* Electrochemistry :- It is the branch of chemistry that deals with the study of the interconversion of electrical energy and chemical energy that takes place through oxidation reduction (redox) reactions.

- In oxidation, a species loses one or more electrons resulting in an increase in the oxidation number.

$$M \rightleftharpoons M^{n+} + ne^- \quad \text{------ oxidation}$$

- In reduction, a species gains one or more electrons resulting in a decrease in the oxidation number.

$$M^{n+} + ne^- \rightleftharpoons M \quad \text{------ reduction}$$

Redox reaction : It is a reaction that involves both oxidation and reduction.

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu.$$

* Electrochemical cells :-

An electrochemical cell is a device which converts chemical energy into electrical energy or electrical energy into chemical energy.

Thus, there are two types of electrochemical cells –

1) Galvanic /Voltaic cell :- the one which converts chemical energy into electrical energy.
Eg :- Dry cell (primary reversible cell), lead storage battery (secondary cells), nickel cadmium cell, Daniell Cell.

2) Electrolytic cell :- The one which converts electrical energy into chemical energy. Electrical energy is supplied from an external source so as to bring about a non-spontaneous chemical change. Eg. Electrolysis of molten NaCl, molten HCl, aqueous KOH

* Electromotive force (EMF) of the cell :-
Current cannot flow from one point to another unless there is a potential difference between the two points. Hence, flow of electrons from anode to cathode in a galvanic cell indicates that the two electrodes have different potentials.

(2-M) " The potential difference between the two electrodes of a galvanic cell which causes the flow of current from one (higher potential) electrode to the other (lower potential) is called as electromotive force (EMF) of the cell."

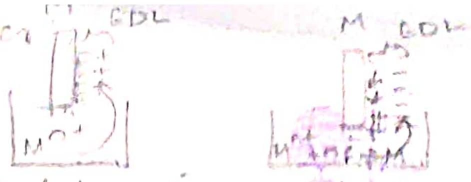
Emf of a cell is denoted by E_{cell}.

The Emf of a cell represents the driving force of a cell reaction, which is represented by the thermodynamic reaction,

$$\Delta G = -nFE$$

where, ΔG = free energy accompanying a cell reaction
n = no of electrons transfer during the cell

Formation of Electrical double layer gives rise to potential



Oxidation − $\bar{e}$. Reduction.

reaction.

F = Faraday.

released electrons accumulate on the surface, + ions attracted & form EDL at interface.

+ ions, develops a layer of + charge on the electrode surface which attracts − ions at interface.

* Electrode Potential :-

It is the measure of the tendency of a metal to lose or gain electrons when it is in contact with the solution of its own ions.

(2-M) * Single Electrode Potential :-

Single Electrod Potential is defined as "the potential developed at the interface between the metal and the solution, when it is in contact with a solution of its own ions."

* Standard Electrode Potential :-

Standard Electrode Potential is the electrode potential when the electrode is in contact with the solution of unit concentration at 298K. (If the electrode involves a gas then the gas at one atmospheric pressure).

* Electrochemical Series :-

The arrangement of elements in the increasi order of their standard electrode potential is known as electrochemical series.

Table :- Electrochemical Series.

M^{n+}/M	E° (Volts)
Li^+/Li	−3.05 (Anode)
K^+/K	−2.93
Ba^{2+}/Ba	−2.90
Ca^{2+}/Ca	−2.87
Na^+/Na	−2.71
Mg^{2+}/Mg	−2.37
Al^{3+}/Al	−1.66
Zn^{2+}/Zn	−0.76
Fe^{2+}/Fe	−0.44
Cd^{2+}/Cd	−0.40
Sn^{2+}/Sn	−0.14
Pb^{2+}/Pb	−0.13
H^+/H_2	0.00 (Reference)
Cu^{2+}/Cu	0.34
Ag^+/Ag	0.80
Hg^{2+}/Hg	0.85
Pt^{2+}/Pt	1.20
Au^{3+}/Au	1.38 (Cathode)

- A negative value indicates oxidation tendency & a positive value indicates reduction tendency with respect to hydrogen.
- Metals with lower electrode potential have the tendency to replace the metals with higher electrode potential from their solutions.

