

(AR)

UNIT -2

ELECTROCHEMISTRY

1. What is an electrochemical cell Explain the classification with examples

An electrochemical cell is a device, which is used to convert chemical energy into electrical energy and vice versa. These electrochemical cells are classified into two types as follows.

1) Galvanic or Voltaic cells:

These are the electrochemical cells, which convert chemical energy into electrical energy.

2) Electrolytic cell:

These are the electrochemical cells, which are used to convert electrical energy into chemical energy.

Concentration cells:

These are the electrochemical cells consisting of same metal electrodes dipped in same metal ionic solutions in both the half cells but are different in the concentration of the metal ions.

Ex: copper concentration cell, zinc concentration cell

2. Mention the Cell notations and Cell Conventions

Cell notations

Eg: $\text{Zn (s) / Zn}^{2+} \text{ (aq) // Cu}^{2+} \text{ (aq) / Cu}$.

/ Single vertical line represents phase boundary between the metal and its solution.

// Double vertical line represents salt bridge.

3. Derive Nernst Equation for single electrode potential

In 1889 Nernst derived a quantitative relationship between the electrode potential and the concentrations of metal ions involved.

The decrease in free energy ($-\Delta G$) represents the maximum amount of work that can be obtained from a chemical cell reaction.

$$-\Delta G = W_{\text{max}}$$

$$W_{\text{max}} = n F E$$

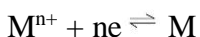
Where, n = No of electrons, E = Electrode potential & F = Faraday constant.

Under standard condition

$$-\Delta G^{\circ} = n F E^{\circ}$$

Where, $-\Delta G^{\circ}$ = Decrease in free energy under standard condition, E° = Standard electrode potential

Consider a reversible electrode reaction of the type



The change in free energy (ΔG) and its equilibrium constant (K) are interrelated by van't Hoff isotherm equation as

$$-\Delta G = -\Delta G^{\circ} - RT \ln K_c$$

Where, K_c = Equilibrium constants = $\frac{[\text{products}]}{[\text{reactants}]}$

$$\frac{1}{[\text{reactants}]}$$

Substitute the value of K_c , we have

$$-\Delta G = -\Delta G^0 - RT \cdot \ln \left[\frac{[M]}{[M^{n+}]}\right]$$

Substitute the value of $-\Delta G$ & $-\Delta G^0$

$$nFE = nFE^0 - RT \cdot \ln \left[\frac{[M]}{[M^{n+}]}\right]$$

Divide the above equation by nF

$$E = E^0 - \frac{RT}{nF} \cdot \ln \left[\frac{[M]}{[M^{n+}]}\right]$$

For a solid metal concentration is unity, so that $[M]=1$

Then, we have

$$E = E^0 - \frac{RT}{nF} \cdot \ln \left[\frac{1}{[M^{n+}]}\right]$$

Converting natural logarithm to the base 10 and the equation becomes as

$$E = E^0 - \frac{2.303RT}{nF} \log \left[1 / M^{n+} \right] \quad \dots\dots\dots 1$$

Substitute the value of $R=8.314\text{J/K/mol}$, $T=298\text{K}$, $F=96500\text{C/mol}$ to the equation (1)

$$E = E^0 - \frac{0.0591}{n} \log \left[1 / M^{n+} \right]$$

This is the expression for Nernst equation for single electrode at 298k

For a cell reaction $aA + bB \rightarrow cC + dD$, The Nernst equation is

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \left[\frac{[C]^c [D]^d}{[A]^a [B]^b} \right]$$

4. Types of Electrodes

Some important types of single electrodes are as follows:

- 1) **Metal ion – metal electrode:** where a metal is in contact with its ionic solution,
E.g.: Cu^{2+}/Cu , Zn^{2+}/Zn , Ag^+/Ag .
- 2) **Gas electrode:** where a gas is in contact with an inert metal dipped in an ionic solution of the gas molecules, E.g.: hydrogen electrode.
- 3) **Metal-metal salt ion electrode:** where a metal is in contact with a solution containing the anion of the salt of the same metal.
E.g.: Calomel electrode, Ag/AgCl electrode.
- 4) **Ion – selective electrode** - where a membrane is in contact with an ionic solution with which it selectively responds to.
E.g.: glass electrode
- 5) **Amalgam electrode** – where a metal dissolved in Hg is in contact with the metal salt solution.

