CH#12:-

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Chap. 12

ELECTROCHEMISTRY

Definition:-

Branch of chemistry which deals with the study of electrical changes during the chemical reaction is called **electrochemistry**. In electrochemistry electrical energy is converted into chemical energy or chemical energy is converted into electrical energy.

Oxidation:- (LEO)

→ Loss of e^- is called oxidation.
→ Increase in oxidation state is called oxidation.
→ Removal of hydrogen is called oxidation.
→ Addition of oxygen is called oxidation.

Reduction:- (GER)

→ Gain of e^- is called reduction.
→ Decrease in oxidation state is called reduction.
→ Addition of hydrogen is called reduction.
→ Removal of oxygen is called reduction.

Redox-reactions:-

Reactions in which oxidation and

reduction take place are called **redox-reactions**.

Oxidation State / Oxidation No. :-

Appearent charge on an atom which may be ⊕ve or ⊖ve is called it's **oxidation state** e.g,

1- HCl

O.S of H = +1

O.S of Cl = -1

2- $KMnO_4$

O.S of K = +1

O.S of Mn = +7

O.S of O = -2

Rules :-

→ O.S of an element is zero in free state.

→ O.S of H is +1 in all compounds except metallic hydride or ionic hydride, in these hydrides, O.S of H is -1.

→ O.S of oxygen is different in different oxides.

(i) O.S of oxygen is -2 in normal oxide.

(ii) O.S of oxygen is -1 in per oxide.

(iii) O.S of oxygen is -1/2 in super oxide.

(iv) O.S of oxygen is +2 in OF_2.

Example. 12.1 :-

Calculate the O.S of Mn in $KMnO_4$.

$KMnO_4$

$+1 + Mn + 4(-2) = 0$

$Mn - 7 = 0$

$\boxed{Mn = +7}$

Example. 12.2 :

Calculate the O.S of Cr in $K_2Cr_2O_7$.

$$K_2Cr_2O_7$$

$$2(+1)+2Cr+7(-2)=0$$

$$2Cr-12=0$$

$$2Cr=12$$

$$\boxed{Cr=+6}$$

Example: 12.3 :

What is O.S of S in SO_4^{-2} ion ?

$$SO_4^{-2}$$

$$S+4(-2)=-2$$

$$S-8=-2$$

$$S=-2+8$$

$$\boxed{S=+6}$$

Self Check Exercise 12.1 :

Identify the compound in which O.S of Fe is +3.

$$FeO\ ,\ Fe_3O_4\ ,\ Fe_2O_3$$

$$FeO$$

$$Fe+(-2)=0$$

$$\boxed{Fe=+2}$$

$$Fe_3O_4$$

$$3Fe+4(-2)=0$$

$$3Fe-8=0$$

$$3Fe=8$$

$$\boxed{Fe=+8/3}$$

Fe_2O_3

$2Fe + 3(-2) = 0$

$2Fe - 6 = 0$

$2Fe = +6$

$\boxed{Fe = +3}$

Thus, in Fe_2O_3, the O.S of Fe is +3.

Example. 12.4 :-

Identify the elements undergoing oxidation or reduction.

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$\overset{-4\ (+1)4}{CH_4}{}_{(g)} + \overset{0}{2O_2}{}_{(g)} \longrightarrow \overset{+4\ (-2)2}{CO_2}{}_{(g)} + \overset{2(+1)\ -2}{2H_2O}{}_{(l)}$$

→ The C atom changes its O.S from -4 in CH_4 to +4 in CO_2. This is due to loss of 8 e's per C atom. Since, O.S of C is increased, therefore, this is oxidation.

→ The O atom changes its O.S from zero in O_2 to -2 in H_2O and CO_2. This is due to gain of 2 e's per O atom. Since, O.S of O is decreased, therefore, this is reduction.

→ Hence, C is oxidized and O is reduced.

Example. 12.5 :-

Identify the substance oxidized and reduced in dry cell.

→ Following reactions occur in dry cell.

At anode :

$$Zn \longrightarrow Zn^{+2} + 2e'$$

At cathode :

$$2NH_4^+ + 2MnO_2 + 2e' \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$$

→ The anode reaction indicates that Zn metal loses 2 e's, therefore it undergoes oxidation.

→ To determine substance reduced, assign O.S to all the atoms that are at cathode.

$$2[\overset{-3}{N}\overset{(+1)}{H}_4\overset{4}{]^{+1}} + 2\overset{+4}{Mn}\overset{(-2)2}{O_2} + 2e' \longrightarrow \overset{2(+3)}{Mn_2}\overset{(-2)3}{O_3} + 2\overset{-3}{N}\overset{(+1)3}{H_3} + \overset{2(+1)}{H_2}\overset{-2}{O}$$

→ In this reaction, Mn changes its O.S from +4 in MnO_2 to +3 in Mn_2O_3. This is due to gain of one e' per Mn atom. This is reduction. Thus, the substance reduced is Mn.

Self Check Exercise 12.2 :-

Identify the atoms undergoing oxidation or reduction in the following reactions.

(i) $N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$

$$\overset{0}{N_2}_{(g)} + \overset{0}{3H_2}_{(g)} \longrightarrow \overset{-3}{2N}\overset{3(+1)}{H_3}_{(g)}$$

→ The H atom changes its O.S from zero in H_2 to +1 in NH_3. Since O.S of H is increased, hence, it is oxidation.

→ The N atom changes its O.S from zero

in N_2 to -3 in NH_3. Since, O.S of N is decreased, hence, it is reduction.

→ Hence, H is oxidized and N is reduced.

(iii) - $4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}$

$$\overset{0}{4Fe}_{(s)} + \overset{0}{3O_2}_{(g)} \longrightarrow \overset{2(+3)\ 3(-2)}{2Fe_2O_3}_{(s)}$$

→ The Fe atom changes its O.S from zero in Fe to +3 in Fe_2O_3. Since, O.S of Fe is increased, therefore this is oxidation.

→ The O atom changes its O.S from zero in O_2 to -2 in Fe_2O_3. Since, O.S of O is decreased, therefore this is reduction.

→ Hence, Fe is oxidized and O is reduced.

(iii) - $C_6H_{12}O_{6(s)} + 6O_{2(g)} \longrightarrow 6CO_{2(g)} + 6H_2O_{(l)}$

$$\overset{0\ 12(+1)\ 6(-2)}{C_6H_{12}O_6}_{(s)} + \overset{0}{6O_2}_{(g)} \longrightarrow \overset{+4\ 2(-2)}{6CO_2}_{(g)} + \overset{2(+1)\ -2}{6H_2O}_{(l)}$$

→ The C atom changes its O.S from zero in $C_6H_{12}O_6$ to +4 in CO_2. Since, O.S of C is increased, therefore this is oxidation.

→ The O atom changes its O.S from zero in O_2 to -2 in CO_2 and H_2O. Since, O.S of O is decreased, therefore, this is reduction.

→ Hence, C is oxidized and O is reduced.

Balancing of Equations V. Imp

By two methods:

1. Oxidation Reduction method
2. Ion-é method / Half Reaction method

Example 12.6:

Balance the following eq. by oxidation No. method.

$$P + HNO_3 + H_2O \longrightarrow H_3PO_4 + NO$$

3e's Gain X 5

$$\overset{0}{P} + \overset{+1\ +5\ -2(3)}{HNO_3} + \overset{(+1)2\ -2}{H_2O} \longrightarrow \overset{+1\ +5\ (-2)4}{H_3PO_4} + \overset{+2\ -2}{NO}$$

5e's lost X 3

$$3P + 5HNO_3 + H_2O \longrightarrow 3H_3PO_4 + 5NO$$

$$3P + 5HNO_3 + 2H_2O \longrightarrow 3H_3PO_4 + 5NO$$

Self Check Exercise 12.3

Using the oxidation No. method, balance the following eq.

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

2e's lost X 3

$$\overset{+1\ +5\ (-2)3}{HNO_3} + \overset{+1\ -2}{H_2S} \longrightarrow \overset{+2\ -2}{NO} + \overset{0}{S} + \overset{+1\ -2}{H_2O}$$

3e's Gain X 2

$$2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + H_2O$$

$$2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + 4H_2O$$

Half-reaction:

A half-reaction is the part of an overall redox reaction that represents,

separately, either an oxidation or a reduction.

Example. 12.7 :-
Split the following reaction into half-reactions.

$$SO_2 + MnO_4^{-1} \longrightarrow SO_4^{-2} + Mn^{+2}$$

$$\overset{+4}{S}\overset{-2}{O_2} + [\overset{+7}{M}n\overset{-2}{O_4}]^{-1} \longrightarrow [\overset{+6}{S}\overset{-2}{O_4}]^{-2} + \overset{+2}{M}n$$

Oxidation half-reaction :-

$$SO_2 \longrightarrow SO_4^{-2}$$

Reduction half-reaction :-

$$MnO_4^{-1} \longrightarrow Mn^{+2}$$

Self Check Exercise 12.4 :-
Split the following reactions into half-reactions.

