

**Semester: II**
**CHEMISTRY OF FUNCTIONAL MATERIALS**
**(Category: Applied Science Course) Stream: EC (Theory and Practice)**

<b>Course Code</b>	<b>:</b>	<b>CM221IB</b>	<b>CIE</b>	<b>:</b>	<b>100 Marks</b>
<b>Credits: L:T:P</b>	<b>:</b>	<b>3:0:1</b>	<b>SEE</b>	<b>:</b>	<b>100 Marks</b>
<b>Total Hours</b>	<b>:</b>	<b>42L+ 30P</b>	<b>SEE Duration</b>	<b>:</b>	<b>3 Hours</b>

**UNIT-V**
**Sensors and Instrumental methods of analysis**
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**Sensors:** Introduction, types, principle, materials used and applications of optoelectronic sensors, piezoelectric sensor, electrochemical sensor and gas sensors.

**Instrumental method of analysis:** Principle, instrumentation: Colorimetry, potentiometry, flame photometry and conductometry.

**Abstract**

*“The students should be able to understand the importance of chemistry behind sensors for engineering, environment, and health applications. The chapter provides the working principle, and applications of pulse oximetry, piezoelectric, ascorbic acid, glucose, and gas sensors. It will provide insights into real world applications of sensors which are purely based on chemistry concepts. The second part of the chapter covers instrumental analysis, which is also based on various sensors, which works on the principle of optoelectronic, potential, conductance phenomena. It will provide the principle and instrumentation and applications of colorimetry, flame photometry, conductometry, and potentiometry.*

**Blow-up Syllabus**

<b>Sl No</b>	<b>Topic to be taught</b>	<b>Duration</b>
1	Introduction to sensor technology, types of sensors	1 hour
2	Optoelectronic sensors- working principle, materials used, applications	1 hour
3	Piezoelectric sensor- working principle, materials used, applications	1 hour
4	Electrochemical sensor- working principle, materials used, applications	1 hour
5	Gas sensors- working principle, materials used, applications	1 hour
6	Colorimetry: Principle, instrumentation, working	1 hour
7	Potentiometry: Principle, instrumentation, working	1 hour
8	Flame photometry: Principle, instrumentation, working	1 hour
9	Conductometry: Principle, instrumentation, working	1 hour

## Sensor

It is device that measures change in a physical (heat, light, sound, pressure etc) and/or chemical (pH, smell, taste, concentration, humidity etc) parameters of interest in an environment and transforms it into an electronic signal.

**Transducer:** A transducer is a device that transforms a signal from one energy form to another energy form.

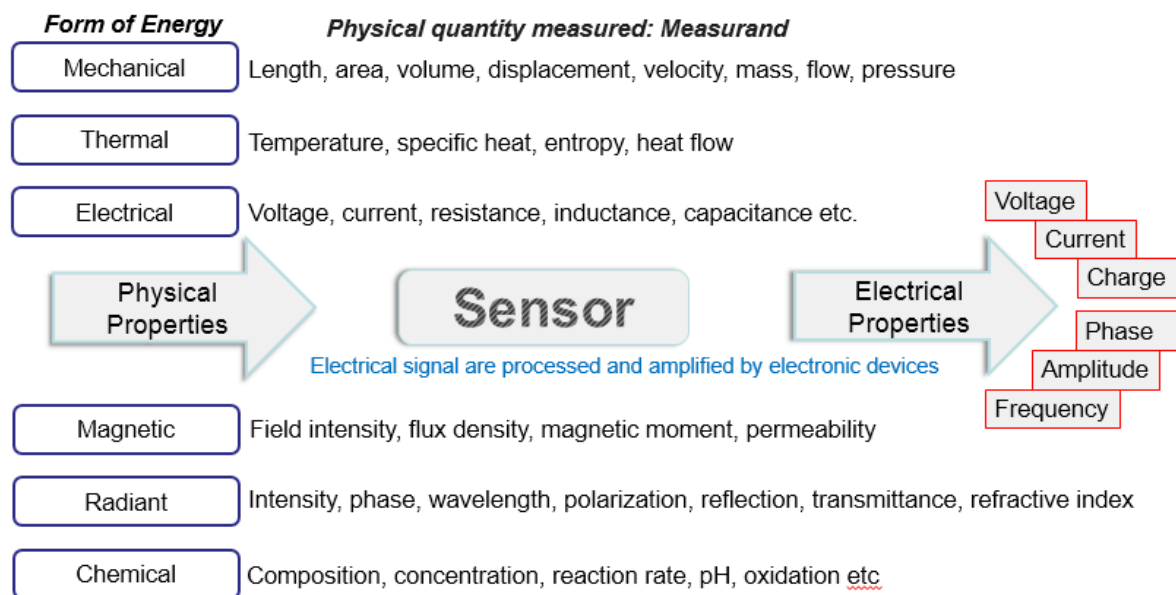
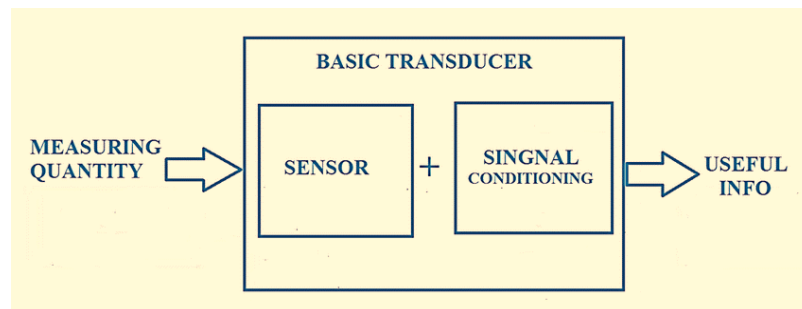


Figure 5.1. (a) Schematic representation of sensor device, (b) Types of sensors based on Input and output properties of sensors

## **Optoelectronic sensors**

It is a sensor that convert light, or a change in light, into an electric signal. The sensor is capable of detecting polarization, wavelength, or frequency of the light rays like visible,

infrared, and ultraviolet, converts that change into electric signal via photoelectric effect. It works like photovoltaic (solar cell) cell.

**Example:**

1. **Pulse oximetry:** Pulse oximetry is a valuable non-invasive low cost sensor that provides data regarding the Oxygen saturation (SPO<sub>2</sub>) of haemoglobin in blood in terms of percentage of hemoglobin molecules loaded with oxygen in arterial blood in patients.



*Figure 5.1. (Source and copyright: Copyright © 2015 DNA TECHNOLOGY, INDIA . All Rights Reserved <https://www.dnatechindia.com/basic-working-pulse-oximeter-sensor.html>)*

**Principle:** It works on the principle that Oxygenated hemoglobin absorbs more infrared light and allows more red light to pass through. Whereas Deoxygenated hemoglobin absorbs more red light and allowing more infrared light to pass through.

**Working:** It consists of two light emitting diode, one emitting red light and the other emitting near infrared light, it also has a photodetector. The photodetector measures the intensity of transmitted light at each wavelength. And using the differences in the reading the blood oxygen content is calculated. The probe is placed on a suitable part of the body, usually a fingertip or ear lobe.

**Methods for Monitoring Oxygen Saturation in Blood**

**(a) Transmission Method**

In the transmission method the transmitter i.e. the LED & the receiver i.e. the photo-detector are placed on opposite side of the finger. In this method this finger will be placed between the LED's & the photo-detector. When the finger is placed a part of the light will be absorbed by the finger and some part will reach the photo detector. Now with each heart beat there will be

increase in volume of blood flow this will result in more light getting absorbed by the finger so less light reaches the photo-detector.



