Q.No	Question	CO No	K level
1	What is Galvanic cell? Describe its construction and working process with diagram?	3	K4
2	Derive Nernst equation for electrochemical cell. Calculate the emf of the Zn-Ag cell at 25^0c when Zn^{+2}=0.10M and $[(Ag^+)]$ =10.0M (E^0cell at 25^0c =1.56v).	3	K4
3	What are secondary batteries? Describe the construction and working process of Lead-acid battery. Write cell reactions and applications	3	K4
4	Describe the construction and working of Li-ion battery. It has a future of cells why?	3	K4
5	How do you find out the strength of acid through neutralization in conductometry? Explain in detailed.	3	K2
6	What is an electro chemical sensor? Write the difference between potentiometric and amprometric sensors.	3	K3

COMMON QUESTIONS (2 MARKS)

Short answer questions	1. Define reference electrode? Give one example. 2. Write the chemical equation involved in redox titrations? 3. Recall the limitations of conductometric titrations? 4. What is secondary battery? Give two examples. 5. Explain the working principle of H_2 -O_2 fuel cell?

UNIT-4
POLYMER CHEMISTRY

Q.No	Question	CO No	K level
1	Define Degree of polymerization and explain the free radical mechanism of addition polymerization?	4	K4
2	Compare thermo plastic and thermosetting plastics?	4	K3
3	Illustrate the preparation, properties and applications of Bakelite.	4	K4
4	Give methods of preparation, properties and applications of Buna-S and Buna-N rubbers.	4	K4
5	Define conducting polymers? Explain preparation, conducting nature and applications of poly acetylene.	4	K4

6	Explain the conducting behavior of poly aniline.	4	K4

COMMON QUESTIONS (2 MARKS)

Short answer questions	1. What is meant by Functionality of monomer? Give one example? 2. Recall the chemical reaction involved in the preparation of Teflon. Mention its applications. 3. Write the monomers of Nylon-6,10? 4. Why cannot thermosetting plastics can be reused and reshaped? 5. How does Buna-S differ from Buna-N?

UNIT-5
INSTRUMENTAL METHODS AND APPLICATIONS

Q.No	Question	CO No	K level
1	State Lambert-Beer's law; explain how this law can be used to determine the concentration of colored solutions? Mention its limitations?	5	K3
2	Explain the principle, instrumentation and applications of Uv-Visible spectroscopy?	5	K4
3	Discuss the principle, instrumentation and applications of IR spectroscopy?	5	K4
4	Explain the principle and applications of pH-metry?	5	K2
5	Define auxochromes and chromophores? Give two examples? Write the applications of Uv-Visible spectroscopy?	5	K3
6	What is chromatography? Explain the principle, instrumentation and applications of TLC?	5	K4

COMMON QUESTIONS (2 MARKS)

Short answer questions	1. Write the factors affecting the absorption of radiation? 2. State the Beer - Lambert's law? 3. Define Chromophores? Give two examples? 4. What is the importance of fingerprint region in IR-Spectroscopy 5. Express the principle involved in P^{H}-Metry? Write any two applications?

Sahithi

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ELECTRO CHEMISTRY AND APPLICATIONS

Dr.B.TirumalaRao

Introduction:

Electro Chemistry is one of the branches of physical chemistry, which deals with the chemical applications of electricity that means the conversion of chemical energy into electrical energy or electrical energy into chemical energy.

Electricity + Chemistry → Electrochemistry

Conductors: A substance or material that allows electric current to pass through them is known as conductors.

The ability of material to conduct electric current is called "Conductance".

Examples: All metals, graphite, fused salts, aqueous solutions of Acids, bases etc.

Non-Conductors: Those materials which do not conduct electric current are called Non-conductors or Insulators.

Examples: Plastics, wood, most of the non-metals, etc.

Types of Conductors: The conductors are broadly classified into two types as follows.

(1)Electronic Conductors/ Metallic Conductors: These are solid substances, which conduct electric current due to the movement of electrons from one end to another end. This will not undergo any physical/chemical change after conduction.

The conduction decreases with increase of temperature.

Ex: All metals, graphite etc.

(2)Electrolytic conductors/Ionic conductors: Electrolytic conductors conduct electric current due to the movement of ions in solution or in fused state.

The conduction increases with increase of temperature.

Ex: Acids, bases, electrovalent substances.

Electrolytic conductors are further sub-classified into three types as follows.

(a)Strong electrolytes:- Strong electrolytes are substances which ionise completely almost at all dilutions.

Ex: HCl, NaOH, NaCl, KCl etc.

(b)Weak electrolytes:-Weak electrolytes are substances which ionise to a small extent even at high dilutions.

Ex: CH_3COOH, NH_4OH, $CaCO_3$ etc.

(c)Non-electrolytes:-Non electrolytes are substances, which do not ionise at any dilutions.

Ex: Glucose, Sugar, Alcohol, Petrol etc.

Electrolysis: The process of decomposition of an electrolyte by the passage of electricity is called electrolysis. In this process electrical energy is converted into chemical Energy.

Electrolyte: Electrolyte is a water soluble substance forming ions in solution and conduct an electric current.

Current: Current is the flow of electrons through a wire or any conductor.

Anode: Anode is the electrode at which oxidation occurs.

Cathode: Cathode is the electrode at which reduction occurs.

Nernst equation: To determine the single electrode potential at the given concentration by using Nernst equation.

$E_{cell} = E^o - 2.303RT/nF \log [Oxi/Red]$ (OR)

$= E^o - 0.0591/n \log [Oxi/Red]$

Where, E= Single electrode potential, R=Gas constant, F= Faraday (96000cu.)

E^o= Standard electrode potential, T=Absolute temperature, n= valence of ion

Electrode potential: The tendency of a metallic electrode to gain or lose electrons, when it is in contact with its own salt solution is called electrode potential. It is denoted by E

Generally Reference electrodes are used as,

1. Slandered hydrogen electrode (SHE) - Pt, H_2/HCl (1M)
2. Calomel electrode - Pt, $Hg/HgCl_2/KCl$ (1M)
3. Silver-silver chloride electrode- $Ag/AgCl/KCl$ (1M)

But, the tendency of an electrode which is oxidised by loss of electrons is called its Oxidation potential. ie which is reduced by gain of electrons is called its Reduction potential.

Oxidation potential $\longrightarrow$ **1/Conc. of ions**

Reduction potential $\longrightarrow$ **Conc. of ions**

Standadard electrode potential: The tendency of a metallic electrode to gain or lose electrons, when it is in contact with its own salt solution of unit molar concentration at 25°C. It is called its Standard electrode potential. It is denoted by E^0

For examples, 1.SRP of Cu^{+2}/Cu (1M) = +0.34v

2. SOP of Cu/Cu^{+2} (1M) = 0.34v
3. SRP of Zn^{+2}/Zn (1M) = +0.76v
4. SOP of Zn/Zn^{+2} (1M) = -0.76v
5. SOP of Pb/Pb^{+2} (1M) = -0.13v

Factors affecting electrode potential: 1.The nature of the metal
2. The temperature
3. The concentration of metal ions in solution

Relationship between spontaneity and electrode potential of a cell.

a. If E^0_{Cell} is positive, the cell reaction is spontaneous.
b. If E^0_{Cell} is negative, the cell reaction is non-spontaneous

Electrochemical series/EMF series: -

When the various electrodes (metals) are arranged in the order of their increasing values of standard reduction potential by using SHE as the reference electrode, then the arrangement is called EMF series.