(i) $Mn^{+2} + PbO_2 \longrightarrow MnO_4^{-1} + Pb^{+2}$

$$Mn^{+2} + \overset{+4}{P}b\overset{-2}{O_2} \longrightarrow [\overset{+7}{M}n\overset{-2}{O_4}]^{-1} + Pb^{+2}$$

Oxidation half-reaction :-

$$Mn^{+2} \longrightarrow MnO_4^{-1}$$

Reduction half-reaction :-

$$PbO_2 \longrightarrow Pb^{+2}$$

(ii) $Br_2 + SO_2 \longrightarrow SO_4^{-2} + Br^{-1}$

$$Br_2^{0} + \overset{+4\ -2}{SO_2} \longrightarrow \overset{+6\ -2}{[SO_4]^{-2}} + Br^{-1}$$

Oxidation half-reaction :-

$$SO_2 \longrightarrow SO_4^{-2}$$

Reduction half-reaction :-

$$Br_2 \longrightarrow Br^{-1}$$

(iii) $NO + MnO_4^{-1} \longrightarrow NO_3^{-1} + MnO_2$

$$\overset{+2\ -2}{NO} + \overset{+7\ -2}{[MnO_4]^{-1}} \longrightarrow \overset{+5\ -2}{[NO_3]^{-1}} + \overset{+4\ -2}{MnO_2}$$

Oxidation half-reaction :-

$$NO \longrightarrow NO_3^{-1}$$

Reduction half-reaction :-

$$MnO_4^{-1} \longrightarrow MnO_2$$

Self Check Exercise 12.5 :-

Use the half reaction method / ion e' method to balance the following redox-reactions.

(i) $Co + Cr^{+3} \longrightarrow Co^{+2} + Cr^{+2}$

$Co \longrightarrow Co^{+2}$ (Oxidation)

$Cr^{+3} \longrightarrow Cr^{+2}$ (Reduction)

$Co \longrightarrow Co^{+2} + 2e's$ (Xing by 1)

$Cr^{+3} + 1e' \longrightarrow Cr^{+2}$ (Xing by 2)

$Co \longrightarrow Co^{+2} + 2e's$

$2Cr^{+3} + 2e's \longrightarrow 2Cr^{+2}$

$Co \longrightarrow Co^{+2} + 2e's$

$2Cr^{+3} + 2e's \longrightarrow 2Cr^{+2}$

$Co + 2Cr^{+3} \longrightarrow Co^{+2} + 2Cr^{+2}$

(iii) $Au^{+3} + H_2 \longrightarrow H^+ + Au$

$H_2 \longrightarrow H^+$ (Oxidation)

$Au^{+3} \longrightarrow Au$ (Reduction)

$H_2 \longrightarrow 2H^+$

$Au^{+3} \longrightarrow Au$

$H_2 \longrightarrow 2H^+ + 2e's$ (⊗ing by B)

$Au^{+3} + 3e's \longrightarrow Au$ (⊗ing by 2)

$3H_2 \longrightarrow 6H^+ + 6e's$

$6e's + 2Au^{+3} \longrightarrow 2Au$

$3H_2 + 2Au^{+3} \longrightarrow 6H^+ + 2Au$

(iii) $Cl_2 + I^- \longrightarrow I_2 + Cl^-$

$I^- \longrightarrow I_2$ (Oxidation)

$Cl_2 \longrightarrow Cl^-$ (Reduction)

$2I^- \longrightarrow I_2$

$Cl_2 \longrightarrow 2Cl^-$

$2I^- \longrightarrow I_2 + 2e's$

$Cl_2 + 2e's \longrightarrow 2Cl^-$

$$2I^- \longrightarrow I_2 + 2e's$$
$$Cl_2 + 2e's \longrightarrow 2Cl^-$$
$$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$$

Example. 12.8 :

Balance the following eq. by half reaction method.

$$Cr_2O_7^{-2} + H_2SO_3 \longrightarrow Cr^{+3} + HSO_4^-$$

$$Cr_2O_7^{-2} \longrightarrow Cr^{+3} \quad \text{(Reduction)}$$
$$H_2SO_3 \longrightarrow HSO_4^- \quad \text{(Oxidation)}$$

$$Cr_2O_7^{-2} \longrightarrow 2Cr^{+3}$$
$$H_2SO_3 \longrightarrow HSO_4^-$$

(a) (b)

(a) $Cr_2O_7^{-2} \longrightarrow 2Cr^{+3} + 7H_2O$

$H_2SO_3 + H_2O \longrightarrow HSO_4^-$

$Cr_2O_7^{-2} + 14H^+ \longrightarrow 2Cr^{+3} + 7H_2O$

$H_2SO_3 + H_2O \longrightarrow HSO_4^- + 3H^+$

$Cr_2O_7^{-2} + 14H^+ + 6e's \longrightarrow 2Cr^{+3} + 7H_2O$ — (a)

$H_2SO_3 + H_2O \longrightarrow HSO_4^- + 3H^+ + 2e's$ — (b)

(X)ing eq (a) by 1 & eq (b) by 3

$Cr_2O_7^{-2} + 14H^+ + 6e's \longrightarrow 2Cr^{+3} + 7H_2O$

$3H_2SO_3 + 3H_2O \longrightarrow 3HSO_4^- + 9H^+ + 6e's$

$$Cr_2O_7^{-2} + 5H^+ + 3H_2SO_3 \longrightarrow 2Cr^{+3} + 4H_2O + 3HSO_4^-$$

Example. 12.9 :-

Use the half reaction method to balance the reaction that take place in acidic medium.

$$MnO_4^- + H_2O_2 \longrightarrow Mn^{+2} + O_2$$

$H_2O_2 \longrightarrow O_2$ (Oxidation)

$MnO_4^- \longrightarrow Mn^{+2}$ (Reduction)

$H_2O_2 \longrightarrow O_2$

$MnO_4^- \longrightarrow Mn^{+2} + 4H_2O$

$H_2O_2 \longrightarrow O_2 + 2H^+$

$MnO_4^- + 8H^+ \longrightarrow Mn^{+2} + 4H_2O$

$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e's$ ——— (a)

$MnO_4^- + 8H^+ + 5e's \longrightarrow Mn^{+2} + 4H_2O$ ——— (b)

(X)ing eq(a) by 5 & (b) by 2.

$5H_2O_2 \longrightarrow 5O_2 + 10H^+ + 10e's$

$2MnO_4^- + 16H^+ + 10e's \longrightarrow 2Mn^{+2} + 8H_2O$

$5H_2O_2 + 2MnO_4^- + 6H^+ \longrightarrow 5O_2 + 2Mn^{+2} + 8H_2O$

Self Check Exercise 12.6 :-

1- Balance half reactions that take place in acidic medium.

(a). $NO_3^- \longrightarrow NO_2$

$NO_3^- \longrightarrow NO_2$

$NO_3^- \longrightarrow NO_2 + H_2O$

$NO_3^- + 2H^+ \longrightarrow NO_2 + H_2O$

$NO_3^- + 2H^+ + 1e' \longrightarrow NO_2 + H_2O$

(b). $IO_3^- \longrightarrow I_2$

$2IO_3^- \longrightarrow I_2$

$2IO_3^- \longrightarrow I_2 + 6H_2O$

$2IO_3^- + 12H^+ \longrightarrow I_2 + 6H_2O$

$2IO_3^- + 12H^+ + 10e's \longrightarrow I_2 + 6H_2O$

(c). $ClO_4^- \longrightarrow ClO_3^-$

$ClO_4^- \longrightarrow ClO_3^-$

$ClO_4^- \longrightarrow ClO_3^- + H_2O$

$ClO_4^- + 2H^+ \longrightarrow ClO_3^- + H_2O$

$ClO_4^- + 2H^+ + 2e's \longrightarrow ClO_3^- + H_2O$

2- Balance the following reactions by half-reaction method, which take place in acidic medium.

(a)- $NO_3^- + Br^- \longrightarrow NO + Br_2$

$Br^- \longrightarrow Br_2$ (Oxidation)

$NO_3^- \longrightarrow NO$ (Reduction)

$2Br^- \longrightarrow Br_2$

$NO_3^- \longrightarrow NO$

$2Br^- \longrightarrow Br_2$

$NO_3^- \longrightarrow NO + 2H_2O$

$2Br^- \longrightarrow Br_2$

$NO_3^- + 4H^+ \longrightarrow NO + 2H_2O$

$2Br^- \longrightarrow Br_2 + 2e's$ (⊗ing by 3)

$NO_3^- + 4H^+ + 3e's \longrightarrow NO + 2H_2O$ (⊗ing by 2)

$6Br^- \longrightarrow 3Br_2 + 6e's$

$2NO_3^- + 8H^+ + 6e's \longrightarrow 2NO + 4H_2O$

$6Br^- + 2NO_3^- + 8H^+ \longrightarrow 3Br_2 + 2NO + 4H_2O$

(b)- $Ce^{+4} + H_3AsO_3 \longrightarrow Ce^{+3} + H_3AsO_4$

$H_3AsO_3 \longrightarrow H_3AsO_4$ (Oxidation)

