

UNIT-3

CONTENTS:

- **Electrochemistry and Batteries:** Basic concepts of electrochemistry.
- **Batteries;** Classification and applications of Primary Cells (Dry Cell) and Secondary Cells (Lead Acid battery).
- **Corrosion:** Introduction to corrosion, Types of corrosion, Cause of corrosion, Corrosion prevention and control, Corrosion issues in specific industries (Power generation, Chemical processing industry, Oil & gas industry and Pulp & paper industries).

CONTENTS:

- Chemistry of Engineering Materials: Cement; Constituents, manufacturing, hardening and setting, deterioration of cement, Plaster of Paris (POP)

ELECTROCHEMISTRY

- **Electrochemistry** deals with the relationship between electrical energy and chemical energy and their inter conversion into one another.

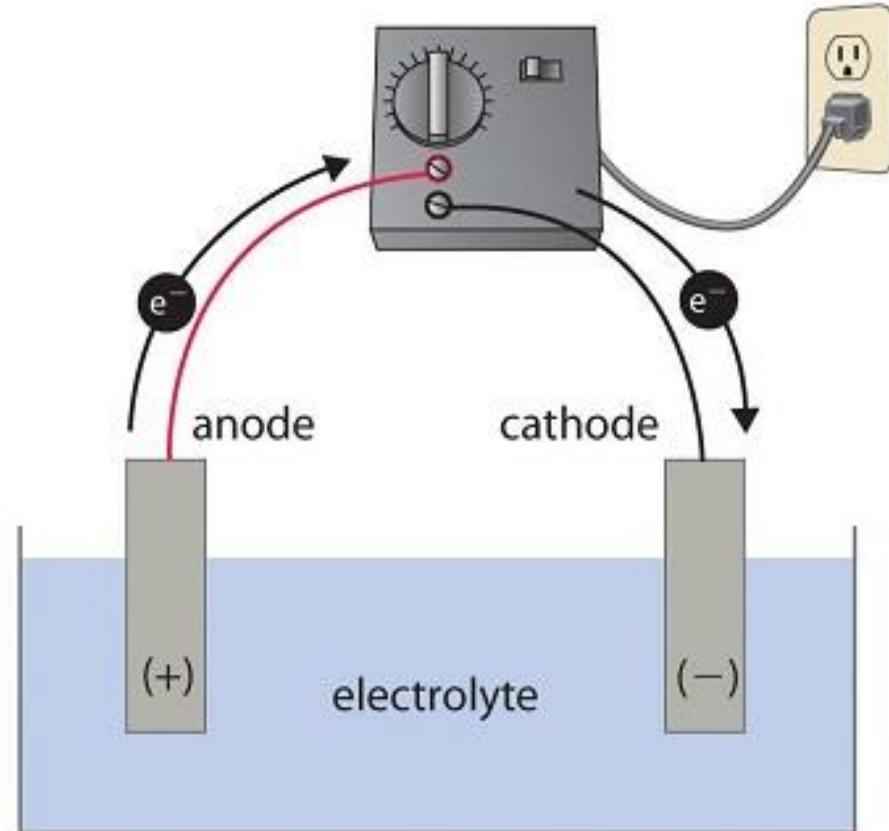
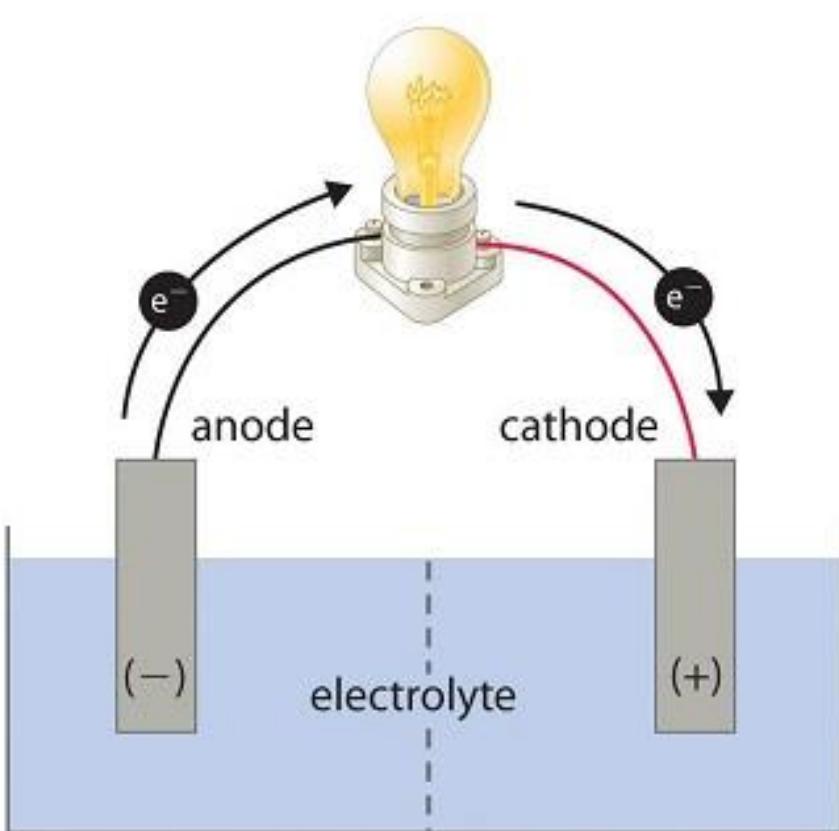
Electrical Energy \longleftrightarrow Chemical Energy

- (i) **Electrolytic cell:** Device in which electrical energy is converted to chemical energy through electrolysis. For Ex. Electrolysis of NaCl produces Na metal and Cl₂ gas.
- (ii) **Electrochemical cells/Galvanic cells:** Device in which chemical energy is converted to electrical energy. For Ex. Daniel cell
- (iii) **Concentration cells:** Device in which electrical energy is produced due to the difference in concentrations of the same substance in the two half cells.

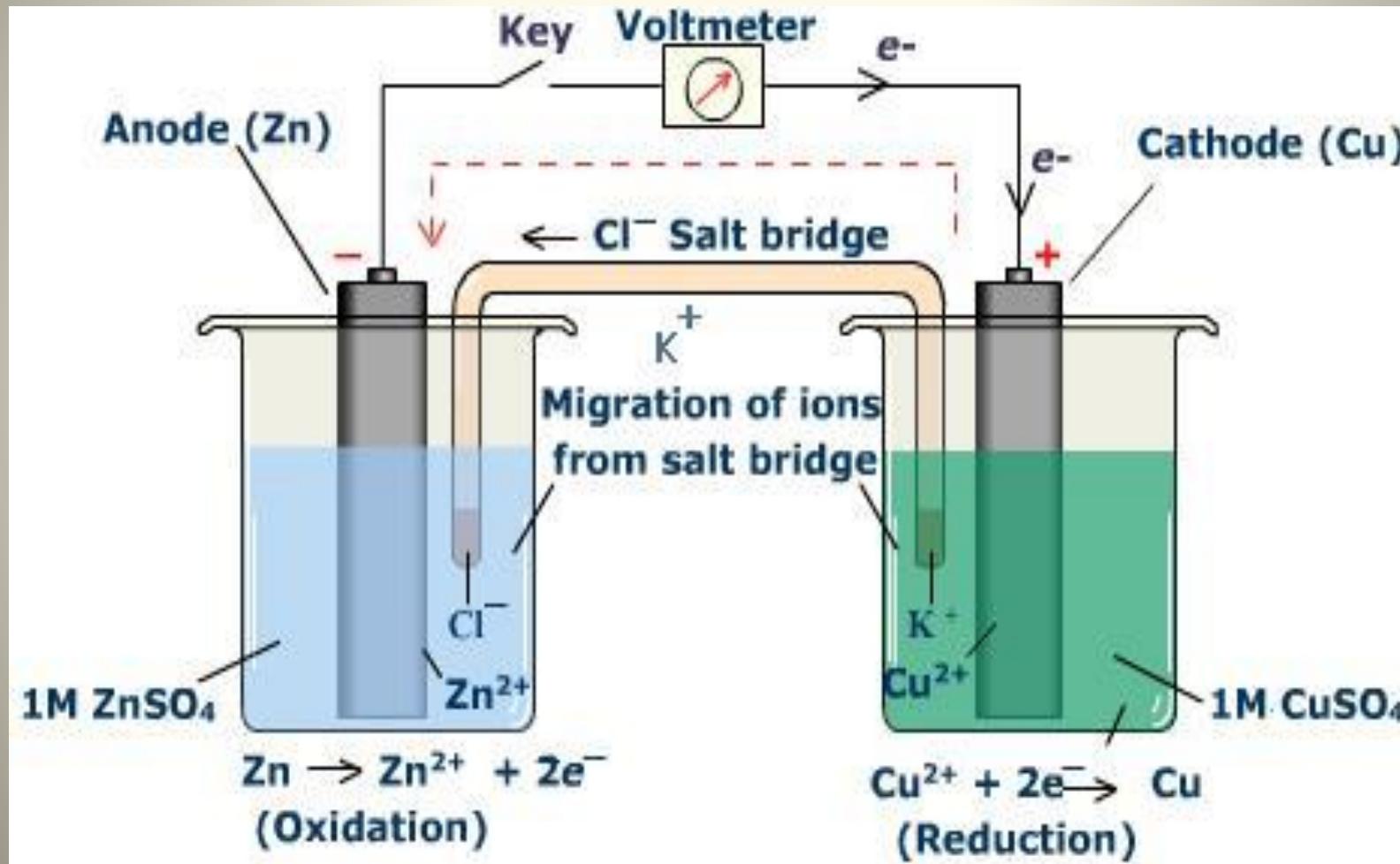
Difference between Electrochemical Cell & Electrolytic Cell

