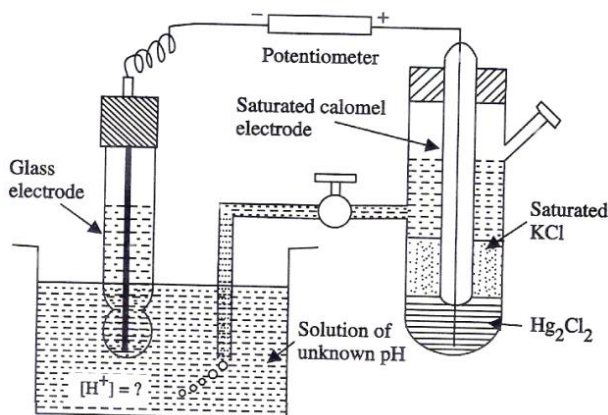
- HCl in the bulb furnishes a constant H^+ ion concentration.
- Glass electrode is used as the “**internal reference electrode**”. The pH of the solutions, especially coloured solutions containing oxidizing or reducing agents can be determined.
- The thin walled glass bulb called glass membrane functions as an ion-exchange resin, and an equilibrium is set up between the Na^+ ions of glass and H^+ ions in solution. The potential difference varies with the H^+ ion concentration, and its emf is given by the expression.

$$E_G = E_G^0 - 0.0592V_{\text{pH}}$$

2.4.3. DETERMINATION OF pH BY USING GLASS ELECTRODE

Principle:

- The H^+ ion concentration inside the electrode is constant. When this electrode is dipped into a solution of unknown H^+ , it becomes sensitive to the outside concentration in the solution.
- The potential difference is developed across the membrane. The e.m.f. of the cell is measured.



The complete cell is represented as:



Procedure

- Unknown solution is taken in the beaker.
- Glass electrodes are dipped in it.
- It is connected to a saturated calomel electrode.
- emf of the cell is measured.

From the EMF, the p^H of the test solution can be calculated as follows:

$$\begin{aligned} E_{\text{cell}} &= E_R - E_L = E_{\text{calomel}} - E_{\text{glass}} \\ E_{\text{cell}} &= 0.2422 \text{ V} - (E_G^0 - 0.0591 \text{ pH}) \\ &= 0.2422 \text{ V} - E_G^0 + 0.0591 \text{ pH} \\ E_{\text{cell}} - 0.2422 \text{ V} + E_G^0 &= 0.0591 \text{ pH} \\ \text{pH} &= \frac{E_{\text{cell}} - 0.2422 \text{ V} + E_G^0}{0.0591} \end{aligned}$$

The E_G^0 value of the glass electrode can be determined by using a solution of known pH.

Advantages of Glass Electrode

- It can be easily constructed and readily used.
- The results are accurate.
- It is not easily poisoned.
- Equilibrium is rapidly achieved.

Limitations

- Since the resistance is quite high, special electronic potentiometers are employed for measurement.

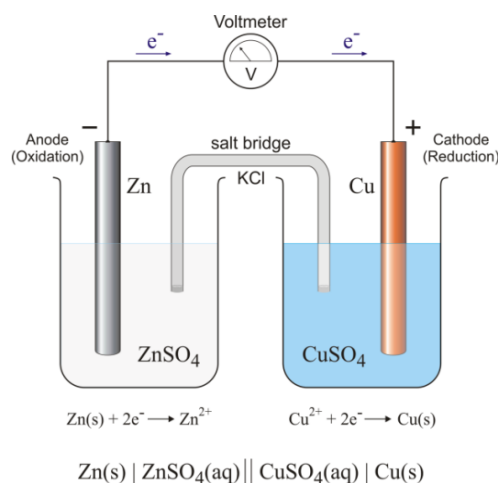
- (ii) The glass electrode can be used in solutions only with a pH range of 0 to 10. However above the pH 12 (high alkalinity), cations of the solution affect the glass and make the electrode useless.

Other Applications of ISEs

- (i) ISEs are used in determining the concentrations of cations like H^+ , Na^+ , K^+ , Ag^+ , Li^+ .
- (ii) ISEs are used for the determination of hardness (Ca^{2+} and Mg^{2+} ions).
- (iii) Concentrations of anions like NO_3^- , CN^- , S^{2-} , halides (X^-) can be determined.
- (iv) ISEs are used in the determination of concentration of a gas by using gas-sensing electrodes.
- (v) pH of the solution can be measured by using a gas-sensing electrode.

2.5. GALVANIC CELLS (ELECTROCHEMICAL CELLS)

- An electrochemical cell is a device which converts Chemical energy into electrical energy. It is also called a galvanic cell or voltaic cell.
- An electrochemical cell consists of two electrodes immersed in one or more suitable electrolytes. When these electrodes are connected externally, redox reactions occur. The electrode at which oxidation occurs is called the anode and the electrode at which reduction occurs is called the cathode. *Example: Daniel Cell*



Cell device (construction): Consists of Zn electrode dipped in 1 M ZnSO_4 solution and a Cu electrode dipped in 1 M CuSO_4 solution. Each electrode is a half cell. The solutions are inter connected by a salt bridge and the two electrodes are connected by wire.

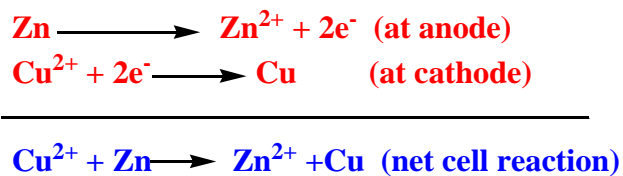
At anode: oxidation takes place with the liberation of e^- .

At cathode: Reduction takes place by the acceptance of e^- .

The electrons liberated in oxidation reactions flow through external wire and are consumed by the copper ions at the cathode.

Salt bridge: It consists of a U-tube containing a saturated solution of KCl or $(\text{NH}_4)_2\text{NO}_3$ in agar – agar gel. It connects the two half cells.

Reactions occurring in the cell



Functions

- Eliminates liquid junction potential.
- Provides a path for the flow of electrons between two half cells.

Representation of a galvanic cell (Cell diagram)

- Anode is written on the LHS and cathode on RHS
- The anode is written with the metal first and then the electrolyte which are separated by a vertical line

Example: Zn/Zn^{2+} (or) Zn/ZnSO_4

- The cathode is written with the electrolyte first and then the metal.

Example : Cu^{2+}/Cu (or) CuSO_4/Cu

- The two half cells are separated by a salt bridge, which is indicated by two vertical lines.

Using the above representation, the galvanic cell is represented as



2.6 CONCENTRATION CELLS

- Concentration cells can be defined as electrochemical cells that consist of two half-cells wherein the electrodes are the same, but they vary in concentration.
- As the cell as a whole strives to reach equilibrium, the more concentrated half cell is diluted and the half cell of lower concentration has its concentration increased via the transfer of electrons between these two half cells.
- Therefore, as the cell moves towards chemical equilibrium, a potential difference is created. A detailed diagram of a concentration cell and its discharge process is given below.

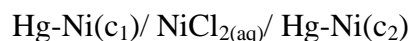
There are two types of concentration cells

- Electrode concentration cells.
- Electrolyte concentration cells.

1. Electrode concentration cell

In this type, two similar electrodes of different composition are in contact with the same electrolyte.

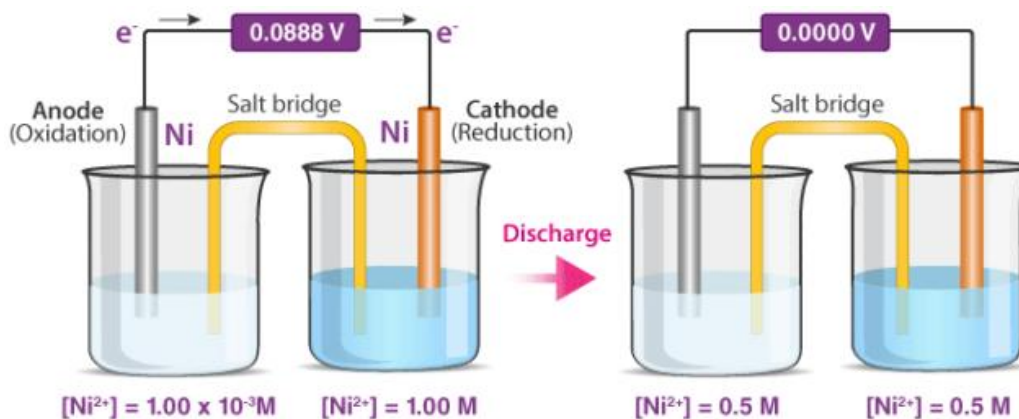
Example : An amalgam with two different compositions of the same metal.



2. Electrolyte concentration cell

In this type, the two electrodes of the same metal are in contact with the same electrolyte of different concentrations.

Example: Nickel ion concentration cell $\text{Ni} / \text{Ni}^{2+} (c_1) // \text{Ni}^{2+} (c_2) / \text{Ni}$



2.6.1 DETERMINATION OF EMF OF A CONCENTRATION CELL

According to the Nernst equation, when a metal is placed in a solution of its own salt of concentration, c , the electrode potential forms between the metal and the solution is determined by the equation.

$$E = E^0 + \frac{2.303RT}{n} \log c$$

$$\text{At } 25^\circ\text{C}, E = E^0 + \frac{0.0591}{n} \log c$$

Now, let us consider a general electrolyte concentration cell in which two half cells are made up of similar electrodes and electrolytes but the concentration of reactive ions around the electrodes are different.

It can be represented as $\text{M} / \text{Mn}^+ (c_1) // \text{Mn}^+ (c_2) / \text{M}$ ($c_2 > c_1$)

Where C_1 and C_2 are the concentration of reactive ions at the two electrodes.

Metal immersed in higher concentration acts as cathode because of high osmotic pressure of solution whereas the metal immersed in lower concentration acts as anode.

The emf of a cell is generally determined by

$$\begin{aligned} \text{Emf of a cell} &= E_{\text{right}} - E_{\text{left}} \\ &= E_{\text{cathode}} - E_{\text{anode}} \end{aligned}$$

Where, E_{cathode} & E_{anode} are half cell potential of cathode and anode respectively.

The half cell potentials can be determined by the Nernst equation.