Anodic

S.No.	Electrode	Electrode Reaction	E° volts	Nature
1.	Li^+/Li	$Li^+ + e^-$ □ Li	-3.0	
2.	Mg^{+2}/Mg	$Mg^{+2}/2e^-$ □ Mg	-2.37	
3.	Pb^{+2}/Pb	$Pb^{+2} + 2e^-$ □ Pb	-1.12	
4.	Zn^{+2}/Zn	$Zn^{+2} + 2e^-$ □ Zn	-0.76	
5.	Fe^{+2}/Fe	$Fe^{+2} + 2e^-$ □ Fe	-0.44	+ve SRP
6.	Sn^{+2}/Sn	$Sn^{+2} + 2e^-$ □ Sn	-0.136	-ve SRP
7.	$2H^+/H_2$	$2H^+ + 2e^-$ □ H_2	0	
8.	Cu^{+2}/Cu	$Cu^{+2} + 2e^-$ □ Cu	+0.34	
9.	Ag^+/Ag	$Ag^+ + e^-$ □ Ag	+0.8	
10.	Au^+/Au	$Au^+ + e^-$ □ Au	+1.50	
11.	½ F_2/F^-	½$F_2 + e^-$ □ F^-	+2.87	

Cathodic

Significance:

1. This series provide more practical information on the relative corrosion tendencies of different metals and alloys.
2. In electrochemical series, -ve SRP values of metals react with acids to give H_2 gas. That is the +ve SRP values of metals react with acids does not give 'H_2' gas.
3. In every cell containing higher value of SRP is indicated as Cathode, Lower value of SRP is indicated as Anode.

Half Cell: Half-cell is a part of a cell, containing electrode dipped in an electrolytic solution.

If oxidation occurs at the electrode that is called oxidation half-cell.
If reduction occurs at the electrode that is called reduction half-cell.

Electrodes – concepts:

Electrode is a material or metallic rod or bar or strip which conduct electrons.

For examples, 1) Copper electrode- Cu^{+2}/Cu 3) Hydrogen electrode - Pt, H_2/H

2) Zinc electrode - Zn^{+2}/Zn 4) Chlorine electrode - Pt, Cl_2/Cl

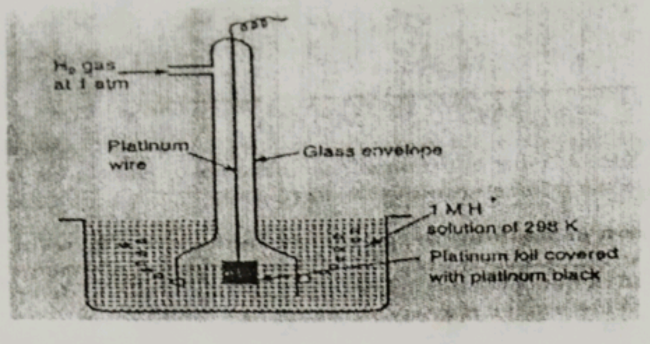
The following types of electrodes as follows,

Reference electrodes:

1 2m* (Electrodes of known potential, with which we can compare the potentials of another electrode, are called reference electrodes.

Example. S.H.E, calomel electrode, Ag – AgCl electrode, Glass electrode, etc.) 2m 1

Standard Hydrogen Electrode:



- It is the best primary reference electrode (since $E^o=0$)
- It consists of a small platinised Pt foil, which is sealed through the end of a glass tube. This tube is surrounded by another tube, which is sealed to the inner glass tube at the top.
- The outer glass tube is provided with a side – arm for passing hydrogen gas into the in-between space. The bottom of the outer tube is opened into a bell, around the Pt electrode.
- Openings in the bell allow the escape of hydrogen gas. The Pt foil is coated with a layer of finely divided Pt, which adsorbs the hydrogen gas and it also speeds up the equilibrium between hydrogen gas and the H^+ ions.
- This electrode, when dipped in 1N HCl and when 1 atm H_2 passed to give SHE.

Anode: $H_2 \longrightarrow 2H^+ + 2e$

Cathode: $2H^+ + 2e \longrightarrow H_2$

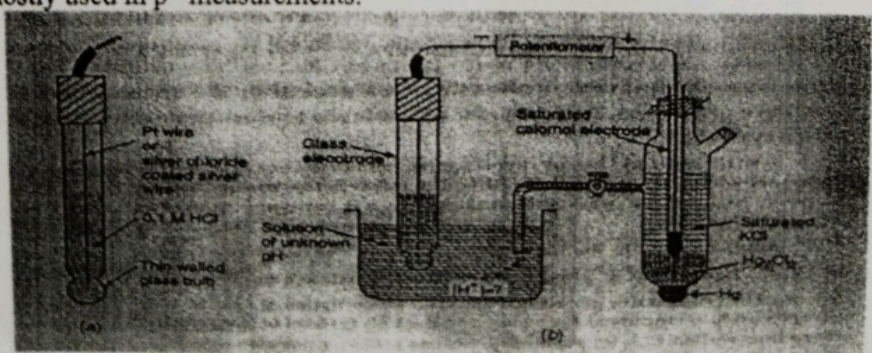
Merits: It is used to find the p^H value of an unknown solution.

Limitations:

- It cannot be used in the presence of ions of many metals.
- It cannot be used in solutions containing redox systems.
- It is difficult to set up
- It cannot be used in redox systems
- It is affected by compounds of Hg, As, S, and oxidizing agents like Fe^{3+}, permanganate, dichromate, etc.

Glass electrode:

- It is also called internal reference electrode or indicator electrode.
- It is highly sensitive to $[H^+]$.
- It is mostly used in p^H measurements.



Construction:

- It consists of a long glass tube with thin walled bulb at the bottom which has low melting point and high electrical conductivity.
- It contains a solution of 0.1 M HCl.
- A Pt wire is inserted inside the tube.
- It is represented as **Pt, HCl $_{(0.1\ M)}$ / Glass**

Determination of p^{H} of solution:

The pH of an unknown solution is found out by coupling the glass electrode with the calomel electrode. The complete cell representation is,

$$\text{Pt, HCl}_{(0.1\ M)}\ /\ \text{Glass}\ /\ H^{+}//\ KCl_{(Satd)},\ Hg_2Cl_{(2)(s)}/Hg\ .$$

The pH of the unknown solution is calculated using the formula

$$p^{H} = (\ 0.2422 - E^{0}_{G} - E_{Cell}\ )\ /\ 0.0591$$

Advantages:

1. It is the most convenient and simple to use.
2. Equilibrium is rapidly achieved.
3. The results are accurate.
4. It is not easily poisoned.

Limitations:

1. It can be used in solutions with pH range of 0 to 10.
2. It requires special electronic potentiometers.

Note: - Glass electrode cannot be used for solution of pH above 9.0?