Electrochemical cell	Electrolytic cell
<ol style="list-style-type: none">1. It is a device which converts chemical energy into electrical energy.2. In this case, the redox reaction is spontaneous.3. The two half cells are set up in different containers and are connected through salt bridge.4. In electrochemical cell, anode is negative and cathode is positive.5. The electrons move from anode to cathode in external circuit.	<ol style="list-style-type: none">1. It is a device which converts electrical energy into chemical energy.2. The redox reaction is non-spontaneous and electrical energy is supplied to make the reaction to occur.3. Both the electrodes are placed in the solution or molten electrolyte in the same container.4. In electrolytic cell, anode is positive and cathode is negative electrode.5. The electrons are supplied by the external battery and enter through cathode and come out through anode.

Difference between Electrochemical Cell & Electrolytic Cell



Galvanic Cell



ELECTROCHEMICAL CELLS/GALVANIC CELLS

A device in which chemical energy is converted into electrical energy.

This conversion is due to redox reactions taking place in the cell. For ex. In Daniel cell.



- The oxidation and reduction occur in separate containers called as half cells and because the redox reaction is taking place, the electricity is produced.
- The resulting cell has voltage of 1.1 V.

- The metallic rods (Zn and Cu) are called as electrodes (anode and cathode).
- In electrochemical cells, oxidation occurs on anode while reduction on cathode.
- Electrons flows from anode to cathode through external circuit. Therefore oxidation occurs at anode (Zn rod) and reduction at cathode (Cu rod).



- ▶ The concentration of Zn^{2+} ions increases while that of Cu^{2+} ions decreases.
- ▶ Zn rod (anode) loses its weight while Cu metal gets deposited on cathode.
- ▶ By convention, anode is kept at left and cathode at right hand side.

Salt bridge ad its Functions

- Salt bridge is an inverted U-tube which connects the two half cells and it contains saturated solution of electrolytes like KCl, KNO_3 etc. in agar-agar jelly or gelatin.
- Salt bridge is used to maintain the electrical neutrality.
- It connects the solutions of the two half cells and completes the circuit.
- It prevents the intermixing of the solutions of both the half cells.

Cell Representation

Metal / Electrolyte (with conc.) // Electrolyte (with conc.) / Metal
(Anode half-cell) (Salt Bridge) (Cathode half-cell)



Electrode Potential

- The electrical potential difference set up between the metal and its solution of is called as electrode potential.

Electrode Potential

- It is of two types:
 - Oxidation Potential:** It is the measure of the tendency of a metallic electrode to lose electrons or to get oxidised. eg.



- **Reduction Potential:** It is the measure of the tendency of a metallic electrode to gain electrons or to get reduced.



Electrode Potential

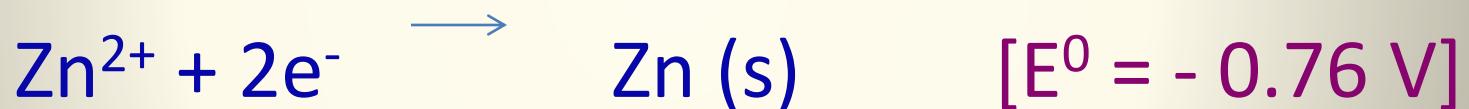
► Oxidation potential is the reverse of reduction potential and vice versa. For e.g.

reduction potential of Zn = - 0.76 V

oxidation potential of Zn = + 0.76 V

Electrode Potential

- The half-cell reactions are always written as reduction half reactions and their potentials are represented as reduction potentials. For ex.



- The electrode potential depends upon:
 1. The nature of the metal and its ions
 2. Concentration of the ions in the solution
 3. Temperature

EMF/CELL POTENTIAL OF A CELL:

- The difference between the electrode potentials of the two electrodes constituting an electrochemical cell is known as electromotive force (EMF) or cell potential of a cell (E_{Cell}).
- This acts as a driving force for the cell reaction (it causes the flow of current from the electrode having higher potential to the electrode having lower potential and flow of electrons in reverse direction).
- It is expressed in volts.

EMF

EMF = Reduction potential of cathode – Reduction potential of anode

OR

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

OR

$$E_{\text{cell}} = E_{(\text{right})} - E_{(\text{left})}$$

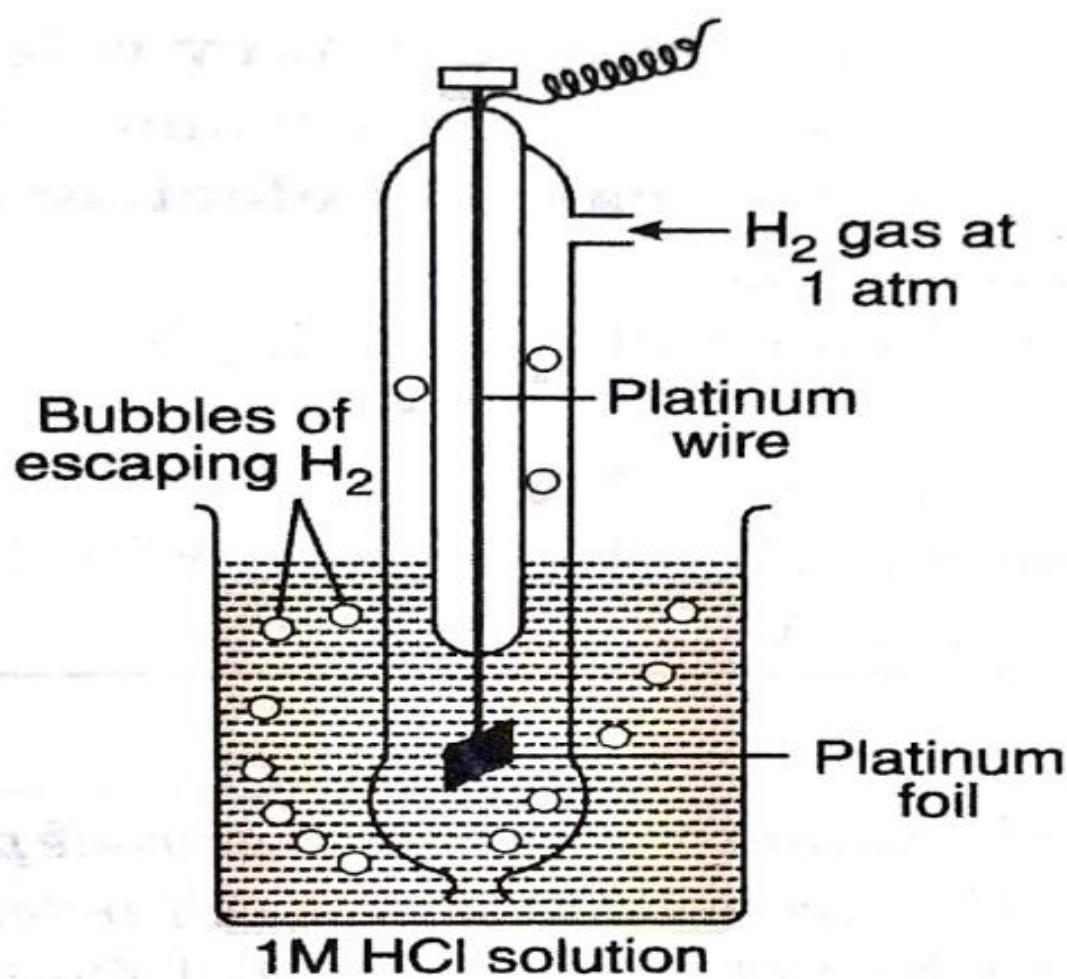
Measurement of Electrode Potential

- It is impossible to measure absolute value of single electrode potential as neither oxidation nor reduction takes place independently, the electrode potential is measured with the help of a reference electrode.
- For this purpose a reference electrode is used.
For ex. Standard Hydrogen Electrode (SHE)

STANDARD HYDROGEN ELECTRODE (SHE)

- It consists of a platinum wire or foil coated with platinum black dipped in 1 M solution of H^+ ions.
- Hydrogen gas at 1 atm Pressure is continuously passed through it at 298 K Temp.

STANDARD HYDROGEN ELECTRODE (SHE)



STANDARD HYDROGEN ELECTRODE (SHE)

- ▶ In a cell when the standard hydrogen electrode acts as anode, the electrode reaction can be written:



- ▶ When the standard hydrogen electrode acts as cathode, the electrode reaction can be written as:



- ▶ The SHE can act as a cathode or an anode depending upon the nature of another electrode to which it is connected. Thus, SHE is also known as reversible electrode.