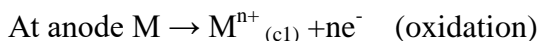
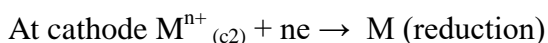
EMF of the concentration cell

$$= [E^0_{\text{M} / \text{Mn}^+} + \frac{0.0591}{n} \log c_2] - [E^0_{\text{M} / \text{Mn}^+} + \frac{0.0591}{n} \log c_1] \text{ At } 25^\circ\text{C}$$

$$= \frac{0.0591}{n} \log c_2 - \frac{0.0591}{n} \log c_1$$

$$= \frac{0.0591}{n} \log \frac{c_2}{c_1} \text{ At } 25^\circ\text{C}$$

The reactions occurring the two half cells are



It is clear from the above equation that there is no net chemical reaction. Therefore the e.m.f. developed is due to the transfer of metal ions from the solution of higher concentration to the lower concentration.

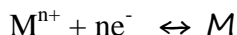
Applications of concentration cells

- (i) Determination of the solubility of a sparingly soluble salt.
- (ii) Determination of valency of an ion

2.7. POTENTIOMETRIC TITRATIONS

Principle

Emf of a cell depends on the concentration of the electrolytes with which the electrodes are in contact. Therefore, the electrode reaction is



As the concentration of M^{n+} changes, the emf of the cell also changes correspondingly.

Thus, the potentiometric titrations involve the measurement of emf between reference electrode and an indicator electrode, with the addition of the titrant.

Types of potentiometric titration

Potentiometric titrations fall into the following three categories.

1. Redox titrations
2. Precipitation titrations
3. Acid-base titrations.

2.7.1. REDOX TITRATION (FeSO₄ Vs K₂Cr₂O₇)

Redox titration : (FeSO₄ Vs K₂Cr₂O₇)

Indicator Electrode :Platinum Foil

Reference Electrode :Standard Calomel Electrode

Pipette Solution :20 ml of ferrous ion solution (Fe²⁺) and 20 ml of dilute sulphuric acid

Burette solution : Potassium dichromate (K₂Cr₂O₇)

Cell configuration : $Pt(s) | Hg^+_{(aq)} | Hg_2 Cl_{2(s)} | KCl || Fe^{3+}(aq) | Fe^{2+}(aq) | Pt(s)$

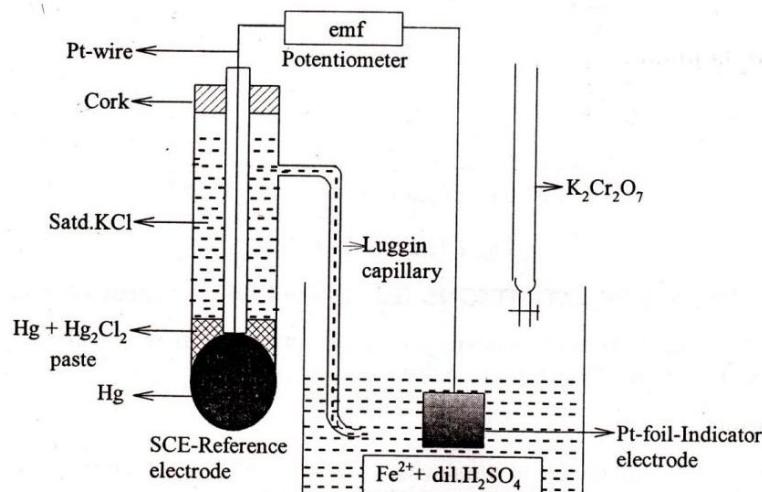
Cell reaction : $K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O + K_2SO_4$

Measurement : EMF due to the oxidation of Fe^{2+} to Fe^{3+}

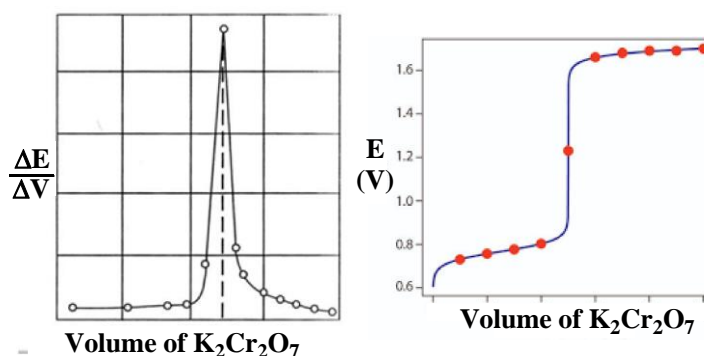
Reference electrode is SCE, the Indicator electrode is Platinum.

End Point : Sudden increase in the EMF as the ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ attains maxima

- The concentration of an ion such as Fe^{2+} can be found by titrating with a strong oxidizing agent such as KMnO_4 (Mn^{7+}) or $\text{K}_2\text{Cr}_2\text{O}_7$ (Cr^{6+})
- When $\text{K}_2\text{Cr}_2\text{O}_7$ is added to ferrous sulphate in acid medium, ferrous ion is oxidized to ferric ion and hexavalent Cr^{6+} is reduced to trivalent Cr^{3+} state. The potential of this system depends on the ratio of ferrous to ferric.



- So the potential of this system will follow the concentration ratio of hexavalent Cr to trivalent Cr. When the potential is plotted against the volume of dichromate added, the following graph is obtained.



- The potential is found to increase with the addition of $\text{K}_2\text{Cr}_2\text{O}_7$. Initially the increase in potential is gradual but at the end point, the increase is very steep because almost all Fe^{2+} would have been converted to Fe^{3+} . Thereafter Fe^{2+} will not be present.
- Beyond the end point, addition of excess Cr^{6+} established equilibrium with Cr^{3+} present in the solution. The potential now depends on $\text{Cr}^{6+}/\text{Cr}^{3+}$. The differential graph is drawn for getting a more accurate end point.

Advantages of potentiometric titrations

1. The necessary apparatus required is cheap and easily available.

2. This method can be used for coloured solutions.
3. Fixing up end points is easier when compared to the titrations in which indicators are used to fix up end points.
4. Very dilute solutions can be titrated with accuracy.
5. Several components may be titrated in the same solution.

Disadvantages of potentiometric titration

- a) More complex than simple acid- base titration.
- b) A Galvanic cell is used to carry out the process.
- c) Overall cost of the process is high.
- d) Continuous supply of electricity is mandatory
- e) Electrolyte used in the reaction must be freshly prepared.
- f) Variation in electrolyte pH alters the result of titration.
- g) There is always a need for some standard electrode like calomel electrode, hydrogen electrode, or other metal chloride electrode.

2.8. AMPEROMETRIC TITRATIONS

Introduction – Amperometric titrations are otherwise called polarographic or polarometric titrations.

Principle:

- The potential applied between polarisable and non-polarisable electrodes is constant and the diffusion current is measured during the titration.
- Potential is applied to an electrode and the variation of the current passing during the titration indicates the end-point.
- During the titrations the concentration of the reducible ion changes and the current also changes.
- Diffusion current \propto concentration of electro reducible ion.
- Potential applied between polarizable & non polarizable is kept constant.
- Hence, at an appropriate applied voltage the apparent diffusion current is measured as a function of the volume of the titrating solution added.
- Now, if a graph is plotted between the ‘current’ against the ‘volume of reagent added’, the end-point will be represented by the point of intersection of two lines indicating the change of current both before and after the equivalence is achieved.

Conditions for performing amperometric titration

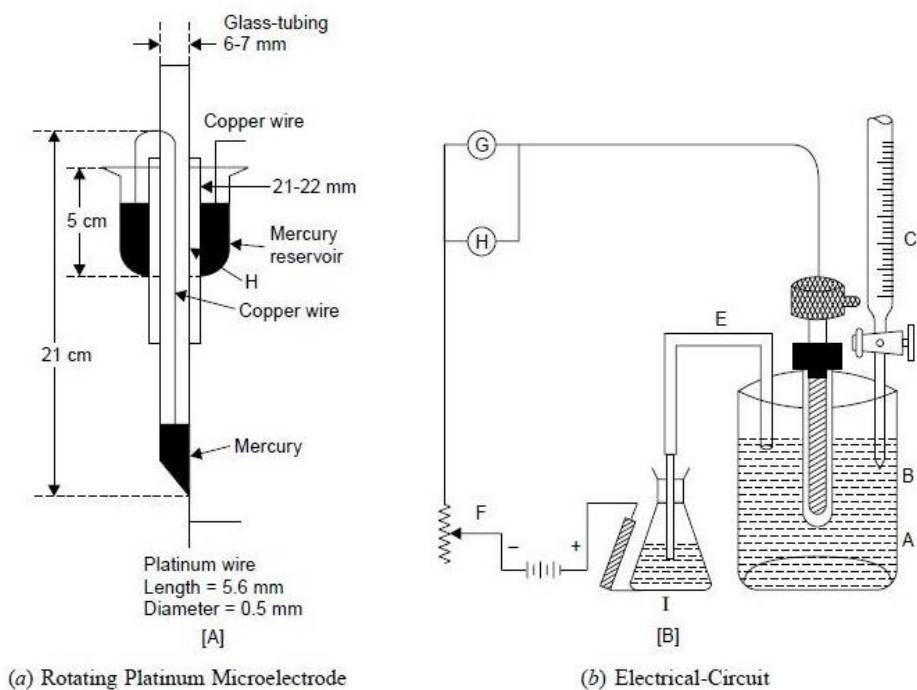
1. Both should be reducible
2. The potential applied should limit current.

Apparatus for Amperometric titration

Rotating platinum microelectrode (RPME):

- It consists of a glass rod with platinum wire at about 600 rpm wire made through mercury. So that the potential can apply and current is measured.

- The rotating platinum microelectrode depicts a simple rotating platinum microelectrode which is made out from a usual standard 'mercury seal'. A platinum wire protrudes from the lower end wall of a 21 cm long 6 mm glass tubing, which is bent at an angle of 90°.
- There are holes (H) in the stem of the mercury reservoir for making electrical contact with it. The mercury reservoir is provided with a flange fitted inward to prevent Hg from being thrown out (Figure a).
- The electrical connection is duly done to the electrode by means of a strong amalgamated Cu-wire passing through the glass tubing to the lower end of the Hg covering the sealed-in platinum wire; the upper end of which passes through a small hole made in the stem of the stirrer and dips well into the Hg present in the Hg seal.



