

MODULE 5: Sensors in Analytical Techniques

Module 2: *Electrode System: Introduction, types of electrodes. Ion selective electrode – definition, construction, working and applications of glass electrode. Determination of pH using glass electrode. Reference electrode - Introduction, calomel electrode – construction, working and applications of calomel electrode. Concentration cell – Definition, construction and Numerical problems.*

Sensors: Introduction, working principle and applications of Conductometric sensors, Electrochemical sensors, Thermometric sensors, and Optical sensors.

Analytical Techniques: Introduction, principle and instrumentation of Colorimetric sensors; its application in the estimation of copper, Potentiometric sensors; its application in the estimation of iron, Conductometric sensors; its application in the estimation of weak acid.

Electrochemical Systems

Ion Selective electrodes

These electrodes selectively respond to a specific ion in a mixture and potential developed is a function of concentration of that ion in the solution. These electrodes consist of a membrane which is capable of exchanging specific ions with solution with which it is in contact. These are also called as membrane electrodes. Eg. Glass electrode.

Glass Electrode

Construction:

The glass electrode consist of glass tube, the bottom of the glass tube is glass bulb made up of very thin glass membrane. The thickness of glass membrane varies from 0.03 mm to 0.1 mm. The membrane is made up of special glass of low melting point and high electrical conductivity. Its

composition is $\text{SiO}_2 - 72\%$, $\text{Na}_2\text{O} - 22\%$, $\text{CaO} - 6\%$. It can sense H^+ ions up to a pH of about 9. Glass bulb contains 0.1 N HCl (Assume concentration is C_2). An Ag/AgCl electrode (internal reference electrode) is placed in the solution and connected by a pt wire for electrical contact.

Glass Electrode

Fig:



The electrode is represented as,

$\text{Ag/AgCl (s) / 0.1N HCl / Glass}$

Working of glass electrode: When the glass electrode is dipped into any solution containing H^+ ions, the Na^+ ions of the glass membrane are exchanged for H^+ ions of the test solution.

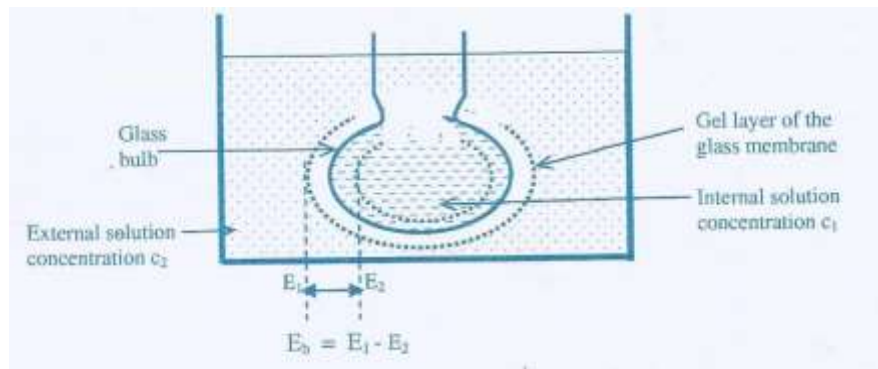
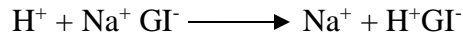


Fig : Boundary Potential

If a thin walled bulb containing an acid is immersed in another solution containing H^+ ions (fig), a potential is developed across the glass membrane. This is called the boundary potential E_b . It is a potential developed across the glass membrane when concentration of the solution inside and outside the glass membrane are different. The E_b is due to the difference in potential ($E_1 - E_2$) developed across the gel layer of the glass membrane between the two liquid.

Mathematically it is represented as,

$$E_b = E_1 - E_2$$

Where, E_1 = Potential due to H^+ present in outside solution (Unknown solution)

E_2 = Potential due to H^+ present in inside solution (known solution)

According to Nernst equation

$$E_b = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

$$E_b = \frac{0.0591}{n} \log C_1 - \frac{0.0591}{n} \log C_2 \dots \dots \dots (1)$$

Where, C_2 is the concentration of H^+ ions of the solution into which glass membrane is dipped. The concentration of H^+ ion inside the bulb (C_1) is constant i.e. $C_1 = 0.1 \text{ M}$.

Thus, $E_b = \frac{0.0591}{n} \log C_2 + K$ or

$$= K + \frac{0.0591}{n} \log C_2$$

Glass electrode selects only H^+ ions ignoring other ions.

Hence $C_2 = H^+$

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

Where, $\log [H^+] = -pH$

$$\text{Thus, } E_b = K - 0.0591pH \text{ -----(2)}$$

The combined glass electrode is dipped into acidic solution, then the potential of the glass electrode is given by....

$$E_G = E_b + E_{Ag-AgCl} \dots \dots \dots (3)$$

From equation 1, theoretically if $C_1 = C_2$, E_b Should be 0, however it has been observed practically that even when $C_1 = C_2$, a small potential is developed which is called as asymmetric potential (E_{asym}). Hence equation 3 can be rewritten as

$$E_G = E_b + E_{Ag-AgCl} + E_{asym} \dots \dots \dots (4)$$

Substituting the value of E_b from equation (2) in equation (4)

$$E_G = K - 0.0591pH + E_{Ag/AgCl} + E_{assy}$$

$$E_G = E_G^\circ - 0.0591pH \dots \dots \dots (5) \text{ Where } (E_G^\circ = K + E_{Ag/AgCl} + E_{assy})$$

The above expression (eq 5) indicate that the potential of glass electrode, E_G varies with the pH of the acidic solution.

Advantages of Glass electrode:

1. It can be used in presence of strong oxidizing /reducing substances and metal ions.
2. It does not get poisoned easily.
3. Equilibrium is easily attained.
4. Portable and compact.