STANDARD HYDROGEN ELECTRODE (SHE)

- The electrode potential (E^0) of SHE is zero.
- The electrode potential of any electrode can be determined by connecting its half-cell with SHE.

STANDARD ELECTRODE POTENTIAL (E^0)

- When E.P. of a metal electrode is determined with respect to SHE, it is called as Standard Electrode Potential (E^0).
- The electrode at which reduction occurs with respect to SHE has +ve reduction potential while the electrode at which oxidation occurs with respect to SHE has -ve reduction potential.

Electrochemical Series

- A series which represents an arrangement of various electrodes in the increasing order of their standard electrode potential (E^0).
- It is also known as Activity series.

Electrochemical Series

Thermodynamics measurement

STANDARD Reduction potential - H_2 as std

WEAK Oxidizing Agent

STRONG Reducing Agent

TOP left
 • Low ↓ tendency gain e
 • $Li^+ + e \rightarrow Li$
 • $E^\circ Li = -3.04V$
 • WEAK oxidizing Agent
 • Red NOT favourable ($E^\circ = -ve$)

Oxidized sp	Reduced sp	E°/V
$Li^+ + e^- \leftrightarrow Li$		-3.04
$K^+ + e^- \leftrightarrow K$		-2.93
$Ca^{2+} + 2e^- \leftrightarrow Ca$		-2.87
$Na^+ + e^- \leftrightarrow Na$		-2.71
$Mg^{2+} + 2e^- \leftrightarrow Mg$		-2.37
$Al^{3+} + 3e^- \leftrightarrow Al$		-1.66
$Mn^{2+} + 2e^- \leftrightarrow Mn$		-1.19
$H_2O + e^- \leftrightarrow H_2 + OH^-$		-0.83
$Zn^{2+} + 2e^- \leftrightarrow Zn$		-0.76
$Fe^{2+} + 2e^- \leftrightarrow Fe$		-0.45
$Ni^{2+} + 2e^- \leftrightarrow Ni$		-0.26
$Sn^{2+} + 2e^- \leftrightarrow Sn$	Compared to H_2 as std	-0.14
$Pb^{2+} + 2e^- \leftrightarrow Pb$		-0.13
$H^+ + e^- \leftrightarrow 1/2H_2$		0.00
$Cu^{2+} + e^- \leftrightarrow Cu^+$		+0.15
$SO_4^{2-} + 4H^+ + 2e^- \leftrightarrow H_2SO_3 + H_2O$		+0.17
$Cu^{2+} + 2e^- \leftrightarrow Cu$		+0.34
$1/2O_2 + H_2O + 2e^- \leftrightarrow 2OH^-$		+0.40
$Cu^+ + e^- \leftrightarrow Cu$		+0.52
$1/2I_2 + e^- \leftrightarrow I^-$		+0.54
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	+ve reduction potential	+0.77
$Ag^+ + e^- \leftrightarrow Ag$		+0.80
$1/2Br_2 + e^- \leftrightarrow Br^-$		+1.07
$1/2O_2 + 4H^+ + 2e^- \leftrightarrow H_2O$		+1.23
$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow 2Cr^{3+} + 7H_2O$		+1.33
$1/2Cl_2 + e^- \leftrightarrow Cl^-$		+1.36
$MnO_4^- + 8H^+ + 5e^- \leftrightarrow Mn^{2+} + 4H_2O$		+1.51
$1/2F_2 + e^- \leftrightarrow F^-$		+2.87

Strong Oxidizing Agent

WEAK Reducing Agent

TOP right
 • High ↑ tendency lose e
 • $Li \rightarrow Li^+ + e$
 • $E^\circ Li = +3.04V$
 • STRONG reducing Agent
 • Oxi favourable ($E^\circ = +ve$)

BOTTOM left
 • High ↑ tendency gain e
 • $F_2 + 2e^- \rightarrow 2F^-$
 • $E^\circ F_2 = +2.87V$
 • STRONG oxidizing Agent
 • Red favourable ($E^\circ = +ve$)

BOTTOM right
 • Low ↓ tendency lose e
 • $F^- \rightarrow 1/2F_2 + e$
 • $E^\circ F_2 = -2.87V$
 • WEAK reducing Agent
 • Oxi NOT favourable ($E^\circ = -ve$)

$E^\circ_{cell}/Cell$ Potential = EMF in volt

EMF when half cell connect to SHE std condition
 Std potential written as std reduction potential

Electrode	Electrode reaction or Half-Cell reaction	Standard Electrode Potential (E°) in (Volt)
$\text{Li}^+ \text{Li}$	$\text{Li}^+ + e^- \rightleftharpoons \text{Li}$	-3.05
$\text{K}^+ \text{K}$	$\text{K}^+ + e^- \rightleftharpoons \text{K}$	-2.93
$\text{Ba}^{2+} \text{Ba}$	$\text{Ba}^{2+} + 2e^- \rightleftharpoons \text{Ba}$	-2.91
$\text{Sr}^{2+} \text{Sr}$	$\text{Sr}^{2+} + 2e^- \rightleftharpoons \text{Sr}$	-2.89
$\text{Ca}^{2+} \text{Ca}$	$\text{Ca}^{2+} + 2e^- \rightleftharpoons \text{Ca}$	-2.87
$\text{Na}^+ \text{Na}$	$\text{Na}^+ + e^- \rightleftharpoons \text{Na}$	-2.71
$\text{Mg}^{2+} \text{Mg}$	$\text{Mg}^{2+} + 2e^- \rightleftharpoons \text{Mg}$	-2.36
$\text{Al}^{3+} \text{Al}$	$\text{Al}^{3+} + 3e^- \rightleftharpoons \text{Al}$	-1.66
$\text{Mn}^{2+} \text{Mn}$	$\text{Mn}^{2+} + 2e^- \rightleftharpoons \text{Mn}$	-1.18
$\text{Zn}^{2+} \text{Zn}$	$\text{Zn}^{2+} + 2e^- \rightleftharpoons \text{Zn}$	-0.76
$\text{Cr}^{3+} \text{Cr}$	$\text{Cr}^{3+} + 3e^- \rightleftharpoons \text{Cr}$	-0.74
$\text{Fe}^{2+} \text{Fe}$	$\text{Fe}^{2+} + 2e^- \rightleftharpoons \text{Fe}$	-0.44
$\text{Cd}^{2+} \text{Cd}$	$\text{Cd}^{2+} + 2e^- \rightleftharpoons \text{Cd}$	-0.40
$\text{Co}^{2+} \text{Co}$	$\text{Co}^{2+} + 2e^- \rightleftharpoons \text{Co}$	-0.28
$\text{Ni}^{2+} \text{Ni}$	$\text{Ni}^{2+} + 2e^- \rightleftharpoons \text{Ni}$	-0.25
$\text{Sn}^{2+} \text{Sn}$	$\text{Sn}^{2+} + 2e^- \rightleftharpoons \text{Sn}$	-0.14
$\text{Pb}^{2+} \text{Pb}$	$\text{Pb}^{2+} + 2e^- \rightleftharpoons \text{Pb}$	-0.13
$\text{Fe}^{3+} \text{Fe}$	$\text{Fe}^{3+} + 3e^- \rightleftharpoons \text{Fe}$	-0.036
$2\text{H}^+ \text{H}_2$	$2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2$	0.00
$\text{Sn}^{4+} \text{Sn}^{2+}$	$\text{Sn}^{4+} + 2e^- \rightleftharpoons \text{Sn}^{2+}$	+0.14
$\text{Cu}^{2+} \text{Cu}$	$\text{Cu}^{2+} + 2e^- \rightleftharpoons \text{Cu}$	+0.34
$\text{I}_2 2\text{I}^-$	$\text{I}_2 + 2e^- \rightleftharpoons 2\text{I}^-$	+0.54
$\text{Fe}^{3+} \text{Fe}^{2+}$	$\text{Fe}^{3+} + e^- \rightleftharpoons 2\text{Fe}^{2+}$	+0.77
$\text{Hg}^{2+} \text{Hg}$	$\text{Hg}^{2+} + 2e^- \rightleftharpoons \text{Hg}$	+0.796
$\text{Ag}^+ \text{Ag}$	$\text{Ag}^+ + e^- \rightleftharpoons \text{Ag}$	+0.80
$\text{Br}_2 2\text{Br}^-$	$\text{Br}_2 + 2e^- \rightleftharpoons 2\text{Br}^-$	+1.09
$\text{Pt}^{2+} \text{Pt}$	$\text{Pt}^{2+} + 2e^- \rightleftharpoons \text{Pt}$	+1.20
$\text{Cl}_2 2\text{Cl}^-$	$\text{Cl}_2 + 2e^- \rightleftharpoons 2\text{Cl}^-$	+1.36
$\text{Au}^{3+} \text{Au}$	$\text{Au}^{3+} + 3e^- \rightleftharpoons \text{Au}$	+1.40
$\text{F}_2 2\text{F}^-$	$\text{F}_2 + 2e^- \rightleftharpoons 2\text{F}^-$	+2.87

APPLICATIONS OF ELECTROCHEMICAL SERIES

1. Oxidizing & reducing properties:

All the metals having higher value of reduction potential (E°) in the series behave as a good oxidizing agents and having lower values of reduction potential (E°) as good reducing agents. For e.g. Li, K; best reducing agents, F_2 ; very powerful oxidizing agents.

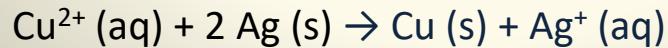
2. Comparison of reactivity of metals:

Metals having lesser E° values can displace the metals from their solutions which are having comparatively higher E° values. For e.g. Cu displaces Ag from $AgNO_3$ solution as $E^\circ_{Cu} = + 0.34$ V and $E^\circ_{Ag} = + 0.80$ V



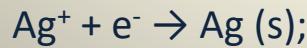
3. Calculation of EMF of the cell: $E^\circ_{Cell} = E^\circ_R - E^\circ_L$

4. Predicting the feasibility of a redox reaction:



From series we know; $Cu^{2+} + 2 e^- \rightarrow Cu (s)$;

$$E^\circ_{Cu^{2+}/Cu} = + 0.34 \text{ V}$$



$$E^\circ_{Ag^+/Ag} = + 0.80 \text{ V}$$

APPLICATIONS OF ELECTROCHEMICAL SERIES

Higher the E^0 , higher the tendency to get reduced, therefore Ag^+ should be reduced to $\text{Ag} (s)$. So, this reaction is not feasible. But to make it feasible the reaction should be reversed.

5. Hydrogen displacement behaviour of Metals:

It Any metal above hydrogen in the electrochemical series can liberate H_2 from an acid solution.

For example: Zn lying above hydrogen in the electrochemical series reacts with dilute H_2SO_4 to liberate H_2 .



6. Corrosion tendency: The anodic or more active metals with high negative electrode potential in the series are more prone to corrosion. The cathodic or more noble metals with less negative electrode potential are less prone to corrosion

NERNST EQUATION:

Dependence of electrode potential and cell potential on concentration

If the concentration of the electrolyte solution is 1 Mol/L (1M) and the temperature is 298 K (25 °C), the electrode potential of the given electrode is called **Standard Electrode Potential (E⁰)**.

However, if the concentration of the electrolyte solution is different from 1M, the electrode potential of the electrode has different value from that of standard electrode potential, E⁰.

This value can be calculated with the help of Nernst Equation. For this purpose, the electrode reaction is always written as reduction reaction.

Consider a general electrode reaction:



We know, Free energy change,

$$\Delta G = \Delta G^0 + R T \ln K \quad \dots \dots \dots (1)$$

Where, ΔG^0 = Standard free energy change, K = Equilibrium constant

Or $\Delta G = \Delta G^0 + R T \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \dots \dots \dots (2)$

Since, $\Delta G = -n F E$ and $\Delta G^0 = -n F E^0$

Putting values of ΔG and ΔG^0 in (2), we get

$$-n F E = -n F E^0 + R T \ln \frac{[M(s)]}{[M^{n+}(\text{aq})]} \quad \dots \dots \dots (3)$$

Nernst Equation for this electrode:

Dividing (3) by $-n F$, we get

$$E = E^0 - \frac{R T}{n F} \ln \frac{[M(s)]}{[M^{n+}(aq)]}$$

Since, Molar concentration of pure solids is taken as unity; $[M(s)] = 1$

$$E = E^0 - \frac{R T}{n F} \ln \frac{1}{[M^{n+}(aq)]}$$

$$E = E^0 - \frac{2.303 R T}{n F} \log \frac{1}{[M^{n+}(aq)]}$$

$$E = E^0 + \frac{2.303 R T}{n F} \log [M^{n+}(aq)]$$

This is the Nernst Equation for this electrode.

Where, E = Electrode Potential

E^0 = Standard Electrode Potential (for a 1M solution of metal ions)

F = Faraday of electricity (96,500 C)

T = Temperature (K)

R = Gas Constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

n = No. of electrons involved in the electrode reduction reaction

$[M^{n+}(aq)]$ = Molar concentration of metal ions

At T = 298 K, Putting the value of R and F, we get:

$$E = E^0 - \frac{0.0591}{n} \log \frac{1}{[M^{n+}(aq)]}$$

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}(aq)]$$

Nernst Equation for a Cell:

Nernst equation can also be applied to any cell reaction such as:



$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{2.303 RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

For e.g. For Galvanic cell;



$$E = E^0 - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+} \text{ (aq)}]}{[\text{Cu}^{2+} \text{ (aq)}]}$$

[\text{Zn (s)}] and [\text{Cu (s)}] = 1

It can be concluded from the Nernst Equation that,

- (a) E increases as $[\text{M}^{n+}]$ increases.
- (b) E decreases as temperature increases.

APPLICATIONS OF NERNST EQUATION:

- (i) Calculation of the Electrode Potential of the Cell
- (ii) To study the effect of Electrolyte Concentration on Electrode Potential
- (iii) Calculation of Equilibrium Constant
- (iv) To find out the Concentration of one of the ionic species in a cell if the Concentration of other species is known
- (v) To find out the pH of a Solution

Relation of EMF with THERMODYNAMIC FUNCTIONS:

The change in thermodynamic properties such as Gibbs function, enthalpy and entropy can be calculated from cell potential measurements.

Gibbs Free Energy and EMF of the Cell:

- The electrical energy produced by a galvanic cell is given by the product of its electromotive force (E) and the quantity of electricity (Q) which passes through it.
- The net electrical work performed by a reaction is the product of electromotive force (E) and the quantity of electricity (Q).

i.e. Net electrical work done = $E Q$ ----- (1)

[If E is measured in Volts and Q in Coulombs, the electrical energy obtained is in Volt-Coulomb or Joules (1 Volt-Coulomb = 1 Joule)].

Also in accordance with Faraday's Law,

Quantity of electricity produced (Q):

$$Q = n F \quad \dots\dots(2)$$

Where, n = number of electrons involved

and F = Faraday of electricity (charge on 1 mole electrons) i.e. 96,500 C

According to Gibbs and Helmholtz, the electrical energy (nFE) of a reversible cell is given by the decrease in free energy ($-\Delta G$) of the cell reaction.

As electrical energy produced by the cell = $n F E$

Hence, $-\Delta G = n F E \quad \dots\dots(3)$

In the cell reaction, if the substances involved are in their standard states i.e. at 1 atm pressure and 298 K temp, then

$$\Delta G^0 = - n F E^0 \quad \dots \dots \dots (4)$$

According to Gibbs-Helmholtz equation,

$$\Delta G = \Delta H - T \Delta S \quad \dots \dots \dots (5)$$

At constant pressure, Entropy change

$$\Delta S = - \left(\frac{\Delta G}{\Delta T} \right)_P$$

Substituting values of ΔG and ΔS in eq. (5), we get,

$$-nFE = \Delta H - T * -\left(\frac{\Delta G}{\Delta T}\right)_P$$

But we know $-\Delta G = \Delta nFE$;

$$-nFE = \Delta H - T \left(\frac{\Delta nFE}{\Delta T}\right)_P \quad (\text{n and F are constants})$$

Now, dividing by $-nF$;

$$E = -\frac{\Delta H}{nF} + T \left(\frac{\Delta E}{\Delta T}\right)_P \quad \dots\dots(6)$$

Thus, by knowing E and $\left(\frac{\Delta E}{\Delta T}\right)_P$ (variation of e.m.f. with temp at constant pressure), the value of heat of reaction (ΔH) occurring in the cell can be calculated.

The change in entropy (ΔS) can also be calculated as:

We have seen,

$$\Delta S = - \left(\frac{\Delta G}{\Delta T} \right)_P$$

Also, $-\Delta G = n F E$;

Substituting the value of $-\Delta G$ in ΔS ;

$$\Delta S = \left(\frac{\Delta n F E}{\Delta T} \right)_P$$

Or $\Delta S = n F \left(\frac{\Delta E}{\Delta T} \right)_P$

NOTE

- When , $\Delta G = -ve$, or $E = +ve$, the reaction is spontaneous.
- If $\Delta G = +ve$, or $E = -ve$, the reaction is non-spontaneous.
-
- If, $\Delta G = 0$, $E = 0$, the reaction is in equilibrium.

$$E = -\frac{\Delta H}{nF} + T \left(\frac{\Delta E}{\Delta T} \right)_P$$

In the above equation (eqⁿ no. 6), n and F are constants and $(\frac{\partial E}{\partial T})_P$ is temperature coefficient of the cell.

The electrical energy (nFE) depends upon the temp. coefficient of the EMF of the cell as:

❖ If the Temp. coefficient $(\frac{\Delta E}{\Delta T})_p = 0$;

Electrical energy (nFE) = Enthalpy of the cell reaction
(ΔH)

❖ If the Temp. coefficient $(\frac{\Delta E}{\Delta T})_p = +ve$;

Electrical energy (nFE) > Enthalpy of the cell reaction
(ΔH)

Here the additional energy has to be supplied by the surroundings otherwise the temp. of the cell falls during the reaction.