$Ce^{+4} \longrightarrow Ce^{+3}$ (Reduction)

$$H_3AsO_3 + H_2O \xrightarrow[Ce^{+4} \longrightarrow Ce^{+3}]{} H_3AsO_4$$

$$H_3AsO_3 + H_2O \xrightarrow[Ce^{+4} \longrightarrow Ce^{+3}]{} H_3AsO_4 + 2H^+$$

$$H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2H^+ + 2e's \quad (a)$$

$$Ce^{+4} + 1e' \longrightarrow Ce^{+3} \quad (b)$$

Qing (eqn @ 1 by 1) 4 (b) by 2.

$$H_3AsO_3 + H_2O \longrightarrow H_3AsO_4 + 2H^+ + \cancel{2e's}$$
$$2Ce^{+4} + \cancel{2e's} \longrightarrow 2Ce^{+3}$$

$$H_3AsO_3 + H_2O + 2Ce^{+4} \longrightarrow H_3AsO_4 + 2H^+ + 2Ce^{+3}$$

(c) $S_2O_8^{-2} + Cr^{+3} \longrightarrow SO_4^{-2} + Cr_2O_7^{-2}$

$Cr^{+3} \longrightarrow Cr_2O_7^{-2}$ (Oxidation)

$S_2O_8^{-2} \longrightarrow SO_4^{-2}$ (Reduction)

$2Cr^{+3} \longrightarrow Cr_2O_7^{-2}$

$S_2O_8^{-2} \longrightarrow 2SO_4^{-2}$

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$2Cr^{+3} + 7H_2O \longrightarrow Cr_2O_7^{-2}$

$S_2O_8^{-2} \longrightarrow 2SO_4^{-2}$

$2Cr^{+3} + 7H_2O \longrightarrow Cr_2O_7^{-2} + 14H^+$

$S_2O_8^{-2} \longrightarrow 2SO_4^{-2}$

$2Cr^{+3} + 7H_2O \longrightarrow Cr_2O_7^{-2} + 14H^+ + 6e's$

$S_2O_8^{-2} + 2e's \longrightarrow 2SO_4^{-2}$ (⊗ing by 3)

$$2Cr^{+3} + 7H_2O \longrightarrow Cr_2O_7^{-2} + 14H^+ + 6e's$$
$$3S_2O_8^{-2} + 6e's \longrightarrow 6SO_4^{-2}$$

$$2Cr^{+3} + 7H_2O + 3S_2O_8^{-2} \longrightarrow Cr_2O_7^{-2} + 14H^+ + 6SO_4^{-2}$$

(d). $MnO_4^- + C_2O_4^{-2} \longrightarrow Mn^{+2} + CO_2$

$C_2O_4^{-2} \longrightarrow CO_2$ (Oxidation)
$MnO_4^- \longrightarrow Mn^{+2}$ (Reduction)

$C_2O_4^{-2} \longrightarrow 2CO_2$
$MnO_4^- \longrightarrow Mn^{+2}$

$C_2O_4^{-2} \longrightarrow 2CO_2$
$MnO_4^- \longrightarrow Mn^{+2} + 4H_2O$

$C_2O_4^{-2} \longrightarrow 2CO_2$
$MnO_4^- + 8H^+ \longrightarrow Mn^{+2} + 4H_2O$

$C_2O_4^{-2} \longrightarrow 2CO_2 + 2e's$ (⊗ing by 5)
$MnO_4^- + 8H^+ + 5e's \longrightarrow Mn^{+2} + 4H_2O$ (⊗ing by 2)

$5C_2O_4^{-2} \longrightarrow 10CO_2 + 10e's$
$2MnO_4^- + 16H^+ + 10e's \longrightarrow 2Mn^{+2} + 8H_2O$

$$5C_2O_4^{-2} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{+2} + 8H_2O$$

Salt Bridge

Salt bridge is a U-shaped tube which is filled with electrolyte like KCl, KNO_3, Na_2SO_4 in gel form.

Functions :-

Salt bridge performs three functions;

→ It is electrical connection between the two solutions.

→ It prevent mixing of two solutions

→ It maintains each portion electrically neutral.

Galvanic Cell / Voltaic Cell

Cell which converts chemical energy into electrical energy is called **galvanic cell**. Reactions take place in this cell are spontaneous reactions.

Anode :-

The electrode at which oxidation occurs is called the anode.

Cathode :-

The electrode at which reduction occurs is called the cathode.

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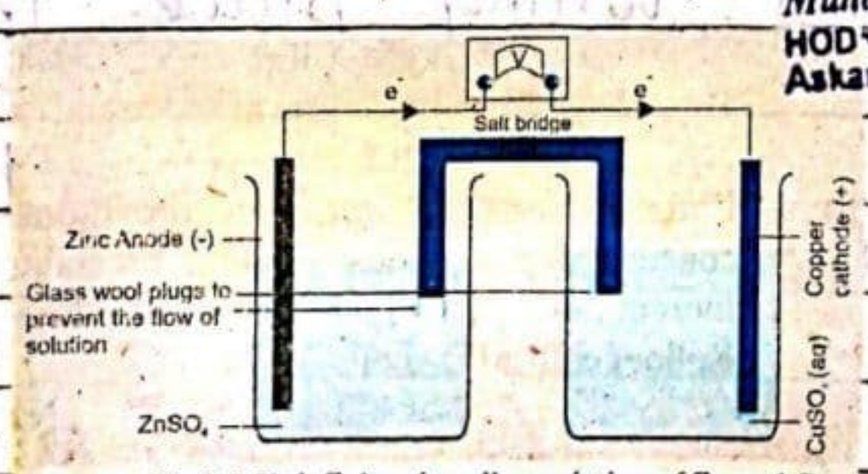

Fig (10.2) A Galvanic cell consisting of Zn and Cu electrodes at 25°C and unit concentration of electrolytic solutions.

Construction of Galvanic Cell :-

1- Zinc rod acts as anode.
2- Copper rod acts as cathode.
3- Zinc rod is dipped in $ZnSO_4$ soln in one container.
4- Copper rod is dipped in $CuSO_4$ soln in another container.
5- The two rods are connected by a copper wire. However, still no current flows through the external circuit.
6- The two solns are connected with a salt bridge. Now the current flows through external circuit and electricity is generated.

Reactions of Galvanic Cell :-

1- In one half-cell oxidation takes place, it is called as oxidation half-cell or anode.
2- In another half-cell reduction takes place, it is called as reduction half-cell or cathode.
3- The reaction taking place in oxidation half-cell is called oxidation half-reaction.
4- The reaction taking place in reduction half-cell is called reduction half-reaction.
5- Zn has greater tendency to lose e's than Cu.
6- Therefore, Zn electrode gets $\ominus$ve charge relative to Cu electrode.
7- Thus, e's flow from Zn electrode through

The external circuit to Cu electrode.
The reactions at the two electrodes are;

At anode : (Oxidation half reaction)

$$Zn_{(S)} \longrightarrow Zn^{+2}_{(aq)} + 2\acute{e}s$$

At cathode: (Reduction half reaction)

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

Overall Cell Reaction :

$$Zn_{(S)} + Cu^{+2}_{(aq)} \longrightarrow Zn^{+2}_{(aq)} + Cu_{(S)}$$

Reaction in Salt bridge form

$$Zn / Zn^{+2} \;//\; Cu^{+2} / Cu$$

Electromotive force (emf)

The force with which $\acute{e}$'s are pushed to flow through the wire from anode to cathode is called **emf**.

Electrode potential

Ability of electrode to lose or gain $\acute{e}$ is called **electrode potential** or **potential difference** which causes the transfer of $\acute{e}$ between two electrodes is called **electrode potential**. It is denoted by E°.

Cell potential

The emf produced by a galvanic

cell is called **cell potential**. It is denoted by E°_{cell}.

Unit:

It is measured in volts (V).

When the passage of one coulomb is able to accomplish one Joule of work, then emf is **one volt**.

Standard Conditions for a cell potential:

The standard conditions are;

→ Concentration of soln = 1 mol dm^{-3}.

→ T = 25°C [298 K]

→ P = 1 atm

The standard cell potential E°_{cell} or emf of cell is the algebraic difference b/w the standard reduction potentials of the two half-cells.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{Anode}$$

The cell potential has **positive value** for any spontaneous redox reaction.

Standard Hydrogen Electrode (SHE)

A standard hydrogen electrode consists of a platinum foil coated with finely divided platinum. It is surrounded by H_2 gas at 1 atm pressure in contact with 1 M HCl soln at 298 K.

Its electrode potential is arbitrarily chosen as zero at all temperatures. The half-cell

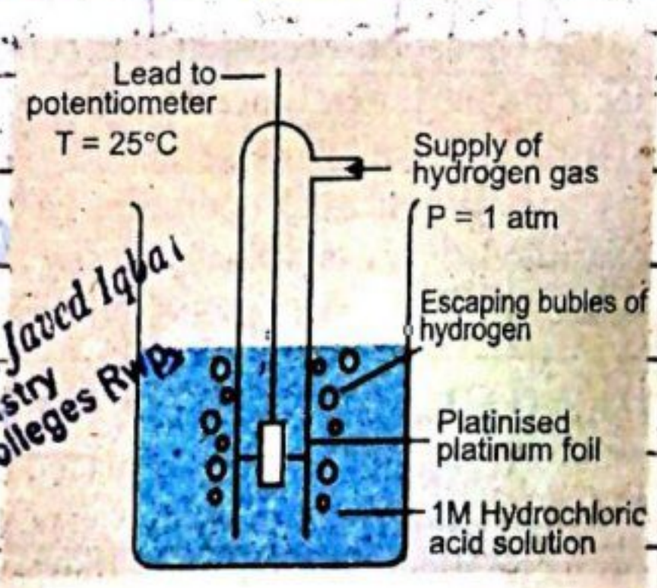

Fig. (10.4) Standard hydrogen electrode (S.H.E)

potential for reduction of $H^+_{(aq)}$ to H_2 gas or the potential for the oxidation of H_2 to $H^+_{(aq)}$ in the standard Hydrogen half-cell is defined exactly 0.00V.