Limitation of glass electrode:

1. It can be used up to pH 13 but becomes sensitive to Na^+ ions above pH 9 resulting in an alkaline error.
2. It does not function satisfactorily in pure alcohol.
3. It has to be handled with care because of glass electrode, and is very fragile.

Determination of pH using glass electrode

To determine the pH of given solution, glass electrode is dipped in a solution whose pH is to be determined. It is combined with a saturated calomel electrode (ref electrode) through a salt bridge. The cell assembly is represented as

$\text{Hg} / \text{Hg}_2\text{Cl}_2 / \text{Cl}^- // \text{solution of unknown pH} / \text{glass} / 0.1\text{N HCl} / \text{AgCl} / \text{Ag}$

EMF of the So formed cell is determined by using electronic voltmeter.

$E_{\text{cell}} = E_{\text{Cathode}} - E_{\text{anode}}$ (Conventionally glass electrode is cathode)

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

Substituting value of E_G from Eq. 5 into above equation

$$E_{\text{cell}} = E_G^\circ - 0.0591\text{pH} - E_{\text{cal}}$$

$$\text{pH} = \frac{E_G^\circ - E_{\text{cal}} - E_{\text{cell}}}{0.0591}$$

$$\text{pH} = \frac{K - E_{\text{cell}}}{0.0591}$$

where, K is known as glass electrode assembly constant.

E_G° value or K is evaluated by dipping the glass electrode in a solution of known pH and measuring emf of the cell formed when coupled with a calomel electrode. Next the same assembly is dipped into test solution and the pH of test solution can be determined.

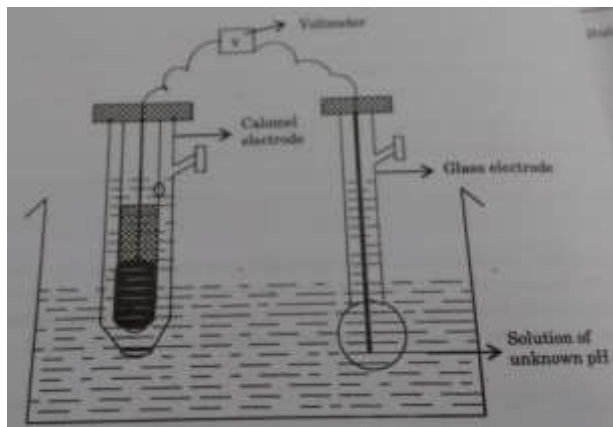


Fig : determination of pH using Glass electrode

Reference Electrodes

Reference electrodes are the electrodes whose potentials are known and they are used for the determination of potentials of other electrodes.

They are of two types;

I. Primary Reference Electrodes: Eg. Standard hydrogen electrode (SHE). Its potential is arbitrarily considered as zero, and it helps to determine the potential of other electrodes.

Limitations of primary reference electrode (SHE)

- (a) Construction and working is difficult on account of difficulties involved in maintaining concentration at unity and pressure in the gas (1 atm).
- (b) Platinum is highly susceptible for poisoning by impurities in the gas.
- (c) It cannot be used in the presence of oxidizing agents.

To overcome all these difficulties, secondary reference electrodes are used.

II. Secondary Reference Electrodes:

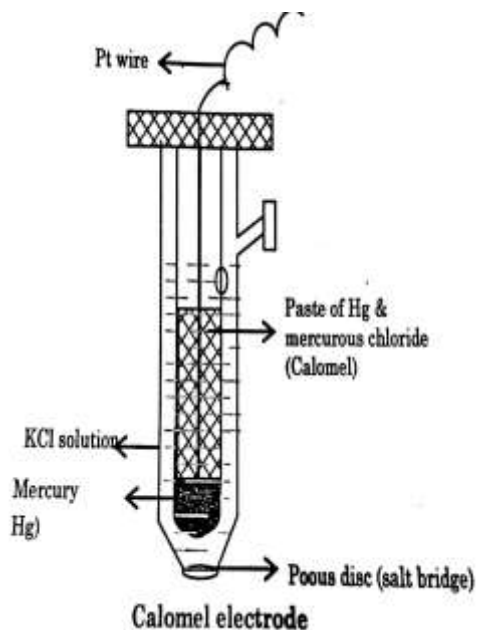
These are the electrode whose potential is known with respect to SHE and are used for determination of potential of other electrodes. Its potential is stable and does not vary much with temperature.

Eg: .Calomel electrode, Silver-silver chloride electrode

Calomel electrode

It is a metal – metal salt ion electrodes and also a secondary reference electrode.

Construction: It consists of mercury, mercurous chloride and a solution of KCl. It is made up of glass tube, Hg is placed at the bottom of the glass tube. It is covered with a paste of calomel (HgCl_2) and KCl solution. A solution of KCl is introduced above the paste through the side tube. Electrical contact is made through Pt wire (dipped in Hg). This glass tube is taken into another glass tube, which has a side tube and a porous plug at the bottom. This porous plug act as salt bridge. The conc of KCl solution used is either decinormal, normal or saturated. Correspondingly, the electrode is known as decinormal, normal or saturated calomel electrode. This constitutes one half cell. Calomel electrode can act as either anode or cathode. It is connected to the other half cell through salt bridge.



Half cell representation

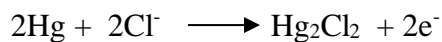
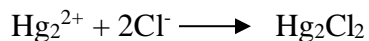
The calomel electrode is represented as, $\text{Hg} / \text{Hg}_2\text{Cl}_2 (\text{s}) / \text{Cl}^- (\text{anode})$

Or $\text{Cl}^- / \text{Hg}_2\text{Cl}_2 (\text{s}) / \text{Hg} (\text{Cathode})$

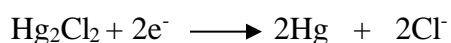
Working

Depending on the potential of electrode with which the calomel electrode is connected, calomel electrode acts as anode or cathode.