❖ If the Temp. coefficient $(\frac{\Delta E}{\Delta T})_p = -ve$;
Electrical energy (nFE) < Enthalpy of the cell reaction
(ΔH)

Here, either the heat is given out to the surroundings otherwise the temp. of the cell will rise during the reaction.

❖ In case of a Daniel cell, the temp. coefficient is very small and therefore, the
Electrical energy $nFE \approx$ Enthalpy of the cell reaction
(ΔH)

ELECTROCHEMISTRY NUMERICALS

Q.1. A Zinc rod is dipped in 0.1 M solution of ZnSO_4 . The salt is 95 percent dissociated at this dilution at 298 K. Calculate the electrode potential, given that; $E^0_{(\text{Zn}^{2+}/\text{Zn})} = -0.76\text{V}$.

Solution: $\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn (s)}$

$[\text{Zn}^{2+}] = 0.1\text{ M} \times \frac{95}{100} = 0.095\text{ M}$; Given:

$E^0_{(\text{Zn}^{2+}/\text{Zn})} = -0.76\text{ V}$ n=2; According to Nernst

Equation; $E = E^0 - \frac{0.0591}{n} \log \frac{[M(s)]}{[M^{n+}(aq)]}$ For pure

solids the concentration is taken as unity, so the

$$\begin{aligned} \text{equation becomes, } E &= -0.76 - \frac{0.0591}{2} \log \frac{1}{0.095} \\ &= -0.76 - 0.03 \end{aligned}$$

$$= -0.79\text{ V}$$

Q. A Zinc rod is dipped in 0.1 M solution of ZnSO_4 . The salt is 95 percent dissociated at this dilution at 298 K. Calculate the electrode potential, given that; $E^0_{(\text{Zn}^{2+}/\text{Zn})} = -0.76\text{V}$.

Q.2. Calculate the potential of Zn^{2+}/Zn electrode in which the Zn^{2+} activity is 0.001 M. $E^0_{(\text{Zn}^{2+}/\text{Zn})} = -0.76 \text{ V}$, $R = 8.314 \text{ J K}^{-1}$, $F = 96,500 \text{ C}$.

Solution: $E = E^0 - \frac{0.059}{n} \log \frac{1}{[\text{Zn}^{2+}]}$

Given; $E^0_{(\text{Zn}^{2+}/\text{Zn})} = -0.76 \text{ V}$; $[\text{Zn}^{2+}] = 0.001 \text{ M}$

$$\begin{aligned} E &= -0.76 - \frac{0.059}{2} \log \frac{1}{0.001} \\ &= -0.76 - \frac{0.059}{2} \times 3 \\ &= 0.76 - 0.0885 \\ E &= -0.8485 \text{ V} \end{aligned}$$

Q. Calculate the potential of Zn^{2+}/Zn electrode in which the Zn^{2+} activity is 0.001
M. $E^0_{(\text{Zn}^{2+}/\text{Zn})} = -0.76 \text{ V}$, $R = 8.314 \text{ J K}^{-1}$, $F = 96,500 \text{ C}$.

Q.3. Calculate the cell potential for the cell reaction: $\text{Al}^{3+} + \text{Fe} \rightarrow \text{Al} + \text{Fe}^{3+}$ $E^0_{\text{cell}} = -1.62 \text{ V}$
The concentration of Al^{3+} and Fe^{3+} are 1.5 M and 2.5 M resp.

Solution: $\text{Al}^{3+} + \text{Fe} \rightarrow \text{Al} + \text{Fe}^{3+}$

Given: $E^0_{\text{cell}} = -1.62 \text{ V}$, $[\text{Al}^{3+}] = 1.2 \text{ M}$, $[\text{Fe}^{3+}] = 2.5 \text{ M}$

According to Nernst Equation,

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n} \times \log \frac{[\text{Al}]}{[\text{Fe}]} \frac{[\text{Fe}^{3+}]}{[\text{Al}^{3+}]} \quad (\text{solids})$$

$$\begin{aligned} E_{\text{cell}} &= -1.62 - \frac{0.0591}{3} \times \log \frac{2.5}{1.5} \\ &= -1.62 - \frac{0.0591}{3} \times \log \frac{5}{3} \quad E_{\text{cell}} = -1.624 \text{ V} \end{aligned}$$

Q. Calculate the cell potential for the cell reaction: $\text{Al}^{3+} + \text{Fe} \rightarrow \text{Al} + \text{Fe}^{3+}$ $E^0_{\text{cell}} = -1.62 \text{ V}$
The concentration of Al^{3+} and Fe^{3+} are 1.5 M and 2.5 M resp.

Q. 4. A cell uses (Zn/Zn²⁺) and (Ag⁺/Ag) electrodes. Write the cell representation, half cell reactions and net cell reaction. Calculate the EMF of the cell. Given $E^0_{(Zn2+/Zn)} = -0.76 \text{ V}$ and $E^0_{(Ag+/Ag)} = 0.8 \text{ V}$.

Ans: Half cell reactions are:



Cell representation : Zn / Zn²⁺ (aq) // Ag⁺ (aq) / Ag (s)

$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{cathode}} - E^0_{\text{anode}} \\ &= 0.8 - (-0.76) = 1.56 \text{ V} \end{aligned}$$

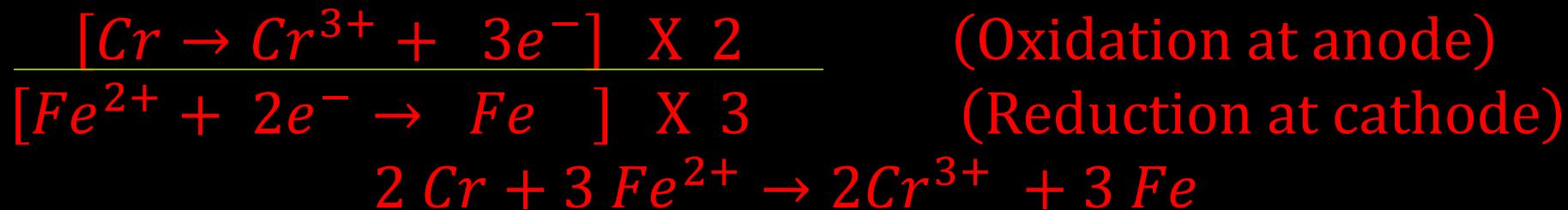
Q. A cell uses (Zn/Zn²⁺) and (Ag⁺/Ag) electrodes. Write the cell representation, half cell reactions and net cell reaction. Calculate the EMF of the cell. Given E⁰_(Zn²⁺/Zn) = - 0.76 V and E⁰_(Ag⁺/Ag) = 0.8 V.

Q.5.Calculate the potential of the cell:



Given: $E^0_{(\text{Cr}^{3+}/\text{Cr})} = -0.74 \text{ V}$; $E^0_{(\text{Fe}^{2+}/\text{Fe})} = -0.44 \text{ V}$

Solution: The half reactions are:



$$\therefore n = 6$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{6} \log \frac{[\text{Cr}^{3+}]^2 [\text{Fe}]^3}{[\text{Fe}^{2+}]^3 [\text{Cr}]^2}$$

For pure solids the activity or the concentration is taken as unity, so the equation becomes,

$$\begin{aligned}
E_{\text{cell}} &= E_{\text{cell}}^0 - \frac{0.0591}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3} \\
&= (E_{\text{cathode}}^0 - E_{\text{anode}}^0) - \frac{0.0591}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3} \\
&= (E_{\text{Fe}^{2+}/\text{Fe}}^0 - E_{\text{Cr}^{3+}/\text{Cr}}^0) - \frac{0.0591}{6} \log \frac{[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^3} \\
&= [-0.44 \text{ V} - (-0.74 \text{ V})] - \frac{0.0591}{6} \log \frac{(0.10 \text{ M})^2}{(0.01 \text{ M})^3} \\
&= 0.3 \text{ V} - \frac{0.0591}{6} \log 10^4 \\
&= 0.3 \text{ V} - 0.0394 \text{ V} = + 0.2606 \text{ V}
\end{aligned}$$

The cell potential = 0.2606 V.

Q. Calculate the potential of the cell:



Given: $E^0_{(\text{Cr}^{3+}/\text{Cr})} = -0.74 \text{ V}$; $E^0_{(\text{Fe}^{2+}/\text{Fe})} = -0.44 \text{ V}$

Q.6. What is the potential of a half cell consisting of zinc electrode in 0.01 M ZnSO_4 solution at 25 $^{\circ}\text{C}$. Given $E^0 = -0.763 \text{ V}$.