E.g.: Pb-Hg/ Pb^{2+}

- 6) **Red-ox electrode:** where an inert metal dips into a solution containing ions in two different oxidation states. E.g.: Pt/ Fe^{2+} , Fe^{3+}

5. Reference Electrodes:

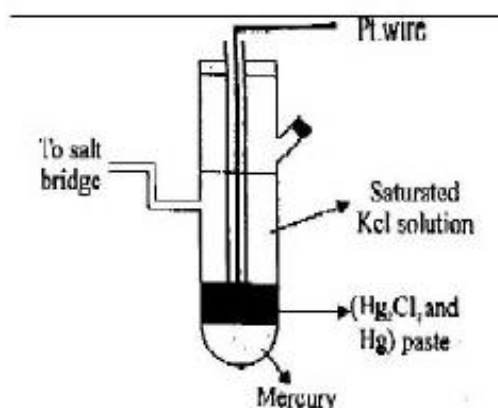
Reference electrodes are electrodes whose potential are known and are used for the determination of potentials of other electrodes. Reference electrodes are of two types:

1. Primary – Standard hydrogen electrode
2. Secondary- Calomel electrode, Ag – AgCl electrode.

Demerits of standard hydrogen electrode:

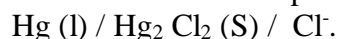
1. It is difficult to maintain 1 atm pressure and unit concentration all the time
2. Hydrogen gas has to be continuously supplied in cylinders.
3. The platinum foil is susceptible to poisoning by fluorides, etc.
4. Construction is difficult.
5. Availability of pure hydrogen gas and its cost.

6. Explain the construction and working of Calomel electrode.



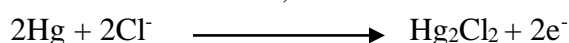
Calomel electrode consisting of a glass container at the bottom of which mercury is placed above which a layer of mercury and mercurous chloride (called calomel) is placed with $\frac{3}{4}$ th of bottle is filled with saturated KCl solution. Electrode potential of the cell depends on the concentration of KCl used.

The calomel electrode can be represented as.

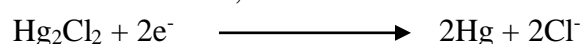


The calomel electrode acts as both anode and cathode depending upon the other electrode used. The platinum wire is used for electrical contact. Salt bridge is used to couple with other half cell.

When it acts as anode, the electrode reaction is



When it acts as cathode, the electrode reaction is



Electrode Potential, $E = E^\circ - (2.303 RT / nF) \log_{10} [\text{Cl}^-]^2$

$$= E^\circ - (2.303 RT / 2F) \log_{10} [\text{Cl}^-]^2 \quad \text{where } n=2$$

$$= E^\circ - 0.0591 \log_{10} [\text{Cl}^-] \text{ at } 298 \text{ K}$$

The electrode potential is decided by the concentration of chloride ions and the electrode is reversible with chloride ions. At 298 K, the electrode potentials are as follows:

$$0.1\text{N KCl electrode} = 0.334\text{V}$$

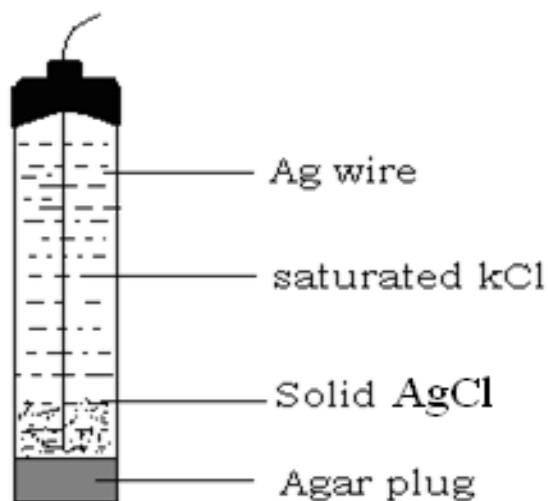
$$1\text{N KCl Electrode} = 0.281\text{ V}$$

$$\text{Saturated KCl electrode} = 0.2424\text{ V}$$

Advantages of Calomel Electrode:

- It is simple to construct.
- The electrode potential is reproducible and stable.
- It is used as a reference electrode.