At pH above 9.0, the ions of the solution affect the glass interface and render the electrode useless.

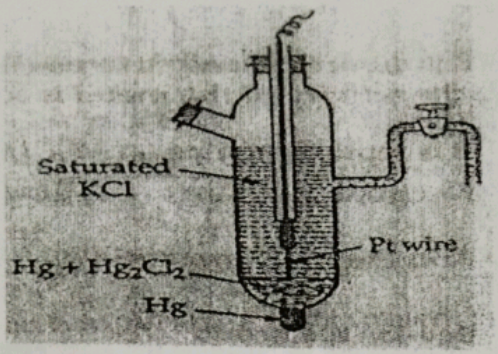
<u>Calomel electrode:</u>

- It is the secondary reference electrode.
- It is the Mercury – Mercurous chloride electrode.
- It contain a layer of mercury at the bottom, over which a paste of Hg + Hg_2Cl_2.
- The remaining part is filled with a saturated solution of KCl.
- A Pt wire, dipping into the Hg layer, is responds electrical contact.
- The side – tube is used for making electrical contact with a salt bridge.
- The potential of calomel electrode is inversely varies with concentration of KCl.

It can be represented as $Hg_2Cl_{2(s)}, KCl_{(Satd\ solution)}.\ \ E^{0} = 0.2422\ V$

Anode reaction: $2\ Hg_{(l)} + 2\ Cl^{-} \longrightarrow Hg_2Cl_{(2)(s)} + 2\ e$

Cathode reaction: $Hg_2Cl_{(2)(s)} + 2\ e \longrightarrow Hg_{(l)} + 2\ Cl^{-}{}_{(aq)}$



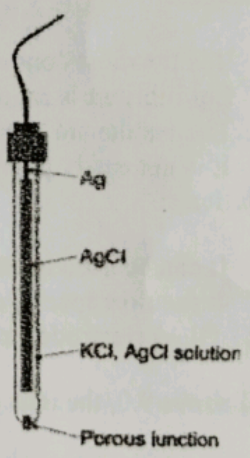
Merits:

- It is simple to construct.
- It gives accurate results and do not vary with T.

<u>Ag-Agcl electrode</u>:-the electrode consists of a silver wire coated **with a layer of silver** chloride dipping into a solution of a chloride like kcl or Hcl

$$AgCl_{(s)} + e^- \rightleftarrows Ag + Cl^- \quad E^0_{red} = 0.2224 \text{ vs. SHE}$$

$$E_{Ag/AgCl} = E^0_{Ag/AgCl} - 0.059 \log_{10} a_{Cl^-}$$



Cell: Cell is a device consisting of two half cells. The two half cells are connected through one wire.

Type of Cells:

A cell is a device consisting of two half cells. Each half cell contains an electrode dipped an electrolytic solution. The two half cells are connected through one wire. The following are two types of cells.

(1) **Electrolytic Cells (2) Electro chemical cells / Galvanic cells**

(1)Electrolytic Cells: Electrolytic cells are cells in which electrical energy is used to bring about the chemical reaction. That means the conversion of electrical energy into chemical energy.

Ex: Electrolysis, Electroplating.

(2)Electro Chemical Cell: Electro chemical cells are cells in which electrical energy is generated by a chemical reaction (redox reaction).

Ex: Galvanic cell, Fuel cell.

Differences between electrolytic and electrochemical cells.

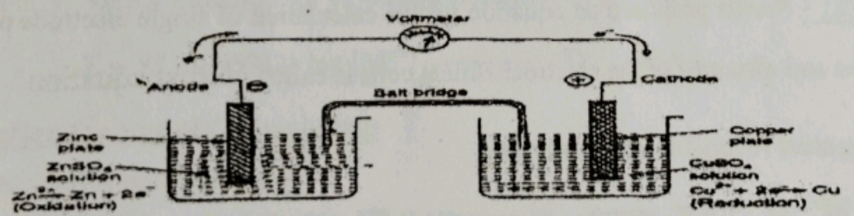
S.No	Electrolytic cell	Electrochemical cell
1	It converts Electrical energy into Chemical energy.	It converts Chemical energy into Electrical energy.
2	Anode carries positive charge.	Anode carries negative charge.
3	Cathode carries negative charge.	Cathode carries positive charge.
4	It is irreversible.	It is reversible.
5	Electron flows from the battery to the electrolyte.	Electron flows from anode to Cathode.

Electro chemical cell:

Electro chemical cell is Galvanic cell in which the electrons transferred due to redox reaction, converted to electrical energy.

Ex: Daniel cell

Construction: Galvanic cell consists of a Zn electrode dipped in 1M $ZnSO_4$ solution and a Cu electrode dipped in 1M $CuSO_4$ solution. Each electrode is known as a half cell. The two solutions are inter connected by a salt bridge and the two electrodes are connected by a wire through the voltmeter.



Working Process: When operating the Galvanic cell as following chemical reactions are involved at anode and cathode.

At Anode: Oxidation takes place in the Zn electrode by the liberation of electrons, so this electrode is called -ve electrode or Anode.

At anode, $Zn \longrightarrow Zn^{+2} + 2e^-$ (Oxidation half-cell reaction)

At Cathode: Reduction takes place in the Cu electrode by the acceptance of electrons, so this electrode is called +ve electrode or Cathode.

At cathode, $Cu^{+2} + 2e^- \longrightarrow Cu$ (Reduction half-cell reaction)

The overall cell reaction can be written as,

At anode, $Zn \longrightarrow Zn^{+2} + 2e^-$

At cathode, $Cu^{+2} + 2e^- \longrightarrow Cu$

$Cu^{+2} + Zn \longrightarrow Zn^{+2} + Cu + E.E$ (Overall cell reaction)

The electrons liberated by the oxidation reaction flow through the external wire and are consumed by the copper ion at the cathode.

Representation of a Galvanic cell:

- A Galvanic cell consists of two electrodes anode and cathode.
- The anode is written on the left hand side while the cathode is written on the right hand side.
- The anode must be written by writing electrode metal by a vertical line or a semicolon. The electrolyte may be written by the formula of the compound or by ionic species.

  Ex: Zn/ Zn^{+2} or $Zn/ZnSO_4$ or $Zn; Zn^{+2}$
- The cathode must be written by writing electrolyte first and then electrode metal. These two are separated by a vertical line or a semicolon.

  Ex: Cu^{+2} / Cu or $CuSO_4/Cu$ or $Cu^{+2}; Cu$
- The two half cells are separated by a salt bridge which is indicated by two vertical lines.

  By using above representation, the Galvanic cell is represented as follows:

  $Zn/ZnSO_4$ // $CuSO_4/Cu$ (or) Zn/Zn^{+2} // Cu^{+2}/Cu (or) $Zn; Zn^{+2};; Cu^{+2}/Cu$

Salt bridge: - It is U shaped tube contains saturated solution of KC or NH_4NO_3 in agar-agar gel. The functions are

1. It maintains electrical neutrality.
2. It eliminates liquid junction potential.
3. It produces connectivity between two half cells.
4. It allows migration of ions from one half cells to another.