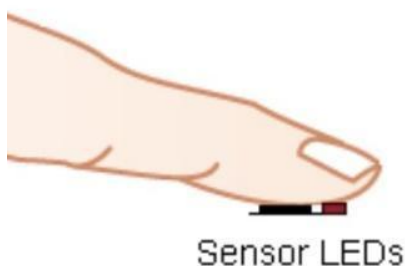
*Fig 5.2. Transmission type pulse oximeter*

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Hence if we see the waveform of received light signal it will consist of peaks in between heart beats and trough (bottom) at each heartbeat. This difference between the trough & the peak value is the reflection value due to blood flow at heart beat.

#### **(b) Reflectance Method**

In Reflective method the LED & the photo-detector are placed on the same side i.e. next to each other. In the reflective method there will be some fixed light reflection back to the sensor due to finger. With each heart-beat there will be an increase in blood volume in the finger this will result in more light reflection back to the sensor.



Hence if we see the waveform of the received light signal it will consist of peaks at each heartbeat. A fixed low value reading is there in between the heart beats this value can be considered as constant reflection and this difference of the peak subtracted from the constant reflection value is the reflection value due to blood flow at heart beat.

*Fig 5.3. Reflectance type pulse oximeter*

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In both above cases you can see the troughs/peaks in reflected light occur at each heartbeat the duration between two spikes can be used to measure the persons Heart Rate. Hence a

typical heart beat sensor Module consists of only on Transmitter LED (mostly infrared) and one photo-detector.

### So exactly how is Oxygen Saturation Calculated?

Now that you have come to know the different methods of sensor placement while measuring the oxygen content in blood (SPO2) we will now see how exactly it works. As said earlier the sensor consist of two transmitting LED's a Red led of approximately 650 nm (nano-meter) and an infra red led which has a wavelength of 950 nm.

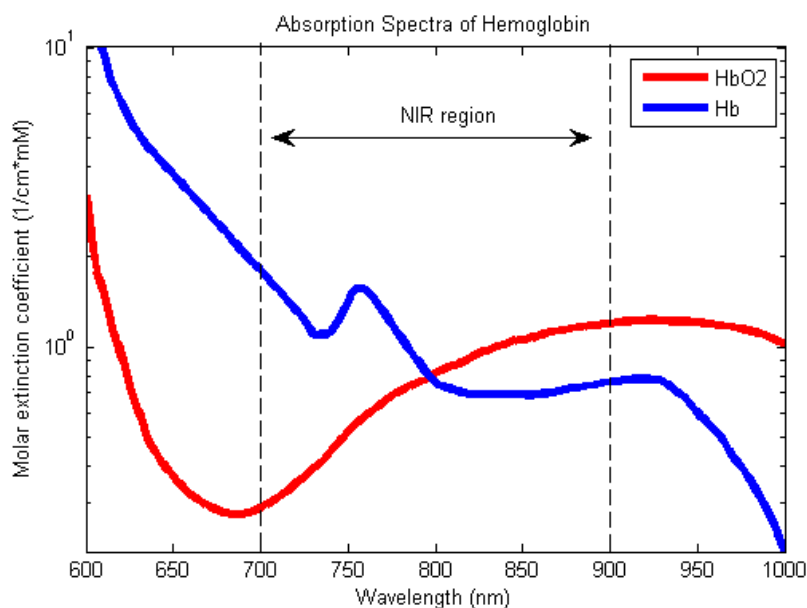


Fig 5.4. Light absorption trend of hemoglobin and oxy-hemoglobin.

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<https://www.dnatechindia.com/basic-working-pulse-oximeter-sensor.html>)

In the above graph you can see the absorbance rate of Oxygenated haemoglobin to various light wavelength. You will see Oxygenated haemoglobin (RED line) absorbs more infrared light than red light. Also the De-Oxygenated haemoglobin (blue line) absorbs more red light as compared to infrared light. The oxygen content in the blood can be easily calculated by comparing how much red light (R) is absorbed as compared to infra-red (IR) light.

Depending on the amount of Oxygenated haemoglobin or De-Oxygenated haemoglobin the ratio of red light absorbed vs Infra-red light (R/IR) absorbed will change. Typically R/IR ratio of 0.5 equates to approximately 100% SpO<sub>2</sub>, a ratio of 1.0 to approximately 82% SpO<sub>2</sub>, while a ratio of 2.0 equates to 0% SpO<sub>2</sub>.

## Piezoelectric (PE) Sensors

“Piezo” is word derived from Greek, it means for “press” or “squeeze”. A piezoelectric sensor is a device, which converts physical parameters like acceleration, strain, pressure, vibration, temperature, or force into an electrical charge which can then be measured. The schematic representation of PE sensor is shown below.

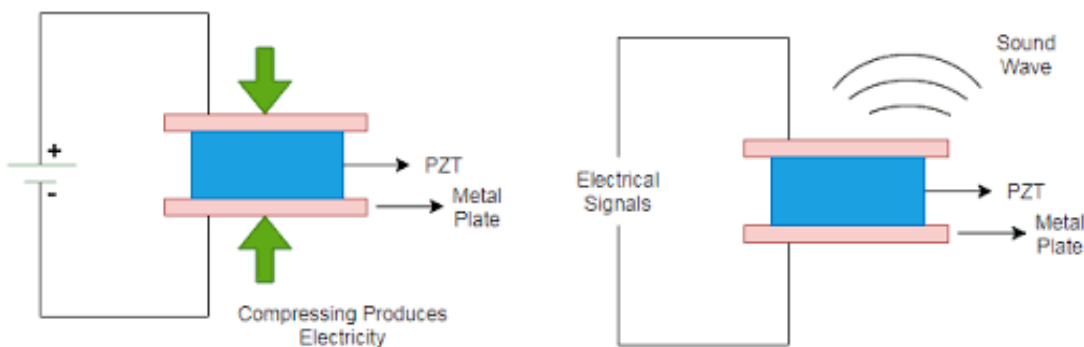


Figure 5.5. Schematic representation of Piezoelectric sensor

The PE sensor is widely used in biomedical, wearable electronics, and self-power energy harvesting devices. The piezoelectric sensors are mostly fabricated by using the perovskite ceramic material (lead zirconate titanate (PZT)) and also other lead-free ceramic piezoelectric sensors using bismuth sodium titanate (BST), barium titanate ( $\text{BaTiO}_3$ ), boride and silicide ceramics ( $\text{TiB}_2$ ,  $\text{TaSi}_2$ ,  $\text{WSi}_2$ , etc.).

### Characteristics of PE sensors:

The good PE sensor should exhibit:

High strength, High stability, High voltage output, Highly flexible, Wide frequency range, Impact resistance, High mechanical strength, Elastic compliance etc

**Strain Sensor:** Upon applying the external force on an object, the strain (permanent/temporary) is induced in the object due to its structural (internal) deformation, this results in change in internal resistance of the object, which can be measured by using the device called strain sensor. Various nanomaterials like graphene, CNT, PVDF, and their hybrids are used in these sensors.

Strain sensors widely used in flexible and wearable electronic devices for medical applications, civil engineering structures, mechanical engineering, aircrafts structures, etc

**Strain sensors** are widely used in medical industry applications, are as follows:

- ❖ **Pulse measurement** – PE sensors are very sensitive to record pulse measurements and effective in monitoring the patients’ health.



- ❖ **Stethoscopes** – Due to high sensitivity and robustness PE sensors, they are often used within stethoscopes.
- ❖ **Anaesthesia Effectiveness** - PE sensors are capable of accurately measuring the muscles stimulations, and hence can be helpful in understanding the effectiveness of anaesthesia.
- ❖ **Sleep Studies** - PE sensors can be attached to various parts of the patient body and can be used to measure the smallest movements of patients during the sleep also.

PE sensors are very popularly finds their application in wearable and stretchable electronics used in healthcare and biomedical engineering, sport performance monitoring, soft robotics, and gaming and virtual reality.

