

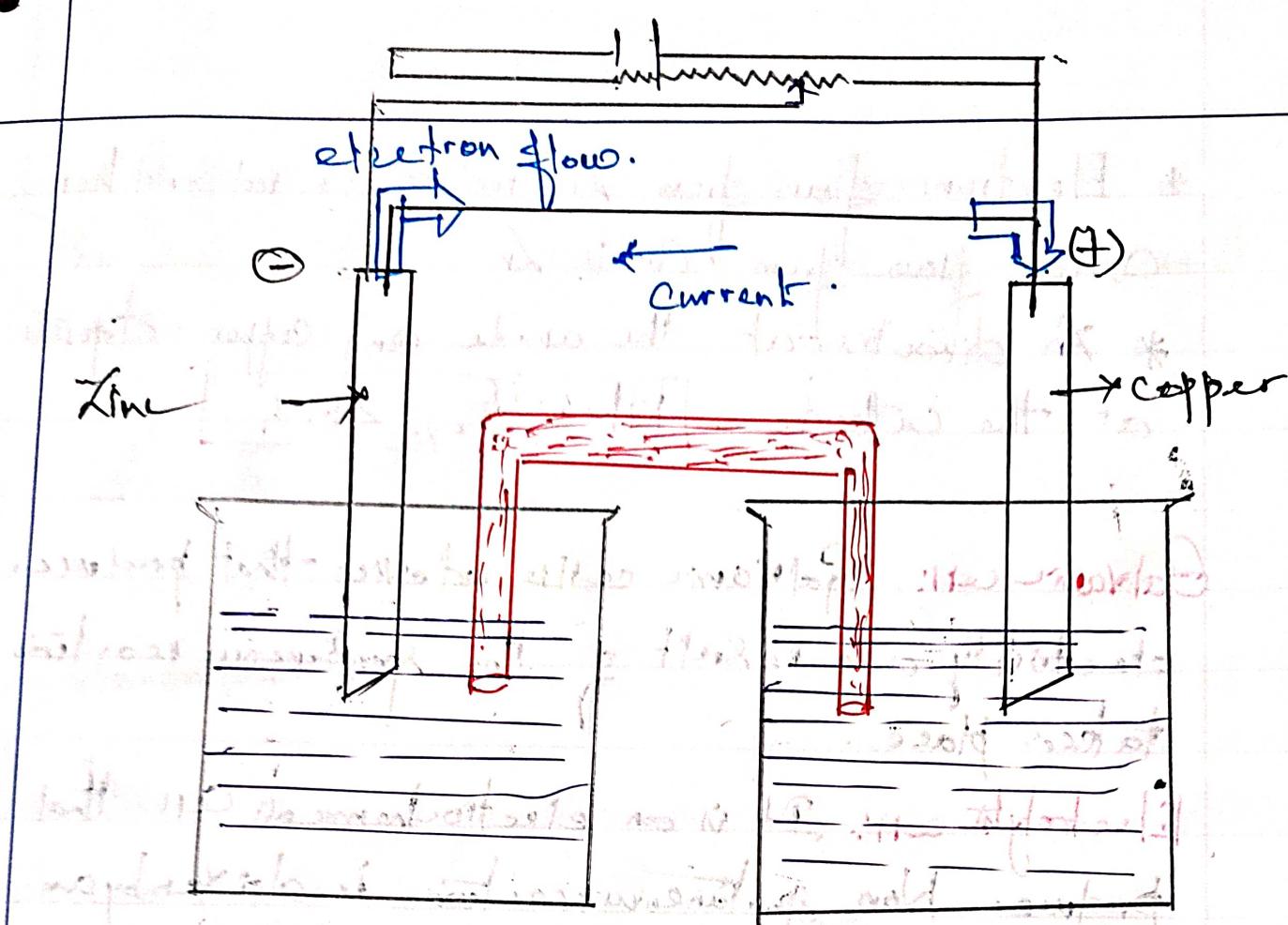
Module No. 9.

Electrochemistry.

Galvanic cell: Introduction about electrochemistry.

A Galvanic cell is a device in which free energy of a physical (or) chemical process is converted into electrical energy. Such a cell consists of two electrodes immersed in one or more suitable electrolytes.