- Subsequently, a wire from the Hg seal is connected to the source of applied voltage. The glass tubing serves as the stem of the electrode that is rotated at a constant speed of 600 rpm (Figure b).

2.8.1 TYPES OF AMPEROMETRY TITRATION

1. Titration of electro-reducible ions vs electro non-reducible ions
Example: Lead (Pb) vs sulphate ions (SO_4^{2-})
2. Titration of electro non-reducible ions vs electro-reducible ions
Example: Chloride (Cl^-) vs Silver (Ag)
3. Titration of electro-reducible Vs Titration of electro-reducible
Example: Lead (Pb) vs Dichromate ions
4. Redox titration (oxidant and reductant)
Example: Ferric (Fe^{3+}) ions vs titanium ions (Ti)

5. End point techniques(Karl fischer).

(Determination of water using Karl fischer reagent)

2.8.2 TITRATION CURVES

1. **Curve (A):** Titration of electro-reducible ions vs electro non-reducible ions

Example: Lead (Pb) vs sulphate ions (SO_4^{2-}).

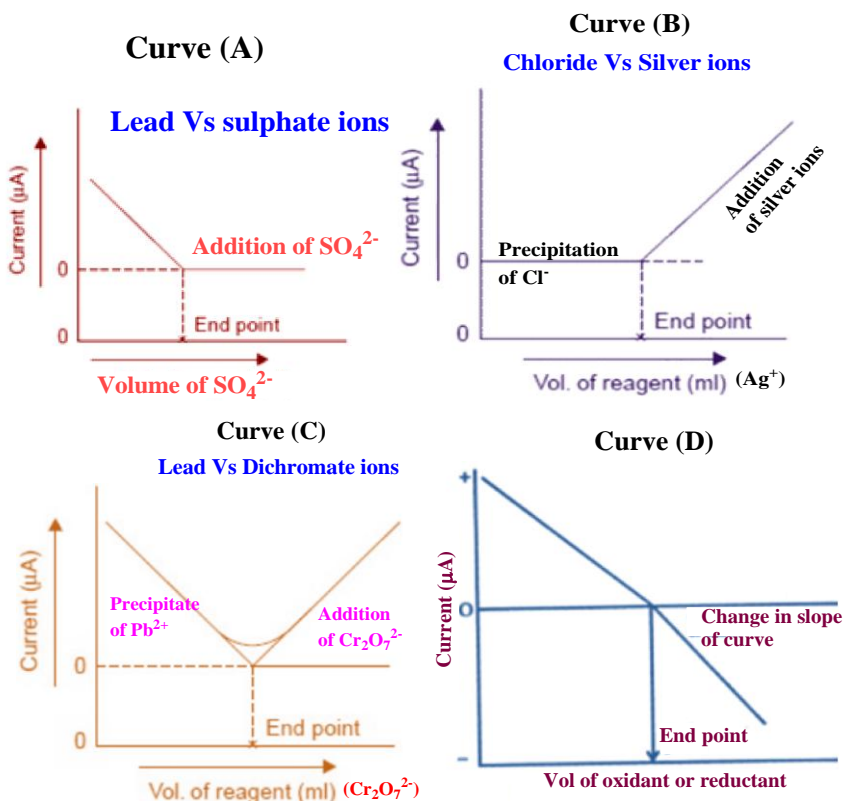
In which lead ions are titrated vs sulphate ions. Current is observed due to lead only.

Decrease current due to decrease concentration of lead ions in solution due to precipitation as lead sulphate by sulphate ions.

2. **Curve (B):** Titration of non-reducible ions vs reducible ions

Example: Titration of chloride ions with silver ions.

- In this titration of chloride ions with silver ions, chloride ions are electro reducible, then current is minimum.
- When the addition of silver ions, the current does not increase and silver chloride precipitate is formed at the end point. Beyond the end point, the diffusion current increases when increasing the concentration of silver ions.



3. **Curve (C):**Titration of reducible ion vs reducible ions

Example: Titration of lead ions with dichromate ions.

- Decrease in current due to decrease in the concentration of lead ions and gradually precipitated as lead chromate.

- After the end point, addition of dichromate ions in solution, the current is increased and V-shaped curve is obtained.

4. Curve (D): Redox Titration (oxidant and reduction)

- Oxidant and reductant give different currents. An eg. Titration of ferric ions against titanium ions.
- 1st part curve decreases current due to decreased concentration of ferric ions. When ferric ions are reduced, the diffusion current is minimum.
- 2nd part of curve current set up by oxidation of titanium ions added. The end point shown by two lines intersect by difference in slope.

Advantages of Amperometric titration

- Both reducible as well as non-reducible ions groups can be determined.
- Dilute solution can be analyzed.
- The reaction carryout can be reducible or irreversible.
- The apparatus is simple and temperature need not be provided constantly.

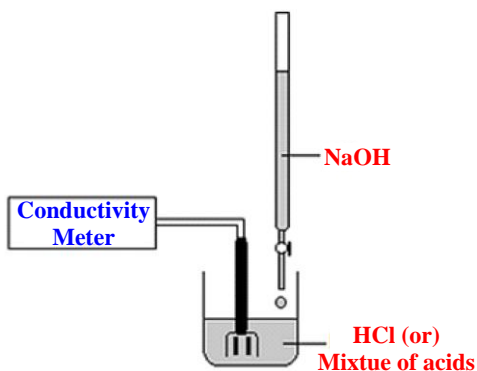
Applications of Amperometric titration

- Amperometric titration (a) quantitative in nature (b) used to determine the end point.
- Determination of water by using Karl fischer reagent.
- Amperometric detectors can detect very low concentrations of reducible ions and they can easily determine.
- Quantification of ions or mixtures of ions.

2.9 CONDUCTOMETRIC TITRATIONS

Principle :

Conductometric titrations are a special type of volumetric analysis in which the end point (or the equivalence point) of the titration is obtained by conductance measurements.

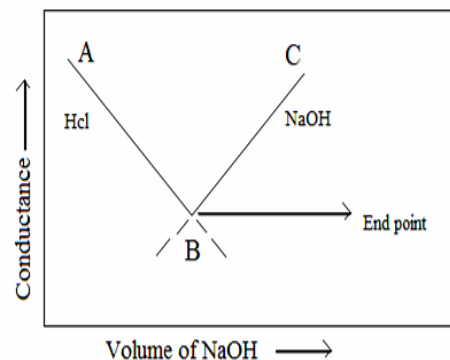


The change in conductance depends on

- The number of free ions in solution
- Nature of ions (size and mobility of ions)

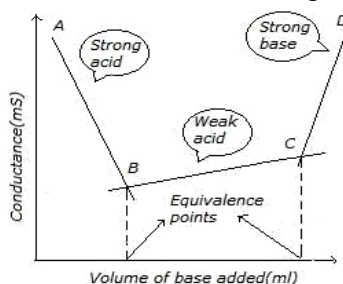
Strong Acid Vs Strong Base: (HCl Vs NaOH)

- Burette solution : NaOH
- Pipette solution : HCl
- Cell : Conductivity cell
- Reaction : $\text{HCl} + \text{NaOH} \rightarrow \text{Na}^+\text{Cl}^- + \text{H}_2\text{O}$
- Conductivity : Initially the conductivity is due to H^+ and Cl^- ions.
- Point A : High Conductance (Due to the presence of fast moving H^+ ions)
- Conductivity : After adding NaOH gradually, the conductivity is due to Na^+ and Cl^- ions.
- Point B : Conductance decreases, due to the replacement of fast moving H^+ ions by slow moving Na^+ ions.
- Conductivity : On further addition of NaOH, the conductivity is due to NaCl and OH^- ions.
- Point C : Conductance begins to increase after reaching a certain minimum value, due to the fast moving OH^- ions.



Weak Acid and Strong acid (Mixture of acids) Vs Strong Base: (HCl + CH_3COOH Vs NaOH)

- Burette solution : NaOH
- Pipette solution : HCl + CH_3COOH
- Cell : Conductivity cell
- Reaction : $\text{HCl} + \text{NaOH} \rightarrow \text{Na}^+\text{Cl}^- + \text{H}_2\text{O}$
 $\text{CH}_3\text{COOH} + \text{NaOH} \rightarrow \text{CH}_3\text{COO}^-\text{Na}^+ + \text{H}_2\text{O}$
- Conductivity : Initially the conductivity is due to completely ionized H^+ and Cl^- ions.
- Point A : High Conductance (Due to the presence of fast moving H^+ ions).
- Conductivity : After adding NaOH gradually, the HCl is neutralized first.
- Point B : Conductance increases.
- Conductivity : After complete neutralization of all HCl, the neutralization of CH_3COOH commences.
- Point C : Conductance further increases due to formation of sodium acetate (Strong electrolyte).
- Conductivity : Neutralisation of acetic acid.
- Point D : Conductance begin to increase after reaching a certain minimum value, due to the fast moving OH^- ions.



Advantages of Conductometric Titration

- It does not require indicators as titration is based on the conductance of the solution and the endpoint or neutralization point is determined graphically.
- It is suitable for colored solutions as well.
- As the endpoint is determined graphically, results are more accurate with minimum error.
- It is used for the analysis of turbid suspensions, weak acids, weak bases, a mix of weak and strong acids, etc.

Limitations of Conductometric Titration

- By conductometric titration technique, only a few specific redox titrations can be carried out.
- It shows less accurate results when the total electrolytic concentration is high in solution. It makes it less satisfactory.

Applications of Conductometric Titration

1. Conductometric titrations are used to determine water purity. It is used to check the levels of pollution present in different small water bodies like lakes, ponds or rivers.
2. Conductometry can also be used to examine the salinity of seawater and the alkalinity of freshwater or freshwater bodies.
3. This type of titration is used significantly in the food industry, specifically by food microbiologists, to trace various microorganisms.
4. Conductometric titration can be used in determining deionized and distilled water purity or freshness by examining the equilibrium of chemicals in ionic reactions.
5. It is also used largely in the pharmaceutical industries to detect many antibiotics and to check the levels of basicity in various organic acids.

2.10 SENSORS

What is a sensor....?

A sensor is a device that detects events or changes in quantities and provides a corresponding output. The output is usually an electrical or an optical signal.