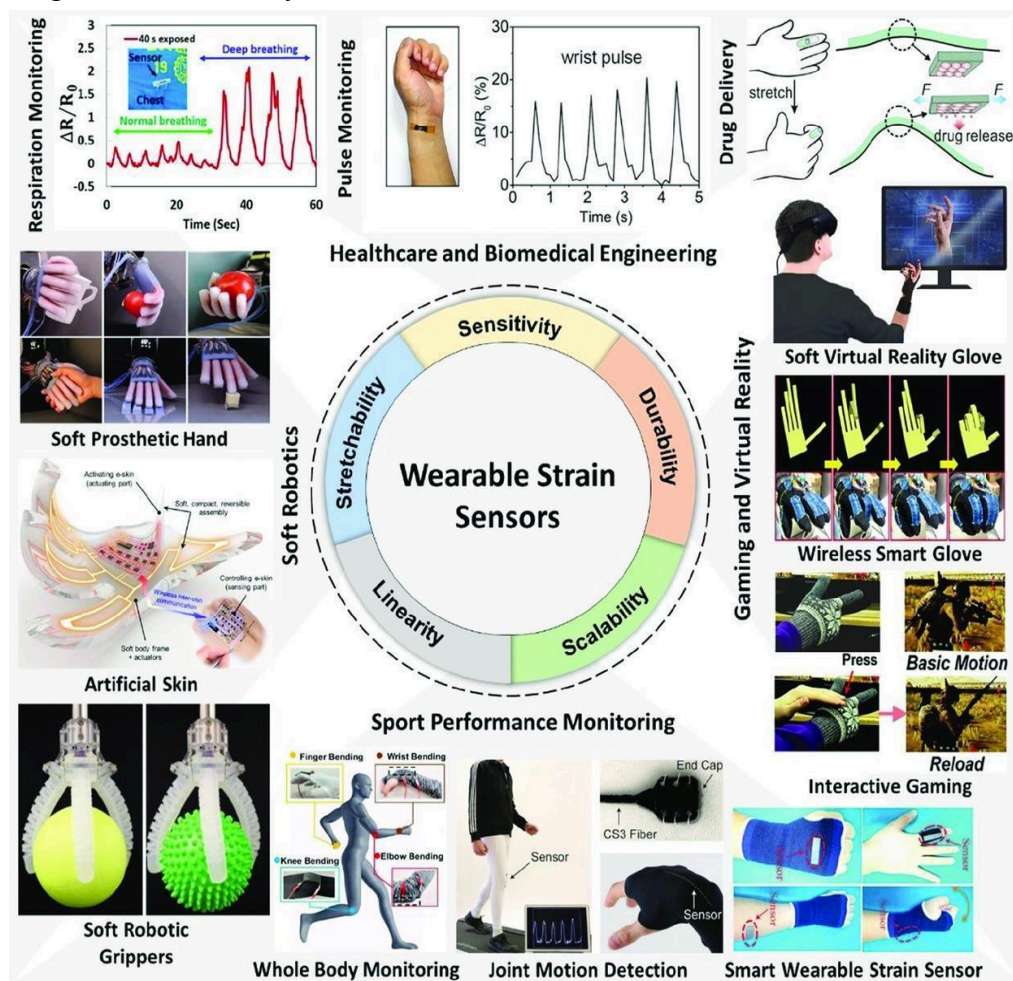


Figure 5.6. Wearable and stretchable strain sensors and their potential applications [for more understanding read: <https://doi.org/10.1002/aisy.202000039>]

**Electrochemical (EC) Sensors:** a device that converts chemical composition data of the analyte into an analytically usable signal.

**Working principle:** The basic principle of EC sensor is that it measures the current produced by chemical reactions in the electrochemical system. The main components of the sensor are (a) electrodes system, (b) transducer (c) amplifier and (d) recorder.

In electrochemical sensor, the electrode system consist of three electrodes such as working electrode, counter/auxiliary electrode and reference electrode. It has a potentiostat, which is an electronic instrument that controls the voltage between two electrodes. Working electrode (WE) is very sensitive to any change in analyte solution, provides the surface for the analyte to undergo reaction, when the potential is applied between WE and RE. The CE helps in completing the circuit by allowing the reaction, which is opposite to WE reaction, to happen. If an oxidation reaction happens at WE, reduction reaction will take place at CE, and vice versa. The RE is independent of the analyte and other ions concentration. Its potential is constant while measuring the potential of WE. By measuring the current of redox reaction, the analyte can be identified. The figure 4.13 represents the electrode system of the EC sensor. For the EC sensor system as shown in figure 4.13(a), the RE can be Standard Hydrogen Electrode (SHE), calomel electrode, silver-silver chloride, CE can be Gold, platinum and carbon electrodes, and WE can be Carbon, glassy carbon electrode (GCE).

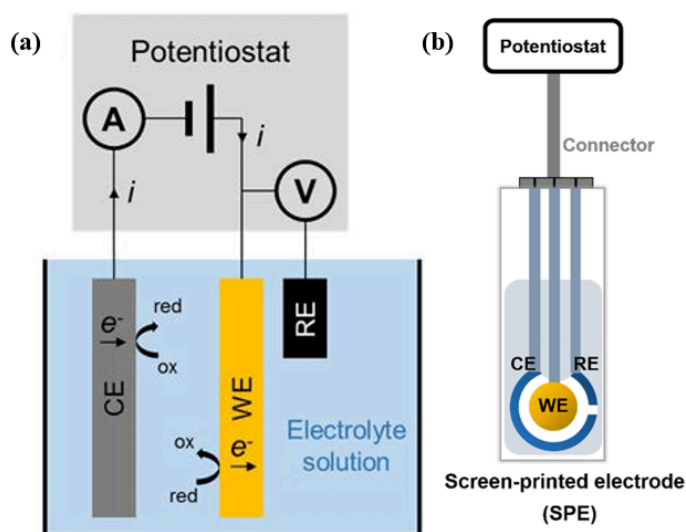


Figure 5.7. Three electrode systems used in electrochemical sensor (a) Combination of three distinct electrodes (b) Screen printed carbon electrode (all three combined)

The electrode shown in figure 4.13(b), is named as screen printed electrode, which is low cost, disposable, which are fabricated by printing the ink of carbon, silver, gold, and platinum on plastic (Flexible Polyester Film) or ceramic substrate. WE are generally printed by graphite or carbon (graphene, CNT) based ink, RE are printed by silver/silver chloride ink and CE is by carbon ink.



The EC sensor used for various analytes such as hydrogen peroxide, glucose, urea, alcohol etc, which are adsorbed on receptors (nanomaterials, Graphene, CNTs metal oxides). They undergo redox reaction upon applying voltage, the resultant current (electrons released) is measured by transducer, which is characteristic property of a biomolecule under study. Then the current is quantified by using amplifier and recorder as shown below.