When an electrode connected externally, internally if required chemical reaction in dilute solution occurs at the one electrode and reduction occurs at the other electrode. According to the latest conversion oxidation occurs at the anode and reduction occurs at the cathode.

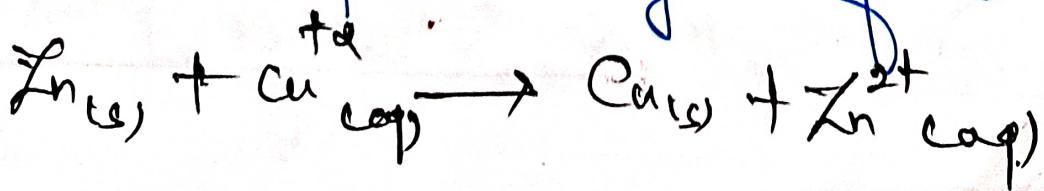


Solution containing salt of Zn

(Solution containing salt of Cu.)

A Copper rod dipping in a solution of a copper sulphate and Zinc rod dipping in a solution of Zinc Sulphate as in the Daniell cell.

The two metal rods are connected through an ammeter through a salt bridge (i.e. an inverted U-tube shaped glass tube filled with KCl). The current starts flowing which is indicated by deflection in ammeter. Represented by the following equation:



- * Electron flows from Zn rod to Cu rod and hence current flows from Cu to Zn.
- * Zn dissolves at the anode and copper deposits at the cathode. Then $E_{\text{ext}} < 0$

Galvanic cell: Galvanic cell is a device that produces electricity as a result of the spontaneous reaction takes place.

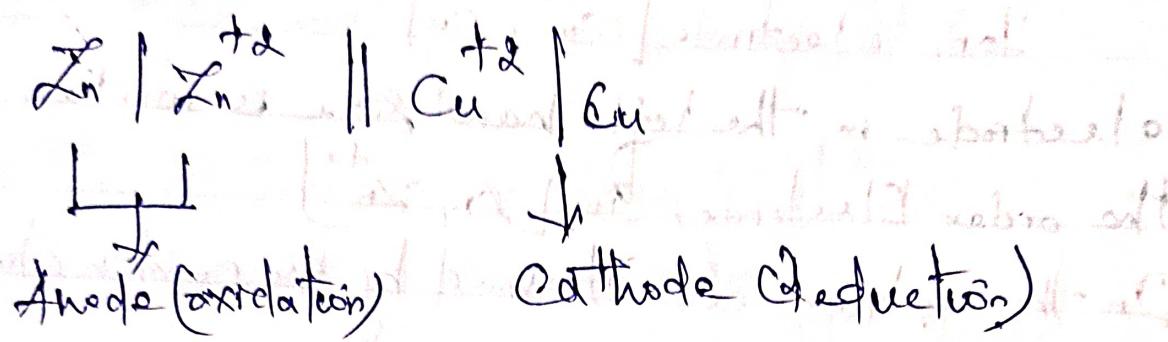
Electrolytic cell: It is an electrochemical cell that produces Non-spontaneous reaction is driven by an external circuit.

Electrode potential:- The tendency of an electrode to lose or gain electrons when it is in contact with its own ion in solution called electrode potential.

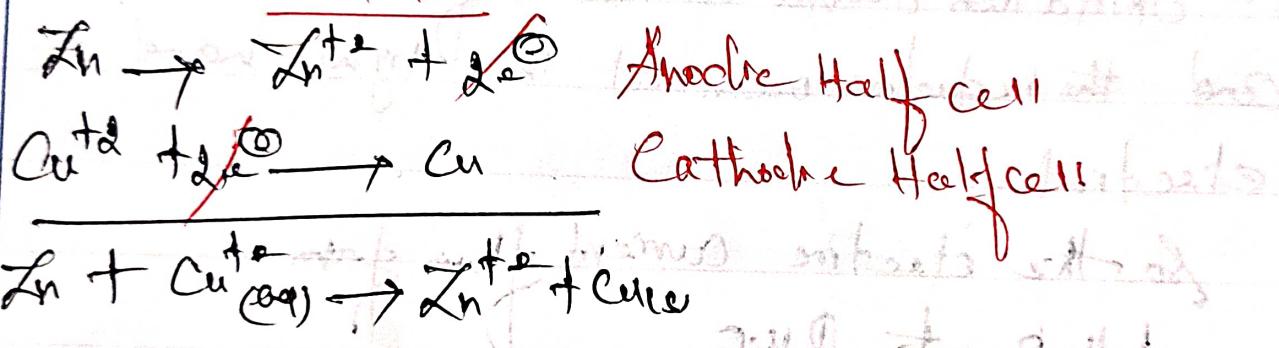
Tendency to gain an electron also the tendency of it to be reduced are called reduction potential.