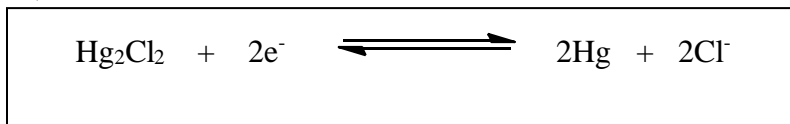
(a). When it acts as anode, electrode reaction is



(b) When it acts as cathode, electrode reaction is



Thus, Net reversible electrode reaction is



Electrode potential is calculated using Nernst equation,

$$\begin{aligned} E_{\text{cal}} &= E^\circ - \frac{2.303RT}{2F} \log [\text{Cl}^-]^2 \\ &= E^\circ - \frac{2.303RT}{F} \log [\text{Cl}^-] \\ &= E^\circ - 0.0591 \log [\text{Cl}^-] \text{ at } 298 \text{ K} \end{aligned}$$

From the above equation it is evident that, the electrode potential of the calomel electrode is mainly depends on the concentration of KCl used. At 298 K the electrode potential are as follows-

For, 0.1 N KCl = 0.334V

1 N KCl = 0.280V

Sat KCl = 0.242 V

Applications:

1. It is used as secondary reference electrode in all potentiometric determinations.
2. Used in glass or combined electrode to determine the pH of the unknown solution.

Advantages:

1. Construction is simple and electrode is portable.
2. The cell potential is stable and reproducible.
3. Cell potential does not vary with temperature.

Limitations:

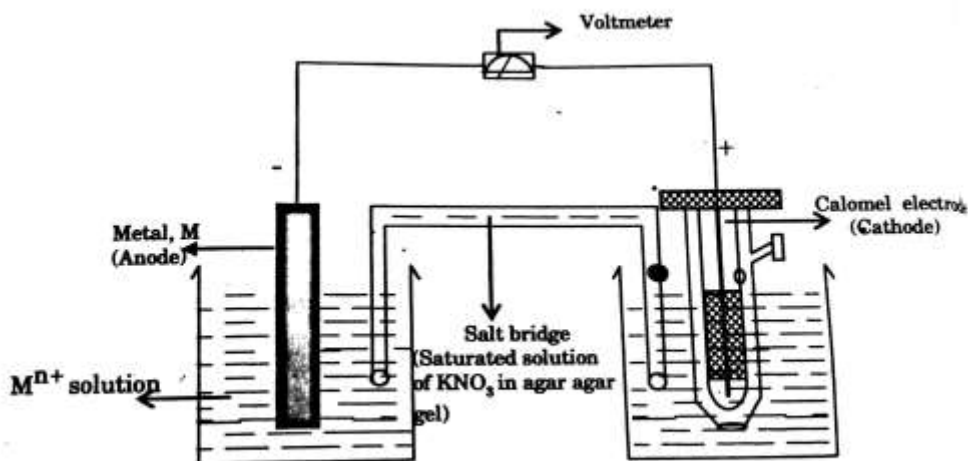
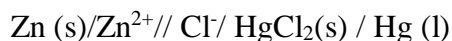
1. Calomel electrode cannot be used beyond a temperature of 60 °C.
2. Hg employed in construction poses pollution problem.

Determination of electrode potential using calomel electrode

To determine the potential of unknown electrode, test electrode eg. Zn/Zn^{2+} is coupled with a saturated calomel electrode to form a cell.

If test electrode is anode:

The cell representation is as follows:



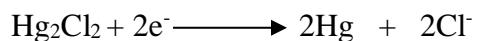
Measurement of electrode potential using calomel electrode

The following reaction takes place at the cell

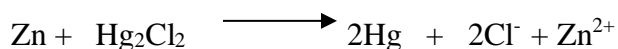
At anode:



At cathode:



Over all reaction:



The EMF of the so formed cell is determined experimentally by potentiometric method.

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

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

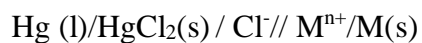
$$= 0.242 - E_{\text{Zn}}$$

Or

$$E_{\text{Zn}^{2+}/\text{Zn}} = 0.242 - E_{\text{cell}}$$

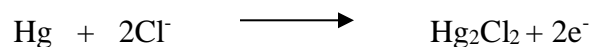
If test electrode is cathode:

The cell representation is as follows:

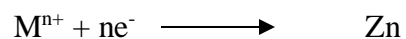


The following reaction takes place at the cell

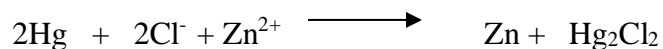
At anode:



At cathode:



Over all reaction:



The EMF of the so formed cell is determined experimentally by potentiometric method.

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

$$= E_{\text{M}^{n+}/\text{M}} - E_{\text{cal}}$$

$$= E_{\text{M}^{n+}/\text{M}} - 0.242$$

Or

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{cell}} + 0.242$$

Concentration Cells

In the case of galvanic cells discussed earlier, the electrical energy arises from the chemical reactions which take place in the cells. There is however another category of cells in which the EMF arises not due to any chemical reaction but due to transfer of matter from one half to the other because of a difference in concentration of the species involved.

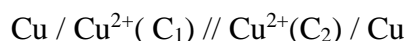
Thus the concentration cell is an electrochemical cell in which both anode and cathode are made up of same elements (identical electrodes) and immersed in same ionic solution (electrolyte) but of different concentration.