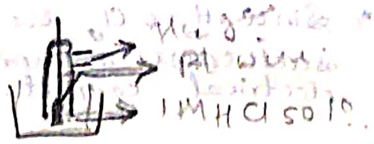
Types of Electrodes :-

Some of the important types of electrodes are :-

1. Metal - metal ion electrode :- where a metal is dipped in a solution containing its own ions.
   Eg :- Zn / Zn^{2+}, Cu / Cu^{2+}, Ag / Ag^{+}.

2. Gas electrode :- Gas is in contact with an inert metal dipped in an ionic solution of the gas molecules.
   Eg :- Hydrogen electrode, $(Pt / H_2 / H^{+})$.
   Chlorine electrode $(Pt / Cl_2 / Cl^{-})$.

3. Metal - metal salt ion electrode (Metal insoluble salt electrode) :- where a metal is in contact with a solution containing the anion of the salt.
   Eg :- Calomel electrode $(Hg / Hg_2Cl_2 / Cl^{-})$;
   (i.e., Hg is in contact $\bar{c}$ KCl solution saturated with Hg_2Cl_2.



Silver - Silver chloride electrode ($Ag / AgCl / Cl^-$).
Lead - Lead sulphate electrode ($Pb / PbSO_4 / SO_4^{2-}$).

4). Ion - selective electrode :- a membrane is in contact with an ionic solution.
Eg :- Glass electrode (exchanges H^+ ions with the solution).
various metal ion selective electrodes, which exchange metal ions with the solution.

(2-M)* Reference Electrodes :-
Reference electrodes are the electrodes with reference to those, the electrode potential of any other electrodes can be measured.
There are two types of reference electrodes -
1) Primary reference electrode - Eg :- Standard hydrogen electrode, SHE, whose potential is arbitrarily taken as zero at all T.
2) Secondary reference electrode - whose potential with respect to SHE are known.
Eg :- Calomel electrode, Ag - AgCl electrode.

Limitations of Standard hydrogen electrode :-
* Construction and working is difficult as it is involves maintaining the concentration at unity and keeping the pressure of gas uniformly at 1 atmosphere.
* Platinum is highly susceptible for poisoning by the impurities present in the gas.
* It cannot be used in the presence of oxidising agents.

(2-M) Secondary reference electrodes :-
To overcome the limitations of primary reference electrode i.e., SHE, there was a need to develop secondary reference electrodes.
The electrodes whose potential with

respect to SHE are known, are referred as Secondary reference electrodes. These can be easily set up.

Eg:- Calomel electrode, Ag - AgCl electrode.

* Calomel electrode :-

(5-M) Calomel electrode is a metal - metal salt ion electrode. It consists of mercury, mercurous chloride and a solution of KCl.

The calomel electrode consists of narrow inner and outer glass tubes.

The bottom of inner glass tube has a layer of mercury followed by a paste of Hg2Cl2.

A platinum wire is dipped into the mercury layer for electrical contact.

The outer glass tube is filled with KCl solution.

KCl solution of different concentration can be used (Molar, Deci molar or saturated)

A porous plug (salt bridge) is fitted at the bottom of outer glass tube.

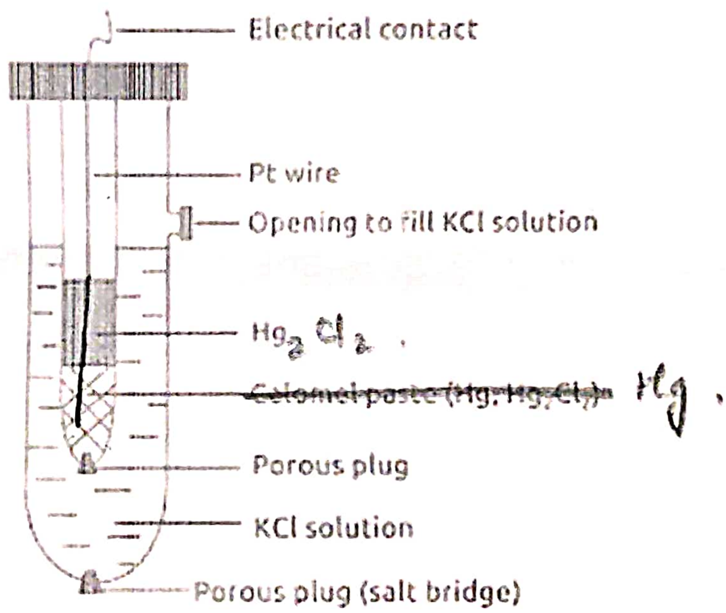
The calomel electrode is represented as , Hg|Hg2Cl2(s)|KCl(aq)