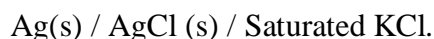
7. Explain the construction and working of Silver-Silver chloride electrode



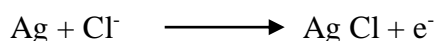
Ag/AgCl Electrode

Ag/AgCl electrode is a metal-metal salt electrode. It consists of narrow glass tube at the bottom of which agar is placed and above which saturated solution of KCl is placed. The silver wire is used for electrical connection and it is coated electrolytically with AgCl.

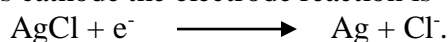
The cell can be represented as.



Electrode acts as both anode and cathode depending on the other electrode used. When it acts as anode the electrode reaction is



When it acts as cathode the electrode reaction is



$$E = E^\circ - (2.303 RT / nF) \log [\text{Cl}^-] \quad (\text{As } [\text{AgCl}] \text{ and } [\text{Ag}] \text{ are taken as } 1)$$

$$= E^\circ - (2.303 RT / F) \log [\text{Cl}^-] \text{ where } n = 1$$

$$= E^\circ - 0.0591 \log [\text{Cl}^-] \text{ at } 298\text{ K}$$

The electrode potential is dependent on the concentration of chloride ions. For 1 molar solution, the electrode potential is 0.223 V and for saturated solution it is 0.199 V at 298 K.

8. What are Ion Selective Electrodes? Explain

These are the electrodes, which responds to specific ions only and develops a potential against that ions while ignoring the other ions present in the solution.

Ex: Glass electrode.

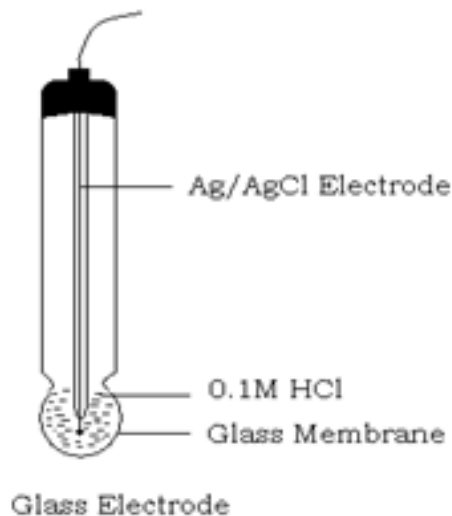
Glass electrode is a pH sensitive electrode widely used for pH determinations. It is consisting of a long glass tube at the bottom of which a thin and delicate glass bulb, which made up of special type of glass (22 % Na₂O, 6% of CaO, 72% of SiO₂) with low melting point and high electrical conductance is used. The

glass bulb is filled with 0.1M HCl and Ag – AgCl is used as internal reference electrode. A platinum wire is used for electrical contact.

The glass electrode can be represented as



The electrode is dipped in a solution containing H^+ ions.



The glass membrane exchanges ions with the solution:



The exchange of ions by the inner and outer membrane gives rise to a boundary potential. This boundary potential consists of two potentials, E_1 and E_2 , which are associated with the outer and inner membrane surfaces respectively.

Then $E_b = E_2 - E_1$

$$= 0.0591 \log (c_2 / c_1) \quad (n = 1 \text{ for } \text{H}^+ \text{ ion})$$

Thus the boundary potential E_b depends only upon the hydrogen ion activities of the solutions. Since the concentration of the inner solution is constant, that is, c_2 is constant.