Examples:

- A mercury thermometer converts the measured temperature into expansion and contraction of a liquid which can be visualized on the calibrated glass tube.
- A thermocouple converts temperature to an output voltage.

Types

Physical sensors: A physical sensor is a device that provides information about a physical property of the system. Ex : pressure sensors, temperature sensors etc.

Chemical sensors: A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. Ex: COD, methane etc.

Classification of chemical sensors:

- Optical sensors
- Electrochemical sensors
- Electrical sensors
- Mass sensitive sensors
- Magnetic sensors
- Thermometric sensors
- Others – radiation detecting sensors

2.10.1 ELECTROCHEMICAL SENSORS

- Electrochemical sensors are one of the broadest and important types of sensors for the quantitative analysis of inorganic ions in electrolyte form making use of different kinds of electrodes.
- By these sensors complex mixtures of metal ions such as Cu^{2+} , Zn^{2+} , Pb^{2+} , Na^+ etc., also can be analyzed. The electrochemical sensors are made use in measuring non metals such as CN^- , Cl^- , Br^- , etc. and also mainly pH.
- Areas where the optical sensors fail due to certain factors, electrochemical sensors are made use of successfully.
- Recent developments in chemically modified electrode sensors, microelectrodes, voltammetric and potentiometric methods such as adsorptive, stripping and potentiometric stripping analysis has made the method more effective for the analysis for the various ions.

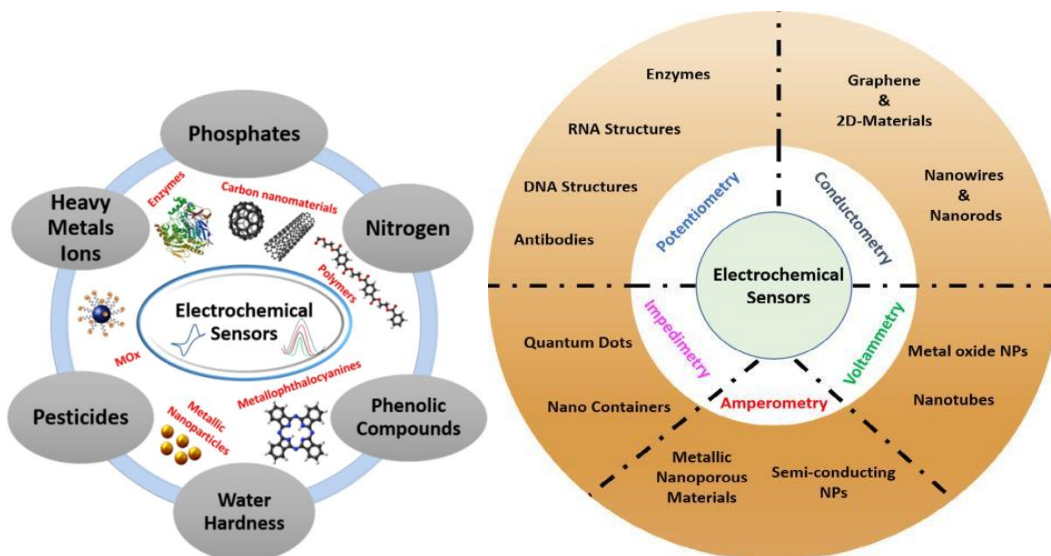
Types:

1. Voltammetric – Current is measured in the DC or AC.
2. Potentiometric - Potential is measured (reference electrode and working electrode).
3. CHEMFET – Chemically Sensitized Field Effect Transistor.
4. Potentiometric Solid Electrolyte Gas Sensors – These are different from potentiometric sensors because these work in high temperature solid electrolytes and are usually applied for gas sensing measurements.

Applications of electrochemical sensors

- Ion selective electrode sensors or electrochemical sensors are now a day's largely used to monitor environmental pollution as well as water pollution.
- Measurement of pH is carried out with the help of hydrogen ion sensitive electrodes along with suitable reference electrodes such as calomel electrodes.

- There are certain special redox electrodes which are used in certain redox (oxidation-reduction) reactions in order to measure certain ion concentrations as well as reaction rates.
- Special electrodes such as Teflon created electrodes are made use for the measurements of dissolved oxygen (DO).
- Electrochemical sensors are playing a significant role in the biomedical field.
- Electrochemical sensors can monitor blood samples and other body fluids for its ionic chemical content concentrations.
- Chemical parameters of the inner eyelid, gastric juice, tissue secretions etc. (chemical concentrations) can be studied with the help of electrochemical sensors.
- The industrial application of electrochemical sensors include the monitoring of various pollutants present in the environment and checking the ionic concentrations of various industrial products including chemicals, pharmaceutical drugs, pesticides, insecticides, fertilizers etc.
- The electrochemical sensors are made use in the measurement of oils and lubricants.
- Electrochemical sensors are also made use for the monitoring of plating baths and rinse systems.
- Electrochemical sensors can also monitor the various stages of corrosion processes.



2.11. POTENTIOMETRIC SENSORS

A potentiometric sensor is a type of chemical sensor that may be used to determine the analytical concentration of some components of the analyte gas or solution. These sensors measure the electrical potential of an electrode when no current is present.

Principle

The signal is measured as the potential difference (voltage) between the working electrode and the reference electrode. The working electrode potential must depend on the

concentration of the analyte in the gas or solution phase. The reference electrode is needed to provide a defined reference potential.

In potentiometric sensors, the zero-current potential (relative to a reference) developed at a selective membrane or electrode surface in contact with a sample solution is related to analyte concentration.

The main use of potentiometric transducers in biosensors is as a pH electrode.

$$E = E_o + \frac{RT}{nF} \ln[\text{analyte}]$$

E_o is a constant for the system; R is the universal gas constant

T is the absolute temperature; z is the charge number

F is the Faraday number;

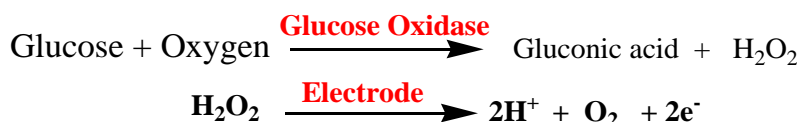
$\ln[\text{analyte}]$ is the natural logarithm of the analyte activity.

The best known potentiometric sensor is the Ion Selective Electrode (ISE).

- Solvent polymeric membrane electrodes are commercially available and routinely used for the selective detection of several ions such as K^+ , Na^+ , Ca^{2+} , NH_4^+ , H^+ , CO_3^{2-} in complex biological matrices.
- The antibiotics nonactin and valinomycin serve as neutral carriers for the determination of NH_4^+ and K^+ , respectively. ISEs used in conjunction with immobilised enzymes can serve as the basis of electrodes that are selective for specific enzyme substrates.

Analysis of Glucose in blood

- For analysis of glucose in blood glucose sensor which is potentiometric sensor is used.
- Glucose is converted into ions, which is detected by ion-selective electrodes (ISE). Glucose is oxidized into gluconic acid which further undergoes decomposition and gives H^+ ions which are detected by pH electrodes.



- H^+ ions are measured by pH meter i.e, glass electrode and a potential difference is set-up between glass electrode and reference electrode which is sensed by a potentiometric sensor which analyses the glucose level in blood.

Analysis of Urea

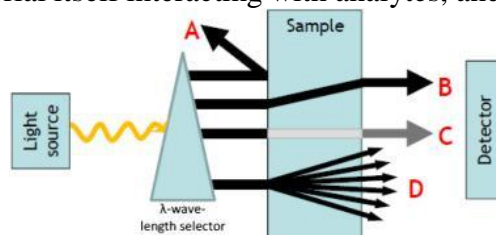
- Analysis of urea in serum or urine samples is very common. For this analysis, enzymatic potentiometric sensors or urea biosensors are used.
- Urea concentration is determined during enzymatic reaction of urea with urease which releases NH_4^+ ions and HCO_3^- ions. By using ammonium ion-selective electrodes analyse the ammonium ions (NH_4^+) concentration.



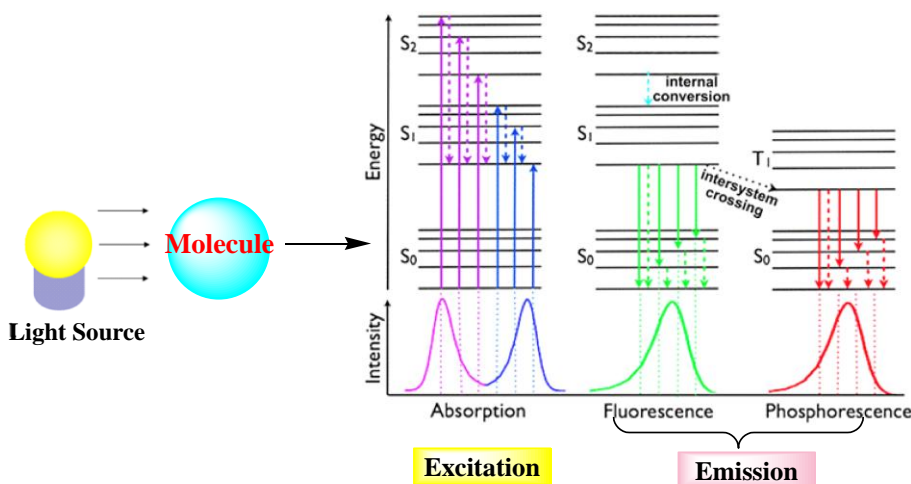
- Electrode is modified with a gel containing the urease enzyme. The signal is determined by a potentiometric biosensor which senses the presence of urea in different samples.

2.12. OPTICAL SENSOR

- Optical sensors have the ability to detect light, typically at a specific range of the electromagnetic spectrum (ultraviolet, visible, and infrared).
- The sensor detects wavelength, frequency, or polarization of light and converts it into an electric signal due to the photoelectric effect.
- Optical sensors can be represented in general terms as a wavelength-selectable light source, the sensor material itself interacting with analytes, and a light detector.



- The detector monitors varies by technique (e.g., refractive index, scattering, diffraction, absorbance, reflectance, fluorescence, photoluminescence, chemiluminescence, etc.), can cover different regions of the electromagnetic spectrum, and can allow measurement of multiple properties (e.g., intensity of light, lifetime, polarization, etc.).
- Fluorometry can provide excellent sensitivity and fluorescent sensors often have some advantages (e.g., sensitivity, depending upon the background fluorescence), although at the cost of a more sophisticated experimental apparatus.
- Fluorescence-based approaches and fluorescence parameters (e.g., Stokes shift, fluorescence intensity and anisotropy, emission and excitation spectra, and fluorescence lifetime) can provide substantial flexibility as an analytical approach.



2.12.1. FLUORESCENCE BASED SENSOR

An analyte responsive fluorescent molecule/supramolecule which changes its fluorescence characteristics in the presence of an analyte.

A fluorescence sensor device (optical sensing device):

The sensor device contains

- the light source
- the analyte-responsive (supra) molecular moiety properly immobilized

- the optical system
- the light detector (photomultiplier or photodiode) connected to appropriate electronics for displaying the signal.

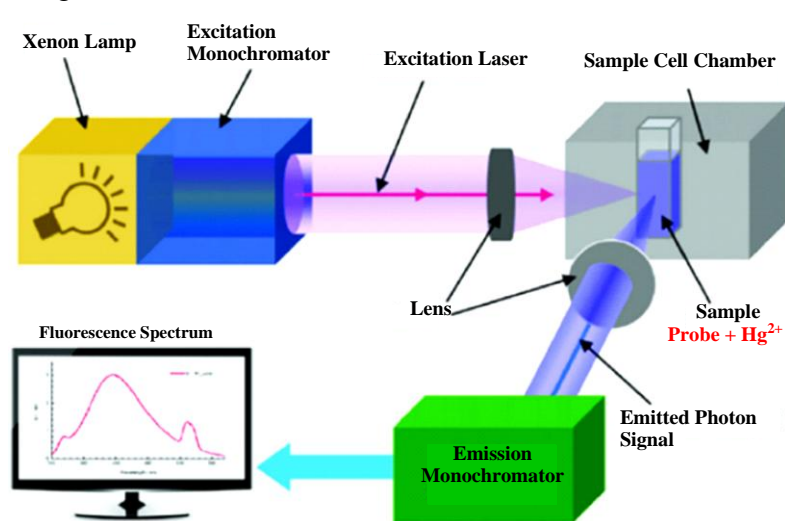


Fig. Instrumentation of Fluorescence sensor device

Types of Sensors: Based on Fluorophore/signal transducer converting the information into an optical signal)

- Chemical sensors (chemosensors): Analyte-responsive moiety is of abiotic origin.
- Biosensors: Biological macromolecules (e.g. protein) as fluorescent molecular sensors.

Importance of Fluorescent sensors

- Analytical chemistry
- Clinical biochemistry
- Medicine and
- Environment

Applications

Detection of chemical and biochemical analytes,

- Cations: H^+ , Li^+ , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Pb^{2+} , Al^{3+} , Cd^{2+} , etc.
- Anions: halide ions, citrates, carboxylates, phosphates, ATP, etc.
- Neutral molecules: sugars, e.g. glucose, etc.
- Gases: O_2 , CO_2 , NO, etc.

2.12.2 Fluorescence Hg^{2+} ion detection

- Mercury (Hg^{2+}) is well known as one of the most toxic metals, and is widespread in air, water, and soil, generated by many sources such as gold production, coal plants, thermometers, barometers, caustic soda, and mercury lamps.
- A major absorption source is related to daily diets such as fish.
- This can cause harmful effects, such as nerve, brain, and kidney damage, lung irritation, eye irritation, skin rashes, vomiting, and diarrhea.

- Metallic mercury mainly causes health effects including neuromuscular changes, minamata disease, headaches, changes in nerve responses, tremors, insomnia, etc. Low level detection of mercury is important.

Detection of Hg^{2+} using fluorescence sensor method

- A sensor probe is a molecule (nanoparticles or organic molecules) that can interact with the toxic analyte like Hg^{2+} ions and produce detectable signals in the mercury recognition process in a solution medium.
- The Hg^{2+} binds to the coordination sites of the probe and shows the color changes & optical changes (absorption and emission).
- To function as a sensor, Hg^{2+} -binding must alter either the electronic structure or the molecular structure of the sensor (probe).
- In a fluorogenic sensor, the interaction between the coordination site and the Hg^{2+} shows the changes in fluorescence behavior of the signaling unit.
- Based on the fluorescence property the detection limit of Hg^{2+} to be calculated.

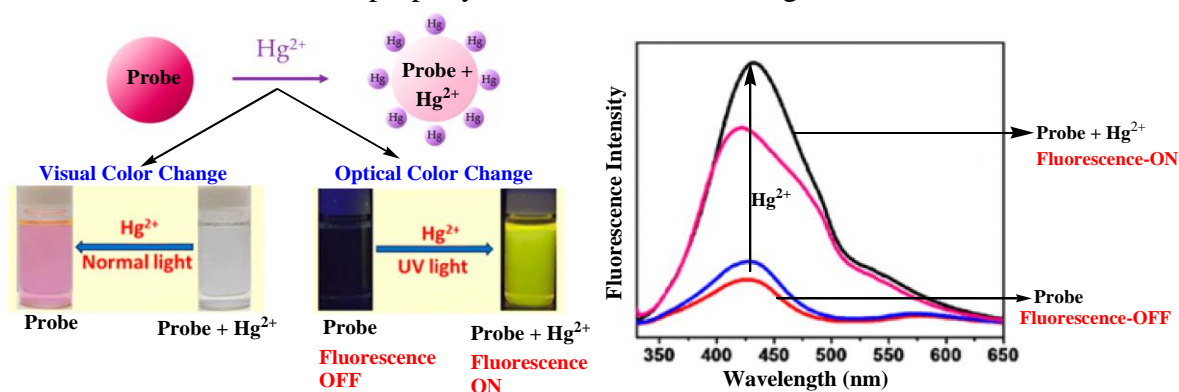


Fig: Schematic representation of Hg^{2+} detection using fluorescence method

2.13. THERMAL SENSOR

Thermal sensors are construction elements to measure temperature and engage functional dependence of a particular physical property of the sensory material on the temperature, which is routinely identified and well defined.

How does a thermal sensor work?

- Temperature sensors work by providing readings via electrical signals. Sensors are composed of two metals that generate an electrical voltage or resistance when a temperature change occurs by measuring the voltage across the diode terminals. When the voltage increases, the temperature also increases.
- The most basic way to measure temperature is using a thermometer; this measures how hot or cold something is. With advances in technology, we now have access to a variety of temperature sensors that are much more accurate.

Types of temperature sensors

- Thermometer

- Thermostat
- Thermistors
- Thermocouples.
- Negative Temperature Coefficient (NTC) Thermistors.
- Resistance Temperature Detectors (RTDs)
- Semiconductor-Based Sensors

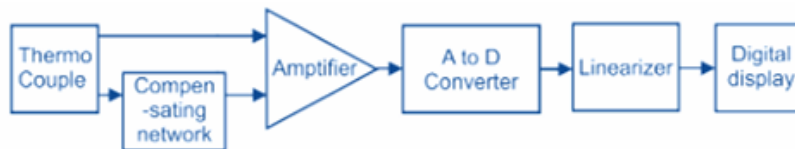
2.13.1. THERMOMETER TEMPERATURE SENSOR

- This type of temperature sensor is the standard temperature sensor, particularly the mercury-filled glass tube. However, thermometers exist in several types. Glass thermometers can contain either ethanol or mercury, although nowadays the main liquid used in these thermometers is ethanol.
- Many problems are associated with the use of mercury thermometers for clinical purposes. These days' digital thermometers are available in which mercury is not used. Digital thermometers are accurate and easy to handle.

Digital Thermometer

Digital thermometer helps in measuring the body temperature. It has an LCD screen that shows an accurate temperature. It is also designed with the last reading recall feature.

Block diagram of digital thermometer



Construction of digital thermometer

It consists of a temperature sensor like thermocouple. The compensating network provides the reference temperature to the thermocouple. Signal conditioner like amplifier. Analog to digital converter (ADC), and electronic display unit for direct display of the temperature.

Working of digital thermometer



(a) The thermocouples sense the temperature and produce proportional thermoelectric e.m.f. (voltage) in response to the changes in temperature.

(b) The compensating network provides the reference point for the thermocouple by producing the compensating voltage proportional to the reference temperature.

(c) The output of the thermocouple is further amplified by the amplifier.

(d) This amplified analog signal is fed as input to the ADC which converts it into an equivalent digital form.

(f) Electronic display unit to give the digital display of the corresponding measured temperature.

Advantages of digital thermometer

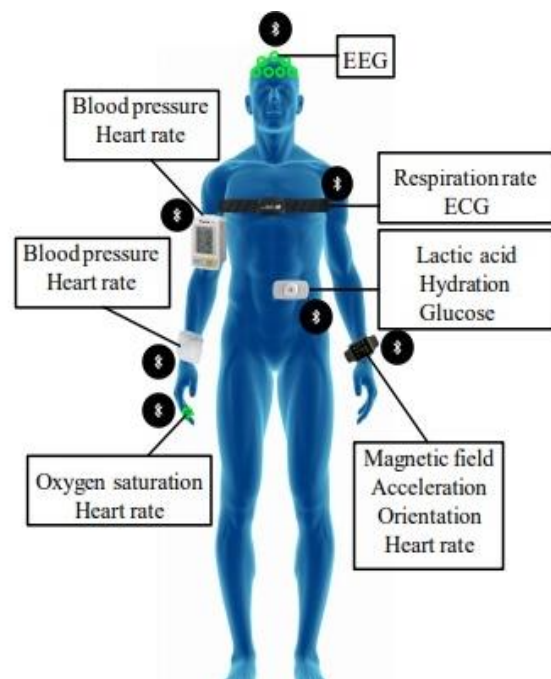
- The temperature readout is simple
- High accuracy
- Small in size, Low price

Application of thermal sensor

- It can be used to monitor the temperature of solids, liquids or gases over an extremely wide temperature range.
- Temperature sensors are utilized to monitor various environments and machinery, power plants, and manufacturing. Temperature sensors are used to measure water temperatures in reservoirs and boreholes.
- They can also be used to interpret temperature-related stress and changes in volume in dams. Temperature sensors are also utilized in the study of the temperature effect on other installed instruments.
- Temperature sensors are used in many electrical appliances, from our refrigerators and freezers to help regulate and maintain cold temperatures as well as within stoves and ovens to ensure that they heat to the required levels for cooking, air confectioners/heaters.
- Temperature sensors are utilized in the monitoring of patients, in medical devices, in thermolulution, in humidifiers, gas analysis, cardiac catheters, ventilator flow tubes, and dialysis fluid temperature.
- Temperature sensors are used for measuring inlet air temperature, exhaust gas, engine temperature, and oil temperature.