Reduction : (act as cathode)

$$2H^+_{(aq)} + 2e's \longrightarrow H_{2(g)} \quad E^\circ_{H^+/H_2} = 0.00V$$

Oxidation : (act as anode)

$$H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e's \quad E^\circ_{H_2/H^+} = 0.00V$$

Reduction Half-reaction	E^0 (Volts)
$Li^+ + \bar{e} \rightleftharpoons Li$	-3.05
$K^+ + \bar{e} \rightleftharpoons K$	-2392
$Ba^{2+} + 2\bar{e} \rightleftharpoons Ba$	-2.90
$Ca^{2+} + \bar{e} \rightleftharpoons Na$	-2.76
$Na^{2+} + 2\bar{e} \rightleftharpoons Na$	-2.71
$Mg^{2+} + 2\bar{e} \rightleftharpoons Mn$	-2.38
$Al^{3+} + 3\bar{e} \rightleftharpoons Al$	-1.67
$Mn^{2+} + 2\bar{e} \rightleftharpoons Mn$	-1.03
$2H_2O + 2\bar{e} \rightleftharpoons H_2 + 2OH^-$	-0.83
$Zn^{2+} + 2\bar{e} \rightleftharpoons Zn$	-0.76
$Cr^{3+} + 3\bar{e} \rightleftharpoons Cr$	-0.74
$Fe^{2+} + 2\bar{e} \rightleftharpoons Fe$	-0.44
$PbSO_4 + 2\bar{e} \rightleftharpoons Pb + SO_4^{2-}$	-0.36
$Ni^{2+} + 2\bar{e} \rightleftharpoons Ni$	-0.25
$Sn^{2+} + 2\bar{e} \rightleftharpoons Sn$	-0.14
$Pb^{2+} + 2\bar{e} \rightleftharpoons Pb$	-0.13
$Fe^{3+} + 3\bar{e} \rightleftharpoons Fe$	-0.04
$2H^+ + 2\bar{e} \rightleftharpoons H_2$	0.00
$AgCl + \bar{e} \rightleftharpoons Ag + Cl^-$	+0.22
$Hg_2Cl_2 + 2\bar{e} \rightleftharpoons 2Hg + 2Cl^-$	+0.27
$Cu^{2+} + 2\bar{e} \rightleftharpoons Cu$	+0.34
$Cu^+ + 1\bar{e} \rightleftharpoons Cu$	+0.52
$I_{2\,(aq)} + 2\bar{e} \rightleftharpoons 2I^-$	+0.54
$Fe^{3+} + \bar{e} \rightleftharpoons Fe^{2+}$	+0.77
$Ag^+ + \bar{e} \rightleftharpoons Ag$	+0.80
$Br_{2\,(aq)} + 2\bar{e} \rightleftharpoons 2Br^-$	+1.09
$O_2 + 4H+ + 4\bar{e} \rightleftharpoons 2H_2O$	+1.23
$MnO_2 + 4H+ + 2\bar{e} \rightleftharpoons Mn^{2+} + 2H_2O$	+1.28
$Cr_2O_{72-} + 14H+ + 6\bar{e} \rightleftharpoons 2Cr^{3+} + 7H_2O$	+1.33
$Cl_2\,(g) + 2\bar{e} \rightleftharpoons 2Cl^-$	+1.36
$2ClO_3 + 12H+ + 5\bar{e} \rightleftharpoons Cl_2 + 6H_2O$	+1.47
$8H^+ + MnO_4^- + 5\bar{e} \rightleftharpoons Mn^{2+} + 4H_2O$	+1.49
$PbO_2 + SO_4^{-2} + 4H^+ + 4\bar{e} \rightleftharpoons PbSO_4 + 2H_2O$	+1.69
$H_2O_2 + 2H+ + 2\bar{e} \rightleftharpoons 2H_2O$	+1.7
$S_2O_3^{-2} + 2\bar{e} \rightleftharpoons 2SO_4^{-2}$	+2.00
$F_2 + 2\bar{e} \rightleftharpoons 2F^-$	+2.87

Some Important Points w.r.t the Table

→ In moving down to top, reactivity increases because E°_{red} decreases, So they will oxidize when they are combine with SHE and hydrogen will reduce.

→ In moving top to down, reactivity decreases because E°_{red} increases. So, they will reduce when they are combine with SHE and hydrogen will oxidize.

→ In moving down to top E°_{red} decreases, So they will easily dissolve in water and also easily corrode.

→ In moving top to down, we see that there are good oxidizing agents.

→ In moving down to top, we see that there are good reducing agents

Determination of Cell Potential

Reduction takes place in the half-cell having greater value of reduction potential. Oxidation takes place in the half-cell having the smaller value of reduction potential.

Example. 12.10

Calculate E°_{Cell} for Zn-Cu cell and write cell reactions. Show direction of é flow.

Half Cell reaction	Reduction potential
i- $Zn^{+2}_{(aq)} + 2e's \rightarrow Zn_{(s)}$	-0.76 V
ii- $Cu^{+2}_{(aq)} + 2e's \rightarrow Cu_{(s)}$	+0.34 V

Data shows that the E°_{red} of first is less. Now reverse the first eq. and add it to the second eq. to get cell reaction.

$$Zn_{(s)} \longrightarrow Zn^{+2}_{(aq)} + 2e's \quad \text{(Oxidation half-reaction)}$$

$$Cu^{+2}_{(aq)} + 2e's \longrightarrow Cu_{(s)} \quad \text{(Reduction half-reaction)}$$

$$Zn_{(s)} + Cu^{+2}_{(aq)} \longrightarrow Cu_{(s)} + Zn^{+2}_{(aq)} \quad \text{(Cell reaction)}$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = E^\circ_{Cu} - E^\circ_{Zn}$$

$$= +0.34 - (-0.76)$$

$$E^\circ_{cell} = +1.10\ V$$

e's will flow from anode to cathode i.e from Zn electrode to Cu electrode.

Example: 12.11

The standard reduction potentials for the following reactions are;

$$Ni^{+2}_{(aq)} + 2e's \longrightarrow Ni_{(s)} \quad E^\circ = -0.25V$$

$$Mg^{+2}_{(aq)} + 2e's \longrightarrow Mg_{(s)} \quad E^\circ = -2.38V$$

Calculate E°_{cell} for Ni-Mg cell, write cell reactions, show direction of e' flow & identify the anode of the cell.

Data shows that E°_{red} of second is less. Now reverse the second eq. and add

it to the first eq. to get the cell reaction.

$$Mg_{(s)} \longrightarrow Mg^{+2}_{(aq)} + 2e's \quad \text{(Anode reaction)}$$

$$Ni^{+2}_{(aq)} + 2e's \longrightarrow Ni_{(s)} \quad \text{(Cathode reaction)}$$

$$Mg_{(s)} + Ni^{+2}_{(aq)} \longrightarrow Mg^{+2}_{(aq)} + Ni_{(s)} \quad \text{(Cell reaction)}$$

Thus Mg will act as anode and Ni as cathode, e's will flow from Mg to Ni.

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{Anode}$$

$$E^\circ_{cell} = E^\circ_{Ni} - E^\circ_{Mg}$$
$$= -0.25 - (-2.38)$$
$$= 2.13\,V$$

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Self Check Exercise 12.7

The E°_{red} for the following half-reactions are;

$$Cu^{+2}_{(aq)} + 2e's \longrightarrow Cu_{(s)} \quad E^\circ = +0.34\,V$$

$$Cl_{2(g)} + 2e's \longrightarrow 2Cl^-_{(aq)} \quad E^\circ = +1.36\,V$$

Calculate E°_{cell} for Cu-Cl_2 cell, write cell reactions, identify cathode & show the direction of e' flow.

Data shows that the E°_{red} is less of the first eq. Now reverse the first eq. and add it to the second eq. to get the cell reaction. As, E°_{red} of Cl_2

half-cell is greater than Cu half-cell. So reduction reaction will occur in Cl_2 half-cell and oxidation in the Cu half-cell.

$$Cu_{(s)} \longrightarrow Cu^{+2}_{(aq)} + 2e's \quad \text{(Oxidation half reaction)}$$

$$Cl_{2(g)} + 2e's \longrightarrow 2Cl^-_{(aq)} \quad \text{(Reduction half reaction)}$$

$$Cu_{(s)} + Cl_{2(g)} \longrightarrow Cu^{+2}_{(aq)} + 2Cl^-_{(aq)} \quad \text{(Cell reaction)}$$

Feasibility of a Chemical Reaction

The sign of E°_{cell} value can give information about the spontaneity of a chemical reaction.