The potential of the glass electrode E_G has three components:

1. The boundary potential (E_b)
2. The potential of the internal Ag / AgCl reference electrode (E_{ref}) and
3. A small asymmetry potential (E_{asy}).

$$\begin{aligned} E_G &= E_b + E_{\text{ref}} + E_{\text{asy}} \\ &= 0.0591 \log C_1 + 0.0591 \log C_2 + E_{\text{ref}} + E_{\text{asy}} \\ &= E_G^0 + 0.0591 \log C_2 \\ &= E_G^0 + 0.0591 \log [\text{H}^+] \quad \text{Where } C_2 = [\text{H}^+] \\ E_G &= E_G^0 - 0.0591 \text{ pH} \quad \text{Where pH} = -\log [\text{H}^+] \end{aligned}$$

Where E_G^0 is a combination of three constant terms,

$$E_G^0 = E_{\text{ref}} + E_{\text{asy}}$$

Asymmetric potential arises due to the difference in responses of the inner and outer surface of the glass bulb to changes in H^+ ion activity. This may originate as a result of differing conditions of strain in the two

glass surfaces (due to difference in curvature). This asymmetric potential varies with time and therefore, glass electrode must be standardized frequently by placing a solution of known H^+ activity (pH).

Advantages:

- Can be used in oxidizing and reducing environments.
- Accurate results are obtained between pH range 1 – 9.
- However, by using special glass electrodes, pH 1 – 14 can be measured.
- Electrode does not get poisoned.

Disadvantages:

Because of the high resistance of glass, simple potentiometers cannot be used. It requires sensitive electronic potentiometers for emf measurement.

9. Explain the determination of pH using glass electrode.

1. The E_G^0 is determined first by dipping the glass electrode in a solution of known pH. E_G^0 value is evaluated by dipping the glass electrode in a solution of known pH and measuring the emf of the cell formed when combined with a calomel electrode.

$$E_{\text{cell}} = E_{\text{glass}} - E_{\text{calomel}}$$

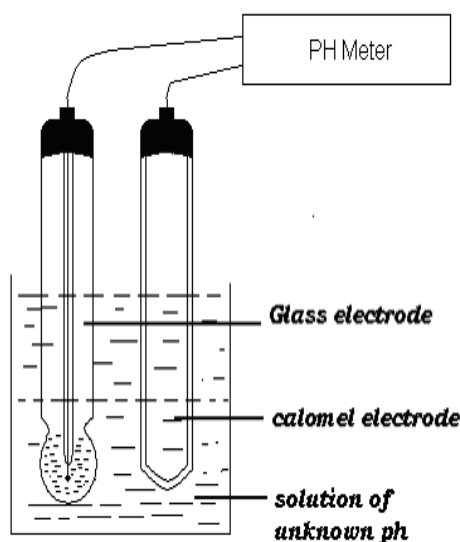
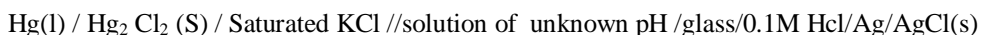
$$= E_G^0 - 0.0591 \text{ pH} - E_{\text{calomel}}$$

$$\implies E_G^0 = E_{\text{cell}} + 0.0591 \text{ pH} + E_{\text{calomel}}$$

By substituting the values of E_{cell} , pH and E_{calomel} , E_G^0 is obtained.

2. To determine pH of unknown solution the glass electrode is combined with secondary reference electrode such as calomel electrode and the glass - calomel electrode assembly is dipped in the solution whose pH is to be determined. The two electrodes are connected to potentiometer or pH meter.

The combined electrodes can be represented as.



The emf of the above cell is given by

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

$$E_{\text{cell}} = E_{\text{glass}} - E_{\text{calomel}}$$

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

$$= E_G^0 - 0.0591 \text{ pH} - E_{\text{cal}}$$

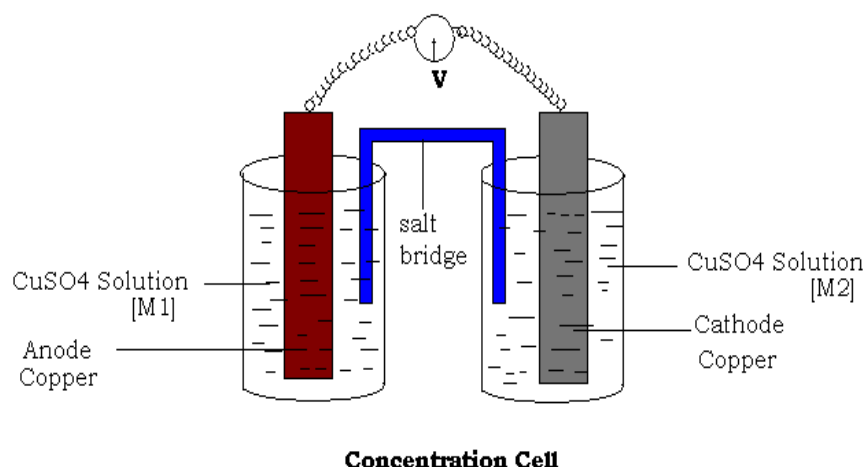
$$\text{pH} = (E_G^0 - E_{\text{cal}} - E_{\text{cell}}) / 0.0591$$