Solution: The half-cell reaction is:



$$E = E^0 - \frac{0.059}{n} \log \frac{1}{[\text{Zn}^{2+}]}$$

$$= -0.763 - \frac{0.059}{2} \log \frac{1}{0.01}$$

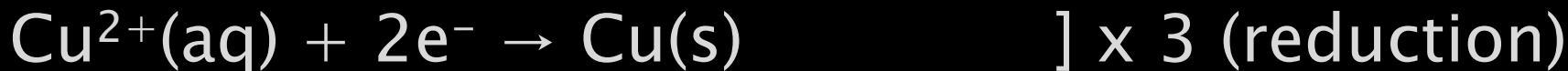
$$= -0.763 - 0.0591$$

$$= -0.8221 \text{ V}$$

Q. What is the potential of a half cell consisting of zinc electrode in 0.01 M ZnSO_4 solution at 25 $^{\circ}\text{C}$. Given $E^0 = -0.763$ V.

Q.7. Calculate the equilibrium constant at 298 K for the reaction taking place between copper sulphate and aluminium. Given $E^0_{\text{cell}} = 2.0 \text{ V}$.

Solution: The equations for the reaction is:



Thus, $n = 6$

Nernst Equation for a cell,

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[\text{Al}^{3+}]^2 [\text{Cu}]^3}{[\text{Al}]^2 [\text{Cu}^{2+}]^3}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log K_c$$

But at equilibrium , the cell reaction is balanced, i.e. at the equilibrium concentration of the two metal ions, there is no potential difference between the two electrodes and the cell potential becomes zero. The Nernst equation may now be written as:

$$0 = E_{\text{cell}}^0 - \frac{0.0591}{n} \log K_c$$

$$\log K_c = \frac{nE_{\text{cell}}^0}{0.0591}$$

$$\log K_c = \frac{6 \times 2}{0.0591}$$

$$= 203.39 \text{ or } K_c = \text{Antilog } 203.39$$

$$= 2.5 \times 10^{203}$$

Q. Calculate the equilibrium constant at 298 K for the reaction taking place between copper sulphate and aluminium. Given $E^0_{\text{cell}} = 2.0 \text{ V}$.

Q.8. Determine the concentration of Cd²⁺ ions in the following electrochemical cell:



Given: $E^0_{(\text{Zn}^{2+}/\text{Zn})} = -0.76 \text{ V}$; $E^0_{(\text{Cd}^{2+}/\text{Cd})} = -0.40 \text{ V}$
 $E_{\text{cell}} = 0.3305 \text{ V}$ at 298 K

Solution: The cell reaction is:



$$\begin{aligned} E^0_{\text{cell}} &= E^0_{(\text{Cd}^{2+}/\text{Cd})} - E^0_{(\text{Zn}^{2+}/\text{Zn})} \\ &= -0.40 - (-0.76) = 0.36 \text{ V} \end{aligned}$$

According to Nernst Equation;

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]}$$

$$0.3305 = 0.36 - \frac{0.0591}{2} \log \frac{0.1}{x}$$

$$-0.0295 = -0.0295 \log \frac{1}{10x}$$

$$\frac{-0.0295}{-0.0295} = \log \frac{1}{10x}$$

$$\log \frac{1}{10x} = 1$$

$$\frac{1}{10x} = \text{antilog } 1 = 10$$

$$\frac{1}{x} = 100, \quad x = 0.01 M$$

Q. Determine the concentration of Cd^{2+} ions in the following electrochemical cell:



Given: $E^0_{(\text{Zn}^{2+}/\text{Zn})} = -0.76 \text{ V}$; $E^0_{(\text{Cd}^{2+}/\text{Cd})} = -0.40 \text{ V}$

$$E_{\text{cell}} = 0.3305 \text{ V at } 298 \text{ K}$$

Q.9. Derive Nernst equation. The voltage of the cell Pb/PbSO₄/Na₂SO₄/Hg is 0.9647 V at 25 °C. Its temperature coefficient is 1.74 x 10⁻⁴ VK⁻¹. Calculate the value of ΔG, ΔS and ΔH. (2018-19)

Solution: We know,

$$\begin{aligned}\Delta G &= - n F E \\ &= - 2 \times 96,500 \times 0.9647 \\ &= - 2 \times 96,500 \times 0.9647 \text{ J} \\ &= - 186,187.1 \text{ J} \\ \Delta G &= - 1.86 \times 10^5 \text{ J}\end{aligned}$$

$$\Delta S = n F \left(\frac{\partial E}{\partial T} \right)_p$$

$$= 2 \times 96,500 \text{ C} \times (1.74 \times 10^{-4} \text{ V K}^{-1})$$

$$= 335,820 \times 10^{-4} \text{ J K}^{-1}$$

$$\Delta S = \mathbf{33.582 \text{ J K}^{-1}}$$

$$\Delta H = -n F E + T n F \left(\frac{\partial E}{\partial T} \right)_p$$

$$= -2 \times 96,500 \text{ C} \times 0.9647 \text{ V} + \{ 298 \text{ K} \times 2 \times 96,500 \text{ C} \times (1.74 \times 10^{-4} \text{ V K}^{-1}) \}$$

$$= -186,187.1 + 10007.436$$

$$= -176,179.664 \text{ J}$$

$$\Delta H = \mathbf{-1.76 \times 10^5 \text{ J}}$$

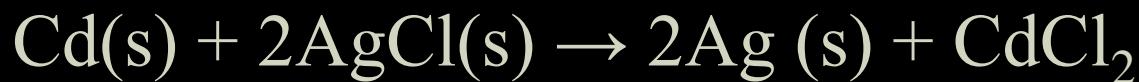
Q. Derive Nernst equation. The voltage of the cell Pb/PbSO₄/Na₂SO₄/Hg is 0.9647 V at 25 °C. Its temperature coefficient is 1.74×10^{-4} VK⁻¹. Calculate the value of ΔG , ΔS and ΔH . (2018-19)

Q.10. Consider the cell:



The emf of a cell at 15 °C is 0.67531 V and its temp coefficient is 0.00065 Vdeg⁻¹. Calculate the value of ΔG, ΔS and ΔH, if the process is carried reversibly.

Solution Hint: Cd/CdCl₂.2H₂O/AgCl(s)/Ag



$$\Delta G = - n F E$$

$$\Delta S = n F \left(\frac{\partial E}{\partial T} \right)_p$$

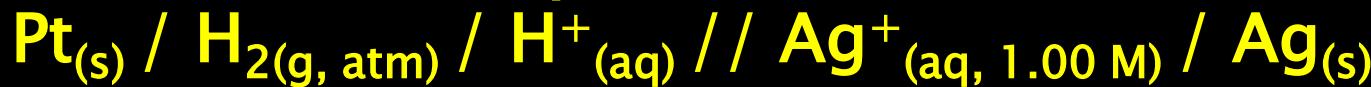
$$\Delta H = - n F E + T n F \left(\frac{\partial E}{\partial T} \right)_p$$

Q. Consider the cell: Cd/CdCl₂.2H₂O/AgCl(s)/Ag
The emf of a cell at 15 °C is 0.67531 V and its temp coefficient is 0.00065 Vdeg⁻¹. Calculate the value of ΔG, ΔS and ΔH, if the process is carried reversibly.

Q.11. For a Weston cell emf is 1.018 V at 293 K. Its temp coefficient $(\frac{\partial E}{\partial T})_p$ is $-4.00 \times 10^{-5} \text{ V K}^{-1}$. Calculate the value of ΔG , ΔS and ΔH for the cell reaction of the cell.

NOTE: Do it by your own.

Q. Calculate the pH of the cell:



Given: $E = 0.900 \text{ V}$ at 25°C

$$E^0_{\text{Ag}^+/\text{Ag}} = + 0.80 \text{ V}$$

Solution:

Chemical reactions taking place are:



$$n = 2 \quad E^0_{\text{cell}} = 0.80 - 0 = 0.80 \text{ V}$$

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n} \log \frac{[H+]^2}{p_{\text{H2}} \times [\text{Ag}+]^2}$$

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{0.0591}{n} \log \frac{[H+]^2}{1 \text{ atm} \times [1M]^2}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log [H^+]^2$$

$$\log [H^+]^2 = (E_{\text{cell}}^0 - E_{\text{cell}}) \times \frac{n}{0.0591}$$

$$2 \log [H^+] = 0.80 - 0.90 \times \frac{2}{0.0591}$$

$$= -0.10 \times \frac{2}{0.0591} = -3.381$$

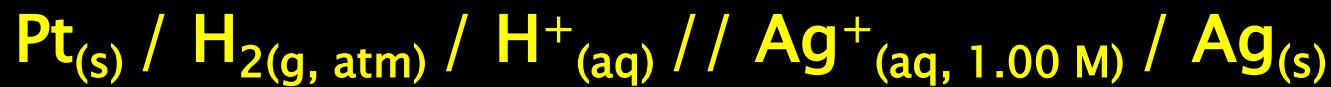
$$2 \log [H^+] = -3.381$$

$$\log [H^+] = \frac{-3.381}{2} = -1.695$$

$$pH = -\log [H^+] = 1.695$$

$$= 1.7 \text{ (approx.)}$$

Q. Calculate the pH of the cell:



Given: $E = 0.900 \text{ V}$ at 25°C

$$E^0_{\text{Ag}^+/\text{Ag}} = + 0.80 \text{ V}$$

Q. 12. The emf of a cell measured by means of a hydrogen electrode against a saturated calomel electrode at 298K is 0.4188 V. If the pressure of the H₂ (g) was maintained at 1 atm, calculate the pH of the unknown solution, given potential of reference calomel electrode is 0.2415 V.

