

Module-5 Sensors

Sensors: Introduction, working principle and applications of Electrochemical sensors, Conductometric sensors, and Optical sensors. Sensors for the measurement of dissolved oxygen (DO). Electrochemical sensors for the pharmaceuticals and hydrocarbons. Electrochemical gas sensors for SO_x and NO_x. Disposable sensors in the detection of biomolecules and pesticides.

Analytical Techniques: Introduction, principle and instrumentation of Conductometry; its application in the estimation of weak acid. Potentiometry; its application in the estimation of iron.

Self-learning: Types of electrochemical sensor, Gas sensor - O₂ sensor, Biosensor - Glucose sensors.

Introduction: A sensor is a device that measures or detects a physical quantity, such as temperature, pressure, humidity, light, sound, motion, or position. Sensors are used to convert the physical quantity into an electrical signal that can be processed by a computer or other electronic system.

Sensors are found in a wide range of applications, from industrial automation and control to consumer electronics and healthcare. For example, sensors are used in automobiles to monitor engine performance, in smart phones to detect user input and orientation, and in medical devices to monitor vital signs.

Sensors: Sensors are electronic devices or modules that detect and measure physical/chemical phenomena into an electrical signal.

Physical/Chemical phenomena: Temperature, pressure, motion, light, or sound/ concentration.

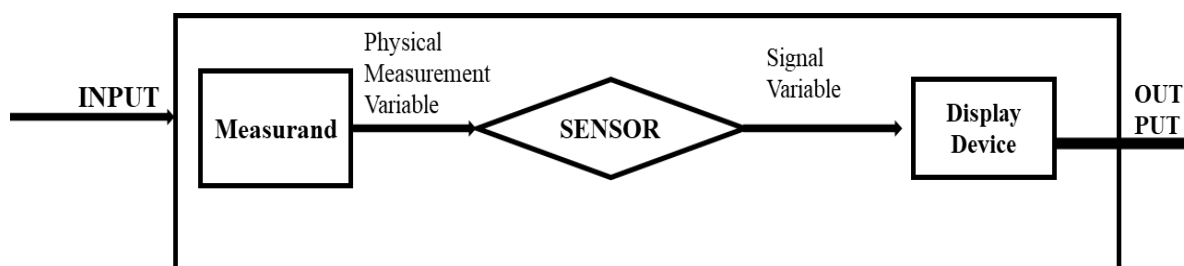


Fig: 1.1 Function of Sensor

Transducer: It is a device that is capable of converting a physical quantity or non- electrical signal into an electrical signal (one form of energy into another form).

Actuator: An actuator is a device that receives a signal or input and produces a physical output (Converts electrical energy into mechanical energy).

Measurement process for the instrumentation model

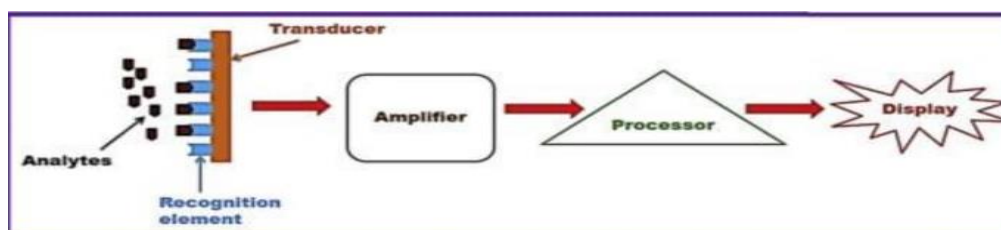
- Sensor input- The physical value or measurand (X) is observed by the sensor device.
- Sensor output – The sensor generates a signal variable (S) output which is normally electrical.
- Signal conditioning- The signal is transmitted and conditioned if needed (amplified, converted, filtered, etc.)
- Display of measurement – the measurement is then displayed by the output device.

Electrochemical sensors:

Sensors which convert the effect of electrochemical reaction between analyte and electrode surface into a useful signal are known as electrochemical sensors. Electrochemical sensors divided into several types based on their mechanism of operation and the type of reaction involved.