2

Nernst equation: - Nernst proposed an equation for the calculation of single electrode potentials of unknown electrodes and also emf of the electrochemical cells is called Nernst equation

Let us consider a general reversible redox reaction,

$$M^{n+}{}_{(aq)} + n\,e^- \rightleftharpoons M_{(s)} \text{ ---------- } (1)$$

The chemical equilibrium constant can be written as,

$$Kc = [M] / [M^{+n}]$$

According to **Van't Hoff reaction isotherm equation,**

i.e Now for a reversible reaction the free energy change (ΔG), standard free energy change (ΔG^0) and its equilibrium constant (K) are inter-related as,

$$\Delta G = \Delta G^0 + RT \ln Kc \text{ ----------- } (2)$$

We know that, In a reversible reaction, the electrical energy is produced is the same as decrease in free energy.

$$\text{i.e. } -\Delta G = nFE \text{ and } -\Delta G^0 = nFE^o \text{ ------- } (3)$$

Where, E = electrode potential, E^0 = standard electrode potential and F = Faraday (96,500 Coulomb).

Apply the equation (3) in equation (2), we get

$$-nFE = -nFE^0 + RT \ln \{[M] / [M^{n+}]\}$$

Since the concentration of metal, M is unity, we have

$$-nFE = -nFE^0 + RT \ln \{1 / [M^{n+}]\}$$

$$-nFE = -nFE^0 - RT \ln [M^{n+}] \text{ ----------- (4)}$$

Both side divide above equation by –nF, we get

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

$$E = E^0 + (2.303\ RT / nF) \log [M^{n+}] \quad \text{.... (5)}$$

Where, E = Electrode potential, T = 298 K, E^o= Standard electrode potential, n = No of electrons involved, R = Gas constant (8.314 J/K/mole), F = 96500 coulombs

- Substituting R, T, F values in eq (5) we get,

$$\mathbf{E = E^0 - 0.0591/n \log \{[M] / [M^{n+}]\}}$$

- At 25^0C, $\mathbf{E = E^0 + 0.0591/ n \log [M^{n+}]}$**-----(6)** since [M] =1
- This equation is called Nernst Equation for **single electrode potential** or **reduction potential of electrode.**
- Similarly, Nernst Equation for **oxidation potential of electrode** can be written as,

$$\mathbf{E = E^0 - 0.0591/n \log [M^{n+}]} \text{ ----------- (7)}$$

Nernst equation for emf of Galvanic cell:

The Galvanic cell is represented as

$Zn/ZnSO_4$ (1M) // $CuSO_4$ (1M) /Cu

The emf of a cell is given by

$$E^0_{cell} = E^o\ Cu^{+2}/Cu - E^o\ Zn^{+2}/Zn$$
$$E_{cell} = E^o_R - E^o_L \text{ .... (1)}$$

We know that, the Nernst equation for reduction potential of copper,

$$E^o\ Cu^{+2}/Cu = E^0_{cell} + 0.0591/2 \log [Cu^{+2}] \text{ --------- (2)}$$

Similarly the Nernst equation for reduction potential of Zinc,

$$E^o\ Zn^{+2}/Zn = E^0_{cell} \pm 0.0591/2 \log [Zn^{+2}] \text{ ------------- (3)}$$

Substituting equation 2 & 3 in equation 1 we get

$$E_{cell} = \{E^o\ Cu^{+2}/Cu - E^o\ Zn^{+2}/Zn\} + 0.0591/2 \log [Cu^{+2}/ Zn^{+2}]$$

$$\boxed{\mathbf{E_{cell} = E^0_{cell} + 0.0591/2 \log [Cu^{+2}/ Zn^{+2}]}}$$

Significance of Nernst equation:

1. If $[M^{n+}]$ increases, the E_{cell} is also increases and vice versa.

2. If T increases, the E_{cell} is also increases and vice versa.

Applications:

1. It is used to study the effect of electrolyte concentration.
2. It is used for the calculation of cell.
3. It is used to calculate pH of a solution.
4. It is used for finding the valence of an ion.

Numerical Problems:

1. To calculate the resulting EMF of a cell. The following half-cell reactions are

(a) $Zn \longrightarrow Zn^{+2} + 2e^-$ (E = -0.76 volts)

$Cu^{+2} + 2e \longrightarrow Cu$ (E = 0.34v)

(b) $Cl_2 + 2e \longrightarrow 2Cl^-$ (0.36v)

$Zn^{+2} + 2e \longrightarrow Zn$ (-0.76v)

2. Write the half-cell reactions, net cell reaction and the emf of the cell represented as

Zn/Zn^{+2} // H^+ (1atm) /H_2 (1atm) at 25c (E^0 Zn^{+2}/Zn = -0.763 v). **[Ans.0.763v]**

3. Calculate the emf of the Zn-Ag cell at 25c when Zn^{+2}=0.10M and **$[(Ag^+)]$ =10.0M (E^0cell at 25c** =1.56v). [Ans.1.62v]

4. Calculate the standard emf of Ni-Ag cell whose E^0_{Ni} and E^0_{Ag} are -0.25 and 0.83V respectively and also write the Cell representation. [Ans.1.08v]

5. The EMF of a cell, Mg/Mg^{+2} (0.01M//cu^{+2} (M)/ Cu is found to 2.78 v at 300k.The standard electrode potential of Mg electrode is -2.371 v. What is the electrode potential of copper electrode? [Ans.0.35v]

BATTERIES

Batteries are having many applications both in science and in our daily life.

"Battery is an electro chemical cell or several - electro chemical cells connected in series that can be used as a source of direct electric current at constant voltage.

A device which converts chemical energy to electrical energy is called **"Battery"**.

A Cell: It contains only one anode and cathode.

A Battery: It contains several anodes and cathodes.

Requirements of a battery: A useful battery should fulfil the following requirements.

(1) It should be light and compact for easy transport.
(2) It should have long life both when it is being used and when it is not used.
(3) The voltage of the battery should not vary appreciably during its use.

Types of Battery: Batteries are classified into three types. They are:

(1) Primary battery / Non-reversible battery
(2) Secondary battery / Reversible battery
(3) Flow battery / Fuel cells

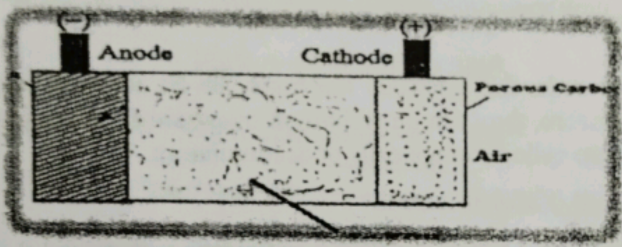
(1)**Primary cells:** In these cells, the electrode reactions cannot be reversed by passing an external electrical energy. So that, the reactions occurs only once and after use they become dead. Therefore, they are not chargeable.

Examples: Dry cell, Mercury cell

1. **Zn-air battery :**

A zinc-air battery is a primary battery. It is a non-rechargeable battery because of the electrode reactions cannot be reversible. It is an example of alkaline battery.