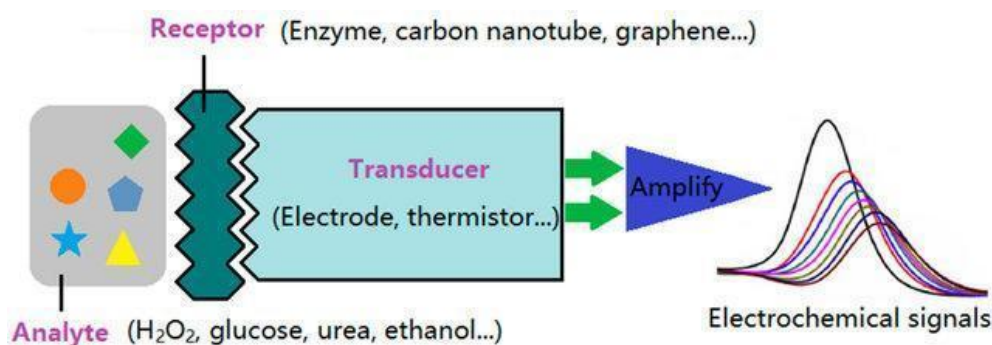
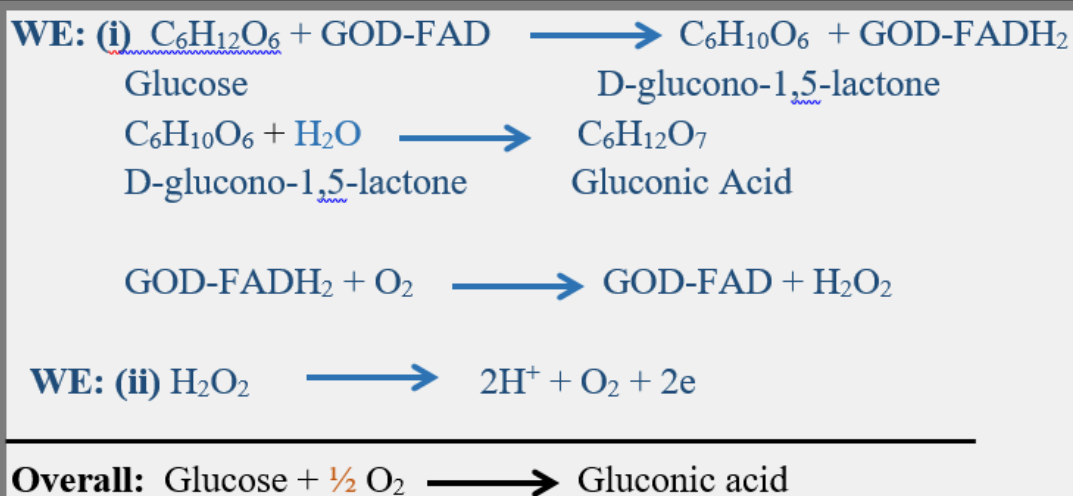


Figure 5.8. Electrochemical sensor components; Analyte, Receptor, Transducer and recorder

## Applications of Electrochemical sensor for biomolecules

### Glucose sensor in diabetes management

In EC sensor, glucose and oxygen react in the presence of nanomaterials or glucose oxidase (GOx) functionalized WE, and thus oxygen is consumed and hydrogen peroxide is produced (as shown in equation below). Further, the glucose concentration can be detected indirectly by electron liberated at WE as shown in reaction.



## Ascorbic acid sensor

Ascorbic acid (AA) is also called as Vitamin C, an essential nutrient and antioxidant required for the human body. Unfortunately, the human body cannot produce/synthesize this biomolecule, and hence it should be consumed by food and drugs. The deficiency of AA lead to scurvy, mental disorder, cancer, etc.

Similar to glucose, the AA can also be analyzed in EC sensor and the following schematic representation depicts the sensor mechanism of AA.

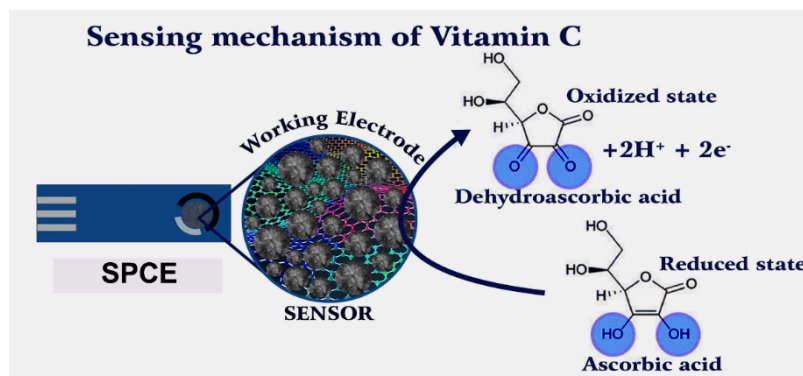


Figure 5.9. The SPCE is functionalized with nanomaterials and possible redox reaction of AA at WE.

## VOCs sensor

Volatile organic compounds are the organic molecules having very low solubility in water and exhibit a high vapor pressure. They are liberated in industries such as pharma, biotech, paints, vanishes. Some examples of VOCs are Phosgene, benzene, ethylene glycol, formaldehyde, methylene chloride, tetrachloroethylene, toluene, xylene, acetone, alcohol, and 1,3-butadiene etc. These VOCs are very dangerous to health upon inhaling, which effects to the liver, kidneys, or central nervous system, even some VOCs are suspected or proven carcinogens. Further, the healthy individual's exhaled breath has major VOCs such as isoprene (12-580 ppb), acetone (1.2-1,880 ppb), ethanol (13-1,000 ppb), methanol (160-2,000 ppb) and other alcohols. Today, human exhaled breath analysis using gas sensors and e-noses (as shown below), is helping the diagnosing a wide range of diseases.

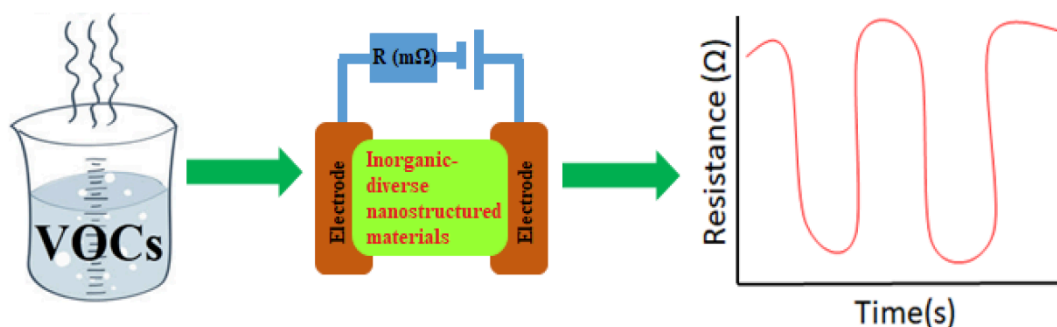


Figure 5.10. Schematic illustration of device based sensing of diverse nanostructures to volatile organic compounds (VOCs). [<https://doi.org/10.3390/s21020633>]

## Electrochemical Gas sensors

Electrochemical gas sensors also called as electrochemical gas detectors, which are designed to identify and measure the quantity of the concentration of gasses like oxygen, carbon dioxide, carbon monoxide, hydrogen, NO<sub>x</sub>, SO<sub>x</sub>, PO<sub>x</sub>, LPG, H<sub>2</sub>S etc . These gases are produced from industrial emissions, vehicle exhaust and open burning of garbage waste, which needs to be monitored. Therefore the electrochemical gas sensors can be effective tool for analyzing them, as it consumes less power than other conventional gas sensors.

The schematic representation of working electrochemical has sensor with respect to CO is represented as follows. [<https://doi.org/10.1016/j.sintl.2021.100116>]

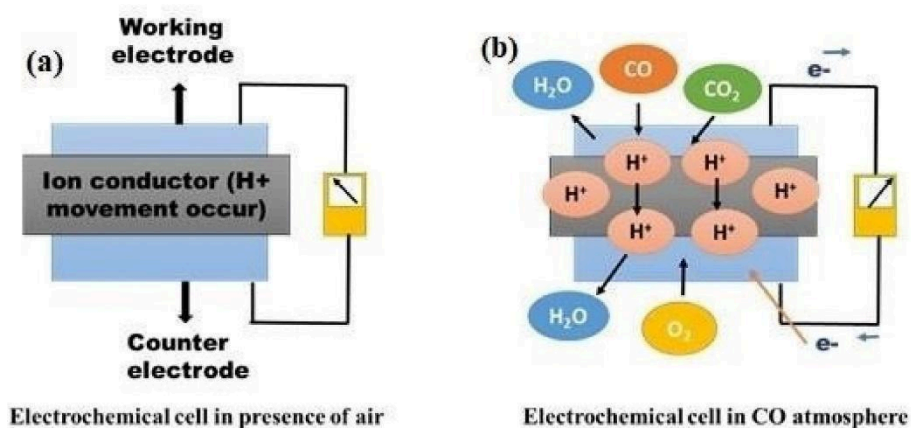


Figure 5.11. Schematic illustration of EC sensor (a) air , (b) carbon monoxide.