- Potentiometric (measure voltage)
- Amperometric (measure current)
- Conductometric (measure conductivity)

Working Principle



- Electrochemical sensor consists of a transducer element covered by a recognition element.
- The recognition element interacts with target analyte and signal is generated.
- Electrochemical transducers transform the chemical changes into electrical signals
- The electric signals are related to the concentration of analyte.
- Electrochemical sensing always requires a closed circuit. Current must flow to make a measurement.
- Since we need a closed loop there should be at least two electrodes. These sensors are often called an electrochemical cell.

Applications

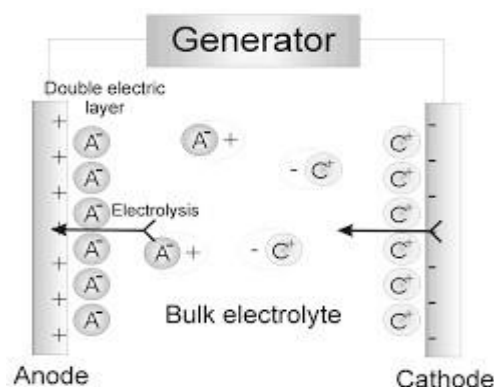
- Electrochemical sensors used for the detection of blood glucose
- Electrochemical sensors are used for pH measurements
- Used to detect pesticides
- Used in the detection of hydrocarbon pollutants

Conductometric Sensors:

Conductometric sensors are chemical sensors that measure changes in electrical conductivity when a specific analyte interacts between the electrodes.

Principle:

The conductometric sensor is composed of two electrodes coated with a highly sensitive material that responds to a specific analyte. When the analyte of interest meets the electrode coating, it binds to the surface, causing a change in the electrical properties of the sensor. The change in conductivity is measured and correlated with the concentration of the analyte in the sample. The final output is a quantitative measure of the concentration of the analyte.



Working

The conductivity is result of dissociation an electrolyte, into ions. The migration of the ions is induced by an electrical field. When a potential difference is applied to the electrode, there is an electrical field within the electrolyte, so the positively charged ions move towards cathode and negatively charged ions are move towards anode. (Figure). Thus, the current in the electrolyte is caused by the ion movement towards the electrodes where the ions are neutralized and isolated as neutral atoms (or molecules).

This chemical change is recognized by working electrode and transducers converts this chemical change into electrical signal.

Applications:

- Monitoring of water quality
- Detection of gas and vapor
- Analysis of biochemical compounds
- Measurement of ionic strength and pH levels in solutions
- Food and beverage industry

Optical sensors:

Optical sensors are devices that use light and converts in to electric signals for detecting and measuring physical or chemical properties of a sample.

Example: (photometric) Colorimetric Sensors

Principle: When a sample solution is interacted with a light of suitable wavelength, certain quantity of light is absorbed by the analyte solution a chemical or physical change occur. This change in the sensing material's properties observed by a sensor and transducer converts intensity of absorbed light into electrical signal. The change in intensity at certain wavelength within visible (400–800nm) range can be determined using special instrumentation.

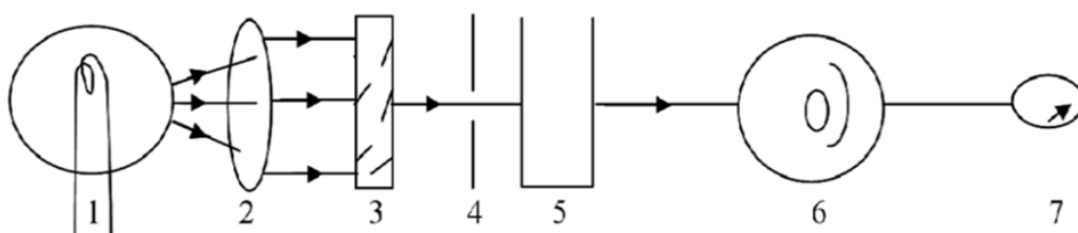
Working:

Fig.1.6 Components of Colourimetric Sensors

- When a monochromatic light is made to pass through analyte solution, certain amount of light is absorbed and remaining is transmitted through the analyte.
- Based on the amount of light absorbed photodetector (sensor) converts optical signal into electrical signal.
- Where the absorbance is displayed in the output device.
- The amount of absorbance is governed by Beer- lamberts law which states that absorbance is directly proportional to the concentration and thickness of the solution ($A \propto CT$).