Construction:- zinc-air battery consists of Zn act as anode and porous carbon plate acting as a cathode and electrolyte is Aqueous KOH.



The cell may be represented as;

Zn/ KOH $_{(aq)}$// Air, C

Working process: When the zinc-air battery operates, the following reactions occur.

At anode: Zn is oxidised to Zn^{+2} ions, which further combines with OH^- ions to form ZnO and H_2O.

$$Zn_{(s)} \longrightarrow Zn^{+2} + 2e^-$$

$$Zn^{+2} + 2OH^- \longrightarrow ZnO + H_2O$$

$$Zn_{(s)} + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$$

At Cathode: The electrons produced at the anode pass through the external wire to the cathode, where it is absorbed by oxygen and water to produce hydroxide ions.

$$1/2O_2 + 2e^- \rightarrow O^{-2}$$

$$O^{-2} + H_2O \rightarrow 2OH^-$$

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

The overall cell reaction can be written as,

$$Zn(s) + 2OH^- \rightarrow ZnO + H_2O + 2e^-$$

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

$$Zn(s) + 1/2O_2 \rightarrow ZnO + Energy$$

From the above cell reactions it is clear that, the cell functions as long as the reacting agents are in supply and directly converted into electrical energy.

The emf of Zn-air battery = 1.59 V

Zinc–air batteries cannot be used in a sealed battery holder since some air must come in; the oxygen in 1 litre of air is required for every ampere-hour of capacity used.

Applications:-

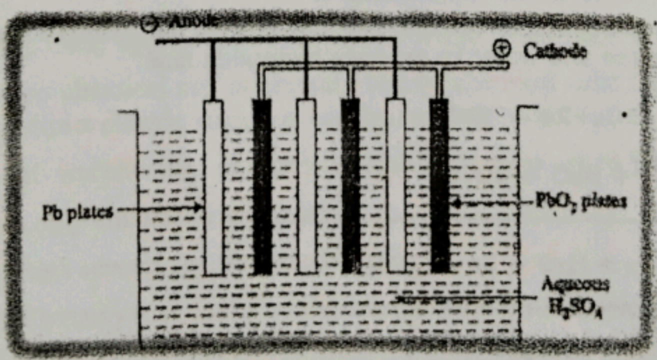
1. The system is well known as a primary battery.
2. Used as power source in hearing aids.
3. Used in electronic pagers.
4. Used in Military radio receivers.
5. Used in voice Transmitters

(2)**Secondary cells:** In these cells, the electrode reactions can be reversed by passing an external electrical energy. Therefore, they can be recharged by passing electric current and used again and again. These are also called storage cells or accumulators.

Examples: Lead-acid cell, Lithium-ion cell

1.) **Lead-acid storage cell:** A Lead-acid cell is a secondary battery and it is also called storage cell or Accumulator or rechargeable battery.

Construction: A lead-acid storage battery consists of a number of voltaic cells (3 to 6) connected in series to get 6 to 12v battery. In each cell, the anode is made of Lead. The cathode is made of PbO_2. A number of lead plates (anodes) are connected in parallel and a number of PbO_2 plates (cathodes) are also connected in parallel. Various plates are separated from the adjacent ores by insulators like rubber or glass fibre. Later, the entire combinations are immersed in dil.H_2SO_4 having a density of 1.30 gm/ml.



The cell may be represented as,

$$Pb/PbSO_4\,//\,H_2SO_4\,/\,PbO_2\,/\,Pb$$

Working Process:

When the lead-acid storage battery operates, the following reactions occur.

At anode: Lead is oxidised to Pb^{+2} ions, which further combines with SO_4^{-2} forms insoluble $PbSO_4$.

$$Pb(s) \longrightarrow Pb^{+2} + 2e^-$$

$$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4(s)$$

$$Pb(s) + SO_4^{-2} \longrightarrow PbSO_4(s) + 2e^- \quad (O.H.R)$$

At cathode: PbO_2 is reduced to Pb^{+2} ions, which further combines with SO_4^{-2} forms insoluble $PbSO_4$.

$$PbO_2 \longrightarrow Pb^{+4} + 2O^{-2}$$

$$Pb^{+4} + 2e^- \longrightarrow Pb^{+2}$$

$$Pb^{+2} + SO_4^{-2} \longrightarrow PbSO_4(s)$$

$$2O^{-2} + 4H^+ \longrightarrow 2H_2O$$

$$PbO_2 + 4H^+ + SO_4^{-2} + 2e^- \longrightarrow PbSO_4 + 2H_2O \ (R.H.R)$$

The overall cell reaction can be written as,

At Anode: $Pb\ (s) + SO_4^{-2} \longrightarrow PbSO_4(s) + 2e^-$

At Cathode: $PbO_2 + 4H^+ + SO_4^{-2} + 2e^- \longrightarrow PbSO_4 + 2H_2O$

$$Pb + PbO_2(s) + 2H_2SO_4 \longrightarrow 2PbSO_4(s) + 2H_2O + \text{Energy (Overall cell reaction)}$$

- From the above cell reactions, it is clear that, $PbSO_4$ is precipitated at both the electrodes and H_2SO_4 is used up. As a result, the concentration of H_2SO_4 decreases and hence the density of H_2SO_4 falls below 1.30 gm/ml. So, the battery need for recharging.

Recharging the Battery: The cell can be charged by passing electric current in the opposite direction. The electrode reactions get reversed. As a result, Pb is deposited on anode and PbO_2 on the cathode. The density of H_2SO_4 is also increases.

The net cell reaction during charging is,

$$2PbSO_4(s) + 2H_2O + \text{Energy} \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftharpoons}} Pb(S) + PbO_2(S) + 2H_2SO_4\,(aq)$$

The emf of lead-acid cell is above 2.0 volts.

Uses:

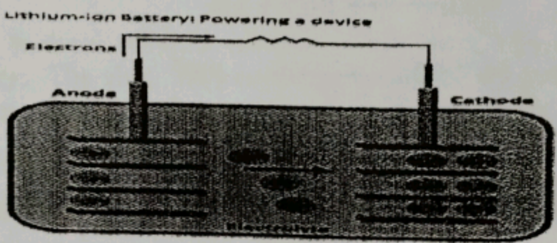
1. This cell is used to supply current mainly in automobiles such as cars, buses, and tractors.
2. It is also used in gas engine ignition, telephone exchanges, hospitals, power stations, etc.

(2) Lithium-ion Battery:

Lithium ion battery is a solid state battery because instead of liquid or a paste electrolyte, solid-electrolyte is used.

Construction:

The Lithium ion battery consists of a Lithium Cobalt oxide ($LiCoO_2$) act as anode and Graphite (C) act as cathode. A solid electrolyte (polymer) is packed in between the electrodes. The electrolyte permits the passage of ions but not that of electrons.



Working Process:

When the anode is connected to cathode, Lithium Cobalt oxide ($LiCoO_2$) is oxidised and produce lithium ions (Li^+) which move from anode to cathode. The cathode is a material capable of receiving the lithium ions and electrons.