10. What are concentrations cells? Explain with an example

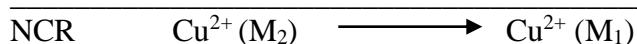
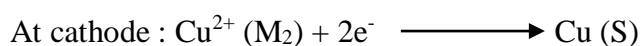
These are the galvanic cells consisting of same metal electrodes dipped in same metal ionic solution in both the half cells but are different in the concentration of the metal ions.

Ex: Consider the following concentration cell constructed by dipping two copper electrodes in CuSO_4 solutions of M_2 molar and M_1 molar where $M_2 > M_1$.

The two half-cell are internally connected by a salt bridge and externally connected by a metallic wire through voltmeter or ammeter.



The electrode, which is dipped in less ionic concentrations solutions (M_1) act as anode and undergoes oxidation. The electrode, which is dipped in more ionic concentration (M_2) act as cathode and undergoes reduction.



$$E \text{ of cell} = E \text{ cathode} - E \text{ anode}$$

$$E \text{ cell} = \left[E^\circ + \frac{0.0591}{n} \log (M_2) \right] - \left[E^\circ + \frac{0.0591}{n} \log (M_1) \right]$$

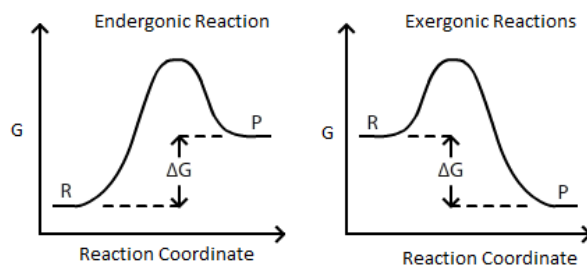
$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{[M_2]}{[M_1]}$$

Note:

- Where, $(M_2) > (M_1)$ cell potential will be positive.
- $(M_2) < (M_1)$ cell potential will be Negative.
- $(M_2) = (M_1)$ cell potential will be Zero

Gibbs Energy (ΔG , Free energy)

ΔG is the change of Gibbs (free) energy for a system and ΔG° is the Gibbs energy change for a system under standard conditions (1 atm, 298K). On an energy diagram, ΔG can be represented as:



Where ΔG is the difference in the energy between reactants and products. In addition ΔG is unaffected by external factors that change the kinetics of the reaction. For example if E_a (activation energy) were to decrease in the presence of a catalyst or the kinetic energy of molecules increases due to a rise in temperature, the ΔG value would remain the same.

The change in free energy is the maximum amount of energy that is available to do useful work. In an electrochemical cell, this free energy is equal to electrical work which is equal to the product of number of electrons, Faraday constant, and electrochemical cell's emf.

$$\Delta G = nFE_{\text{cell}}$$

Where, n – number of electrons transferred in the reaction

F – Faraday constant (96,500 coulombs)

E_{cell} – EMF of the cell

Single electrode potential and its origin:

The potential that is developed at the interface of a metal when dipped in a solution of its ions is called single electrode potential. It tells about the tendency of the metal to lose or gain electrons. But, by definition, it represents the reduction reaction, that is, to gain electrons.

Depending on the nature of the metal, dissolution may be faster or deposition may be faster. If the dissolution of metal ions is faster, electrons accumulate on the surface of the metal making it negatively charged. This attracts the positively charged metal ions to the surface forming a layer. This causes formation of double layer. This is also called Helmholtz double layer (HDL). This gives rise to a potential across the interface, called electrode potential. HDL depends on the size of the ions, charge separation, nature of the ion, etc.

Figure: