UNIT-3 ELECTROCHEMISTRY

Introduction – Electrode potential – Nernst equation and problems - Electrochemical series - Conductometric titrations (acid - base & precipitation titration)
Electrodes: Construction, working and applications of Standard and reference electrode (Hydrogen & Calomel) – Ion selective (glass electrode) – determination of pH using glass electrode.

3.1 INTRODUCTION

Electrochemistry is the branch of science which deals with the relationship between chemical reaction and electricity. Electrochemistry is the study of the process involved in the interconversion of electrical energy to chemical energy and vice – versa.

Electric current is a flow of electrons generated by a cell or a battery when the circuit is completed. A substance which allows electric current to pass through it, is called a conductor, e.g. metals, graphite, fused metallic salts while non – conductor is a substance which does not conduct the electric current e.g. plastics, wood, non – metals etc.

IMPORTANT TERMS INVOLVED IN ELECTROCHEMISTRY

1. **Cell:** Cell is an assembly of two electrodes and an electrolyte. Generally, it consists of two half cells. Each half cell contains an electrode material in touch with electrolyte.
2. **Current:** Current is a flow of electricity through a conductor. It is measured in ampere. Electrode is a material rod/bar/strip that conduct electrons.
3. **Anode:** Anode is an electrode at which oxidation occurs
4. **Cathode:** Cathode is an electrode at which reduction occur
5. **Electrolyte:** Electrolyte is a liquid or solution that conducts electric current. There are three types of electrolytes.
   (a) **Strong electrolytes:** these are the substances which ionize completely at any concentration.

   Example: HCL, aqueous solutions of NaOH, NaCl and KCL

   (b) **Weak electrolytes:** Weak electrolytes are the substance which ionize partially in solution.
   Example: CH_3COOH, NH_4OH and aqueous solution of Na_2CO_3

   (c) **Non-electrolyte:** Non-electrolyte are the substances which do not ionize at any dilutions.
   Example: Glucose, Sugar, alcohol, petrol, etc.

6. **Galvanic (or) Voltaic (or) Electrochemical cell**

- It is a device that produces electrical energy at the expense of chemical energy produced in a reaction.
- A cell consists of two half cells or electrodes.
- A half-cell or electrode contains a metal rod dipped in an electrolytic solution.

7. **Electrolytic cell:** It is a cell in which electrical energy brings about a chemical reaction.

Differences between electrolytic cell and electrochemical cell.

Electrolytic Cell	Electrochemical cell
1. Electrical energy brings about a chemical reaction.	1. Electrical energy is produced at the expense of chemical energy.
2. Anode is positively charged.	2. Anode is negatively charged.
3. Cathode is negatively changed.	3. Cathode is positively charged.
4. Electrons move from anode to cathode through external circuit.	4. Electrons move from cathode to anode through external circuit.
5. The extent of chemical reaction at the electrode is governed by Faraday's laws of electrolysis.	5. The emf of the cell depends on concentration of electrolyte and nature of the metal electrode.
6. The amount of electricity passed is measured by a coulometer.	6. The emf of the cell is measured by a potentiometer.
7. One electrolyte and two electrodes of the same element are generally used in these cells.	7. Two different electrolytes and two different electrodes are used.

TYPES OF CELL

1. Electrolytic cell

It is a device in which chemical reaction proceed at the expense of electrical energy.

Example: Electro plating and Electrolysis of NaCl

The cell is constituted by dipping two platinum electrodes in an appropriate electrolyte (NaCl in water). The electrodes are connected to the two terminals of a battery. The electrode connected to positive terminal acts as anode (attracts anions) and the other electrode connected to the negative terminal acts as cathode (attracts cations). Chlorine is liberated at anode and hydrogen is liberated at cathode

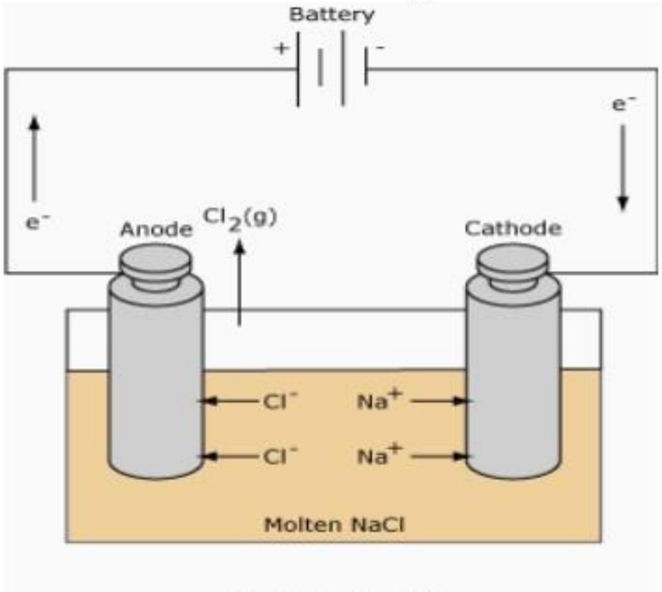
Cell reaction:

At anode: $2\,Cl^- \longrightarrow Cl_2 \uparrow + 2e^-$

At cathode: (i) $2Na^{+} + 2H_2O \longrightarrow 2NaOH + 2H^{+}$

(ii) $2H^{+} + 2e^{-} \longrightarrow H_2\uparrow$

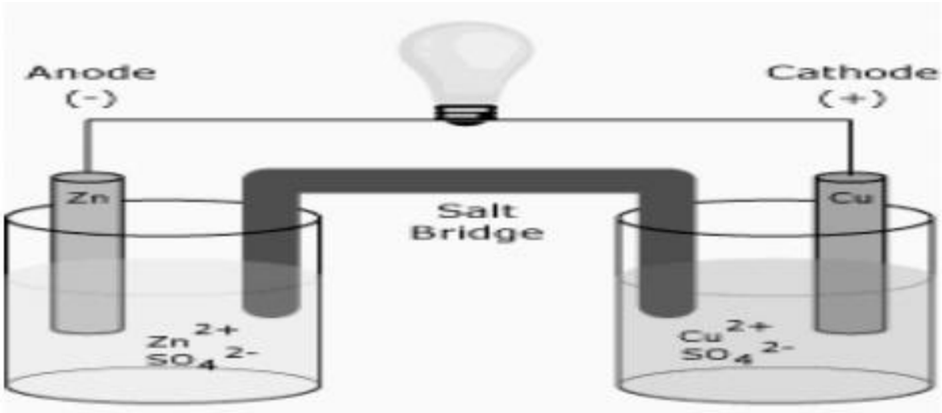
Net reaction: $2NaCl + 2H_2O \longrightarrow 2NaOH + H_2 + Cl_2$



Electrolytic Cell

2. Electrochemical Cell or Galvanic cell

- It is a device in which a redox reaction is used to derive electrical energy.
- During the working of the cell the stored chemical energy decreases and this decrease is gained as electrical energy.
- In the electrochemical cell the electrode at which oxidation occurs is called anode (− ve) and the electrode at which reduction occurs is called cathode (+ ve).
- Example: Zn acts as anode and Cu acts as cathode in Daniel cell.



Daniell Cell

It consists of zinc electrode dipped in 1M zinc sulphate solution and a copper electrode dipped in 1M copper sulphate solution. Each electrode acts as a half cell connected by a salt bridge through a voltmeter. The two solutions can seep through the salt bridge without mixing.

At anode: Oxidation takes place

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

At cathode: Reduction takes place.

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

Net reaction: $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

Representation of a galvanic cell

1. Galvanic cell consists of two electrodes, anode and cathode.
2. The anode is written on the left-hand side while the cathode is written on right side.
3. The anode is written with the metal first and then the electrolyte. The two are separated by a vertical line or semicolon.

   Ex: Zn / Zn^{2+} (or) $Zn / ZnSO_4$ (or) $Zn; Zn^{2+}$
4. The cathode is written with electrolyte first and then the metal both are separated by vertical line or semicolon.

   Ex: Cu^{2+} / Cu (or) $CuSO_4 / Cu$ (or) $Cu ; Cu^{2+}$
5. The two half cells are connected by a salt bridge which is indicated by two parallel lines.

$$\overset{-}{Zn} / ZnSO_4\ (1M)\ \|\ CuSO_4\ (1M) / Cu^{+}$$

Salt bridge: It consists of a U tube filled with a saturated solution of KCl or $(NH_4)_2NO_3$ in agar-agar gel. It connects the two half cells and performs the following

Functions

- It eliminates the liquid junction potential.
- It provides path for the flow of electrons between two half cells.
- Completes the circuit.
- Maintains electrical neutrality in the two compartments by migration of ions
- through the porous material thus ensures the chemical reactions proceed without hindrance.
- Prevents mixing of the electrode solutions.

3.1.1 Single electrode potential (or) electrode potential:

It is a measure of the tendency of the metal electrode to lose or gain electrons, when it is in contact with its own salt solution. It is developed due to the formation of a double layer around the metal rod.

Oxidation potential

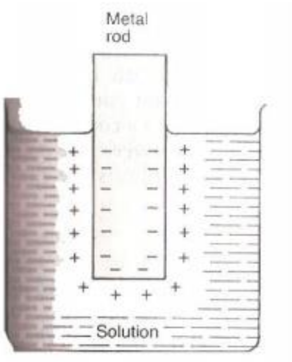
When a metal M is dipped in its salt solution, one of the following reactions occurs depending on the metal:

Positive metal ions pass into the

$$\text{solution : } M \rightarrow \square M^{n+} + ne^{-}$$
$$\text{(oxidation)}$$

(e.g.) When Zn rod is dipped in $ZnSO_4$ solution, Zn goes into solution as Zn^{2+}.

The electrons attach to Zn rod, giving it a negative charge. The negative charge on the rod attracts positive ions from solution. Thus, a double layer of ions is formed close to the rod.

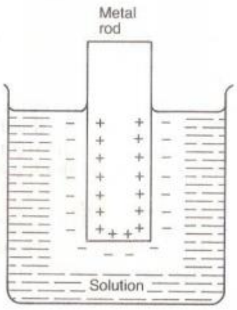


Reduction Potential

Positive ions from the solution deposit over the metal.

$$M^{n+} + ne^{-} \rightarrow \square\ M \qquad \text{(reduction)}$$

When Cu rod is dipped in $CuSO_4$ solution, Cu^{2+} ions from the solution deposit on metal rod. They attract negative ions from solution. Thus, a double layer of ions is formed close to the metal rod. This is called Helmholtz double layer.



As a result, a potential difference is set up between the metal and the solution. The equilibrium value of the potential difference is known as electrode potential.

Factors affecting electrode potential or emf of Cell:

1. Nature of the metal
2. Temperature
3. Concentration of metal ions in the solution

Standard electrode potential:

It is a measure of the tendency of the metal electrode to lose or gain electrons, when it is in contact with its own salt solution of 1M strength at 25°C.

Measurement of single electrode potential:

It is impossible to determine the value of a single electrode potential. But we can always measure the potential difference between two electrodes using a potentiometer, by combining the two electrodes to form a cell. For this purpose, we use reference electrode. Standard hydrogen electrode is called primary reference electrode. Calomel electrode is called secondary reference electrode.

What is Nernst Equation?

The **Nernst equation** provides the relation between the cell potential of an electrochemical cell, the standard cell potential, temperature, and the reaction quotient.

Expression of Nernst Equation

Nernst equation is a fundamental equation in electrochemistry that predicts the voltage at which an electrochemical reaction takes place. It is used to calculate the standard electrode potential of an electrochemical cell and the voltage of a galvanic cell under non-standard conditions. Nernst equation is an important tool for understanding the behaviour of batteries and other electrochemical devices. Even under non-standard conditions, the cell potentials of electrochemical cells can be determined with the help of the Nernst equation.

Nernst Equation for Single Electrode Potential

$$E_{cell} = E^0 - [RT/nF] \ln Q$$

Where,

- E_{cell} = cell potential of the cell
- E^0 = cell potential under standard conditions
- R = universal gas constant
- T = temperature
- n = number of electrons transferred in the redox reaction
- F = Faraday constant
- Q = reaction quotient

The calculation of single electrode reduction potential (E_{red}) from the standard single electrode reduction potential ($E°_{red}$) for an atom/ion is given by the Nernst equation.

For a reduction reaction, the Nernst equation for a single electrode reduction potential is given as,

$$M^{n+} + ne^- \longrightarrow nM \text{ is;}$$

$$E_{red} = EM^{n+}/M = E^oM^{n+}/M - [2.303RT/nF] \log [1/[M^{n+}]]$$

Where,

- R is the gas constant = 8.314 J/K Mole
- T = absolute temperature,
- n = number of mole of electron involved,
- F = 96487 (≈96500) coulomb/mole = charge carried by one mole of electrons.
- $[M^{n+}]$ = active mass of the ions. For simplicity, it may be taken as equal to the molar concentration of the salt.

Nernst Equation at 25ºC

For measurements carried out 298 K, the Nernst equation can be expressed as follows:

$$E = E^0 - 0.0592/n \log_{10} Q$$

Therefore, as per the Nernst equation, the overall potential of an electrochemical cell is dependent on the reaction quotient.

Derivation of Nernst Equation

Consider a metal in contact with its own salt-aqueous solution. Reactions of metal losing an electron to become an ion and the ion gaining an electron to return to the atomic state are equally feasible and are in an equilibrium state.

$$M^{n+} + ne^{-} \rightarrow nM$$

In the reduction reaction, 'n' moles of an electron are taken up by the ion against a reduction potential of $E_{red.}$

1. The work done in the movement of electron

$$W_{red} = nFE_{red}$$

Where,

- F is Faraday = 96487 coulomb = electrical charge carried by one mole of electrons

2. Change in the Gibbs free energy is an indication of spontaneity, and it is also equal to the maximum useful work (other than volume expansion) done in a process.

Combining work done and Gibbs free energy change:

$$W_{red} = nFE_{red} = -\Delta G \text{ or } \Delta G = -nFE_{red}$$

3. Change in the free energy at standard conditions of 298 K and one molar /one atmospheric pressure conditions is ΔG°. From the above relation, it can be written that

$$\Delta G^\circ = -nFE^\circ_{red}$$

Where,

- E°_{red} is the reduction potential measured at standard conditions.

4. During the reaction, concentration keeps changing, and the potential also will decrease with the rate of reaction.

To get the maximum work or maximum free energy change, the concentrations have to be maintained the same. This is possible only by carrying out the reaction under a reversible equilibrium condition.

For a reversible equilibrium reaction, Van't Hoff isotherm says:

$$\Delta G = \Delta G^\circ + RT \ln K$$

Where,

- K is the equilibrium constant
- K = Product/Reactant = $[M]^n/[M]^{n+}$
- R is the Gas constant =8 .314J/K mole
- T is the temperature on the Kelvin scale.

5. Substituting for free energy changes in Van't Hoff equation,

$$-\ nFE_{red} = -\ nFE^{\circ}_{red} + RT \ln [M]/[M^{n+}]$$

$$= -\ nFE^{\circ}_{red} + 2.303\ RT \log [M]^n/[M^{n+}]$$

Dividing both sides by – nF,

$$E_{red} = E^{\circ}_{red} - \frac{2.303RT}{nF1} \log \frac{[M]^n}{[M^{n+}]}$$

or,

$$EM^{n+}/M = E^{o}M^{n+}/M - \frac{2.303RT}{nF1} \log \frac{[M]^n}{[M^{n+}]}$$

The activity of the metal is always considered as equal to unity.

$E_{red} = E^{\circ}_{red}$ – or

$$EM^{n+}/M = E^{o}M^{n+}/M - \frac{2.303RT}{nF} \log \frac{1}{[Mn^{n+}]}$$

This relation connecting reduction potential measurable at conditions other than standard conditions to the standard electrode potential is the Nernst equation.

For reactions conducted at 298 K but different concentrations, the Nernst equation is:

$$EM^{n+}/M = E^{o}M^{n+}/M - \frac{2.303 \times 8.314 \times 293}{n96500} \log \frac{1}{[Mn^{n+}]}$$

$$= E^{o}M^{n+}/M - \frac{0.0591}{n} \log \frac{1}{[Mn^{n+}]}$$

Determining Equilibrium Constant with Nernst Equation

When the reactants and the products of the electrochemical cell reach equilibrium, the value of ΔG becomes 0. At this point, the reaction quotient and the equilibrium constant (K_c) are the same. Since ΔG = -nFE, the cell potential at equilibrium is also 0.

Substituting the values of Q and E into the Nernst equation, the following equation is obtained.

$$0 = E^0_{cell} - (RT/nF) \ln K_c$$

Converting the natural logarithm into base-10 logarithm and substituting T = 298 K (standard temperature), the equation is transformed as follows.

$$\mathbf{E^0_{cell} = (0.0592V/n) \log K_c}$$

By rearranging this equation, the following equation can be obtained.

$$\log K_c = (nE^0_{cell})/0.0592V$$

Thus, the relationship between the standard cell potential and the equilibrium constant is obtained. When K_c is greater than 1, the value of E^0_{cell} will be greater than 0, implying that the equilibrium favours the forward reaction. Similarly, when K_c is less than 1, E^0_{cell} will hold a negative value which suggests that the reverse reaction will be favoured.

Nernst Equation Applications

The Nernst equation can be used to calculate the following:

- Single electrode reduction or oxidation potential at any conditions
- Standard electrode potentials
- Comparing the relative ability as a reductive or oxidative agent
- Finding the feasibility of combining such single electrodes to produce an electric potential
- Emf of an electrochemical cell
- Unknown ionic concentrations
- The pH of solutions and solubility of sparingly soluble salts can be measured with the help of the Nernst equation.

Limitations of Nernst Equation

The activity of an ion in a very dilute solution is close to infinity and can, therefore, be expressed in terms of the ion concentration. However, the ion concentration is not equal to the ion activity for solutions having very high concentrations. In order to use the Nernst equation in such cases, experimental measurements must be conducted to obtain the true activity of the ion.

Another shortcoming of this equation is that it cannot be used to measure cell potential when a current flow through the electrode. This is because the current flow affects the ions' activity on the surface of the electrode. Also, additional factors such as resistive loss and overpotential must be considered when a current flow through the electrode.

Solved Examples on NERNST Equation

1. The standard electrode potential of zinc ions is 0.76V. What will be the potential of a 2M solution at 300 K?

Solution:

The Nernst equation for the given conditions can be written as follows:

$$E_{M^{n+}/M} = E^o – [(2.303RT)/nF] \times \log 1/[M^{n+}]$$

Here,

- $E° = 0.76V$
- $n = 2$
- $F = 96500$ C/mole
- $[M^{n+}] = 2$ M
- $R =8.314$ J/K mole
- $T =300$ K

Substituting the given values in the Nernst equation, we get,

$$E_{Zn^{2+}/Zn} = 0.76 – [(2.303\times8.314\times300)/(2\times96500)] \times \log ½$$

$$= 0.76 – [0.0298 \times (-0.301)]$$

$$= 0.76 + 0.009 = \mathbf{0.769\ V}$$

Therefore, the potential of a 2 M solution at 300 K is 0.769 V.

2. From the following standard potentials, arrange the metals in the order of their increasing reducing power.

- $Zn^{2+}(aq) + 2e^– \rightarrow Zn(s)$: $E° = -0.76$ V
- $Ca^{2+}(aq) + 2e^– \rightarrow Ca(s)$: $E° = -2.87$ V
- $Mg^{2+}(aq) + 2e^– \rightarrow Mg(s)$: $E° = -2.36$ V
- $Ni^{2+}(aq) + 2e^– \rightarrow Ni(s)$: $E° = -0.25$ V
- $Ni(s) \rightarrow Ni2^+(aq) + 2e^–$: $E° = +0.25$ V

Reducing power of a metal increases with its ability to give up electrons, i.e., lower standard potentials. Arranging the reduction potentials in decreasing order gives the increasing order of reducing the power of metals.

Increasing order of reduction potentials is Ni (-0.25V) < Zn (-0.76V) < Mg(-2.36V) < Ca (-2.87).

3. What is the Cell Potential of the electrochemical cell in which the cell reaction is: $Pb^{2+} + Cd \rightarrow Pb + Cd^{2+}$? Given that $E^o_{cell} = 0.277$ volts, temperature = 25^{o}C, $[Cd^{2+}] = 0.02$ M, and $[Pb^{2+}] = 0.2$ M.

Solution

Since the temperature is equal to 25^{o}C, the Nernst equation can be written as follows:

$$E_{cell} = E^0_{cell} – (0.0592/n) \log_{10}Q$$

Here, two moles of electrons are transferred in the reaction. Therefore, n = 2. The reaction quotient (Q) is given by $[Cd^{2+}]/[Pb^{2+}] = (0.02M)/(0.2M) = 0.1$.

The equation can now be rewritten as:

$$E_{cell} = 0.277 – (0.0592/2) \times \log_{10}(0.1)$$
$$= 0.277 – (0.0296) (-1)$$
$$= \mathbf{0.3066\ Volts}$$

Thus, the cell potential of this electrochemical cell at a temperature of 25°C is 0.3066 volts.

4. The Cu^{2+} ion concentration in a copper-silver electrochemical cell is 0.1 M. If $E^o(Ag^+/Ag)$ = 0.8 V, $E^o(Cu^{2+}/Cu)$ = 0.34V, and Cell potential (at 25°C) = 0.422 V. Find the silver ion concentration.

Solution

Here, the silver electrode acts as a cathode, whereas the copper electrode serves as the anode. This is because the standard electrode potential of the silver electrode is greater than that of the copper electrode. The standard electrode potential of the cell can now be calculated, as shown below:

$$E^o_{cell} = E^o_{cathode} – E^o_{anode}$$
$$= 0.8V – 0.34V$$
$$= 0.46V$$

Since the charge on the copper ion is +2 and the charge on the silver ion is +1, the balanced cell reaction is:

$$2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$$

Since two electrons are transferred in the cell reaction, n = 2, the Nernst equation for this electrochemical cell can be written as follows:

$$E_{cell} = E^0_{cell} – (0.0592/2) \times \log (0.1/[Ag^+]^2)$$
$$0.422V = 0.46 – 0.0296 \times (-1 – 2\log [Ag^+])$$

Therefore,

$$-2\log [Ag^+] = 1.283 + 1 = 2.283$$

Or,

$$\log [Ag^+] = -1.141$$
$$[Ag^+] = \text{antilog} (-1.141)$$
$$= \mathbf{0.0722\ M}$$

5. Calculate the reduction potential of lead electrode in contact with a solution of 0.015M Pb^{2+} ions.(E^0 = -0.13 volt)

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Std Oxidation potential is given as $Pb^{2+} + 2e^- \rightarrow Pb$; $E^0 = -0.13v$

Concentration of Pb^{2+} = 0.015M

Solution

The Nernst equation for reduction potential is

$$E = E^0_{red} + 0.0591/n \log(Pb^{2+})$$

$$E = -0.13 +.o2955(-1.824)$$

$$E = -0.1839V$$

Oxidation potential of Pb = -0.1839V