At anode: $LiCoO_2 \longrightarrow Li_{(x-1)}CoO_2 + xLi^+ + xe^-$

At cathode: $Graphite + xLi^+ + xe^- \longrightarrow xLi - Graphite$

Netcell reaction is, $LiCoO_2 + Graphite \rightleftharpoons x\,Li - Graphite + Li_{(x-1)}CoO_2 + Energy$

Recharging the battery: - The lithium ion battery can be recharged by supplying an external current, which drives the Lithium ions back to the anode.

The net cell reaction during charging is,

$$xLi - Graphite + Li_{(x-1)}CoO_2 + Energy \underset{\text{Discharging}}{\overset{\text{Charging}}{\rightleftharpoons}} LiCoO_2 + Graphite$$

The emf of a Li-ion cell is 3v.

Advantages of Li-ion battery: It has a future cell, why?

(1)Its cell voltage is high 3.0v

(2)Li is a light weight metal, only 7 gm. (1 mole) material is required to produce 1 mole of electrons.

(3)Li has the most -ve E° value. So, it generates a higher voltage than the other types of cells.

(4)All the constituents of the battery are solids. So, there is no risk of leakage from the battery.

(5)This battery can be made in a variety of sizes and shapes.

3. Fuel Cells:

A fuel cell is an electrochemical cell, which converts the chemical energy into electrical energy by the oxidation of fuel without combustion. In these cells, the reactions, products and electrolytes continuously pass through the cell.

$$\textbf{Fuel + Oxygen} \longrightarrow \textbf{Oxidation products + Electricity}$$

A fuel cell is always represented as follows,

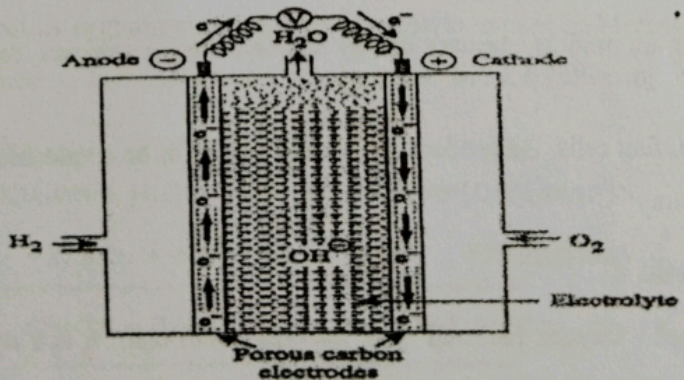
Fuel / Anode / electrolyte / Cathode / oxidant

Examples: - (1) H_2 - O_2 fuel cell. (2) CH_3OH- O_2 fuel cell.

(1)H_2 - O_2 fuel cell:

This cell was developed by **Sir William Robert Grove** by using Pt electrodes. Hydrogen - Oxygen fuel cell is the simplest and most successful fuel cell. In which the fuel Hydrogen and the oxidiser - oxygen and the liquid electrolyte are continuously passed through the cell.

Construction: The cell consists of two inert porous carbon electrodes with Pt or Pd coated act as anode and Ag coated act as cathode. In between them 25% KOH electrolyte is filled. Now the two electrodes are connected through the Voltmeter.



Working Process: The fuel-Hydrogen is passed through the anode compartment, where it is oxidised. The oxidiser-Oxygen is passed through the cathode compartment, where it is reduced. Then, the following chemical reactions are occurred.

At anode: Hydrogen molecules are oxidised at the anode with the liberation of electrons, which are combine with hydroxide ions to form water.

$$H_2 \longrightarrow 2H^+ + 2e^-$$
$$\cancel{2H^+} + 2OH^- \longrightarrow 2H_2O$$

$$H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$$

At cathode: The electrons produced at the anode pass through the external wire to the cathode, where it is absorbed by oxygen and water to produce hydroxide ions.

$$1/2O_2 + 2e^- \longrightarrow \cancel{O^{-2}}$$
$$\cancel{O^{-2}} + H_2O \longrightarrow 2OH^-$$

$$1/2O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

The overall cell reaction can be written as,

$$H_2 + \cancel{2OH^-} \longrightarrow \cancel{H_2O} + \cancel{2e^-}$$
$$1/2O_2 + \cancel{H_2O} + \cancel{2e^-} \longrightarrow \cancel{2OH^-}$$

$$H_2 + 1/2O_2 \longrightarrow H_2O + \text{Energy}$$

From the above cell reactions it is clear that, the cell functions as long as the reacting gases are in supply, the heat of combustion is directly converted into electrical energy.

The standard emf of H_2-O_2cell = **1.23v**

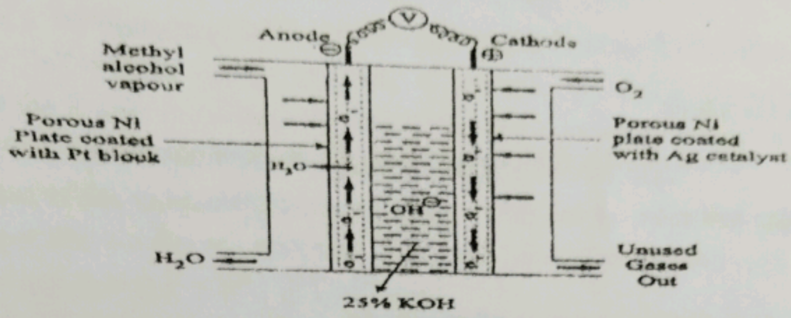
Applications:

1. H_2 - O_2 fuel cells are used as auxiliary energy source in space vehicles, submarines and military vehicles.
2. In case of H_2 - O_2 fuel cells, the product of water is proved to be a valuable source of fresh water by the astronauts.

(2)<u>CH_3OH - O_2 fuel cell:</u>

Methanol - Oxygen fuel cell is an important fuel cell. It is a sub-category of proton-exchange fuel cell. This fuel cell is based on the oxidisation of methanol to form CO_2.

Construction: The cell consists of two inert porous nickel electrodes with Pt coated act as anode and Ag coated act as cathode. In between them 25% KOH or Proton exchange membrane electrolyte is filled. Now the two electrodes are connected through the voltmeter.



Working Process: The fuel-Methanol is passed through the anode compartment, where it is oxidised. The oxidiser - Oxygen is passed through the cathode compartment, where it is reduced. (i.e Methanol and water are absorbed on Pt catalyst and lose of protons and electrons until CO_2 is formed. These protons are transferred across through membrane and also electrons passed through external wire to cathode. They undergo reduction to form water.) Thus, the following chemical reactions are involved.

At anode: $CH_3OH + 6OH^- \longrightarrow CO_2 + 5H_2O + 6e^-$ (Oxidation)

At cathode: $3/2\ O_2 + 3H_2O + 6e \longrightarrow 6OH^-$ (Reduction)

Net cell reaction: $CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2H_2O +$ Energy

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From the above cell all reactions it is observed that, for the formation of the final product CO_2 reaction of one molecule of Methanol, 3/2 O_2 molecules of water will be reduced to H_2O molecules. Then heat of combustion is directly converted into electrical energy.