Applications:

- Medical diagnostics: Colorimetric sensors are used to detect the presence of biomolecules, such as glucose, cholesterol, and haemoglobin, in bodily fluids such as blood and urine.
- Security and defence .
- Food safety testing.
- Copy machines
- Photography

Electrochemical Sensor for the measurement of Dissolved Oxygen (DO)

Electrochemical DO sensors, also known as amperometric or Clark-type sensors, measures dissolved oxygen concentration in water based on electrical current produced

Galvanic Sensor is a Electrochemical sensor, which is used to measure DO

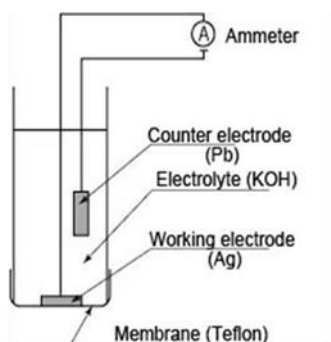


Fig:1.9 Galvanic Sensor for DO measurement

Components:

Cathode: Working Electrode-Ag

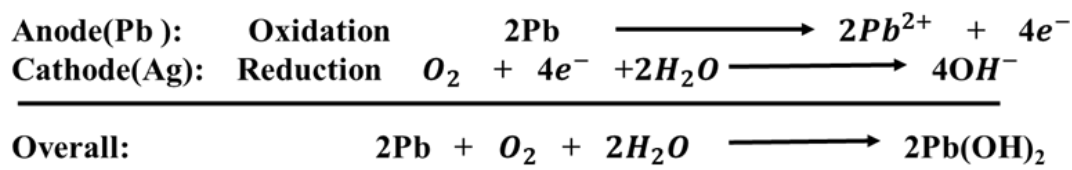
Anode: Zn, Pb or any other active metal

Electrolyte: KOH, NaOH or any other inert electrolyte

Membrane: Teflon

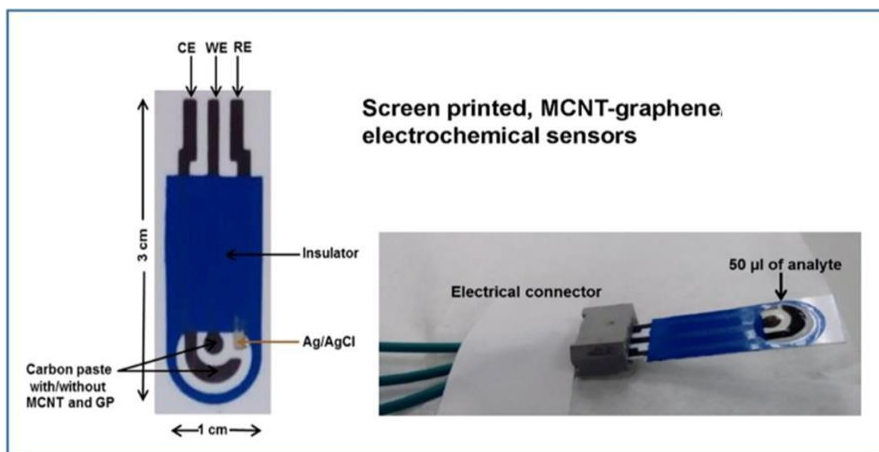
Working Principle

- The difference in potential between the anode and the cathode should be at least 0.5V.
- DO sensor is immersed in water sample.
- Oxygen molecule diffuses across the oxygen-permeable membrane (Teflon) and the rate of diffusion is proportional to the pressure of oxygen in the water.
- Molecular Oxygen reduces to OH⁻ at cathode.
- This reaction produces an electrical current that is directly related to the oxygen concentration.
- This current is carried by the ions in the electrolyte and runs from the cathode to the anode.