The EC gas sensor system consists of combination of two or three electrodes which are called reference, working, auxiliary/counter electrodes and ionic conductor between them as shown in figure 4.17. In this setup, the ionic conduction of the electrolyte, which in contact with WE and CE, complete the circuit. When gas molecules (CO) reacted with WE as shown in reaction below, @WE,  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$  : The electrons released at WE are

made to pass through externally and the  $H^+$  ion internally towards CE. By measuring the current flow, the type and quantity of gas sensor can be measured.

## Instrumental method of analysis:

### 1. Colorimetry: Principle, instrumentation

Colorimeter is a form of photometer which deals with the measurement of light transmitting power of a colored solution in order to determine the concentration of light absorbing substances present within it. It was invented by Louis J Dubosca in 1870 [Ref: <https://doi.org/10.1021/ed071p967>]. The concentration of colored solute in a solution is estimated by comparing its color intensity with that of standard solution containing a known concentration of solute.

#### Principle of Colorimeter :

When a beam of incident light of intensity  $I_0$  passes through a solution, following events occur:

- A part of incident light is reflected. It is denoted by  $I_r$
- A part of incident light is absorbed. It is denoted by  $I_a$
- Remaining incident light is transmitted. It is denoted by  $I_t$

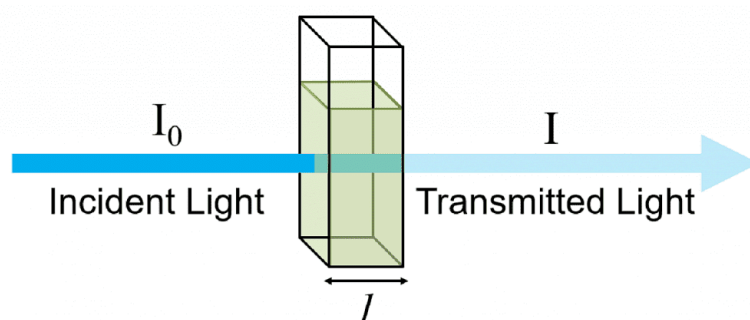
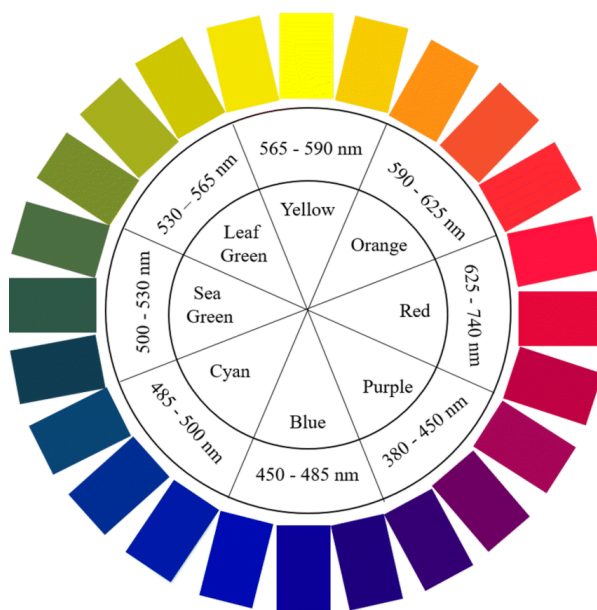


Figure 5.12. Light absorption by colored solution

As  $I_r$  is kept constant by using cells with identical properties, The light that is not absorbed is transmitted through the solution and gives the solution its color. Note that *color of the incident light should be complementary to that of color of the solution* as shown below:



*Figure 5.13. Complementary colors*

The ratio of the intensity of transmitted light ( $I_t$ ) to the intensity of incident light ( $I_0$ ) is called **transmittance (T)**. Photometric instruments measure transmittance. In mathematical terms,  $T = I_t/I_0$

The **absorbance (A)** of the solution (at a given wavelength) is defined as equal to the logarithm (base 10) of  $1/T$ .

That is,  $A = \log (1/T)$

These measurements are dependent on two important laws:

### 1. Beer's law:

When monochromatic light passes through a colored solution, the amount of light absorbed is directly proportional to the concentration (C) of solute in the solution.

### 2. Lambert's law:

When monochromatic light passes through a colored solution, the amount of light absorbed is directly proportional to the length (l) or thickness of the solution.

3. **Beer-Lambert's law:** When monochromatic radiation passes through a homogeneous medium, then the rate of decrease in the intensity of the transmitted radiation with the increase in the thickness of the medium and the concentration of the solution varies directly with the intensity of incident radiation

**Absorbance (A)  $\propto$  Cl**

Or,  $A = \epsilon Cl$

where  $\epsilon$  is a constant known as **absorption coefficient**.

As the path length is same (as same cuvette is used), Concentration of an unknown solution can be determined by using equation:

$$\text{Concentration of Test} = \frac{\text{Absorbance of Test}}{\text{Absorbance of Standard}} \times \text{Concentration of Standard}$$

### Colorimeter instrumentation:

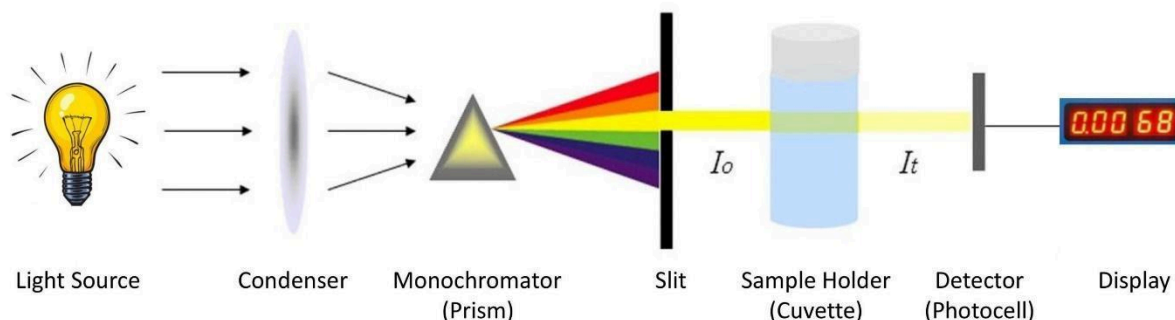


Figure 5.14. Schematic representation of colorimeter

#### 1. Light Source:

The light source should produce energy at sufficient intensity throughout the whole visible spectrum (380-780nm). Tungsten lamp is frequently used.

**2. Slit:** It allows a beam of light to path and minimize unwanted light.

**3. Condensing lens: Give parallel beam of light.**

**4. Monochromator:** It is used to produce monochromatic radiation (one wavelength band) from polychromatic radiation (white light) produced from light source. It allows required wavelength to pass through it. Prism, gelatin filters, grating monochromators or interference filters can be used.

**5. Sample Holder (Cuvette):** Must be transparent. Glass or clear plastic cuvettes are preferred.

**6. Photo detectors:** Detector of colorimeter basically receives the resultant light beam once it has passed through the sample and converts it into electrical signal. Selenium photocell, silicon photocell, phototube, photomultiplier tube etc are used.

**7. Display:** It detects and measures the electric signal and makes visible output.

### Uses and Applications

In clinical laboratory, colorimeter is used for the estimation of various biochemical compounds in variety of biological samples like blood, plasma, serum, urine and other body fluids. All those methods which involve the formation of colored product with specific



analyte, the analyte can be estimated quantitatively. Colorimeters are also widely used for monitoring the growth of bacterial or yeast cells in liquid cultures.

## 2. Potentiometry

Potentiometry principles state that by measuring the change in the potential difference between two electrodes of a cell dipped in a solution, its concentration can be estimated by using Nernst Equation. It determines the analyte concentration by a change in the concentration of ions.

**Example: Potentiometric estimation of any Ferrous ions (reducing agent) using potassium dichromate (oxidising agent) is follows.**

The potentiometry is based on Nernst equation, it gives the relation between the potential at an electrode and the concentration of the active species in the solution.

Oxidized form + ne-      Reduced form
---------------------------------------

**For the reaction,**

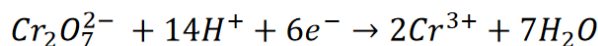
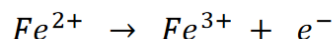
Nernst equation can be written as

$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{[oxidized\ form]}{[reduced\ form]}$$

Where  $E^{\circ}$  is the standard electrode potential and the terms within the brackets represent their concentrations.

It is evident from the equation that the potential depends upon the concentrations of the oxidised and the reduced species in the solution. When a reducing agent in solution is oxidized using an oxidizing agent, the concentrations and hence the potential changes. Potentiometry essentially involves the measurement of change in potential as and when a species in solution is oxidized or reduced. When a titration of a reducing agent is carried out against an oxidising agent, the potential gradually changes in the beginning but changes rapidly near the end point. A plot of change in potential against volume reveals a sudden change in potential at the equivalence point. This sudden change in the present experiment

can be explained as follows. **The reactions that take place when dichromate is added to ferrous solution are:**



The potential of the system before the equivalence point is given by

$$E = E^0 + \frac{0.0591}{1} \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

i.e., the potential is dependent on the concentration of  $Fe^{2+}$  and  $Fe^{3+}$  ions. The potential of the solution will be around 0.75V. At the equivalence point the potential is decided by the concentrations of  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Cr_2O_7^{2-}$  and  $Cr^{3+}$  ions. The potential at equivalence point is given by

$$\begin{aligned} E &= \frac{E_{Fe^{3+}/Fe^{2+}}^0 + E_{Cr^{6+}/Cr^{3+}}^0}{2} \\ &= \frac{0.75V + 1.33V}{2} = 1.04V \end{aligned}$$

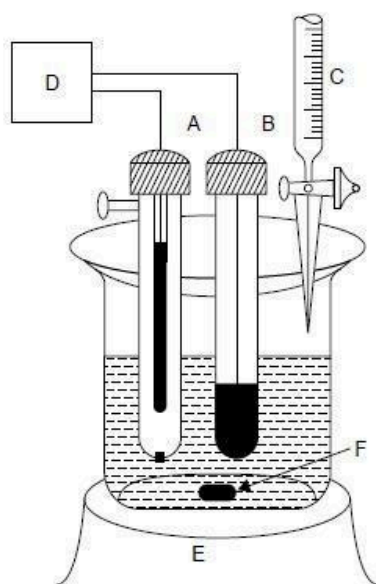
Beyond the equivalence point as no ferrous ions exist, the potential is determined by the concentration of  $Cr_2O_7^{2-}$  and  $Cr^{3+}$  ions and it is given by,

$$\begin{aligned} E &= E^0 + \frac{0.0591}{6} \log [Cr^{6+}] / [Cr^{3+}] \\ &= 1.33V + \frac{0.0591}{6} \log [Cr^{6+}] / [Cr^{3+}] \end{aligned}$$

therefore,

An abrupt increase in the potential is observed at the equivalence point. This increase marks the end point of the titration. Potential change at an electrode cannot be directly measured. The electrode at which the potential changes with concentration (indicator electrode) is connected to another electrode whose potential remains constant [Ex:-calomel electrode (Standard reference electrode)], to form a cell.  $EMF = E_{cathode} - E_{anode}$ . As the potential of the indicator electrode changes, the EMF of the cell also changes. It is the change in EMF that is measured during a potentiometric titration.

## Instrumentation



*The various components shown in Figure, are as follows:*

A = Saturated Calomel Electrode (SCE), (Reference Electrode).

B = Pt electrode (Indicator Electrode).

C = Burette to discharge titrant in the reacting vessel.

D = Potentiometer with an mV scale.

E = Magnetic stirrer with variable speed, and

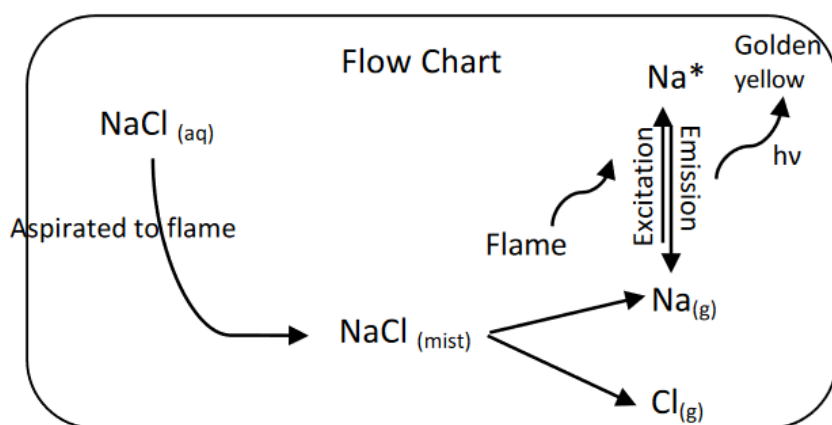
F = Magnetic rotator.

*Figure 5.15. Schematic representation of potentiometer*

## Flame photometry

### Theory:

Flame Photometry is an atomic emission technique used for detection of metals. If a solution containing metallic salts is aspirated into a flame, a vapour will be formed which contains metallic atoms. The electrons from the metallic atoms are then excited from ground state ( $E_1$ ) to higher energy state ( $E_n$ ) where  $n = 2, 3, 4$ , etc., by making use of thermal energy of flame. From higher energy states, these electrons will return to the ground state by emitting radiations  $(E_n - E_1) = h\nu$  where  $n = 2, 3, 4$ , etc., which are the characteristic of each element.



*Figure 5.16. Schematic representation of atomic emission phenomena*

Flame photometer correlates the emitted radiations with the concentration of these elements. It is simple and rapid method for the elements that can be easily excited (Sodium and other alkali metals).

A flame photometer is composed of the pressure regulator, flow meter, an atomizer, burner, optical system, photosensitive detector and output recorder. A filter corresponding to the wavelength of light emitted by the element whose concentration is to be determined, is inserted between the flame and the detector. Propane gas is used as fuel and air or Oxygen is used as oxidant. Combination of these two will give a temperature of 1900°C. The whole analysis depends on the flow rate of the fuel, oxidant, the rate of introduction of the sample and droplet size.

The sample containing the analyte is aspirated into the flame through nebulizer. Radiation from resulting flame is collected by the lens and allowed to pass through an optical filter, which permits only the radiation characteristic of the element under investigation into the photocell. The output from the photocell represents the concentration and nature of the element.