2.14. SENSOR FOR HEALTH CARE

- The recent evolution of electronics and communication systems has been of great importance to the development of comfort devices. Some reasons for this are the easily accessible technology, power systems that allow greater autonomy to devices, and miniaturization of electronic circuits, which are factors that enable the continuous monitoring of individuals.
- Monitoring and analysis of bioelectrical signals and movements can aid diagnosis, prevention, and examination of a wide range of issues, for example, *orthopedic, neurological, cardiovascular, and pulmonary problems*.
- A monitoring system connected to a hospital makes medical assistance at home possible through the *IoT (Internet of Things)* concept.



- Thus, different types of sensors can be used (e.g., *GPS receiver, accelerometer, ECG, blood pressure, blood glucose, body temperature, and breathing sensor*).
- In addition to the sensor data, it is possible to resort to online information provided by neighbors and caregivers.

2.14.1. BIOSIGNALS

A biosignal is any signal in living beings that can be continually measured and monitored. The term biosignal is often used to refer to bioelectrical signals, but it may refer to both electrical and non-electrical signals.

Classification of biosignals

According to the physical nature of biosignals

- Electric – Electrocardiogram (ECG)
- Magnetic – Magnetocardiography (MCG)
- Chemical – Glucose, Pulse oximeter
- Magnetic – Electronic stethoscope
- Thermal – Thermometer, Thermography
- Optical – Immunology

2.14.2. CHEMICAL BIOSIGNALS

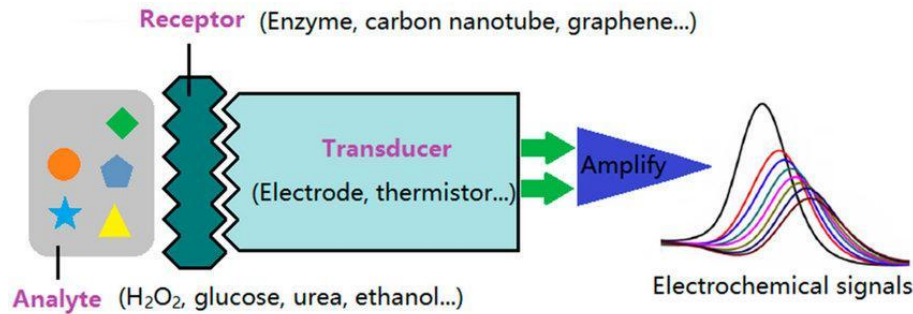
Signals provide information about concentration of various chemical agents in the body.

- Level of glucose (diabetes)
- Blood oxygen level (asthma, obstructive pulmonary disease, heart and kidney failure)
- Gases in blood and breathing airflow (anesthetic gases, carbon dioxide etc.)
- pH

2.15. GLUCOSE SENSOR

Introduction

- With approximately 346 million people living with diabetes worldwide, it is no surprise that this disease is costly. Out of these patients, it is estimated that 3.4 million of them die from poor glucose management. Poor glucose management includes the patient's death and poor monitoring of blood glucose level.
- A lancet device is designed with a needle projecting from one end of the device which is used to prick the patients' finger and draw blood.
- There are two methods used to examine the blood reflectance photometry and the electrochemical technique.



2.15.1 REFLECTANCE PHOTOMETRY

- The glucose from the blood sample makes contact with the catalyzing enzyme (glucose oxidase) embedded on the test strip.
- The enzyme oxidizes the glucose into a molecule that can then react with a dye to form a complex which can be optically measured.
- By shining an LED light onto the complex the colour intensity of the dye complex can be determined.
- A dark dye complex is a clear indication of high glucose concentration.

Working

- Most portable blood glucose monitor (BGMs) with optical detection use reflectance photometry to measure the amount of light (which is produced by an LED) reflected from a reagent-impregnated test pad that has reacted with a drop of blood.
- Once the reagent pad is inserted, light from the LED strikes its surface and is reflected to the photodiode, which measures the light's intensity and converts its energy to electrical signals.
- These signals are amplified, digitized, analyzed by a microprocessor, and converted by the unit's programming to the corresponding glucose concentration for display on the readout, expressed in mmol/L of blood.

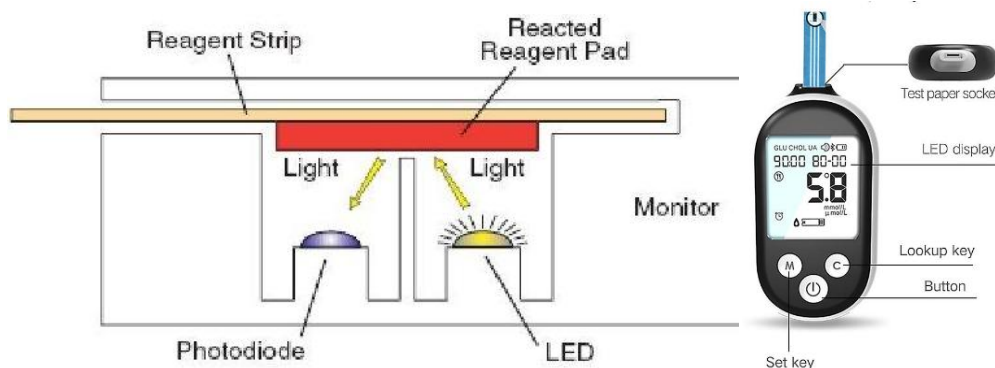


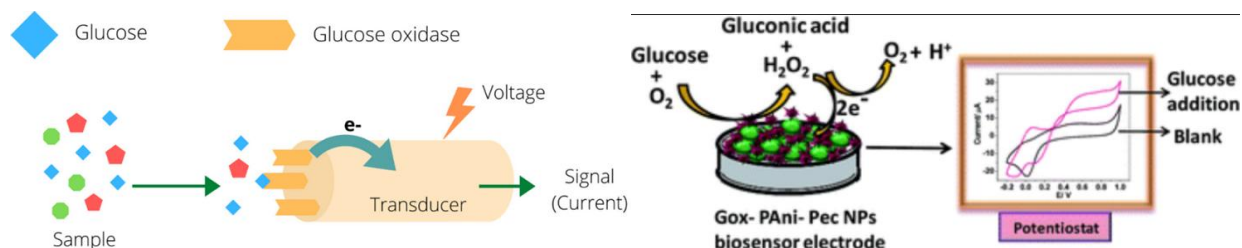
Fig. Blood glucose monitor – Light from the LED reflecting from the reagent pad onto the photodiode

Limitations:

- A large volume of blood samples is required (1-3 μlit).
- Time consuming, when the blood sample processing is considered.
- Regular calibration of this technique is required to ensure the test strip, in order to deliver the most accurate result.

2.15.2. AMPEROMETRIC BIOSENSOR

Amperometric glucose biosensors are prepared by immobilizing glucose oxidase (GOx) molecules onto an electrochemical interface. The enzyme catalyzes the conversion of glucose to gluconic acid and hydrogen peroxide.



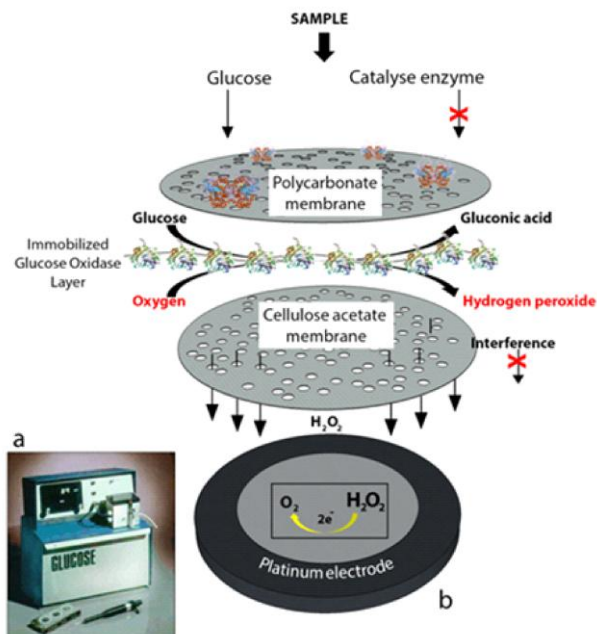
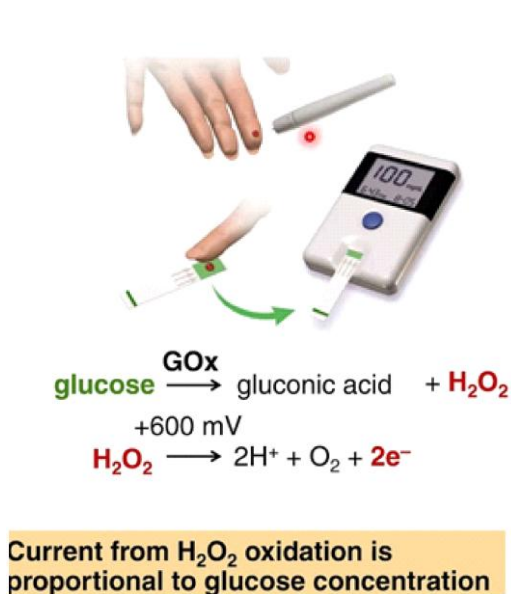
Construction:

Each strip includes layers of electrodes, spacers and immobilized enzymes assembled in a small package.

- The glucose from the blood sample makes contact with the catalyzing enzyme, embedded on the test strip.
- Enzyme oxidizes the glucose molecules to D-gluconic acid
- This reaction generates an electrical current that forces electrons to flow between the working electrodes and counter electrodes.
- Based on this working principle, the more blood glucose present in a sample the stronger the voltage generated.