**Electrochemical sensors for the detection of Pharmaceuticals (diclofenac)**

The electrochemical detection of diclofenac (or any other analyte) typically occurs at the interface between the analyte and the working electrode, where a potential is applied with respect to the reference electrode, and the corresponding current is measured.

- **Electrochemical sensors** and **biosensors** are developed for the analysis of diclofenac.
- Carbon based-electrodes are the most investigated electrodes in diclofenac analysis.
- Carbon nanotubes and graphene-based composites are the most efficient modifiers for diclofenac detection.



Components of disposable screen printed Carbon paste electrode for diclofenac detection (Three electrode sensor)

- **Working electrode:** Carbon Paste with MWCNT or Graphene
- **Counter Electrode:** Carbon Paste with MWCNT or Graphene
- **Reference Electrode:** Ag/AgCl
- **Process:** Screen Printing Technique on PVC substrate. Insulating ink was printed on the PVC surface.

Working:

- The electrochemical oxidation of DCF on carbon-based sensor at pH 7.0 is reversible reaction.
- Oxidation of Diclofenac occurs at carbon electrode to release e⁻, to form radical intermediates and followed by hydrolysis of radical intermediate species.
- The products formed are 2,6 dichloro aniline and 2,2 hydroxyl phenyl acetic acid.
- Reactions on the electrode cause the current to flow.
- The intensity of this current is a function of the number of oxidized / reduced molecules.

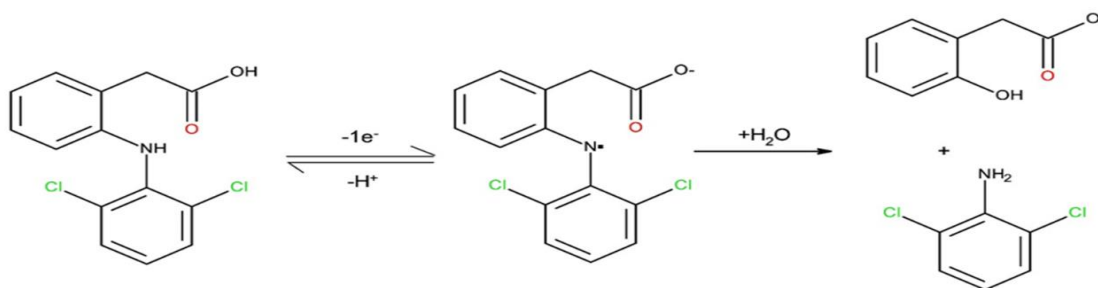


Fig:1.12 The Oxidation mechanism for diclofenac

Products: 2,2 Hydroxy-Phenyl-Acetic Acid and 2,6 Dichloro Aniline

Electrochemical sensors for the detection of Hydrocarbon :1- Hydroxypyrene (Screen Printed Sensor)

NOTE: 1-Hydroxypyrene detection is done for the evaluation of polycyclic aromatic hydrocarbon which is carcinogenic in nature.

Working electrode: PAMAM/Cr-MOF/GO (Composite)

Counter Electrode: PAMAM/Cr-MOF/GO

Reference Electrode: Ag/AgCl Operating

PAMAM: Dendrimer polyamidoamine

Cr-MOF: Chromium-centered metal–organic framework

GO: Graphene Oxide

Working:

When this electrode is used to detect the sample containing 1-Hydroxypyrene (water sample) the following changes takes place:

At the electrode surface electro-oxidation takes place to yield several hydroxylated species and then hydroquinone by losing $2e^-$ and $2H^+$.

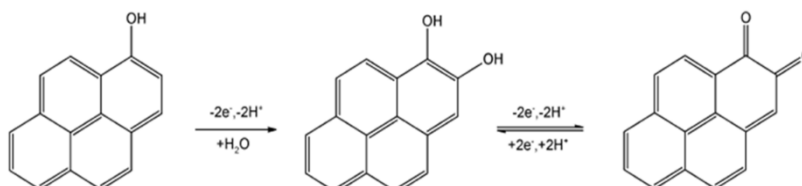


Fig:1.13 The electro-oxidation scheme for 1-Hydroxypyrene

- Reactions on the electrode cause the current to flow.
- The quantity of this current is a function of the number of oxidized / reduced molecules.
- Current produced is directly proportional to the concentration 1-Hydroxypyrene

Electrochemical gas sensors for SO_x and NO_x

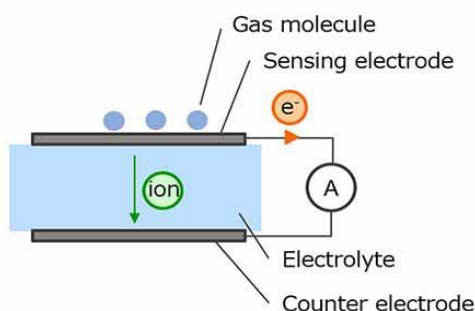
Definition: Electrochemical gas sensors are devices that detect the presence of certain gases in the environment by converting the gas molecules into an electrical signal through electrochemical reactions.

Sensors for SO_x

Sulfur oxides, SO₂ released from thermal power stations and other industrial plants, are gases harmful to the environment. It is very important to detect and control the concentrations of SO_x in industrial processes. The methods usually used to detect SO_x are chemical and electrochemical

Gas sensors typically consist of a sensing element, which is the part that interacts with the gas molecules, and a transducer, which converts the changes in gas concentration into an electrical signal. The sensing element is usually made of materials such as metal oxides, polymers, or semiconductors. When a gas molecule comes into contact with the sensing element, it undergoes a reaction that causes a change in the electrical properties of the material. This change is then measured by the transducer and converted into a signal that can be interpreted by the device.

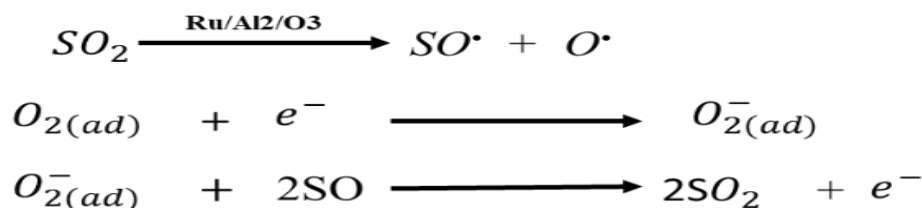
Working Principle:



The working principle of SO_x sensors is based on the electrochemical detection method. These sensors typically consist of three main components: a sensing electrode, a counter electrode, and an electrolyte. The sensing electrode is made of a material that is sensitive to sulfur oxides, such as gold or platinum. When sulfur oxides come into contact with the sensing electrode, a chemical reaction occurs, leading to the generation of an electric current. This current is proportional to the concentration of sulfur oxides present in the environment.

Reactions:

- When SO₂ gas enters the sensor, it undergoes oxidation to produce oxygen free radicals, which are highly reactive species.
- The free radicals then react with other oxygen molecules in the sensor to produce molecular oxygen.



Sensors for NO_x

Electrochemical sensors are widely used for the detection of various gases, including nitrogen oxides (NO_x). NO_x gases, such as nitrogen dioxide (NO₂) and nitric oxide (NO), are major air pollutants that can have harmful effects on human health and the environment. Electrochemical sensors offer a reliable and sensitive method for measuring NO_x concentrations in real-time, making them valuable tools for environmental monitoring and industrial applications.

Principle:

The principle behind electrochemical sensors for NO_x detection is based on the redox reactions that occur at the sensor's electrodes. These sensors typically consist of three main components: a working electrode, a reference electrode, and a counter electrode. The working electrode is usually made of a material that can catalyze the electrochemical reaction of NO_x gases, such as platinum or gold. When NO_x gases come into contact with the working electrode, they undergo a reduction reaction, leading to the generation of electrical current. This current is proportional to the concentration of NO_x gases present in the environment.

- Electrochemical gas sensors for NO_x detection are based on the principle of electrochemical reactions that occur at the surface of the sensor electrodes.
- The working electrode is coated with a material that catalyzes the reduction of NO_x to NO, while the reference electrode provides a stable potential.
- When NO_x gas encounters the working electrode, it undergoes reduction to produce NO, which generates an electrical current proportional to the concentration of NO_x in the environment.

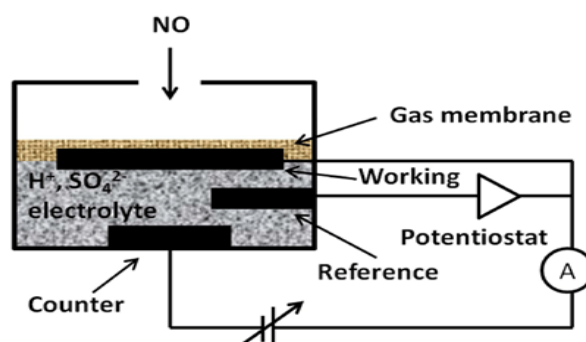
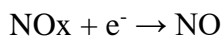


Fig: 1.14 NO_x Gas Sensor

Working:

The sensor uses a working electrode coated with a metal oxide catalyst (silica, alumina), which facilitates the reduction of NO_x to NO. The reference electrode is made of gold, and an electrolyte solution is used to facilitate ion transport between the electrodes. When NO_x gas comes into contact with the working electrode, it undergoes reduction to produce NO, which generates an electrical current proportional to the concentration of NO_x in the environment.

**Disposable sensors**

Disposable sensors are typically made of low-cost materials and easy-to-use sensing devices designed for short term or rapid single-point measurements.

Advantages of Disposable Sensors over Classical Sensors:

- **Cost-effective:** Disposable sensors are typically cheaper than classical sensors.
- **Convenient:** Disposable sensors do not require calibration or maintenance.
- **Hygienic:** Disposable sensors can help reduce the risk of cross contamination in medical and food safety applications.
- **Portable:** Because disposable sensors are typically smaller and lighter than classical sensors.
- **Rapid testing:** Disposable sensors can provide results quickly, allowing for faster decision-making.

Electrochemical disposable sensor Determination of Ascorbic acid (biomolecule) explain with Oxidation of AA to Dehydroascorbic acid.

Ascorbic acid, also known as Vitamin C, is an essential well-known antioxidant and essential nutrient in human diets and is also used as a food preservative. The detection of ascorbic acid can be important in various fields, such as food safety and medical diagnosis.

The detection of AA to DHA oxidation using a graphene-based electrode typically involves the following steps:

- **Fabrication of the electrode:** The graphene-based electrode is fabricated using screen-printing technology. Graphene ink is printed onto a substrate to form the working electrode. The ink contains graphene flakes, binders, and solvents that help to improve the adhesion of the graphene flakes to the substrate.
- **Sample preparation:** The sample is prepared by dissolving the AA in a suitable solvent, such as phosphate-buffered saline (PBS) or water.
- **Detection:** The sample is then applied to the graphene-based electrode, and an electrochemical reaction occurs between AA and the electrode surface. In this reaction, AA is oxidized to form DHA, and electrons are released to the electrode surface. The number of electrons released is proportional to the concentration of AA in the sample.

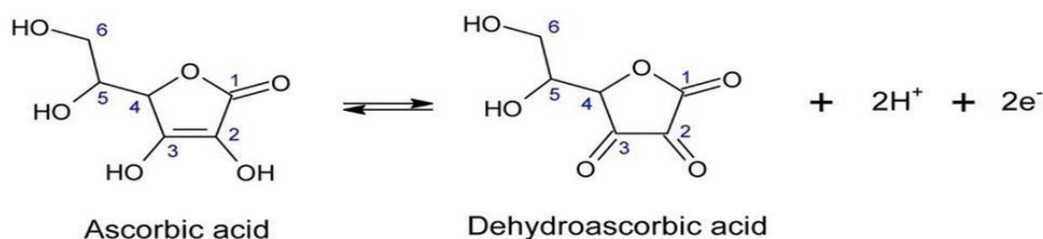


Fig: 1.18 Oxidation of Ascorbic acid

Detection of pesticide such as Glyphosate by electrochemical oxidation method

Glyphosate is a broad-spectrum herbicide and one of the most commonly used pesticides in the world. Glyphosate has become a controversial pesticide due to concerns about its potential impact on human health and the environment. Some studies have suggested that exposure to glyphosate may be linked to

health problems such as cancer, developmental disorders, and endocrine disruption. The sensor is a silicon-based chip comprising of three-electrode system. It is fabricated by electro deposition technique.