REFER FIGURE NEXT PAGE

Calomel electrode can be represented as, $Hg \mid Hg_2Cl_2 \mid Cl^-$.

Calomel electrode can act as anode or cathode depending on the nature of the other electrode of the cell.

When it acts as anode, the electrode reaction is


Electrical contact
Pt wire
Opening to fill KCl solution
Hg_2Cl_2
~~Calomel paste (Hg; Hg2Cl2)~~ Hg
Porous plug
KCl solution
Porous plug (salt bridge)

* SCE = Saturated Calomel electrode.

− if $\frac{O.S}{R.S}$, + if $\frac{R.S}{O.S}$ in Nernst Equation

Hg_2Cl_2 insoluble salt, so its conc is 1; [M] = [salt] = 1 when it is added to water it doesn't impart

$$2Hg \longrightarrow Hg_2^{2+} + 2e^-$$
$$Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_2$$
$$\overline{2Hg + 2Cl^- \longrightarrow Hg_2Cl_2 + 2e^-}$$

When it acts as cathode, electrode reaction is,

$$Hg_2^{2+} + 2e^- \longrightarrow 2Hg$$
$$Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^-$$
$$\overline{Hg_2Cl_2 + 2e^- \longrightarrow 2Hg + 2Cl^-}$$

Net reversible electrode reaction is,

$$Hg_2Cl_{2(s)} + 2e^- \rightleftharpoons 2Hg_{(l)} + 2Cl^-$$

Electrode potential is decided by the concentration of chloride ions and the electrode is reversible with chloride ions.

At 298 K, electrode potentials are as follows,

0.1 N KCl electrode	E = 0.334 V.
1 N KCl	E = 0.281 V.
Saturated KCl	E = 0.2422 V.

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

$K_c = \frac{[Hg]^2 [Cl^-]^2}{[Hg_2Cl_2]}$

$E = E^\circ - \frac{RT}{nF} \ln [Cl^-]^2$

$E = E^\circ - \frac{0.0591}{2} \log [Cl^-]^2$

Electrode potential may be represented by the Nernst equation as,

$E = E^\circ - 0.0591 \log [Cl^-]$

$n = 2$

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

Uses :-

(1-M)

1) It is used as a secondary reference electrode in the measurement of single electrode potential.

2) It is commonly used as reference electrode in all potentiometric determinations.

3) It is simple to construct.

* Determination of single electrode potential using SCE :-

(6-M)

Test electrode (Eg Zn / Zn^{2+}) is coupled with saturated calomel electrode, (SCE), Working:-

At anode: $Zn \rightarrow Zn^{2+} + 2e^-$

At cathode: $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$

$Zn + Hg_2Cl_2 \rightarrow Zn^{2+} + 2Hg + 2Cl^-$

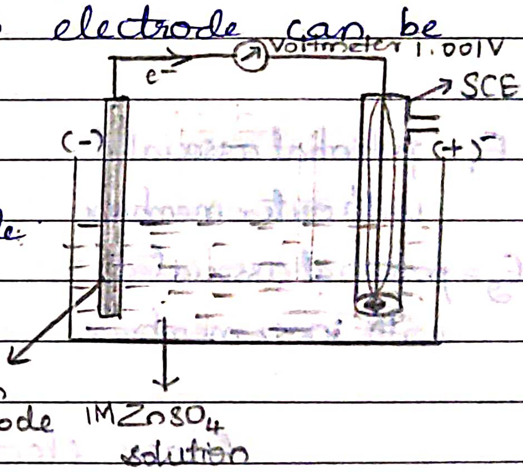
The cell representation is as follows,

$Zn_{(s)} | Zn^{2+} || Cl^- | Hg_2Cl_{2(s)} | Hg_{(l)}$

Emf of the so formed cell is determined experimentally by potentiometric method.