The standard emf of CH_3OH-O_2 cell = **1.21v**

NOTE: -In case of **proton exchange membrane** electrolyte is used in Methanol - Oxygen fuel cell, protons flow from anode to cathode instead of electrons. So, the following chemical reactions are occurred.

At anode: $CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$ **(Oxidation)**

At cathode: $3/2\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$ **(Reduction)**

Net cell reaction: $CH_3OH + 3/2\ O_2 \rightarrow CO_2 + 2H_2O +$ **Energy**

Limitations:

(1) During the methanol oxidation reaction, CO_2 is formed which is strongly absorbed on Pt catalyst, reducing the surface area and lowering the performance.

(2) Methanol is toxic and flammable. Hence care has to be taken.

(3) Limited in the power they produce.

(4) The efficiency of current is low due to the high permeation of methanol through membrane material used which is known as methanol cross over.

Advantages and Disadvantages of fuel cells:

Advantages: 1. Fuel cells are efficient (75%) and take less time for operation.

2. It is pollution free technique

3. It produces electric current directly from the reaction of a fuel and an oxidiser

4. It produces drinking water.

Disadvantages:

1. Fuel cells cannot store electric energy as other cells do.
2. Electrodes are expensive and short lived.
3. Storage and handling of hydrogen gas is dangerous.

Note: When a large number of fuel cells are connected in series. It forms Flow battery.

❖ Potentiometric titrations:

To measure potential difference more accurate as compared to voltmeter but voltmeter is used more often due to its small size and convince.

Basic principle: - Potentiometric titration is a volumetric titration method. It is based on the change in potential of the solution at the end point during the titration. In this titration, change in active ion concentration leads to the change in electrode potential. Thus, the Potentiometric titrations involve the measurement of emf between reference electrode and an indicator electrode, with the addition of the titrant.

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

Types of Potentiometric titration: - These titrations are followed by three types, they are,

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

Ex. Redox titration: ($FeSO_4$ vs $K_2Cr_2O_7$)

- ✓ **Burette solution:** $K_2Cr_2O_7$ solution
- ✓ **Pipette solution:** unknown $FeSO_4$ + dil. H_2SO_4
- ✓ **Electrodes used:** Pt electrode & calomel electrode.
- ✓ **Cell representation:** $Hg / Hg_2Cl_{2(s)}, KCl // Fe^{3+} / Fe^{2+}, Pt$

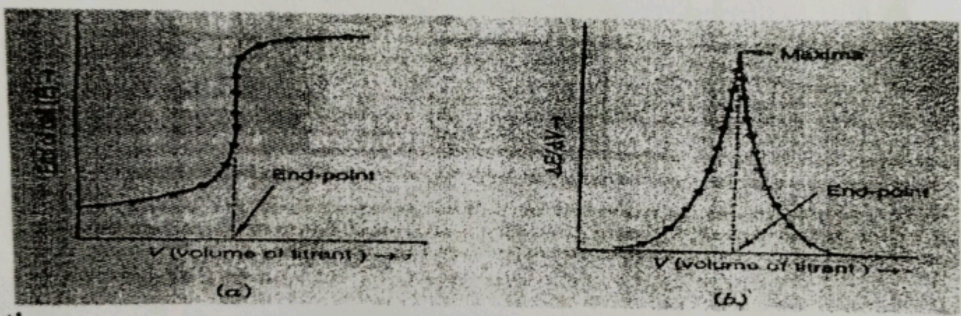
Exp.Procedure:

- ✓ When $FeSO_4$ solution is titrated against $K_2Cr_2O_7$ solution, the following Rdox reaction occurs as follows,

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

- ✓ When $FeSO_4$ solution is titrated against $K_2Cr_2O_7$ solution, Cr^{+6} reduced to Cr^{+3} and Fe^{2+} oxidized to Fe^{+3} and the change in potential is noted. A graph is drawn by taking volume of $K_2Cr_2O_7$ in the X axis and change in potential in the Y axis, from which volume of $K_2Cr_2O_7$ is obtained. From the end point concentration of $FeSO_4$ is calculated.
- ✓ The potential of the indicator electrode (Pt electrode) can be measured using potentiometer by connecting it with a reference electrode (Saturated calomel electrode).
- ✓ The Nernst equation is $E = E^0 + (RT/nF) \log C$
- ✓ The change in potential is noted for each addition of the titrant. The change in potential is small at initial, but it is large at the end point
- ✓ The end point of the titration is obtained from the plot of volume of titrant vs $\Delta E / \Delta V$ against the volume of titrant added. The maxima of the curve give the end point.

Graph:



Calculations:-

- **N1V1= N2V2**
- **N2=N1V1/V2**
- **The strength of given $FeSO_4$ solution= N2* Equivalent wt.of HCl**

❖ Conductometric titrations:

Principle: Conductometric titration is a volumetric titration method. It is based on the change in conductance of the solution during titration. The conductance of the solution depends on the number of free ions, charge on the free ions and mobility of the ions.

Types of Potentiometric titration: - These titrations are followed by three types, they are,

1. Acid-Base titrations.
2. Redox titrations.
3. Precipitation titrations.
4. Complexometric titrations

Ex. Acid-Base titrations: (S.A Vs S.B)

- ✓ **Burette solution:** NaOH solution
- ✓ **Pipette solution:** unknown HCl solution + 100 ml distilled water
- ✓ **Electrodes used:** Pt electrode & conductivity cell.

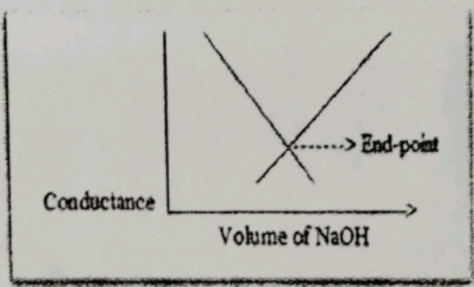
Exp.Procedure:-

- ✓ When HCl solution is titrated against NaOH solution, the following neutralization reaction occurs.

$$NaOH + HCl \rightarrow NaCl + H_2O$$

- ✓ The concentration of fast moving H+ ions of acid neutralized by OH – ions of base to form water.
- ✓ The conductance first decreases and then increases after the end point. A graph is drawn by taking volume of NaOH in X axis and conductance in Y axis, from which volume of NaOH is obtained. From the end point the concentration of HCl is calculated.

Graph:



Calculations:-

$$N1V1= N2V2$$

$$N2=N1V1/V2$$

The strength of given HCl solution= N2* Equivalent wt.of HCl

Advantages:

1. It gives more accurate end points.
2. It requires no indicators.
3. It is very useful in case of coloured solution.
4. It is very useful for dilute solutions.
5. It is very useful for titrating weak acids against weak bases.
6. In this method, no keen observance is near the end point, since it is detected graphically.

❖ SENSORS:

Sensor is a device which is able to detect in physical or chemical quantity of a sample and provides information continuously in discrete steps in the form of an electrical signal is termed as a sensor.