→ If E°_{cell} value is **positive**, the reaction occurs is **spontaneous** or **feasible**.

→ If E°_{cell} value is **negative**, the reaction occurs is **non-spontaneous** or **non-feasible**.

Example. 12.12 :-

Is the following reaction feasible ?

$$Sn + Fe^{+2} \longrightarrow Sn^{+2} + Fe$$

$$E^\circ_{Sn} = -0.14\,V, \quad E^\circ_{Fe} = -0.44\,V$$

Reduction

$$Sn^\circ + Fe^{+2} \longrightarrow Sn^{+2} + Fe^\circ$$

Oxidation

Sn is acting as anode and Fe as cathode. The above reaction consists of the following two half-cell reactions.

$Sn \longrightarrow Sn^{+2} + 2e's$ (Oxidation half reaction)

$Fe^{+2} + 2e's \longrightarrow Fe$ (Reduction half reaction)

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$= -0.44 - (-0.14)$

$= -0.30\ V$

As, E°_{cell} is negative, therefore the given reaction is not feasible. However reverse reaction would be spontaneous.

Self Check Exercise 12.8

Using emf data, explain the following,

1. Can Fe displace Cu from a soln of Copper (II) Sulphate.

$Fe + CuSO_4 \longrightarrow FeSO_4 + Cu$

$Fe + Cu^{+2} \longrightarrow Fe^{+2} + Cu$

In this Rxn, Fe is loosing e's to Cu^{+2} is gaining e's, Thus Fe is acting as anode, Cu as cathode.

$Fe \longrightarrow Fe^{+2} + 2e's$ (Oxidation half reaction)

$Cu^{+2} + 2e's \longrightarrow Cu$ (Reduction half reaction)

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$E^\circ_{cell} = E^\circ_{Cu} - E^\circ_{Fe}$

$= +0.34 - (-0.44)$

$= +0.78\ V$

Since, E°_{cell} is positive therefore the given reaction is feasible. Thus, Fe can displace Cu from a soln of $CuSO_4$.

2- Can Iodine displace Bromine from aq. soln of potassium bromide ?

$$I_2 + 2KBr \longrightarrow 2KI + Br_2$$
$$I_2 + 2Br^{-1} \longrightarrow 2I^{-1} + Br_2$$

Br^{-1} is loosing e's & I_2 is gaining e's. Bromine act as anode & Iodine act as cathode.

$$2Br^{-1} \longrightarrow Br_2 + 2e's \quad \text{(Oxidation half reaction)}$$
$$I_2 + 2e's \longrightarrow 2I^{-1} \quad \text{(reduction half reaction)}$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = E^\circ_{I} - E^\circ_{Br}$$
$$= +0.54 - (+1.08)$$
$$= -0.55\,V$$

Since, E°_{cell} is negative hence the given reaction is not feasible. Thus, iodine cannot displace bromine from aq. soln of potassium bromide.

Electrochemical Series

Series of elements in which elements are arranged by increasing order of their E°_{red} is called electrochemical series.

Applications of Electrochemical Series :-

1- Prediction of Feasibility of a reaction :-

If cell potential is ⊕ve, reaction is feasible. If it's ⊖ve, reaction is not feasible.

2- Calculation of Voltage of Cell :-

With the help of electrochemical series, voltage of the cell can be calculated.

3- Comparision metal acts Anode or Cathode :-

Element having low E°_{red} will oxidize and act as anode and element having high value of E°_{red} will reduce and act as cathode e.g, Zn act as anode and Cu act as cathode.

4- Reactivity :-

Elements having low E°_{red} will more reactive and vice versa.

Example. 12.13 :-

Predict a replacement reaction will occur or not.

a) Mg ribbon is in a soln of silver nitrate.

Mg is above Ag. Thus, Mg will displace Ag^+.

$$Mg + AgNO_3 \longrightarrow MgNO_3 + Ag$$

b) A small piece of Ca is added to a beaker of water.

Ca is higher in activity series than hydrogen. Hence, it will displace hydrogen from water.

$$Ca + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$$

c) A copper wire is dipped in 1M HCl.

Copper is below in activity series than hydrogen, hence it cannot displace hydrogen from HCl.

Self Check Exercise 12.9

Predict whether a reaction occurs or not.

a) An iron nail is placed in 1M HCl.

Iron is higher in activity series than hydrogen. Hence, it will displace hydrogen from HCl. Thus, iron is oxidized and H^+ ion is reduced.

$$2Fe + 6HCl \longrightarrow 2FeCl_3 + 3H_2$$

b) Lead (II) oxide is heated with powdered zinc.

Zn is higher in activity series than lead. Hence, it will displace lead from PbO. Thus, Zn is oxidized & Pb^{+2} is reduced.

$$Zn + PbO \longrightarrow ZnO + Pb$$

c) Nickel wire is placed into a soln of silver nitrate.

Nickel is higher in activity series than silver. Hence, it will displace silver from silver nitrate. Thus nickel is oxidized & silver is reduced.

$$Ni + 2AgNO_3 \longrightarrow Ni(NO_3)_2 + 2Ag$$

Electro-chemical Cells

A cell which convert electrical energy into chemical energy and vice versa are called **electro-chemical cells.**

Types :-

1- Galvanic cell
2- Electrolytic cell

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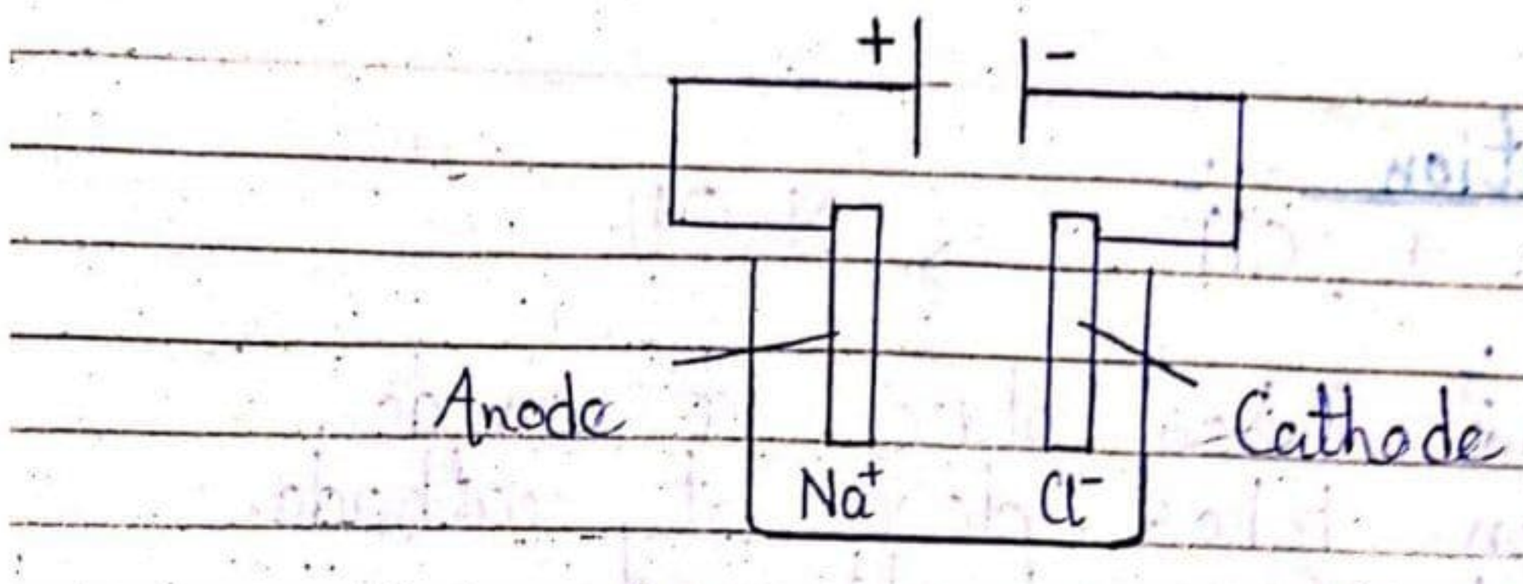
Electrolytic Cell

Cell which converts electrical energy into chemical energy is called electrolytic cell.

For example :

1- **Down cell :-**
It is used when salt is present in molten state.

2- **Nelson cell :-**
It is used when salt is present in aqueous form
e.g, Molten form.



At anode :- $2Cl^- \longrightarrow Cl_2 + 2e's$

At cathode :- $2Na^+ + 2e's \longrightarrow 2Na$

Over all Reaction :-

$2NaCl \longrightarrow 2Na + Cl_2$

Results :-

1. Cl_2 is obtained at anode.
2. Na is obtained at cathode.
3. Down cell is used in this process.
4. Oxidation is occur at anode.
5. Reduction is occur at cathode.

e.g, Nelson cell (Aqueous form)

$NaCl + H_2O \longrightarrow$ Brine

$NaCl \rightleftharpoons Na^+ + Cl^-$

$H_2O \rightleftharpoons H^+ + OH^-$

At anode :- $2Cl^- \longrightarrow Cl_2 + 2e's$

At cathode :- $2H^+ + 2e's \longrightarrow H_2$

OR

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

In solution :-

$$Na^+ + OH^- \longrightarrow NaOH$$

Result :-

1- Oxidation takes place at anode.
2- Reduction takes place at cathode.
3- At anode, Cl_2 is obtained.
4- At cathode, H_2 is obtained.
5- Nelson cell is used in this process.