Working Electrode: A gold electrode of 4 mm diameter coated with 200nm thickness gold nanoparticles

Counter electrode: A gold electrode of 4 mm diameter coated with 20nm thickness gold nanoparticles

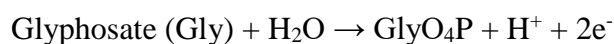
Reference Electrode: Ag/AgCl/Cl⁻

Electrolytes are added to increase the conductivity of the solution and minimizes the resistance between the working and counter electrode.

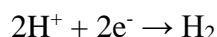
A potential of 0.78V is applied to the working electrode, which is made of gold. When the glyphosate molecules come into contact with the electrode surface, they undergo oxidation, which leads to a change in the current in the electrolyte medium. The change in the current is directly proportional to the concentration of glyphosate in the sample.

Reactions:

At the anode: (working electrode, which is positively charged):



At the cathode: (counter electrode, which is negatively charged):



ANALYTICAL TECHNIQUES

CONDUCTOMETRY

Conductance is the ability of a metal or a solution to allow passage of electricity through it. It is the reciprocal of resistance i.e, $C=1/R$. Conductance is measured in seimen or ohm^{-1} called mho.

Theory: For a conductor having uniform length (l cm) & cross section ('a' cm^2) resistance is

$$R \propto l/a$$

$$R = s * l/a$$

Where 's*' is proportionality constant & is known as specific resistivity.

$$\text{Now } C = 1/R$$

$$= 1/s*(l/a)$$

$$= K (a/l)$$

Where $K=1/s$ is called specific conductance.

Specific conductance: It is the conductance of the solution placed between 2 parallel electrodes having unit area of cross-section and unit distance apart.

When $a=1 \text{ sq cm}$ & $l = 1 \text{ cm}$ then $C= K$.

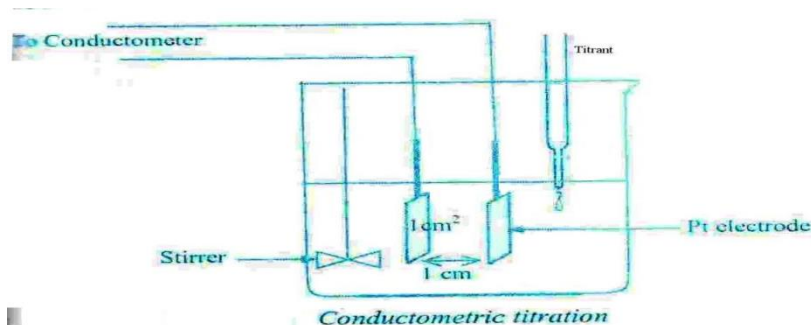
Specific conductance of a solution depends on

- Charge of the ion.
- Mobility of the ion.
- Concentration of the solution

Instrumentation

Conductivity cell consists of 2 parallel platinum electrodes each having unit area of cross-section & placed at unit distance apart, it is dipped in electrolytic solution taken in a beaker & it is connected to conductance measuring device. The conductance of the solution is measured after the addition of each

ml of titrant added from the burette. The equivalence point of the titration is found by plotting the graph of conductance Vs volume of the titrant.