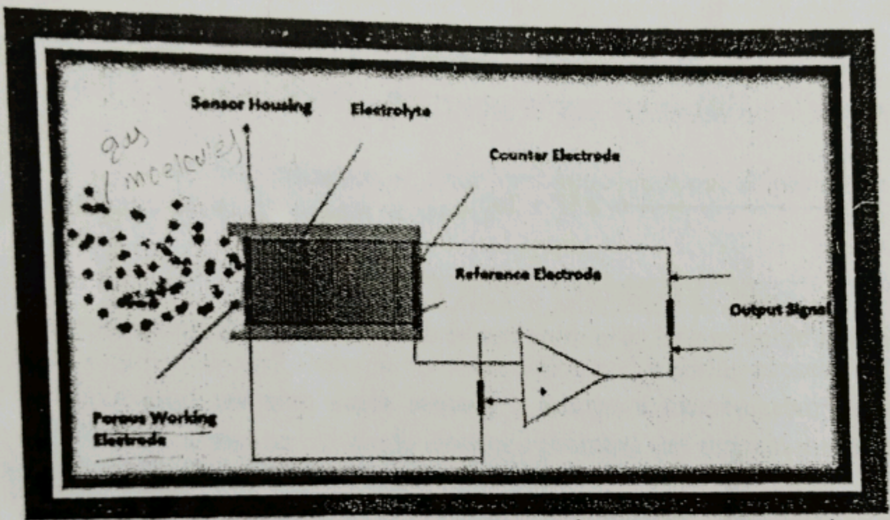
Sensors are various types, such as Chemical sensors (58%), Optical sensors (24%), Mass sensors (12%) and Thermal sensors (6%) will constitute the electrochemical sensors.

Electrochemical sensors:- These are electro analytical devices that owe their popularity and success to the scientific discipline electrochemistry.

These sensors are will provide information about the chemical environment and the growing need for reliable sources of information which guarantees their future. In these sensors chemical information is directly converted into an electrical signal.

An electrochemical sensor has an outer frame containing an electrolytic gel three electrodes (such as Measuring electrode, Counter electrode and Reference electrode). At the top it has gas permeable membrane. The electrodes used in sensors should have high sensitivity, durability and large surface area. Special filter electrodes are also arranged for getting quick signals.

These are devices that evaluate information about sample from measurement of some electrical parameter variations.



Instrumentation of electrochemical sensor

Types of Electrochemical sensors

According to the measures of electrical parameters, electrochemical sensors are divided into 3 types.

1. Potentiometric sensors: - If we measure difference of two potentials.
2. Amprometric sensors/Volta metric sensors: - If the parameter is current.
3. Conductometric sensors:-If we measure Resistance or Conductance.

The basic principle involved in any electrochemical sensor is **"Ohm's law"**

The Ohm's law states that, the potential difference is equal to the product of electric current and the resistance.

$$E=IR$$

In all sensors have two things are in common. First, the measurement should be done with closed electrical circuit, measuring that a test charge can be passed through the electrical circuit and returned to its origin. Secondly, electrical neutrality is to be maintained.

1. **Potentiometric sensors:** - It is used to determine the concentration of ions of interest in the test solution used for electro-analysis.
   A good sensor will have greater ability to respond to the species of interest even in the presence of other species called interferons.

Working principle- The concentration of the ionic species present in the test solution is determined directly by using potentiometric sensor. This is because, the concentration of the species is related directly to the potential difference in volt developed in the system.
In potentiometric sensor, Ion-selective electrode (ISE) is used for electro analysis. Most of the Ion-selective electrodes are membrane electrode, Glass electrode etc.
For example-1. Analysis of Glucose,

For analysis of Glucose initially neutral Glucose molecule is to be converted in to its ions. The ions are selectively detected as shown below. During the analysis of Glucose, It is oxidized in the presence of oxidize enzyme to Gluconic acid.

Finally, the subsequent measurement of the liberated H^+ ions are carried out by using Glass electrode through P^H is determined.
The following are the electrochemical reactions that occur during the analysis of Glucose through potentiometric sensor.

1. $$\text{D-Glucose} + O_2 + H_2O \xrightarrow{\text{Glucose oxidize enzyme}} \text{D-Gluconicacid} + H_2O_2$$

2. $$H_2O_2 \longrightarrow 2\,H^+ + 2e^-$$

Applications:-

1. The glucose levels in blood as well as in urine can be determined by using potentiometric Sensors.
1. The urine glucose measurement integrates a glucose value over the time required for the bladder to fill.
2. The concentration of H^+ ions released during the decomposition of Carbonic acid formed by the hydrolysis of CO_2 can also be determined.

$$H_2O + CO_2 \longrightarrow H_2CO_3 + 2H^+ + CO_3^{-2}$$

2. **<u>Amprometric sensors: -</u>** It is used for the measurement of current between the working electrode and counter electrode which is induced by a Redox reaction. At the working electrode.

In Amprometric sensors, an electrochemical signal finds .its place in accordance with the diffusion current developed. The diffusion current is directly proportional to the concentration of the species which is being electrochemically transformed at the electrode. The electrochemical reactions will occur quickly when their charge transfer resistance is very low. On the other hand, when the charge transfer resistance is very high, the electrochemical reactions will occur slowly.
The size of electrode also plays an important role in the performance of Amprometric sensor. Amprometric sensors having electrodes of diameter <20m, will exhibit best performance.

For example- 1. Analysis of Uric acid,

For analysis of Uric acid can be carried out in the presence of an enzyme or in the absence of an enzyme by using Amprometric sensor.

The following electrochemical reactions occur during the analysis of Uric acid through Amprometric sensor.

Case-I. In the presence of an Uricase enzyme, Uric acid ($C_4H_4N_4O_3$) is oxidized to Allantoin.

1. $\text{Uricacid} + O_2 + 2H_2O \xrightarrow{\text{Uricase enzyme}} \text{Allantoin} + CO_2 + H_2O_2$

2. $H_2O_2 \longrightarrow 2\,H^+ + 2e^-$

Case-II. In the absence of enzyme, Uric acid containing containing Ascorbic acid is analysed by using differential pulse voltammetry. In this determination two different peaks for Uric acid and Ascorbic acid are identified with suitable separation.

Applications:-

1. The measurement of water quality by using Amprometric oxygen sensor (Clark electrode).
2. It is employed in gas analysis in diverse areas, such as food industry, beverage industry to detect explosive materials and toxic gases such as NO_2, SO_2, CO_2, H_2S etc.
3. It is used to determine the concentrations of ionic chemical content in blood, Urine and other biological samples.
4. It is used for the determination of trace level concentrations of pesticides, fertilizers, drugs and pharmaceuticals etc. from sample matrix.

IMPORTANT QUESTIONS

1. What is Galvanic cell? Describe its construction and working process?
2. Derive Nernst equation for single electrode potential and explain the terms involved in it. Write its applications.
3. Explain the construction and working of Lead – acid storage battery.
4. Explain the construction and working of Li – ion battery.
5. What are fuel cells? Explain the construction and working of Proton exchange fuel cell.
6. Write a short notes on, a.) $H_2 - O_2$ cell b.) Lithium ion cell
7. Explain NaoH vs HCl titration conductometrically.
8. Write a short notes on, a.) Potentiometric sensors b.) Amprometric sensors

Q/B
1, 2, 3, 5,