First Law of Faraday

It states that; "The amount of chemical reaction taking place at an electrode is directly proportional to the quantity of charge that flows through the electrode during the process."

Second Law of Faraday

It states that; "If same quantity of charge is passed through different electrolytic cells, the chemical change in each case is proportional to the gram equivalent mass of each parent species."

Equivalent weight

The amount of a substance produced during electrolysis by passing one Faraday of electricity is called its **equivalent weight.**

Example. 12.14 :-

In the electrolysis of molten $ZnCl_2$, how much Zn can be deposited at the cathode by passage of 0.01 A of 1 hr ?

Time = 1 hr = 3600s

Current = 0.01 A

$$\text{Current} = \frac{\text{Charge}}{\text{Time (s)}}$$

$$\text{Charge} = \text{Current} \times \text{Time}$$

$$= 0.01\ A \times 3600\ s$$

$$= 36\ C$$

As,

$$96500\ C = 1\ F$$

$$1\ C = \frac{1}{96500}\ F$$

$$36\ C = \frac{36}{96500}\ F = 3.73 \times 10^{-4}\ F$$

In the electrolysis of molten $ZnCl_2$, the cathode reaction is

$$Zn^{+2} + 2e's \longrightarrow Zn$$

It shows that for every 2 moles of e's, 1 mole of Zn is produced.

Since, 1F = 1 mole of e'

$\therefore$ 2F = 2 mole of e's = 1 mole of Zn

So,

2F charge produces Zn = 1 mole

3.73×10^{-4} F " " $= \frac{1 \times 3.73 \times 10^{-4}}{2}$

$= 1.86 \times 10^{-4}$ moles

Atomic mass of Zn = 63.37 g/mol

So, to 1 mole of Zn = 63.37 g

1.86×10^{-4} moles $= 63.37 \times 1.86 \times 10^{-4}$

$= 0.012$ g

Example. 12.15 :-

A constant current was passed through the soln of $AuCl_4^-$ ions b/w gold electrodes. After a period of 10 mins, the cathode increases its weight by 1.314 g.

(i) How much charge was passed ?

(ii) What was the amount of current ?

(iii) What Vol. of Cl_2 was collected at anode at 1 atm and 25°C.

Mass of Au produced = 1.314 g

Atomic mass of Au = 179 g/mol

No. of moles of Au = $\frac{1.314 \text{ g}}{179 \text{ g/mol}} = 6.67 \times 10^{-3}$ moles

The reaction at cathode is the reduction of Au (III) to Au metal.

$AuCl_4^- + 3e's \longrightarrow Au + 4Cl^-$

It means that for every 3 Faraday of electricity used up, 1 mole of Au is produced.

i/- Charge = 6.67×10^{-3} moles Au X $\frac{3 \text{ Faraday}}{\text{1 moles of Au}}$

$= 2 \times 10^{-2}$ Faraday

ii/- $\text{Current} = \frac{\text{Charge}}{\text{Time (s)}}$

Time = 10 min = $10 \times 60 = 600$ s

$\text{Current} = \frac{(2 \times 10^{-2})(96500)}{600}$

$= 3.22$ A

iii/- The reaction at anode is oxidation of Cl^- ions.

$2Cl^- \longrightarrow Cl_2 + 2e$

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For every 2 Faraday of electricity 1 mole of Cl_2 was produced.

For every 1 Faraday of electricity = 1/2 moles of Cl_2 was produced.

For 2×10^{-2} Faraday of electricity = $1/2 \times 2 \times 10^{-2}$ moles of Cl_2 was produced.

$= 1 \times 10^{-2}$ moles of Cl_2 was produced

By Ideal gas eq.,

$PV = nRT$

$V = \frac{nRT}{P}$

$= \frac{1 \times 10^{-2} \times 0.08205 \times 298}{1}$

$V = 0.245 \text{ dm}^3$

Self Check Exercise 12.10 :-

1/- Bauxite ore is used for the commerical preparation of Al. For this purpose, bauxite ore is first purified to produced pure alumina, Al_2O_3. Alumina is then electrolyzed.

$$2Al_2O_{3(s)} \longrightarrow 4Al_{(s)} + 3O_{2(g)}$$

Calculate mass of Al that collects at the cathode and vol. of oxygen that collects at anode when Al_2O_3 is electrolyzed for 10 hrs with a 15 A of current at 1 atm and 25°C.

Time = 10 hrs = 10 X 60 X 60 = 36000 s

Current = 15 A.

Current = $\frac{\text{Charge}}{\text{Time (s)}}$

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= Charge = Current X Time

= 15 A X 36000 s

= 540000 C

As, 96500 C = 1 F

540000 C = $\frac{1\text{ F} \times 540000}{96500}$

= 5.596 F

In the electrolysis of molten bauxite, the cathode reaction is;

$$Al^{+3} + 3e's \longrightarrow Al$$

It shows that for every 3 moles of e's, 1 mole of Al is produced.

Self Check Exercise 12.10 :-

1/- Bauxite ore is used for the commerical preparation of Al. For this purpose, bauxite ore is first purified to produced pure alumina, Al_2O_3. Alumina is then electrolyzed.

$$2Al_2O_{3(s)} \longrightarrow 4Al_{(s)} + 3O_{2(g)}$$

Calculate mass of Al that collects at the cathode and vol. of oxygen that collects at anode when Al_2O_3 is electrolyzed for 10 hrs with a 15 A of current at 1 atm and 25°C.

Time = 10 hrs = 10 X 60 X 60 = 36000 s

Current = 15 A.

Current = $\frac{\text{Charge}}{\text{Time (s)}}$

= Charge = Current X Time

= 15 A X 36000 s

= 540000 C

As, 96500 C = 1 F

540000 C = $\frac{1\text{ F} \times 540000}{96500}$

= 5.596 F

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In the electrolysis of molten bauxite, the cathode reaction is;

$$Al^{+3} + 3e's \longrightarrow Al$$

It shows that for every 3 moles of e's, 1 mole of Al is produced.

Since, 1 F = 1 mole of e⁻
∴ 3F = 3 mole of e⁻ = 1 mole of Al
So,
3F charge produces Al = 1 mole
5.596 F " = $\frac{1 \times 5.596}{3}$
= 1.865 moles
Atomic mass of Al = 27 g/mol
So, 1 mole of Al = 27 g
1.865 moles " = 27 × 1.865
= 50.355 g
The reaction at anode is oxidation of O^{-2} ions.

$$2O^{-2} \longrightarrow O_2 + 4e^-$$

It shows that for every 4 moles ..... of e's, 1 mole of O_2 is produced.
Since, 1 F = 1 mole of e⁻
4F = 4 moles of e⁻ = 1 mole of O_2
So,
4F electricity produce O_2 = 1 mole
5.596 F " " = $\frac{1 \times 5.596}{4}$
= 1.399 moles of O_2

By Ideal gas eq.,

$$PV = nRT$$
$$V = \frac{nRT}{P}$$
$$= \frac{(1.399)(0.0821)(298)}{1}$$
$$V = 34.229 \text{ dm}^3$$

2/- Which of the following compounds will give more mass of metal, when 15 A of current is passed through molten mass of these salts for 1 hr.

(a) NaCl (b) $CaCl_2$

Time = 1 hr = 3600 s

Current = 15 A

$$\text{Current} = \frac{\text{Charge}}{\text{Time (s)}}$$

$$\text{Charge} = \text{Current} \times \text{Time (s)}$$

$$= 15\,A \times 3600\,s$$

$$= 54000\,C$$

As, 96500 C = 1 F

$$54000\,C = \frac{1}{96500} \times 54000$$

$$= 0.5596\,F$$

(a) - NaCl

In the electrolysis of molten NaCl, the cathode reaction is;

$$Na^{+1} + 1e' \longrightarrow Na$$

It shows that for every 1 mole of e', 1 mole of Na is produced.

Since,

1 F = 1 mole of e' = 1 mole of Na

So,

1 F' charge produces Na = 1 mole

0.5596 F " " = 1 X 0.5596

= 0.5596 moles

Atomic mass of Na = 23 g/mol

So,

1 mole of Na = 23g

0.5596 moles of Na = 23 X 0.5596

= 12.871 g

(b) $CaCl_2$

In the electrolysis of molten $CaCl_2$, the cathode reaction is;

$Ca^{+2} + 2e's \longrightarrow Ca$

It shows that for every 2 moles of e's, 1 mole of Ca is produced.