Concentration cells are of two types:

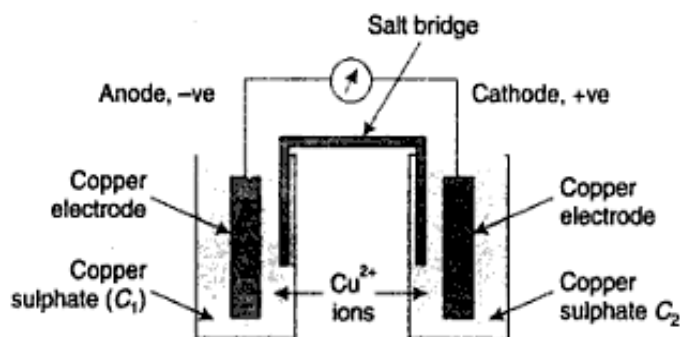
- 1) Electrolyte concentration cell
- 2) Electrode concentration cell

1. Electrolyte concentration cell: In these cells, the two electrodes of same element is in contact with solution of same metal ion (electrolyte) but of different concentration.

Eg. Two copper electrodes immersed in copper sulphate solutions of different concentrations C_1 and C_2 . Cell is represented as

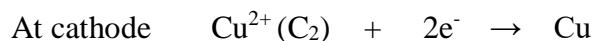
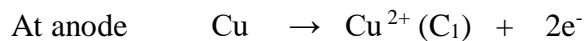


Construction:



Electrolyte Concentration cell

The Electrode reactions are as follows:



EMF of cell is given by

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

$$= \left[E^\circ + \frac{2.303RT}{nF} \log C_2 \right] - \left[E^\circ + \frac{2.303RT}{nF} \log C_1 \right]$$

$$E_{\text{cell}} = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

Where C_2 is the concentration at cathode while C_1 is the concentration at anode.

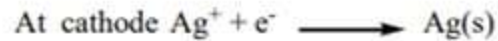
The following conclusions are drawn from the above eq.

1. When two solutions are of the same concentration i.e. $C_2 = C_1$, no current flows. The cell reaction is a change in concentration as a result of which current flows. Therefore cell can operate only as long as concentration terms are different.
2. For above cell to be operative, E_{cell} should be positive which is possible only if $C_2 > C_1$. Thus the direction of spontaneous reaction is from the more concentrated one to the less concentrated one.
3. In a concentration cell, electrode with lower electrolyte concentration acts as anode and the

one with higher electrolyte concentration acts as cathode. Higher the ratio $\left[\frac{C_2}{C_1} \right]$, higher is the emf.

Write the electrode reactions and Calculate the EMF of the given concentration cell at 298K, $\text{Ag(s)} | \text{AgNO}_3 (0.018\text{M}) || \text{AgNO}_3 (1.2\text{M}) | \text{Ag(s)}$.

Ans:



$$E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{C_2}{C_1} \right) \quad \text{at 298K}$$

$$E_{\text{cell}} = 0.0591 \log \left(\frac{1.2}{0.018} \right) \quad (n=1)$$

$$E_{\text{cell}} = 0.1078 \text{ V.}$$

Calculate the emf of Copper concentration cell at 25⁰ C, where the copper ions ratio in the cell is 10.

Given: $\frac{[\text{Cu}^{2+}]_{\text{cathode}}}{[\text{Cu}^{2+}]_{\text{anode}}} = \frac{C_2}{C_1} = 10$

Ans: $E_{\text{cell}} = \frac{0.0591}{n} \log \left(\frac{C_2}{C_1} \right); \quad \text{at 298 K}$

$$E_{\text{cell}} = \frac{0.0591}{2} \log(10)$$

$$E_{\text{cell}} = 0.0296 \text{ V.}$$

Sensors

Introduction

A sensor is a detection device that can sense the measured data and convert it into electrical signals or other required forms of information output according to particular rules, in order to meet the requirements of data transmission, processing, storage, and display, as well as recording and control.

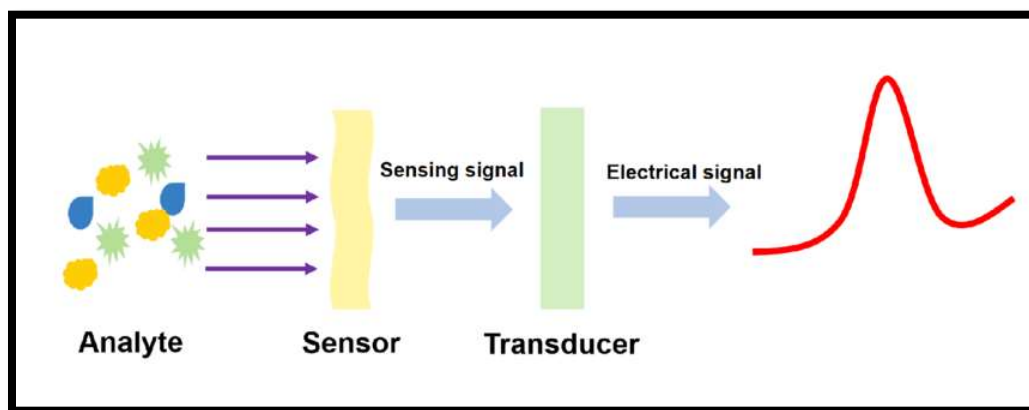
Sensors enable objects to have senses such as touch, taste, and smell, and they gradually become alive as a result of their evolution. *Thermal elements, photosensitive elements, gas-sensitive elements, force-sensitive elements, magnetic-sensitive elements, humidity-sensitive elements, sound-sensitive elements, radiation-sensitive elements, color-sensitive elements, and taste-sensitive elements* are the ten categories according to their basic sensing functions.

Sensors are frequently categorized based on their functioning principle, input data, and application scope. They may be loosely split into three types based on their diverse functioning principles:

- 1) **Physical sensor** – Sensors built with the physical qualities of specific transforming components and the special physical properties of certain functional materials are known as physical sensors.
- 2) **Chemical sensor** – Chemical sensors convert the composition and concentration of inorganic and organic chemical compounds into electrical signals using the electrochemical reaction concept.
- 3) **Biological sensor** - It's a sensor that detects and measures biochemical compounds using biologically active chemicals.

Conductometric sensor:

Working Principle: The relationship between conductance and receptor techniques is the basis for developing conductometric detection. The conducting material acts as an electrochemical transducer to convert the sensing signals into electrical signals.



The basic principle of conductometric detection involves a reaction that can change the ionic species concentration. This reaction leads to changes in electrical conductivity or current flow. In this method, two inert metal electrodes are used. The two electrodes are separated at a certain fixed distance before applying AC voltage, which later causes current flow. The change in conductance between the electrodes due to ionic composition changes during recognition is measured. The speed, practicality, specificity, sensitivity, near real-time detection, and need for low sample volume are some advantages of conductometric sensors.

Applications of conductometric sensors:

- (i) Detection of foodborne pathogens.
- (ii) Detection of alkali metal ions, organic acids,
- (iii) Detection of circulating tumor cells.
- (iv) Toxic heavy metal ion detection

(v) Conductometric sensors for gas sensing.

Additional Material: Conductometric detection is based on measurement of specific conductance of an analyte and is preferable because it can be applied for detection of both electroactive and electroinactive species. The conductivity electrodes can either be in contact with the solution or insulated using a thin layer. Conductivity detection is mostly associated with capillary electrophoresis (CE).

***Contact-mode conductivity measurement**, the electrodes are in direct contact with the sample. Although better contact with sample results in good sensitivity and lesser response time, it is accompanied with the increased risk of degradation of electrodes and contamination of sample*

***Contactless conductivity detection**, on the other hand, does not suffer from electrode instability. In this case, the electrodes are separated from the buffer or sample by a thin layer of insulation. For achieving good capacitive coupling, the insulation layer needs to be as thin as possible.*

***Conducting polymers are also used for conductance-based detection.** They are organic conjugated compounds with an extended π -orbital system allowing movement of electrons from one end to other. Conducting polymers have unique electrical and optical properties that can be tuned by reaction with redox active agents. Electrical conductivity of these types of polymers depends on their ability to transport charge carriers along the polymer backbone. Interaction with redox active species results in the change in conductivity of the polymers which can be measured either in DC or AC conditions. Commonly used conducting polymers are polyaniline, polyacetylene, polypyrrole, polyfluorine, etc.. The advantages of conducting polymers are their environment stability, easy processibility, compatibility with biomolecules, ability to be coated on the surface of desired dimensions, and modification to bind to biomolecules. These properties taken together have paved the way for developing conducting polymer-based sensors for detection of bacteria, proteins, trace metal ions, and many more. Such a conductometric biosensor was developed by Dixit et al. [80] in which polyaniline thin film doped with Fe-Al was deposited on glass substrate. On top of this film, an interdigitated Au electrode array was designed for detection of *E. coli* in liquid samples. The current–voltage characteristics of the film upon exposure to microorganism were measured using source measuring unit. Change in conductivity of the film is due to the interaction of charged microorganism with the polymer film resulting in redox reactions at the polymer film interface.*

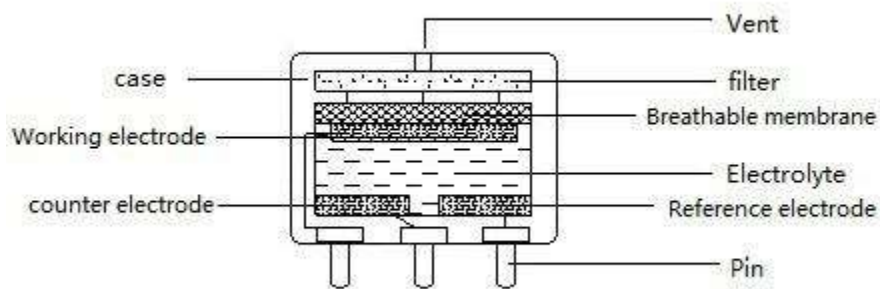
Electrochemical sensors

Electrochemical sensors are devices that give information about the composition of a system in real time by coupling a chemically selective layer (the recognition element) to an electrochemical transducer. **Electrochemical sensors** are made on the basis of ion conduction. According to the formation of their electrical characteristics, electrochemical sensors can be divided into potential sensors, conductivity sensors, electricity sensors, polarographic sensors, and electrolytic sensors.

Electrochemical sensors are mainly used to analyze gas, liquid, or solid components dissolved in liquids, the measurement of liquid pH, conductivity, and oxidation-reduction potential.

Working Principle

The electrochemical sensor works by reacting with the measured gas and generating an electric signal proportional to the gas concentration. A typical electrochemical sensor consists of a sensing electrode and a counter electrode and is separated by a thin electrolytic layer.



The gas first reacts with the sensor through the tiny capillary-shaped opening, then the hydrophobic barrier layer, and finally reaches the electrode surface. Using this method can allow an appropriate amount of gas to react with the sensing electrode to form a sufficient electrical signal while preventing electrolytes from leaking out of the sensor. The electrochemical sensor contains the following main components:

- Breathable membrane** (also called hydrophobic membrane): The breathable membrane is used to cover the sensing (catalytic) electrode, and in some cases, it is used to control the molecular weight of the gas reaching the electrode surface.
- Electrode**: The electrode material should be a catalytic material that can perform semi-electrolytic reactions over a long period of time. Generally, electrodes are made of precious metals, such as platinum or gold, which react effectively with gas molecules after catalysis.
- Electrolyte**: The electrolyte must be able to carry out the electrolysis reaction and effectively transfer the ionic charge to the electrode.
- Filter**: Sometimes a scrubber filter is installed in front of the sensor to filter out unwanted gas. The most commonly used filter material is activated carbon.

Advantages and disadvantages of electrochemical sensors

Advantages of electrochemical sensors

- The use of electrochemical sensors can accurately measure some odors, analyze proteins, and can also be used for new drug development and disease treatment.
- Detection speed is relatively fast, very simple, convenient.
- The cost is relatively low.
- Electrochemical sensors are useful in many aspects, such as medicine and industrial analysis.

Disadvantages of electrochemical sensors

- Short lifespan. They usually need to be replaced every one to three years.
- Electrolytic solution, need to replenish it regularly, which is a bit troublesome.

Application of electrochemical sensors

- i. **Humidity sensor** - The sensor used to measure relative humidity is coated with piezoelectric quartz crystal, which is made of small quartz crystal by photolithography and chemical etching technology.
- ii. Detection of toxic gases like nitrogen oxide, hydrogen sulfide and sulfur dioxide with high selectivity and sensitivity.

Optical Sensors

The method of sensing light rays is known as optical sensing. The sensor type used for optical sensing is known as optical sensor. Optical Sensor converts light rays into electrical signal. The purpose of an optical sensor is to measure a physical quantity of light and, depending on the type of sensor, then translates it into a form that is readable by an integrated measuring device.

Working principle:

The operating principle is the transmitting and receiving of light in an optical sensor, the object to be detected reflects or interrupts a light beam sent out by an emitting diode. Depending on the type of device, the interruption or reflection of the light beam is evaluated. This makes it possible to detect objects independently of the material they are constructed from (wood, metal, plastic or other). Special devices even allow for a detection of transparent objects or those with different colors or variations in contrast.

Optical sensors use visible or ultraviolet light to interrogate sensors for analysis. 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 (Fig.). What the detector monitors varies by technique (e.g., refractive index, scattering, diffraction, absorbance, reflectance, 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.).

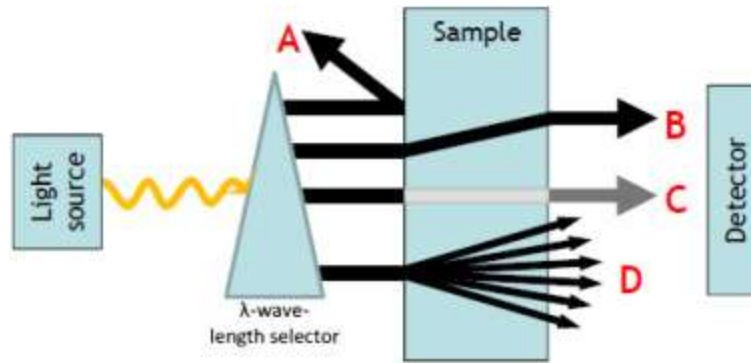


Figure: Working operation of optical sensing. General arrangement of spectroscopic measurements: (A) light reflection; (B) light refraction; (C) light absorption; (D) fluorescent emission.

Applications:

Following are the applications of optical sensors:

- It is used in remote sensing satellite.
- Used in imaging
- Quality and Process Control applications
- Metrology
- Medical instruments

Thermometric sensor

Temperature sensors quantify the quantity of heat energy or even coldness produced by an item or system, allowing us to “sense” or detect any physical change in that temperature, generating an analog or digital output.

Classification:

The temperature sensor is one of the most frequently used sensors, which is widely used in computers, automobiles, kitchen appliances, air conditioners, and household thermostats. The five common types of temperature sensors include,

- i. Thermocouples,
- ii. Thermistors,
- iii. RTDs (Resistance Temperature Detectors),
- iv. Analog thermometer IC, and
- v. Digital thermometer IC.

Working principle:

Different types of temperature sensors have different working principles:

Resistance temperature detectors (RTD) measures the temperature according to the rule that the resistance of the conductor changes with temperature. The temperature-sensing element

of resistance thermometers are commonly made of metal wires as platinum and copper, and at low temperatures, carbon, germanium, and rhodium iron are often used for the element. Because they are almost made of platinum, we often call them platinum resistance thermometers.

As the temperature changes, the resistance value of the metal also changes.

And for different metals, the resistance value changes differently with the temperature, which can be directly used as the output signal.

Resistance changes in 2 different ways:

Positive temperature coefficient

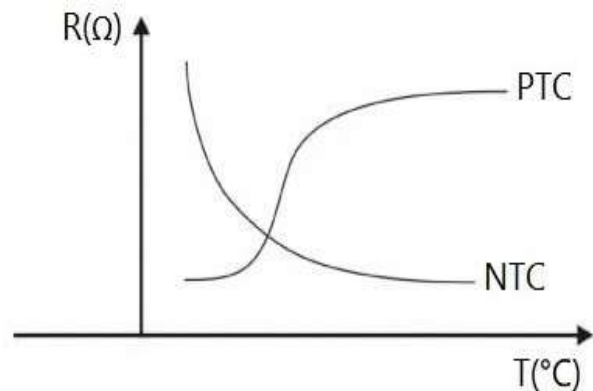
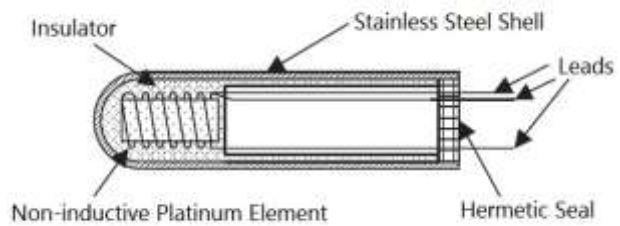
- temperature increases & resistance increases
- Temperature decreases & resistance decreases

Negative temperature coefficient

- temperature increases & resistance decreases
- Temperature decreases & resistance increases

Application:

1. **Sensing Application** - The thermal conversion method of temperature sensors is often used to measure physical quantities, such as flow rate, radiation, gas pressure and type, humidity, thermochemical reaction, etc.
2. **Biomedical Domain** - Special temperature sensors are often applied for biomedical applications. These temperature sensors have low power consumption, long-term stability, and high reliability, with an accuracy of less than 0.1°C between 32°C and 44°C
3. **Industrial Application** - Integrated temperature sensors can be applied in automation and microbe thermal detection.
4. **Consumer Products** - Many low-cost integrated temperature sensors and transmitters have been used in consumer products such as washing machines, refrigerators, and air conditioners.



Analytical Techniques:

1. Colorimetric Sensors: Principle, Instrumentation and applications of Colorimetry

Principle: Colorimetry is a scientific technique that is used to determine the concentration of colored compounds in solutions.

When a beam of incident light of intensity I_0 passes through a solution, a part of the incident light is reflected (I_r), a part is absorbed (I_a) and rest of the light is transmitted (I_t)

Thus, $I_0 = I_r + I_a + I_t$

In colorimeter, I_r is eliminated. For this purpose, the amount of light reflected (I_r) is kept constant by using cells that have identical properties. (I_0) & (I_t) is then measured.

Colorimetry measurements are based on Beer-Lambert's law which states that when a monochromatic light passes through a transparent medium, the amount of light absorbed is directly proportional to the concentration and path length of the solution.

$$A = \epsilon ct$$

Where A is absorbance, ϵ is the molar extinction coefficient, c is the concentration, t is the path length. If t, the path length is kept constant, then, $A \propto c$. Hence a plot of absorbance against concentration gives a straight line.

Instrumentation: Photoelectric colorimeter consists of

- (i) Tungsten lamp as the light source.
- (ii) A filter which provides the desired wavelength range wherein the solution gives the maximum absorbance.
- (iii) A sample cell
- (iv) A photocell detector: Detector are photosensitive elements which converts light energy into electrical energy

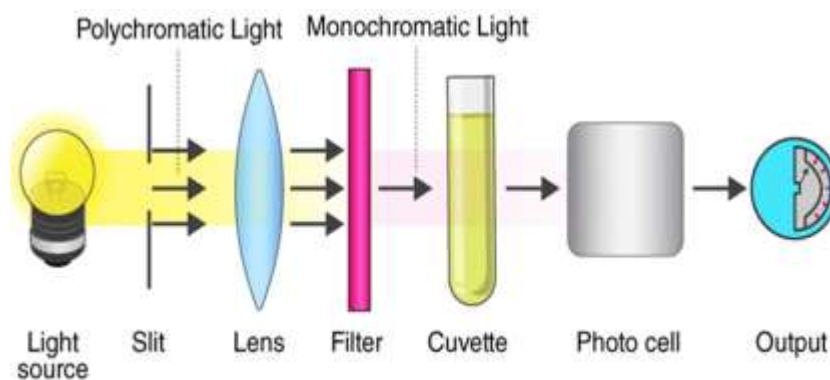


Fig: Schematic layout of colorimeter

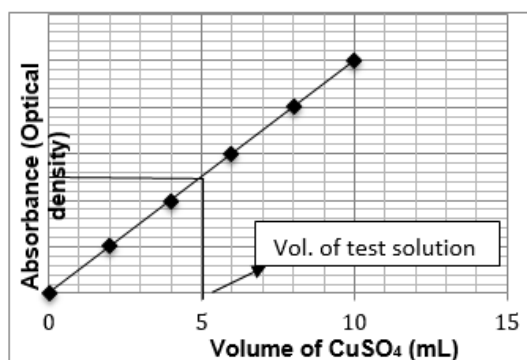
Application: (i) Colorimetry is versatile method of determining the concentration of metals and nonmetals present in small quantities in ores, soil, samples and alloys.

(ii) For the determination of the course of the reaction by measuring the rate of formation and disappearance of the light-absorbing compound

(iii) A compound can be identified by determining the absorption spectrum in the visible region of the light spectrum

(iv) For determination of the concentration of a colored compound

(v) **Colorimetric estimation of Cu in CuSO₄**. Draw out 2, 4, 6, 8, and 10 ml cm³ of the Copper sulphate solution into 50cm³ volumetric flask. Add 5cm³ of ammonia solution to each of them and dilute upto the mark with distilled water and mix well. Prepare a blank solution by diluting 5cm³ of ammonia solution in 50cm³ volumetric flasks. For test solution add 5ml of NH₃ and make up to the mark. Measure the absorbance of each of these against blank solution at 620 nm. Plot a graph of absorbance (OD) against volume of copper sulphate solution and determine the volume of copper sulphate solution in the test sample as shown in the figure and find the amount of copper present in it.



2. Potentiometric Sensor: Principle, Instrumentation and applications of Potentiometry

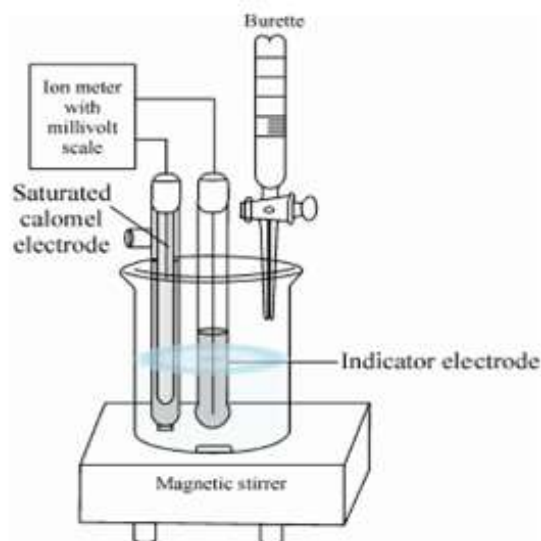
Principle: The procedure of using measurement of emf to determine the concentration of ionic species in solution is called as potentiometry also known as potentiometric titration.

When a metal M is immersed in a solution containing its own ions Mⁿ⁺, the electrode potential is given by Nernst equation.

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

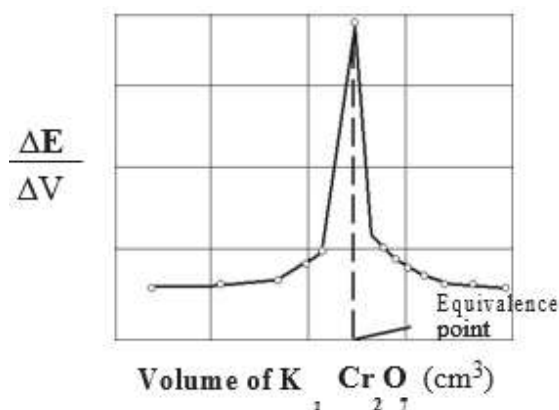
Thus, the concentration can be calculated, provided E^o of the electrode is known. The principle involved in potentiometric titration is the measurement of emf between two electrodes, an indicator electrode, (the potential of which is function of the concentration of the ion to be determined) and a reference electrode of constant potential. In this method, the measurement of emf is made while the titration is in progress. The equivalence point of the reaction is revealed by a sudden change in potential in the plot of emf readings against the volume of titrant.

Instrumentation: A potentiometer consists of: (i) Calomel electrode as a reference electrode, (ii) Platinum electrode as an indicator electrode, (iii) a device for measuring the potential and (iv) Magnetic stirrer.



Application: Potentiometric estimation of FAS using standard $K_2Cr_2O_7$ solution: Pipette out 25ml of FAS into a beaker. Add 1 t.t dil H_2SO_4 , immerse calomel electrode + platinum electrode into it. Connect the assembly to a potentiometer and measure the potential by adding $K_2Cr_2O_7$ in the increments of 0.5ml.

Plot graph $\Delta E / \Delta V$ against volume of $K_2Cr_2O_7$, and determine the equivalence point. From the normality and volume $K_2Cr_2O_7$, solutions calculate the normality and the weight of FAS in the given solution.



3. Conductometric Sensors: Principle, Instrumentation and applications of Conductometry

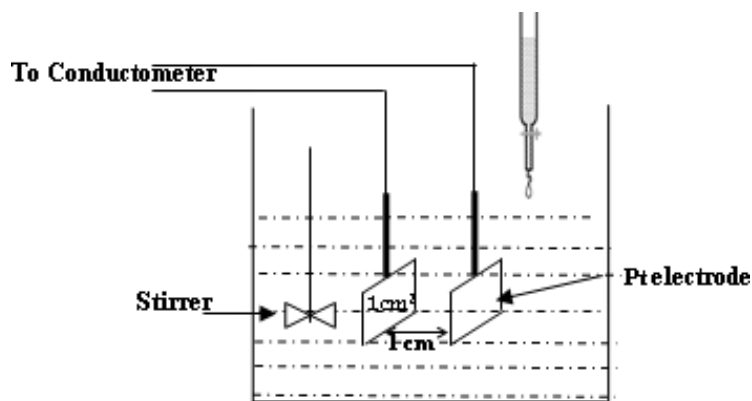
Principle: Conductometry is based on Ohm's law which states that the current i (amperes) flowing in a conductor is directly proportional to the applied electromotive force, E (volts), and inversely proportional to the resistance R (ohms) of the conductor.

$$i = \frac{E}{R}$$

The reciprocal of the resistance is called the conductance (Ease with which electric current flows through a conductor). Specific conductance of a solution is defined as the conductance of a solution present between two parallel electrodes which have 1cm^2 area of cross section and which have kept 1 cm apart.

The conductance of solution depends on the number and mobility of ions. The substitution of ions with different ionic mobility affects the electrolytic conductivity. Therefore, the equivalence point can be determined by means of conductivity measurement for a neutralization reaction between an acid and a base. Equivalence point is determined graphically by plotting conductance against titer values.

Instrumentation: Conductometer consists of: (1) conductivity cell having two platinum electrodes; and a (ii) conductometer. A simple arrangement of conductometric titration is depicted in figure. The solution to be titrated is taken in the beaker.



Application in the estimation of weak: Pipette out 50ml of sample into a beaker. Immerse the conductivity cell into it. Connect the conductivity cell to a conductivity meter and measure the conductance by adding NaOH from the burette by increment of 1 ml. Plot a graph of conductance against volume of NaOH. Determine the neutralization point from the graph as shown below.

Weak acid with a strong base: (CH_3COOH Vs NaOH): In the conductometric titration of a weak acid with a strong base, the conductance of the acid will be initially low due to poor dissociation of acetic acid. On complete neutralization of the acid, further addition of base leads to an increase in the number of more mobile OH^- ions. Hence conductance increases sharply.