Solution:

Chemical reactions taking place are:



Given, E_{cell} = 0.4188 V, P = 1 atm, E⁰_{calomel} = 0.2415 V, n = 2

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[H^+]^2}{p_{\text{H}_2} \times [\text{Hg}^+]^2}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log \frac{[H^+]^2}{1 \text{ atm} \times [1M]^2}$$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{0.0591}{n} \log [H^+]^2$$

$$\log [H^+]^2 = (E_{\text{cell}}^0 - E_{\text{cell}}) \times \frac{n}{0.0591}$$

$$2 \log [H^+] = 0.2415 - 0.4188 \times \frac{2}{0.0591}$$

$$\log [H^+] = -3$$

$$\text{pH} = 3$$

Q. The emf of a cell measured by means of a hydrogen electrode against a saturated calomel electrode at 298K is 0.4188 V. If the pressure of the H_2 (g) was maintained at 1atm, calculate the pH of the unknown solution, given potential of reference calomel electrode is 0.2415 V.

Batteries:

A battery is a combination of electrochemical cells connected in series , that can be used as a direct current.

Types of Cells (Battery):

- 1. Primary Cells**
- 2. Secondary Cells (Storage Cells)**

PRIMARY CELLS:

- In these cells, the electrode reactions cannot be reversed by external electric energy source.
- Reaction occurs only once and after use they become dead.
- They are not chargeable.
- e.g. Dry cell, Mercury cell.

Primary Battery

- Primary batteries, also known as non-rechargeable batteries.
- These batteries cannot get charged and reused.
- These batteries are generally used in watches, clocks, torches, and other electronic devices.
- Primary cells include the Daniell cell, Dry cell, and Mercury cell.

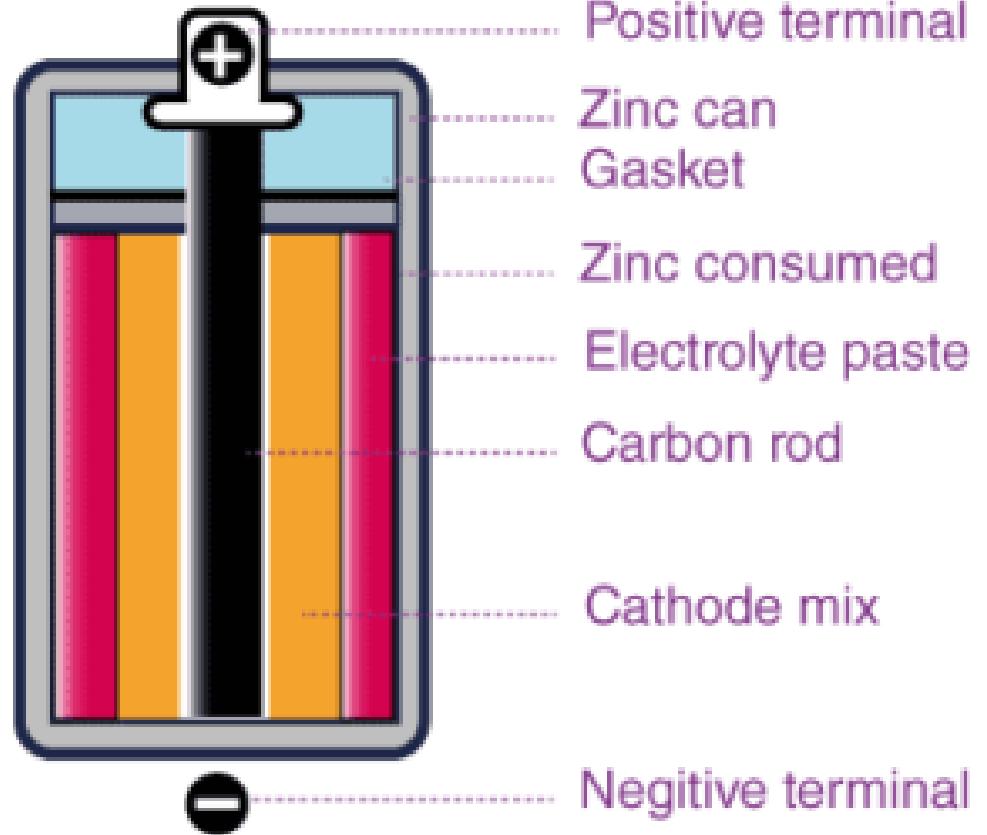
Dry Cell

The dry cell is a simple electrochemical cell that converts chemical energy into electrical energy. They are also called ***Leclanche Cells***.

Construction of dry cell:

- Outer metal covering: The metal covering is made up of zinc metal. It acts as a negative terminal of the cell.
- Anode: The zinc cylinder acts as anode while cathode is a graphite rod (Carbon).
- Cathode: The carbon rod (graphite) is surrounded by a black paste of MnO_2 and carbon powder.
- Electrolyte: Inside the Zinc metal, there is the electrolyte filled between two layers. Electrolyte is a wet pulp of Zinc chloride (ZnCl_2) and Ammonium chloride (NH_4Cl). It is the charge carrier of electricity as it contains negatively charged and positively charged ions.
- Dry cells are sealed with wax or other material to protect the moisture

PRIMARY BATTERY

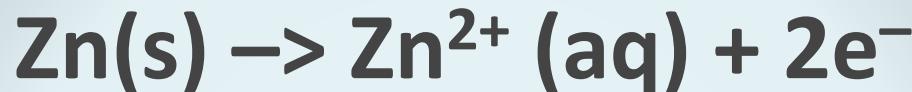


Working of dry cell:

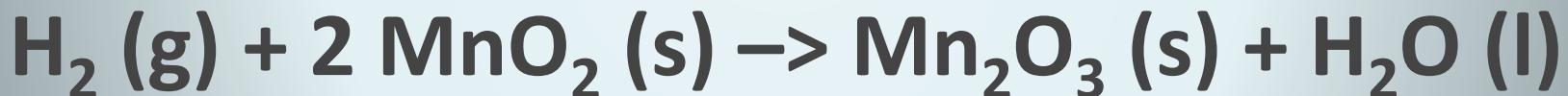
- When the electrodes are connected, the cell operates.
- Chemical reactions take place between the electrolyte, zinc container and graphite rod.
- Because of this, electric charge is produced on the two terminals of the cell and electric current flows in the circuit.

The redox reaction that takes place in these cells is:

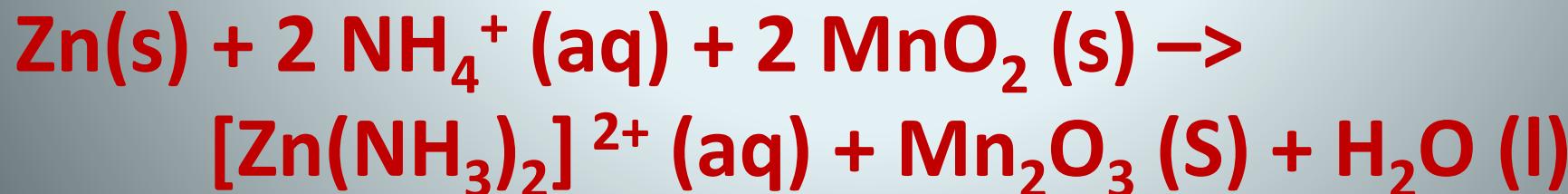
At Anode: (Oxidation)



At Cathode: (Reduction)



Thus, the overall cell equation is:



Advantages :