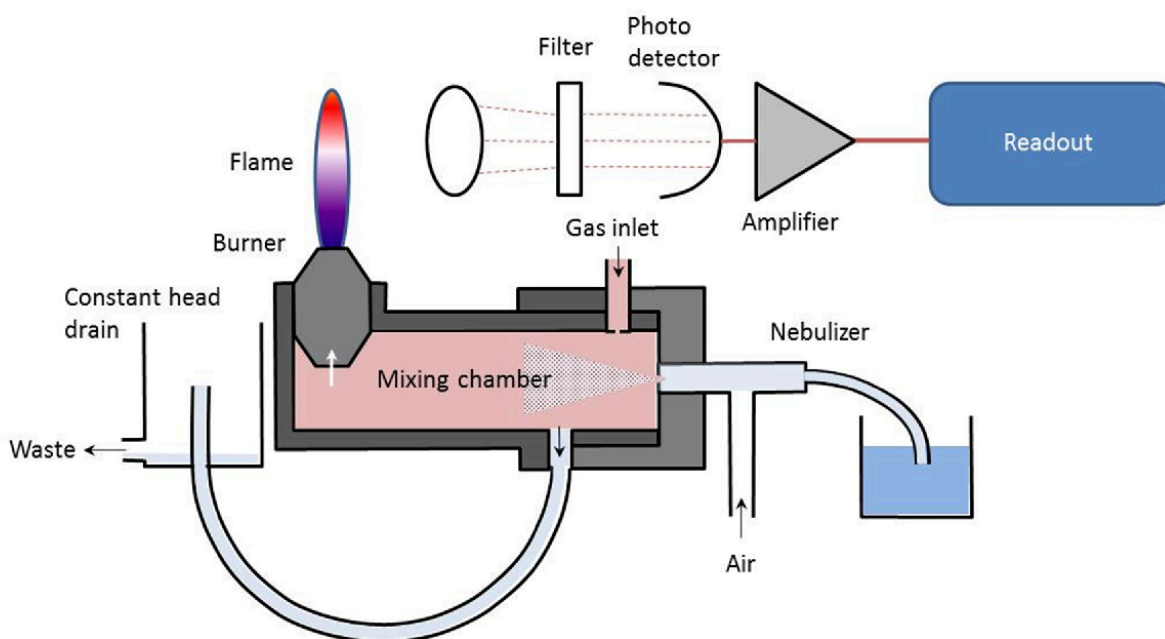


Figure 5.17. Schematic representation of flame photometer

## Conductometry

Conductance of any solution (G) is the ease with which current flows through it. It is the reciprocal of resistance (R) offered by the solution.

$$G = 1/R$$

### Specific Conductivity

The extent to which a given sample of electrolytic solution can conduct an electric current is called its conductance. Conversely, the extent to which the given sample of electrolytic solution can resist the flow of electric current is called its resistance. Of course, the conductance is the reciprocal of the resistance of that particular electrolytic solution. The SI unit of conductance is S (Siemens).

The conductivity or specific conductivity is the measure of the ability of an electrolytic solution to conduct electricity. The SI unit of specific conductivity is Siemens per meter, better represented as S/m.

$$R = \rho l/A$$

$$\Rightarrow \rho = AR/l$$

According to the definition of conductivity

$$\kappa = 1/\rho$$

$$\Rightarrow \kappa = l/AR$$

$$\Rightarrow \kappa = l/A \times 1/R$$

Here,  $l/A$  is a constant value called the cell constant. And  $1/R$  gives the conductance of the electrolytic solution, therefore,

$$k = \text{Cell constant} \times \text{Conductance (G)} \text{ Siemens/metre}$$

### The difference between specific conductance and conductance?

Conductance means the flow of current through the liquid conductor. Specific conductance is defined as the conducting capacity of a solution of the dissolved electrolyte and the whole solution is being placed between two electrodes are 1 sq. cm and length 1 cm.

### The conductivity of electrolytic solutions depends on:

- The nature and the concentration of the electrolyte added
- The size of the ions produced and their solvation.
- Solvent nature and viscosity.
- Temperature.

**Molar conductivity ( $\Lambda_m$ ):** The conductance of that volume of solution containing one mole of an electrolyte is known as molar conductivity.

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

Where  $\Lambda_m$  = Molar conductivity  
 $\kappa$  = Conductivity  
 $M$  = Molarity of Solution

**Equivalent conductivity ( $\Lambda_{eq}$ ):** The conductance of that volume of solution containing one equivalent of an electrolyte is known as equivalent conductivity.

$$\Lambda_{\text{eq}} = \frac{\kappa \times 1000}{N}$$

$$= \frac{\text{S cm}^{-1}}{\text{equivalent cm}^{-3}} = \text{or } \frac{\text{Ohm}^{-1} \text{ cm}^2 \text{ equivalent}^{-1}}{\text{S cm}^2 \text{ equivalent}^{-1}}$$

**Table:** Ionic Species and Molar Conductivity values

Cation	$\Lambda^\infty / (\text{S cm}^2 \text{ mol}^{-1})$	$\Lambda^\infty / (\text{S cm}^2 \text{ eq}^{-1})$	Anion	$\Lambda^\infty / (\text{S cm}^2 \text{ mol}^{-1})$	$\Lambda^\infty / (\text{S cm}^2 \text{ eq}^{-1})$
H <sup>+</sup>	349.8	349.8	OH <sup>-</sup>	198.3	198.3
Li <sup>+</sup>	38.7	38.7	F <sup>-</sup>	55.4	55.4
Na <sup>+</sup>	50.1	50.1	Cl <sup>-</sup>	76.3	76.3
K <sup>+</sup>	73.5	73.5	Br <sup>-</sup>	78.1	78.1
Be <sup>+2</sup>	90.0	45.0	I <sup>-</sup>	76.8	76.8
Mg <sup>2+</sup>	106.2	53.1	NO <sub>3</sub> <sup>-</sup>	71.5	71.5
Ca <sup>2+</sup>	119.0	59.5	SO <sub>4</sub> <sup>2-</sup>	160.0	80.0
Ba <sup>2+</sup>	127.2	63.6	CH <sub>3</sub> COO <sup>-</sup>	40.9	40.9
Al <sup>3+</sup>	183.0	61.0	C <sub>6</sub> H <sub>5</sub> CO <sup>-</sup>	32.4	32.4
Cu <sup>2+</sup>	107.2	53.6	HCO <sub>3</sub> <sup>-</sup>	44.5	44.5
Ag <sup>+</sup>	61.9	61.9	CO <sub>3</sub> <sup>2-</sup>	138.6	69.3
Zn <sup>2+</sup>	105.6	52.8	Fe(CN) <sub>6</sub> <sup>3-</sup>	302.7	100.9
Ce <sup>3+</sup>	209.4	69.8	Fe(CN) <sub>6</sub> <sup>4-</sup>	442.0	110.5

Instrumentation:



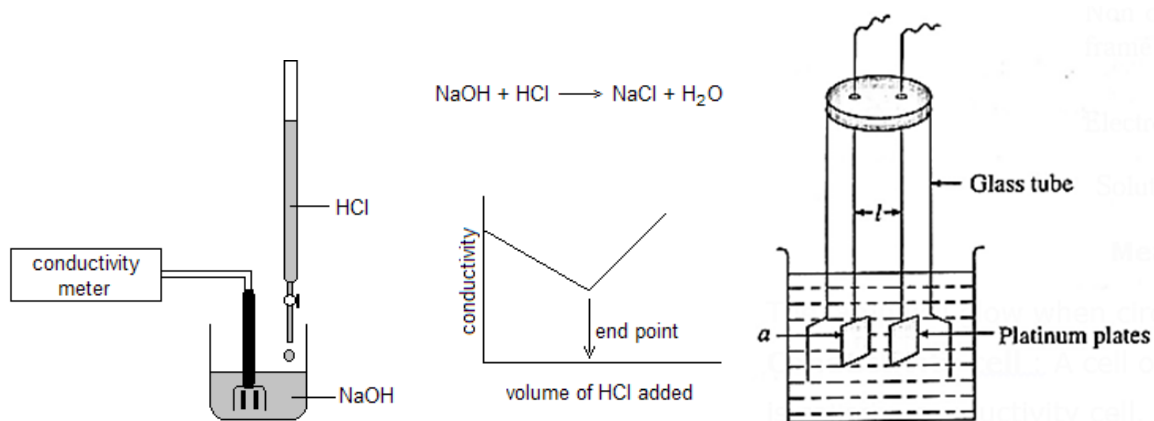


Figure 5.18. Schematic representation of conductometry

### Some Typical Conductometric Titration Curves are:

1. **Strong Acid with a Strong Base**, e.g. HCl with NaOH: Before NaOH is added, the conductance is high due to the presence of highly mobile hydrogen ions. When the base is added, the conductance falls due to the replacement of hydrogen ions by the added cation as  $\text{H}^+$  ions react with  $\text{OH}^-$  ions to form undissociated water. This decrease in the conductance continues till the equivalence point. At the equivalence point, the solution contains only NaCl. After the equivalence point, the conductance increases due to the large conductivity of  $\text{OH}^-$  ions

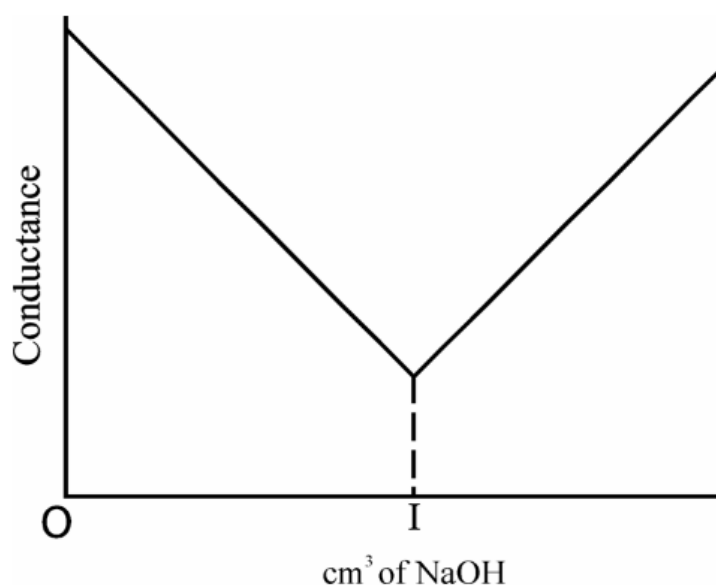


Figure 5.19. Variation of conductance of Strong Acid with a Strong Base

2. **Weak Acid with a Strong Base**, e.g. acetic acid with NaOH: Initially the conductance is low due to the feeble ionization of acetic acid. On the addition of base, there is decrease in conductance not only due to the replacement of  $\text{H}^+$  by  $\text{Na}^+$  but also suppresses the dissociation of acetic acid due to common ion acetate. But very soon, the conductance increases on adding NaOH as NaOH neutralizes the un-dissociated  $\text{CH}_3\text{COOH}$  to  $\text{CH}_3\text{COONa}$  which is the strong electrolyte. This increase in conductance continues raise up to the equivalence point. The graph near the equivalence point is curved due the hydrolysis of salt  $\text{CH}_3\text{COONa}$ . Beyond the equivalence point, conductance increases more rapidly with the addition of NaOH due to the highly conducting  $\text{OH}^-$  ions.

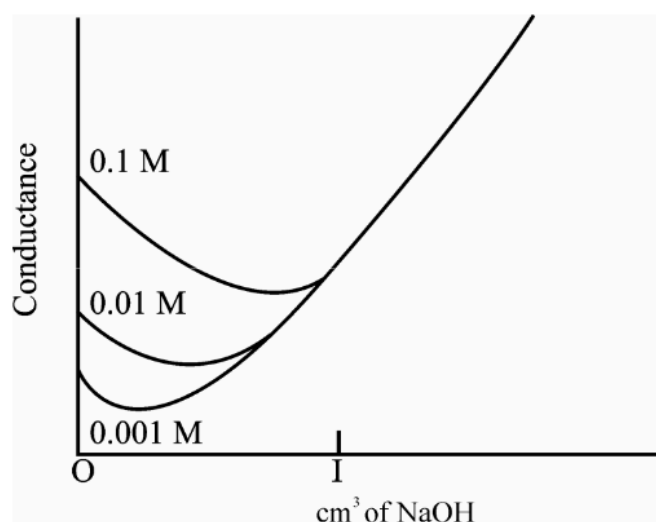


Figure 5.20. Variation of conductance of Weak Acid with a Strong Base

3. **Strong Acid with a Weak Base**, e.g. sulphuric acid with dilute ammonia: Initially the conductance is high and then it decreases due to the replacement of  $\text{H}^+$ . But after the endpoint has been reached the graph becomes almost horizontal, since the excess aqueous ammonia is not appreciably ionised in the presence of ammonium sulphate.

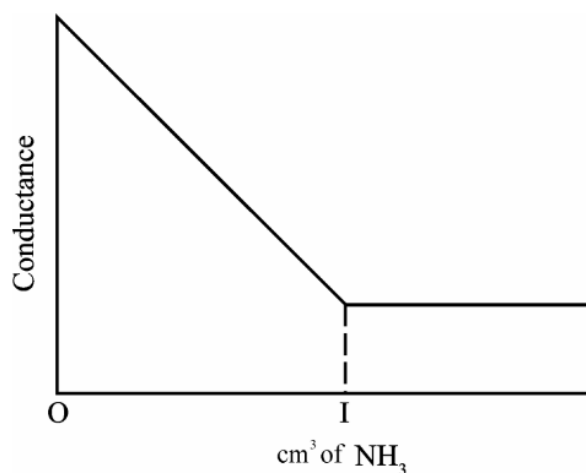
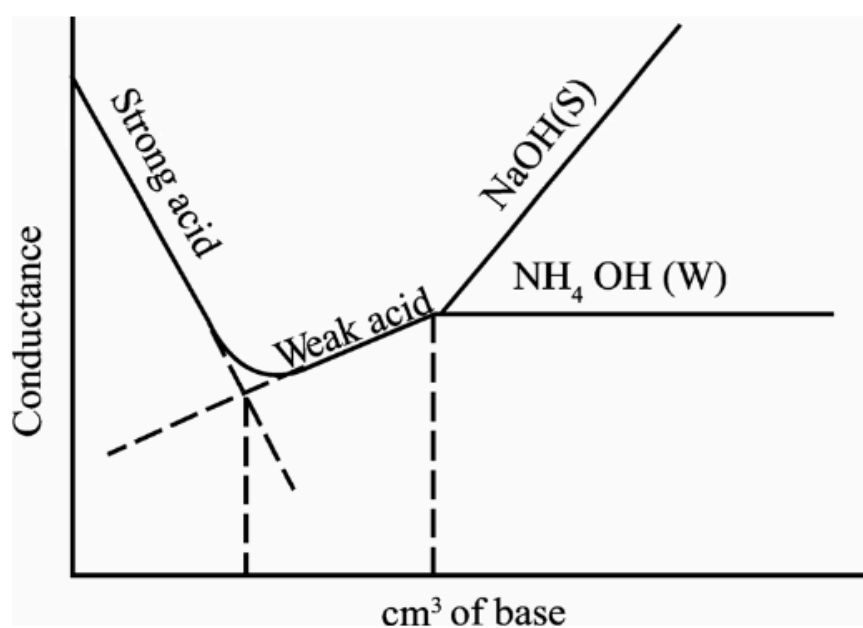


Figure 5.19. Variation of conductance of Strong Acid with a weak Base

#### 4. Mixture of a Strong Acid and a Weak Acid vs. a Strong Base or a Weak

**Base:** In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing. The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of  $\text{OH}^-$  ions in case of a strong base as the titrant. However, when the titrant is a weak base, it remains almost constant after the end point similar to



*Figure 5.19. Variation of conductance of mixture of Strong and weak Acid with a Strong Base*

	Describe the working principle of Electrochemical Gas sensors	4	3	2
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