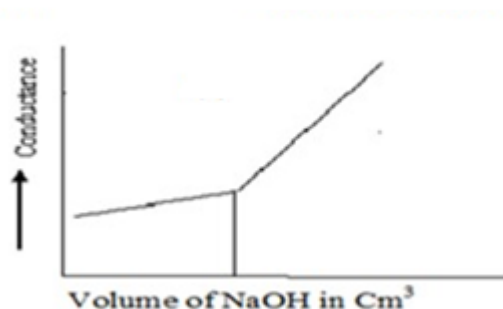


Applications:

Conductometric titration is used for determining accurate end point in acid base titration

Weak acid Vs strong base (CH₃COOH V/S NaOH)

Weak acid partially dissociated in aqueous solution the conductance of the of the acid will be initially low due to poor dissociation. When a strong base is added to the acid, the salt formed is highly ionized and conductance increases on complete neutralization of the acid, further addition of base lead to an increase in the number of more OH⁻ ion and hence conductance increase sharply.



Advantages:

1. Very weak acids can be titrated.
2. Colored solution can also be used.
3. Mixture of acids can be titrated accurately.
4. It can be used where visual & potentiometry titration fails.

POTENTIOMETRY:

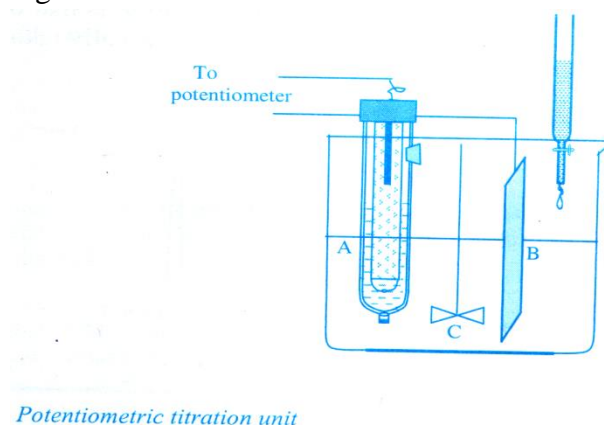
It is an electro analytical technique in which concentration of the solution is measured by measuring the emf of the solution.

Theory: Potentiometric titration involves the measurement of the potential of an indicator electrode with volume of the titrant. The indicator electrode is used in combination with a reference electrode. For an electrode reversible with its ions in a solution the e potential is given by Nern'st equation

$$E = E^0 + \frac{2.303RT}{nf} \log[M^{n+}] \quad (M \rightleftharpoons M^{n+} + ne^-)$$

From the equation it is found that potential depends on concentration of the ion. Therefore for an analyte solution whose concentration is to be determined it is titrated with titrant, initially the change in potential is small. At the equivalence point there will be a sudden raise in potential. Beyond the equivalence point there will be no change in the potential. The equivalence point is determined by plotting change in potential against volume of titrant added.

Instrumentation: A potentiometer consists of a reference electrode, an indicator electrode. The electrode assembly is dipped in the solution whose concentration is to be determined. They are connected to the potentiometer which shows the potential of the solution. The titrant is added in increment of 0.5ml & the potential is measured each time. Near to the equivalence point the potential increases rapidly. A few readings are taken after the end point. End point is determined by plotting a graph of change in potential against volume of titrant added.



Advantages: More accurate than indicator involving titration, useful with colored & turbid solution, useful for weak acid base titration where indicator is not available.

Application: Potentiometric titration is used to determine end point in acid base titration, precipitation titration & redox titration.

Redox titration

The electrode assembly consists of a reference electrode (Calomel), a platinum electrode (indicator electrode) sensitive to redox species present in the solution.

Eg: Consider a redox titration of FAS vs potassium dichromate

In this titration the potential of the Mohr's salt solution(FAS) increases by the addition of potassium dichromate from the burette because the Fe^{2+} ion present in the FAS is oxidized to Fe^{3+} by the added dichromate solution. The electrode potential formed with respect to platinum electrode is given by

$$E = E^0 + \frac{2.303RT}{nF} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

When all the Fe^{2+} ions are converted to Fe^{3+} ions there will be a sharp increase in potential which gives the equivalence point. This is determined by plotting a graph of $\Delta E / \Delta V$ vs volume of potassium dichromate. After the equivalence point no significant change in the potential is found.