- Low Priced
- Voltage-1.5 V

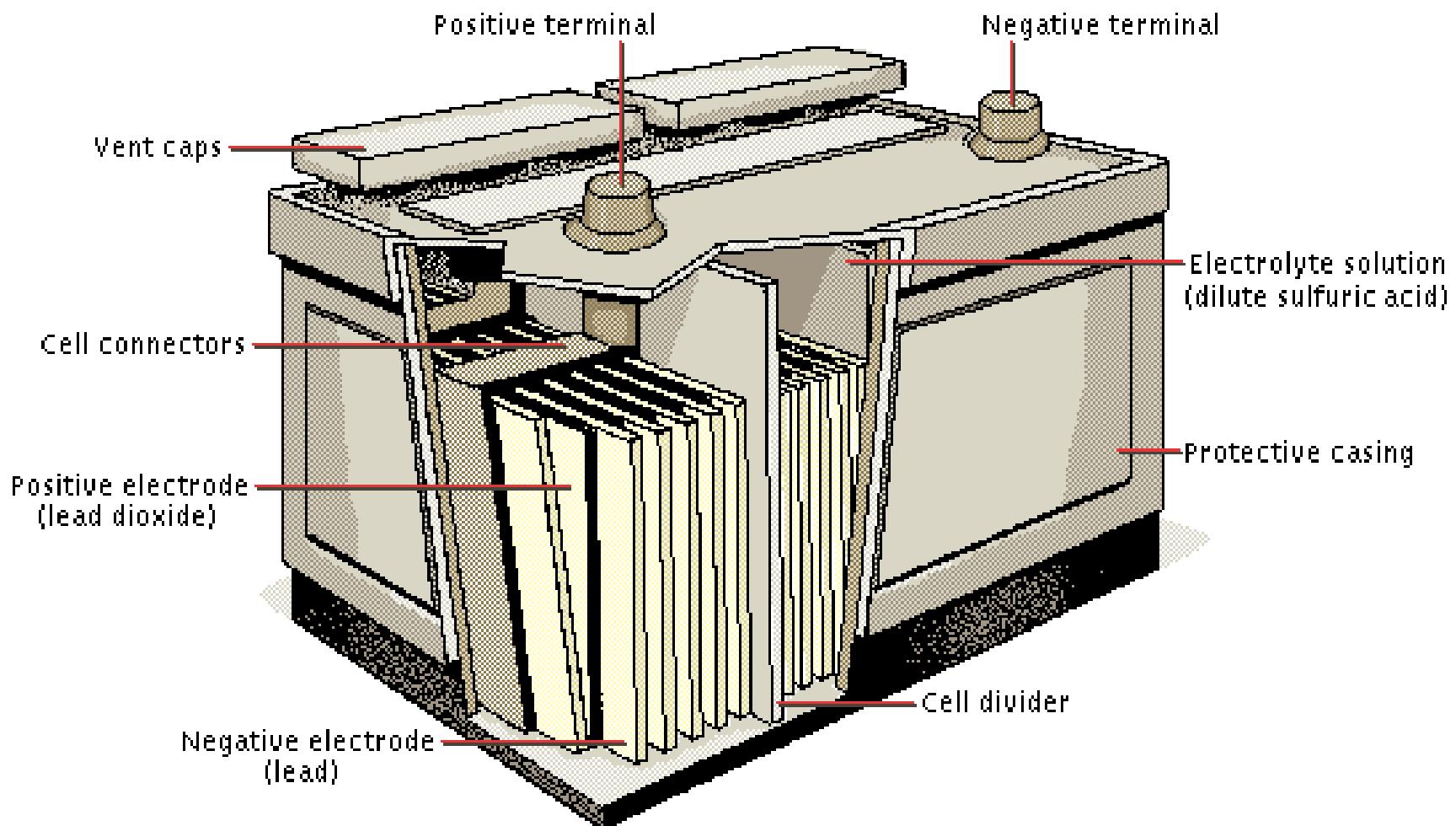
Disadvantages:

- If current is rapidly drawn from it, products get build up on the electrodes, thereby causing drop in voltage.
- A dry cell becomes dead after a long time, even if it is not in use.

SECONDARY CELLS (STORAGE CELLS):

- In these cells the reactions can be reversed by external electric energy source.
- They are chargeable cells.
- e.g. Lead Storage Cell and Nickel-Cadmium storage cell

Lead Storage Battery

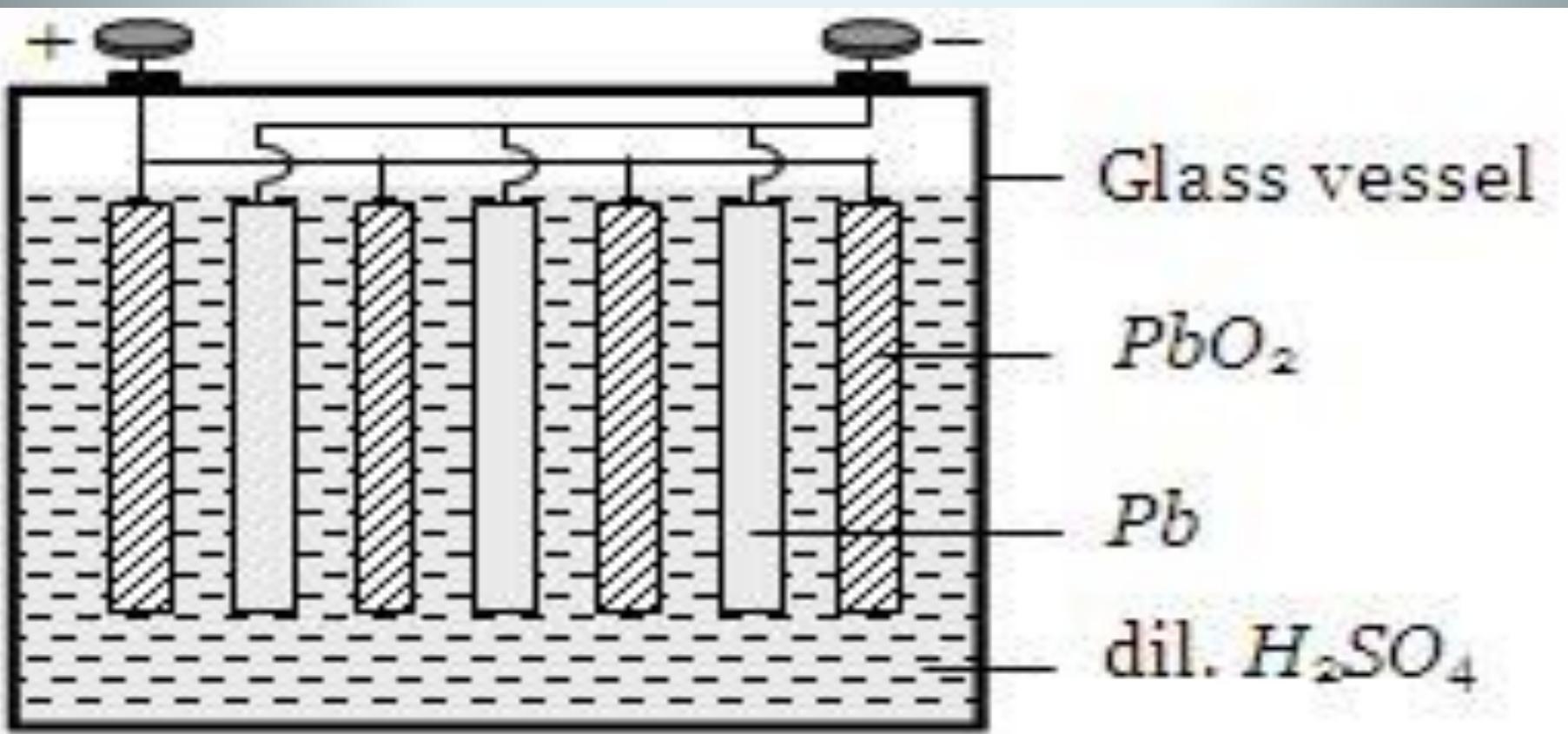


LEAD STORAGE BATTERY

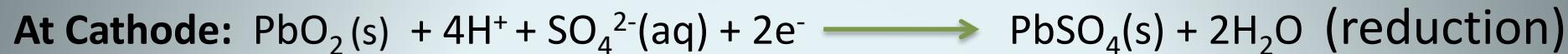
- It is a secondary cell and can be recharged and used again and again as a source of electric current.
- It is used in cars, trucks and buses etc.
- In lead storage battery, a number of voltaic cells are connected in series.
- 3-6 such cells are generally combined to get 6-12 V battery.

In each cell:

- ▶ Anode: A grid of lead packed with finely divided spongy lead
- ▶ Cathode: A grid of lead packed with PbO_2
- ▶ Electrolyte: Aq. H_2SO_4 (38%) having density 1.30 g/mL



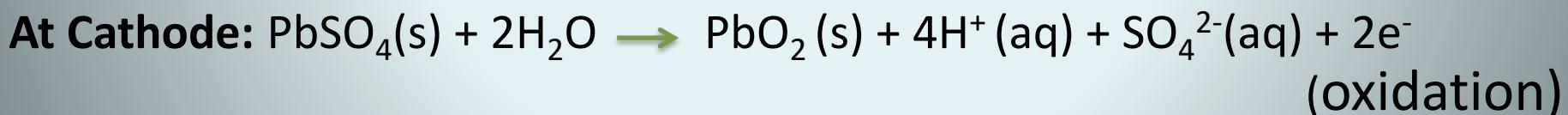
Reaction during Discharging (usage) of Cell



- ▶ Thus, at anode Pb is oxidised and at cathode PbO_2 is reduced.
- ▶ PbSO_4 is formed at each electrode and sulphuric acid is used up.
- ▶ As a result, concentration of sulphuric acid decreases and the density of the solution also decreases.
- ▶ When both anode and cathode become covered with PbSO_4 and the density of acid falls below 1.2 g/mL, the battery needs recharging.

Recharging the battery

- The cell can be charged by passing electric current of a suitable voltage in the opposite direction.
- The electrode reaction gets reversed.
- As a result, Pb is deposited on anode and PbO₂ on cathode.
- The density of acid also increases.
- The reaction is written as:



It may be noted that storage battery acts as voltaic cell as well as electrolytic cell. For ex.

- When it is used to start the engine, it acts as a voltaic cell and produces electric energy.
- During recharging, it acts as an electrolytic cell.

THANK YOU