Since 1 F = 1 mole of e'

∴ 2F = 2 mole of e' = 1 mole of Ca

So,

2F charge produces Ca = 1 mole

0.5596 F " " = $\frac{1 \times 0.5596}{2}$

= 0.2798 moles

Atomic mass of Ca = 40 g/mol

So,

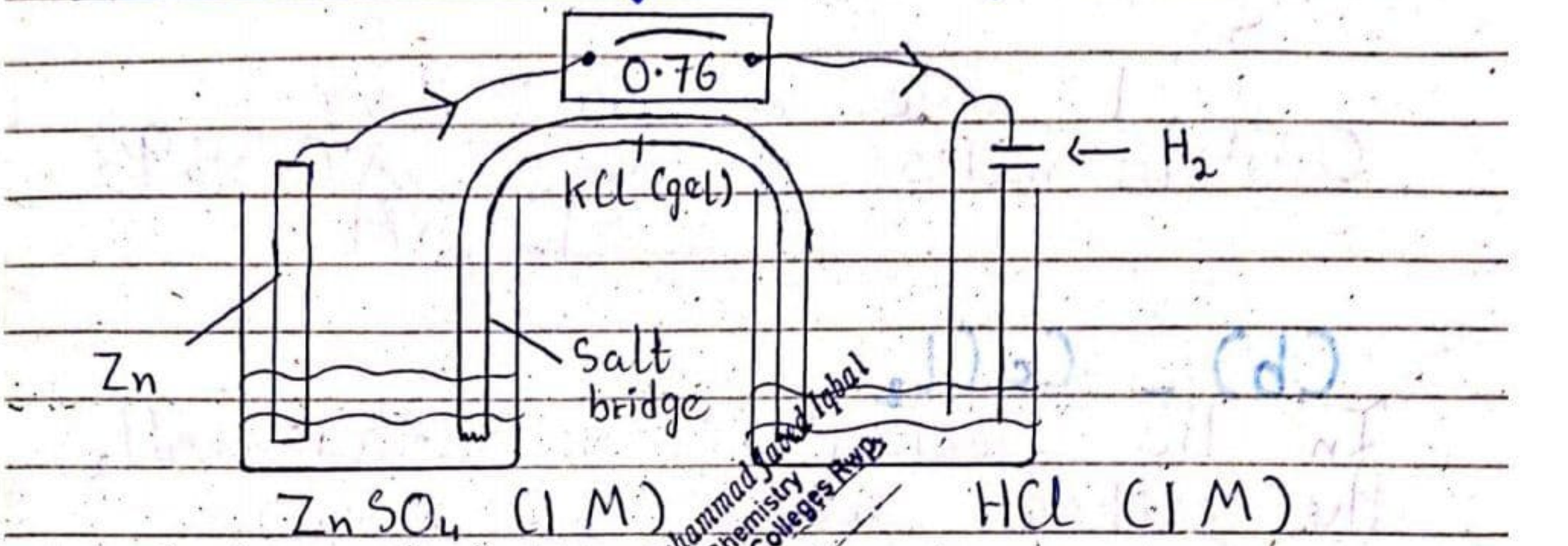
1 mole of Ca = 40g

0.2798 moles of Ca = 40 X 0.2798

= 11.192 g

Hence NaCl will produce more mass of Na.

Determination of E°_{red} of Zn



$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$

At anode :-

$$Zn \longrightarrow Zn^{+2} + 2e's$$

At cathode :-

$$2H^+ + 2e^- \longrightarrow H_2$$

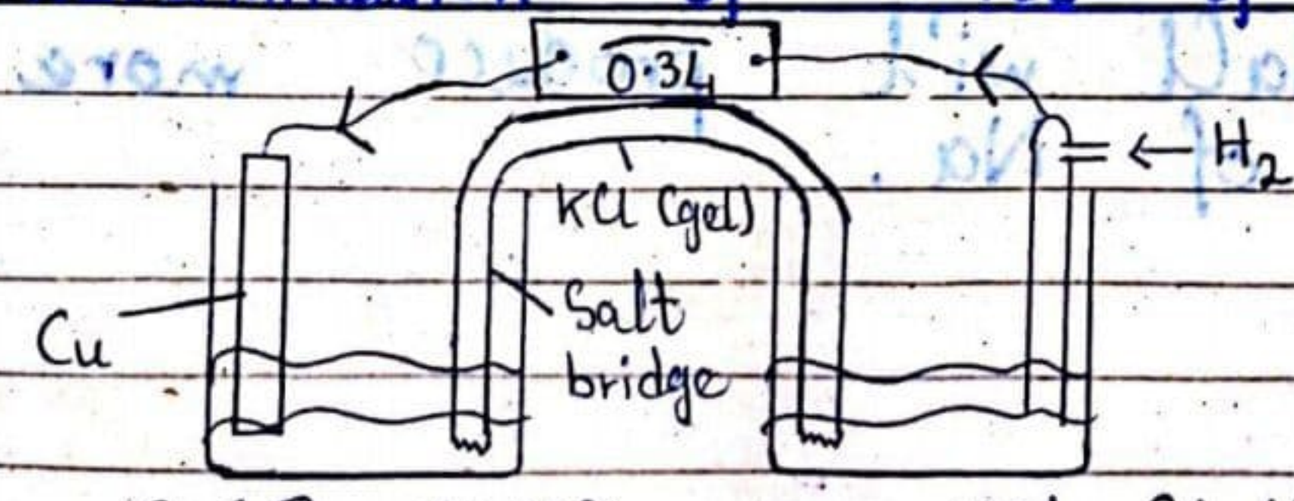
$$0.76 = E^\circ_{Zn/Zn^{+2}} + E^\circ_{H^+/H_2}$$

$$0.76 = E^\circ_{Zn/Zn^{+2}} + 0.00$$

$$E^\circ_{Zn/Zn^{+2}} = 0.76$$

$$E^\circ_{Zn^{+2}/Zn} = -0.76\ V$$

Determination of E°_{red} of Cu



$$E^\circ_{cell} = E^\circ_{ox} + E^\circ_{red}$$

At anode :

$$H_2 \longrightarrow 2H^+ + 2e's$$

At cathode :

$$Cu^{+2} + 2e's \longrightarrow Cu$$

$$0.34 = E^\circ_{H_2/H^+} + E^\circ_{Cu^{+2}/Cu}$$

$$0.34 = 0.00 + E^\circ_{Cu^{+2}/Cu}$$

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

Alkaline Battery : (Dry Cell) (Cell in Remote)

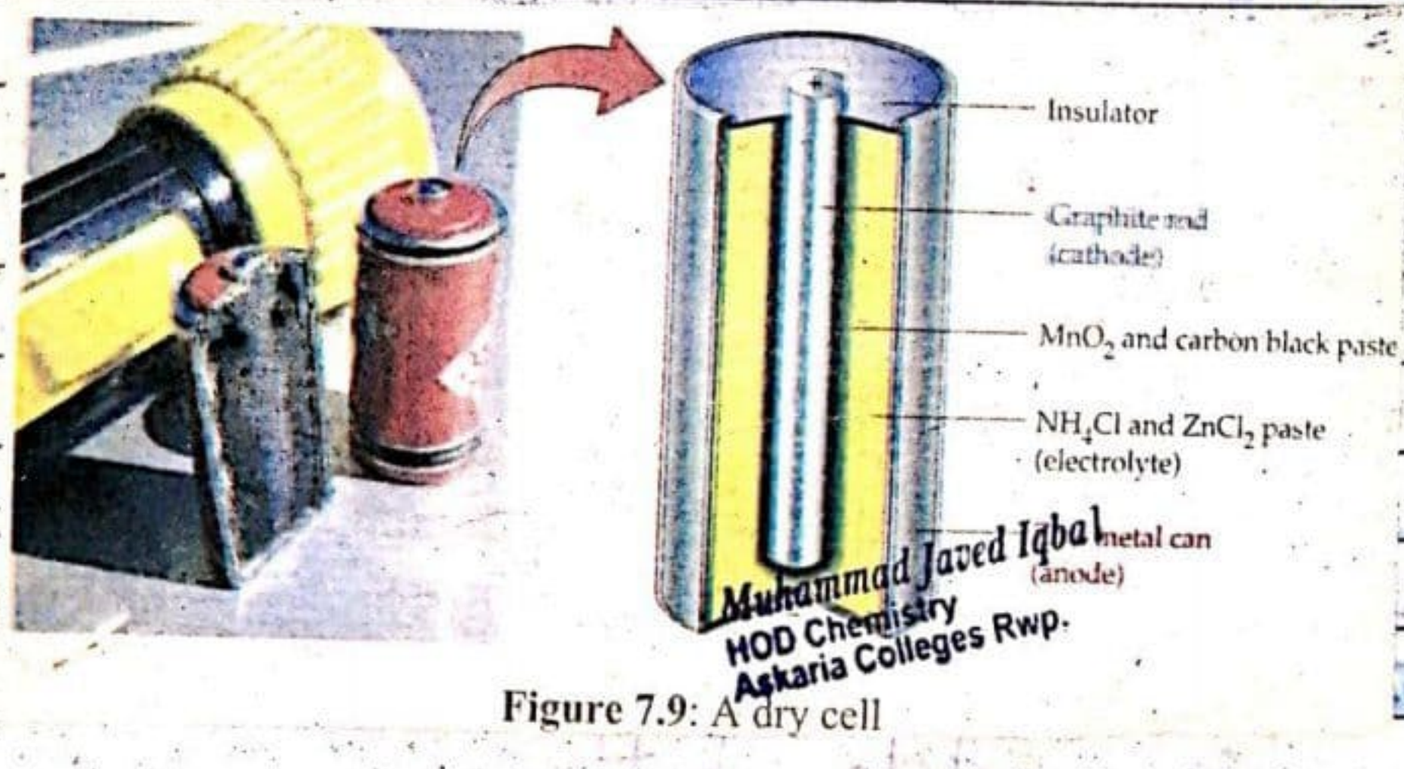


Figure 7.9: A dry cell

Type of cell : Primary cell i.e Non-rechargeable
Cell potential : 1.5 V
Electrolyte : $KOH \rightleftharpoons K^+ + OH^-$
Anode : Zn
Cathode : MnO_2
Discharging :