Emf of a cell is found to be 1.001 V.

$\therefore$ Electrode potential of Zn electrode can be calculated as follows,



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

$$E_{cell} = E_{calomel} - E_{Zn}$$

$$1.001 = 0.2422 - E_{Zn}$$

$$E_{Zn} = 0.2422 - 1.001$$

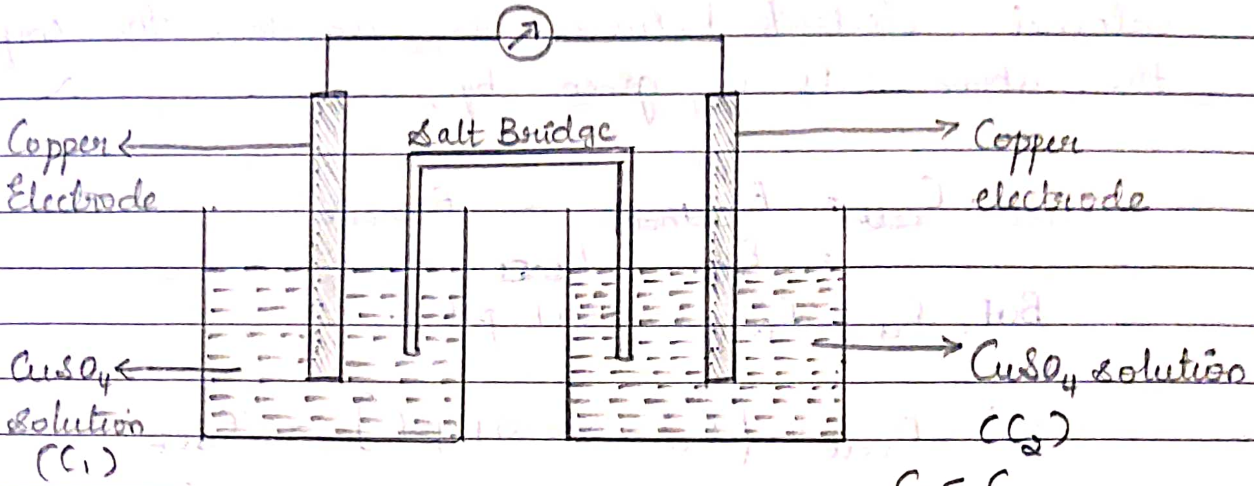
$$E_{Zn} = -0.76\ V.$$

6-M

* Concentration Cells :-

If two electrodes of the same metal are in contact with the solution of its own ions with different concentrations, they differ in their electrode potentials. The coupling of two such electrodes also constitutes a cell and gives rise to emf as the electrodes differ in their electrode potentials. Such cells which consist of two electrodes of the same substance in contact with solutions of different concentrations and the emf arises due to the difference in concentrations are known as Electrolyte Concentration Cells.

Two copper rods are dipped in Copper sulphate solutions of concentrations C_1 & C_2 respectively, where $C_1 < C_2$



$C_1 < C_2$

Cell may be represented as,

$Cu_{(s)} \mid CuSO_4\,(C_1) \parallel CuSO_4\,(C_2) \mid Cu_{(s)}$

At anode, $Cu_{(s)} \rightarrow Cu^{2+}_{(C_1)} + 2e^-$

At cathode, $Cu^{2+}_{(C_2)} + 2e^- \rightarrow Cu_{(s)}$

The emf of ~~the~~ above cell is,

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

$$E_{cell} = E^\circ_{Cu} + \frac{2.303RT}{nF}\log[Cu^{+2}]_{cathode} - \left[E^\circ_{Cu} + \frac{2.303RT}{nF}\log[Cu^{2+}]_{anode}\right]$$

$$= \cancel{E^\circ_{Cu}} + \frac{2.303RT}{nF}\log(C_2) - \cancel{E^\circ_{Cu}} - \frac{2.303RT}{nF}\log(C_1)$$

$$= \frac{2.303RT}{nF}\log\left(\frac{C_2}{C_1}\right)$$

$$E_{cell} = \frac{0.0591}{n}\log\left(\frac{C_2}{C_1}\right) \text{ at } 298\,K.$$

The following conclusions may be drawn from the above equation,

1) When the two solutions are of the same concentrations, $\log\frac{C_2}{C_1} = 0$, and hence no current flows.