Glucose Amperometric Biosensor (Glucometer)

Glucose oxidase to convert glucose to H_2O_2 and oxidizes it

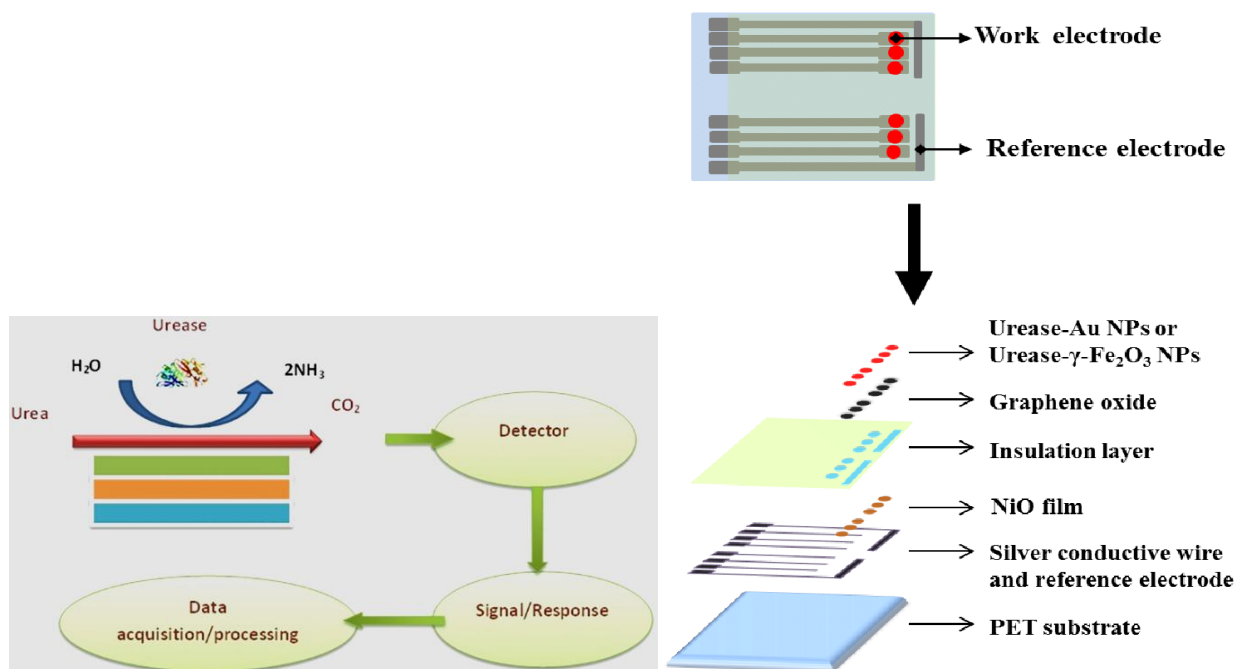


Advantage:

- This technique is more efficient and not more than 1 μ lit of blood needs to be drawn as a sample to test for blood glucose concentration.
- Time taken for a reading to be generated is approximately five seconds.

2.16. UREA BIOSENSOR

- Urea is an organic nitrogenous compound and it is present in nature as well as in living organisms at a significant level. The significant amount of urea in human plasma is 15–40 mg/dl.
- Higher levels of urea in the body provoke a cascade of symptoms, called uremic neuropathy or nerve damage. High risk side effects are urinary tract obstruction, gastrointestinal bleeding and renal failure etc. Lower urea levels contribute to cachexia, nephritic syndrome and liver failure
- The study of this earlier urea biosensor was merely about its ability in ammonium ion identification of a cation-selective glass electrode, provided by urease that was directly proportional to the concentration of urea.
- Two forms of urea biosensors are common enzymatic and non-enzymatic.
- Urease enzyme based urea biosensors hydrolyse the analyte urea into NH_4^+ and HCO_3^- ions.



- The above figure shows a schematic diagram of the mechanism of urease enzymes that catalyses the hydrolysis of urea.
- During the reaction, the urea is measured after the development of generated ions that lead to a change in pH. In fact, it is easy to detect the ammonium ion (NH_4^+) in traces by using a different transducer, aligned with the concentration of urea.

- A variety of urea electrodes have been developed by now, often utilizing ion-responsive field effect transistors, CNT, and gold/silver/zinc-oxide/iron-oxide based transducers. Accomplishments were made to improve the biosensor based on the enzyme coating, leading to greater enzyme stability and lower limits on urea determination.

2.17. GAS SENSOR

A gas sensor is a device which detects the presence or concentration of gases in the atmosphere. Based on the concentration of gases, the sensor produces a corresponding potential difference by changing the resistance of the material inside the sensor, which can be measured as the output voltage.

Based on this voltage value, the type and concentration of the gas can be estimated

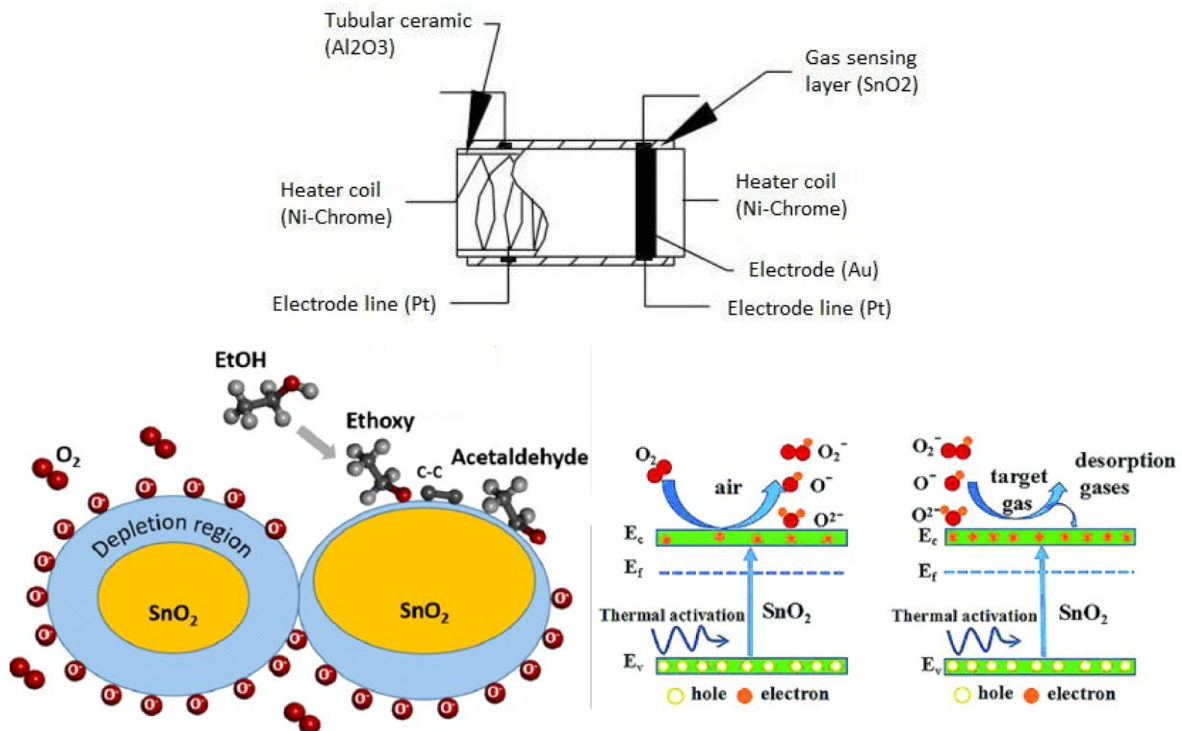
Types:

1. Metal oxide based gas sensor
2. Optical gas sensor
3. Electrochemical gas sensor
4. Calorimetric gas sensor
5. Acoustic based gas sensor

2.17.1. METAL OXIDE GAS SENSOR

Metal oxide semiconductors provide promising materials for detecting, monitoring, and controlling different kinds of toxic gases like CO, NH₃, H₂, HCHO, NO₂, etc.

Due to low cost, low power consumption, superior sensitivity, and ease of preparation method, metal oxide semiconductors are gaining growing interest.

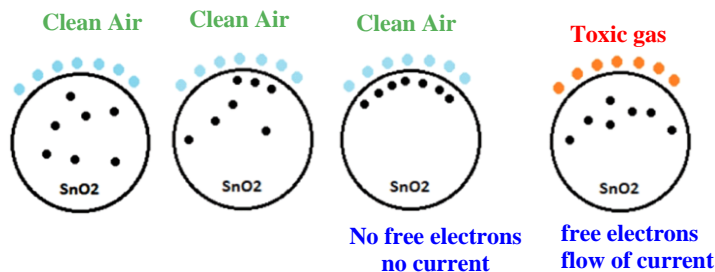


2.17.2. CARBON DIOXIDE SENSOR (CO₂)

A carbon dioxide (CO₂) sensor is a device used to measure the concentration of carbon dioxide gas in the atmosphere.

Working:

- The ability of a gas sensor to detect gases depends on the chemiresistor to conduct current.
- The most commonly used **chemiresistor** is SnO₂ (Tin dioxide) which is an n-type semiconductor that has free electrons.
- Normally the atmosphere will contain more oxygen than combustible gases.
- The oxygen particles attract the free electron present in SnO₂ which pushes them to the surface of SnO₂.
- As there are **no free electrons available**, output current will be zero.
- In the below figure the oxygen molecule (blue color) attracting the free electrons (black color) inside the SnO₂ and preventing it from having free electrons to conduct current.



- When the sensor is placed in the toxic or combustible gases environment (CO₂, NH₃), this reducing gas (orange color) reacts with the adsorbed oxygen particles and breaks the chemical bond between oxygen and free electrons **thus releasing the free electrons**.
- As the free electrons are back to its initial position they can now conduct current. This condition will be proportional to the amount of free electrons available in SnO₂.
- If the gas is highly toxic, more free electrons will be available.

Applications:

- Used in industries to monitor the concentration of toxic gases.
- Used in households to detect emergency incidents.
- Used in air quality check at offices.
- Used in air conditioners to monitor the CO₂ levels.
- Used in detecting fire.
- Used in mines.

2.17.3. OXYGEN SENSORS (O₂)

An oxygen sensor is one type of sensor and it is available in the exhaust system of an automobile.

Types of oxygen sensors

Three types of oxygen sensor

- (i) Concentration cell (zirconia sensors)

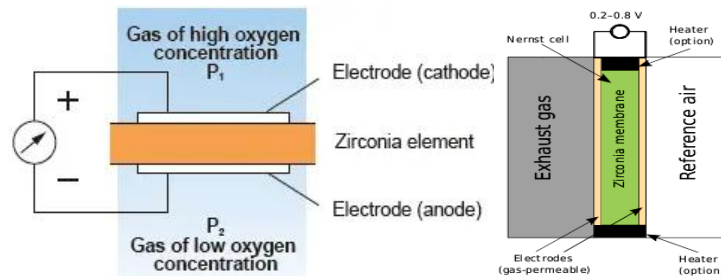
(ii) Oxide semiconductor (TiO_2 sensors)

(iii) Electrochemical pumping oxygen sensors (limiting current sensors).

Thin-film and micromachining technology to the fabrication of oxygen sensors is now in progress and will aid the development of a new generation of sensors.

Zirconia type measurement system: Concentration cell system

- The basic principle is that there is a cathode and an anode submersed in an electrolyte.
- Zirconia oxygen analyzer is specially used to measure the net concentration of oxygen in flue gas.
- Oxygen enters the sensor through a permeable membrane by diffusion and is reduced at the cathode, creating a measurable electric current. There is a linear relationship between the oxygen concentration and the electric current.
- A solid electrolyte like zirconia exhibits conductivity of oxygen ions at high temperature.
- As shown in the figure, when porous platinum electrodes are attached to both sides of the zirconia element to be heated up and gases of different partial oxygen concentrations are brought into contact with the respective surfaces of the zirconia, the device acts as an oxygen concentration cell.
- This phenomenon causes an electromotive force to be generated between both electrodes according to Nernst's equation. And it is proportional oxygen concentration.



Advantages

- Capable of measuring trace oxygen concentration.
- Can be directly installed in a combustion process such as a boiler's flue and requires no sampling system, and response is faster.

Disadvantages

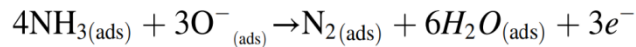
- If the sample gas contains a flammable gas, a measurement error occurs (combustion exhaust gas causes almost no problem because it is completely burned).

2.17.4. AMMONIA SENSORS (NH_3)

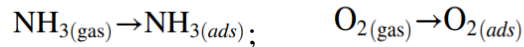
This sensor is designed for higher concentrations of Ammonia. Sensors for lower level detection are in development.

Working Mechanism

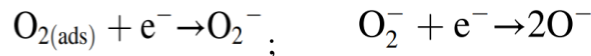
- In environment (air) condition, when the atmospheric oxygen is chemisorbed on the film surface could lead to the removal of an electron from the conduction band.
- Therefore, the oxygen negative species (O_2^-) can create a depletion layer on the film surface resulting in a decrease/or increase in the conductivity/or resistance.
- When the film surface is interacting with the analyte gas molecules (gas atmosphere), the chemisorbed oxygen can release the electrons back to the conduction band of the SnO_2 structure.
- Consequently, the depletion layer becomes reduced, and the conductance of the sensor increases.
- Also, the substitution of Zn ions favors the adsorption of atmospheric oxygen species on the SnO_2 surface; accordingly, it creates more sensing sites to interact with analyte gas molecules.
- The interaction between the adsorbed oxygen and NH_3 species can be considered by the relation.



- Direct adsorption and desorption of oxygen (O_2) and NH_3 in the SnO_2 film surface;



- The formation of negatively charged O_2^- anionic ions on the film surface;



- Based on the above expressions, the release of electrons from the negatively charged adsorbed oxygen sites results in an increase of the current with respect to NH_3 species.

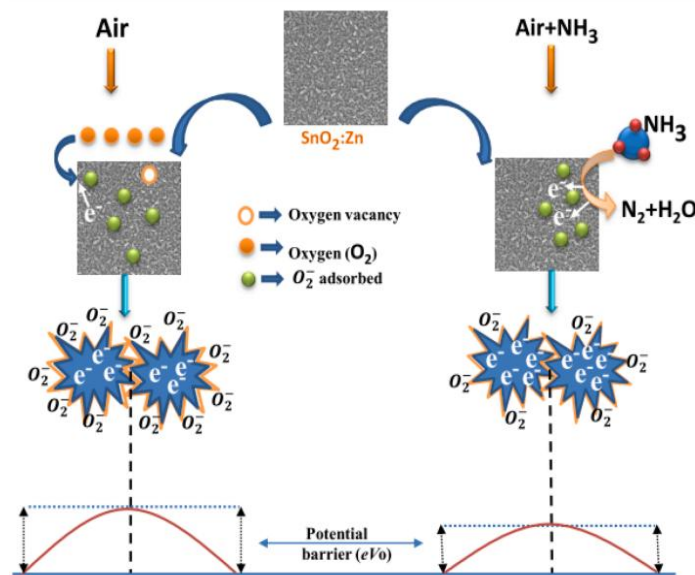


Fig. Possible mechanism for the adsorption of air and NH_3 molecules on the $SnO_2: Zn$ surface at room temperature.

2.18. BLOOD OXYGEN SENSOR

Pulse oximetry is a test used to measure the **oxygen** level (**oxygen** saturation) of the **blood**.

PULSE OXIMETER

Pulse oximeters are medical sensors which are used continuously to measure the oxygen saturation (SPO_2) [Saturation of peripheral oxygen]. of haemoglobin in blood. It displays the percentage of blood that is loaded with oxygen.

Principle of Pulse oximeter

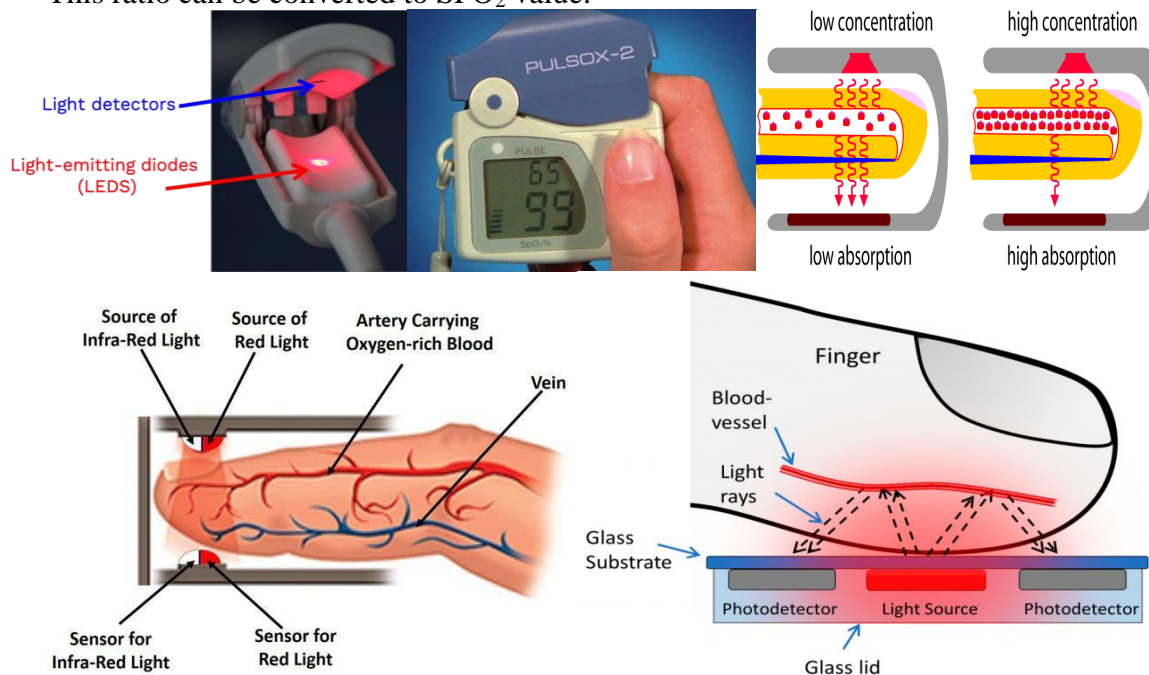
- The principle of pulse oximetry is based on the differential absorption characteristics of oxygenated and deoxygenated haemoglobin.
- Oxygenated haemoglobin absorbs more infrared light and allows more red light to pass through.
- Whereas deoxygenated haemoglobin absorbs more red light and allows more infrared light to pass through.

What is inside the sensor?

- Each pulse oximeter sensor contains two light emitting diodes one emitting red light and the other emitting near infrared light and also has a photo-detector.
- The photo-detector measures the intensity of transmitted light at each wavelength.

Working

- The oxygen content in the blood can be easily calculated by comparing how much red light(R) is absorbed as compared to infrared (IR) light.
- Depending on the amount of oxygenated haemoglobin (or) de-oxygenated haemoglobin, the ratio of red light absorbed to infra-red light (R/IR) absorbed will change.
- This ratio can be converted to SPO_2 value.



How does an oximeter work?

Pulse oximeter probes have light emitting diodes which shine two types of red light through

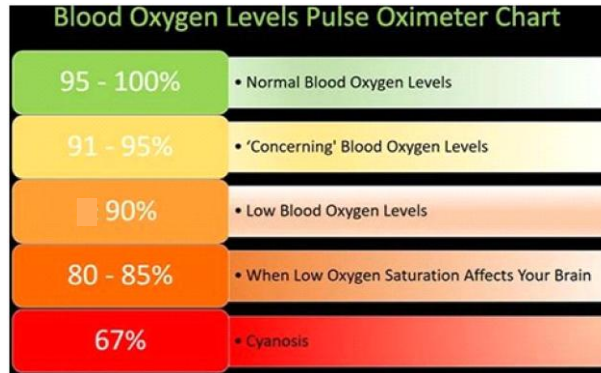
the tissue.

Step – 1: The device is plugged to a person's finger.

Step – 2: Small beams of light pass through the blood in the finger; the sensor on the other side of the tissue picks up the light that is transferred through the tissues.

Step – 3: The oximeter measures oxygen by evaluating changes of light absorption in oxygenated or deoxygenated blood.

Step – 4: The result is displayed on the monitor.



Uses:

- Operating rooms.
- ICU.
- Post anesthesia care units.
- Emergency departments and ambulances.
- Endoscopy suites.
- Sleep laboratories
- Cardiac catheterization laboratories.
- Delivery suites
- Wards.