At anode :-

$$Zn \longrightarrow Zn^{+2} + 2e's$$

$$Zn^{+2} + 2OH^- \longrightarrow Zn(OH)_2$$

At cathode :-

$$2MnO_2 + 2e's + H_2O \longrightarrow Mn_2O_3 + 2OH^-$$

Nickel Cadimum Cell (NICAD) (Mobile Battery)

Type of cell :- Secondary cell i.e Rechargeable
Cell potential :- 1.4 V / 1.5V
Electrolyte :- $KOH \rightleftharpoons K^+ + OH^-$
Anode :- Cd
Cathode :- NiO_2

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Discharging :-

At anode :-

$$Cd \longrightarrow Cd^{+2} + 2e's$$

$$Cd^{+2} + 2OH \longrightarrow Cd(OH)_2$$

At cathode :-

$$NiO_2 + 2e's + 2H_2O \longrightarrow Ni(OH)_2 + 2OH$$

Uses :-

1- Use in mobile batteries.
2- Use in dry cells.

Lead Accumulator : (UPS : Battery)

Type of cell : Secondary cell i.e Rechargeable
Cell potential : 6 cells = 6X2 = 12 volts

Electrolyte : 30% H_2SO_4 having density 1.25 g/cm^3

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^-$$

Anode : Pb act as anode.

Cathode : PbO_2 act as cathode.

Discharging :

At anode :-

$$Pb \longrightarrow Pb^{+2} + 2e's$$

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

At cathode :-

$$PbO_2 + 2e' + H^+ \longrightarrow Pb^{+2} + H_2O$$

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

Recharging :

Cathode :-

$$PbSO_4 \rightleftharpoons Pb^{+2} + SO_4^{-2}$$

$$Pb^{+2} + 2e' \longrightarrow Pb$$

Anode :-

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

$$Pb^{+2} + H_2O \longrightarrow PbO_2 + 2e' + H^+$$

Solar Cell :

Devices that convert solar energy directly into electrical energy are called **solar cells**.

Construction :-

→ A basic solar cell consists of two layers of different types of semi-conductive materials.
→ These materials are joined together to form a junction.

Working :-

→ When one layer is exposed to light, many e's gain enough energy.
→ These e's break away from their parent atoms.
→ Such e's cross the junction.
→ Thus ⊖ve ions are formed on one side of the junction and ⊕ve ions on the other side.
→ Hence a potential difference is developed which causes e's to flow.

Voltage :-

Semi-conductor made of silicon gives **0.5 V** per cell.

Fuel Cell

Type of cell :- Secondary cell i.e Rechargeable
Cell potential :- 0.9 V
Electrolyte :- $KOH \rightleftharpoons K^+ + OH^-$
Discharging :

At anode :-

$$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$$

At cathode :-

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

Electrolyte : 30% H_2SO_4 having density 1.25 g/cm^3

$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^-$$

Anode : Pb act as anode.

Cathode : PbO_2 act as cathode.

Discharging :

At anode :-

$$Pb \longrightarrow Pb^{+2} + 2e's$$

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

At cathode :-

$$PbO_2 + 2e' + H^+ \longrightarrow Pb^{+2} + H_2O$$

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

Recharging :

Cathode :-

$$PbSO_4 \rightleftharpoons Pb^{+2} + SO_4^{-2}$$

$$Pb^{+2} + 2e' \longrightarrow Pb$$

Anode :-

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

$$Pb^{+2} + H_2O \longrightarrow PbO_2 + 2e' + H^+$$

Solar Cell

Devices that convert solar energy directly into electrical energy are called **solar cells**.

Construction :

Cell reaction:

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Corrosion

Chemical decay of metal due to sourrounding medium is called **corrosion.**

Example : Rusting of Iron

Rusting of iron is an electrochemical process. One of the half-reaction in rusting is;

$$Fe^{+2} + 2e' \longrightarrow Fe \qquad E^\circ = -0.44V.$$

Reverse of this reaction is.

$$Fe \longrightarrow Fe^{+2} + 2e' \qquad E^\circ = +0.44V$$

The Fe is oxidized to Fe^{+2} which is further oxidized to Fe^{+3}. The Fe^{+3} form various insoluble hydrated oxides. These are deposited as the red-brown precipitate known as **rust**. The process of corrision occur when metal is in contact with water. A water droplet present on the surface of iron prepares an electrolytic soln. The metal comes in contact with electrolyte and electrochemical reaction starts.

Reduction half reaction :

$$O_2 + H^+ + e' \longrightarrow 2H_2O \qquad E^\circ = +1.23V$$

This is more ⊕ve than Fe^{+2} - Fe couple, so it can derive the following reaction;

Oxidation half reaction :

$$Fe \rightarrow Fe^{+2} + 2e's \text{ (oxidation reaction)}$$

The E°_{cell} of the combined half-reactions is;

$$E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{Anode}$$

$$E^\circ_{cell} = +1.23 - (-0.44)$$

$$E^\circ_{cell} = +1.67V$$

Therefore, there is a strong tendency towards oxidation. Oxidation of iron occurs in an interior region of the droplet whereas reduction of O_2 occurs near the air droplet interface.

Prevention of Corrosion :

Corrosion can be prevented by the following ways;

1- Painting :

Corrosion of metal can be prevented by painting the metal. Thus, it does not come in contact with oxygen or mojsture. Painting also provides visual appeal.

2- Galvanization :

Objects made of iron are dipped in molten Zn and dried. This process is known as **galvanization**.

If a scratch penetrates the Zn layer, iron is still protected because Zn

oxidizes preferentially. It is because Zn is more active metal than iron. Any oxidation that occurs dissolves Zn rather than Fe. Thus Zn acts as sacrifical coating on Fe. This is also known as **sacrifical corrosion**.

$$Fe^{+2} + 2e' \rightleftharpoons Fe \quad E^\circ = +0.44V$$

$$Zn^{+2} + 2e' \rightleftharpoons Zn \quad E^\circ = +0.76V$$

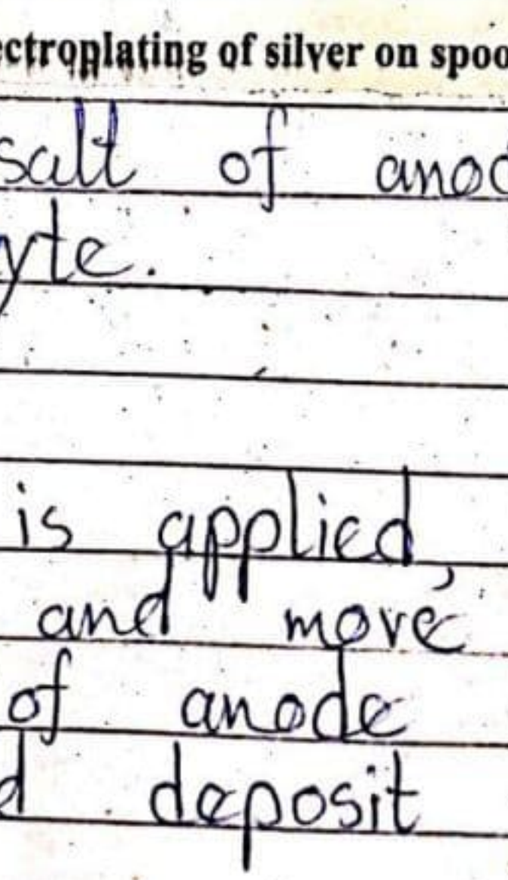
3- Electroplating :

Construction :

Anode : The article to be plated is used as cathode.

Cathode : The metal, which is to be deposited on the article, is used as anode.

Electrolyte : Water soluble salt of anode metal is used as electrolyte.



Electroplating of silver on spoon

Working :

When electrical potential is applied, e's are lost from anode and move into cathode. Metal ions of anode in soln gain the e's and deposit on the article.

Example 1 :- In silver plating, silver rod is used as anode and sodium cyanide is used as electrolyte. Cyanide ions form a complex with silver ions.

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$$

At anode :- (Oxidation)

$$Ag \longrightarrow Ag^+ + e'$$

At cathode :- (Reduction)

$$[Ag(CN)_2]^- + e' \longrightarrow Ag + 2CN^-$$

Example 2 :-

Steel objects are electroplated with aluminum or chromium. These metals form a thin protective coating of oxide which inhibits further corrosion. The potential of the passive oxide coating is like a noble metal.