2) When $C_2 > C_1$, $\log\frac{C_2}{C_1}$ is positive, & hence

PAGE
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E is positive.

Thus, the direction of the spontaneous reaction is from the more concentrated solution C_2 to less concentrated one C_1.

3) Higher the ratio $\frac{C_2}{C_1}$, higher is the cell potential value.

For eg:- if ratio $\frac{C_2}{C_1}$ is increased from 0.001 to 0.01 then, the voltage doubles, & from 0.001 to 0.1, then, voltage increases by three times.

* Numericals :-

Q. The emf of a concentration cell with 0.05M and 0.025 M $AgNO_3$ solution is,

June 2010

Sol:-

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

$C_2 = 0.05\,M$
$C_1 = 0.025\,M$
$n = 1$

$$= \frac{0.0591}{1} \log \frac{0.05}{0.025}$$

$$= 0.0591 \times \log 2.$$

$$= 0.0591 \times 0.3010$$

$$= 0.01779\ V.$$

$$= 0.0178\ V.$$

Q. Calculate the emf of copper concentration cell at 25°c, where the copper ions ratio in the cell is 10.

Sol:-

$$E_{cell} = \frac{0.0591}{n} \log \left(\frac{C_2}{C_1}\right)$$

$\frac{C_2}{C_1} = 10$
and $n = 2$.

$$= \frac{0.0591}{2} \log 10.$$

$$= 0.0295V.$$

$\log 10 = 1$

Q. Calculate the emf of the following concentration cell at 298 K.

$$Ag_{(s)} \,|\, Ag^+ (0.01M) \,||\, Ag^+ (0.5M) \,|\, Ag_{(s)}$$

Sol:- $E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$

$= \frac{0.0591}{1} \log \frac{0.5}{0.01}$

$= 0.0591 \log 50$ $\quad \log 50 = 1.6989.$

$= 0.0591 \times 1.6989$

$= 0.1004$ V.

2019 (3-M)

4. The emf of the cell $Cd \mid CdSO_4 (0.0093\ M) \parallel Cd^{2+} (x\ M) \mid Cd$ is 0.086 V at 25°C. Find the value of x.

Sol:- $E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$

$0.086 = \frac{0.0591}{2} \log \frac{x}{0.0093}$

$0.086 = 0.0295 \log \frac{x}{0.0093}$

$\frac{0.086}{0.0295} = \log \frac{x}{0.0093}$, $\quad 2.9103 = \log \frac{x}{0.0093}$

$\text{Antilog} (2.9103) = \frac{x}{0.0093}$

$813.43 = \frac{x}{0.0093}$

$\therefore x = 813.43 \times 0.0093$

$\therefore x = 7.56$ M.

2006

5. A concentration cell was constructed by immersing two silver electrode in 0.05M and 1M $AgNO_3$ solution. Write the cell representation, cell reactions and calculate the EMF of the cell.

Sol:- Cell representation,

$Ag_{(s)} \mid AgNO_3 (0.05M) \parallel AgNO_3 (1M) \mid Ag_{(s)}$.

At anode, $Ag \longrightarrow Ag^+ (0.05M) + e^-$

At cathode, $Ag^+ (1M) + e^- \longrightarrow Ag$

Net cell reaction: $Ag + \underset{(1M)}{Ag^+} \longrightarrow Ag^+ (0.05M) + Ag$.

$$E_{cell} = \frac{0.0591}{n} \log\left(\frac{C_2}{C_1}\right)$$

$$= \frac{0.0591}{1} \log \frac{1}{0.05}$$ $\log 20 = 1.3010$

$$= 0.0591 \times 1.3010$$

$$= 0.0768 \text{ V.}$$