Tendency to lose an electron also the tendency to get oxidised are called oxidation potential.

Cell Representation In an electrochemical cell the ions will be in the aqueous solution otherwise it is unstable.



Reaction Oxidation / Reduction



E_{cell}° (F. oxidation) Anode + [F. reduction] Cathode

According to the thermodynamic point of view Dextrose dextrorotatory
the Enantiomeric quantity of Reaction is negative

$$F_{\text{ext}} = -E_{\text{ox}} \frac{\partial}{\partial x}$$

Feasibility If the $F_{cell} > 0$ Then the cell is feasible

Electrode on the right hand side is written in the order



electrode in the left hand side is written in the order Electrode, Ion $[\text{Zn}, \text{Zn}^{+}]$

In the Galvanic cell formed by the combination of two electrodes

Oxidation occurs at the left hand electrode and the reduction occurs at the right hand electrode.

so the electric current flows from

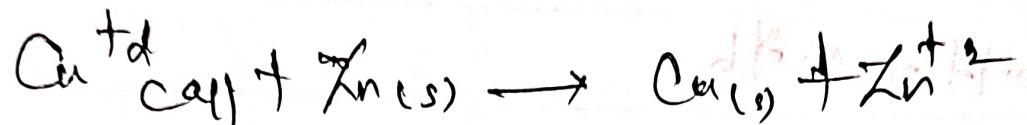
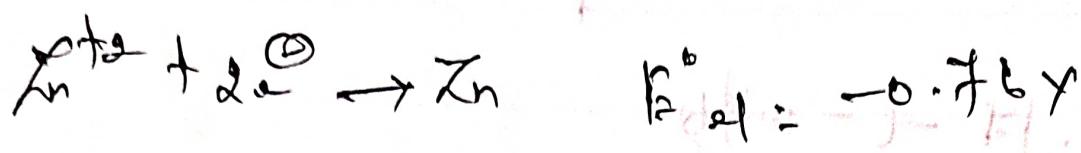
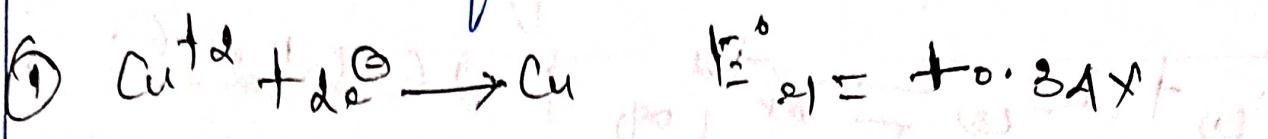
L.H.E to R.H.E

Determination of cell potential and the cell reaction

Both the cell reactions are written in the form of the standard reduction potentials.

the resultant gives the cell potential as well as the feasible cell reaction

The two half cell in the Daniell cell:



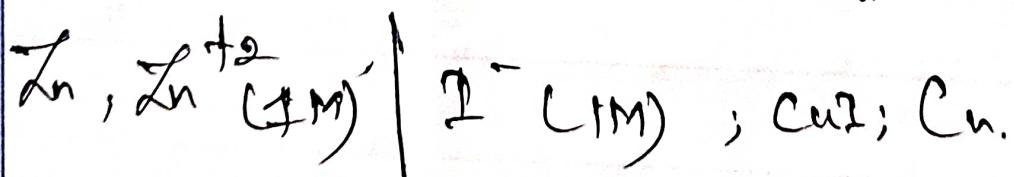
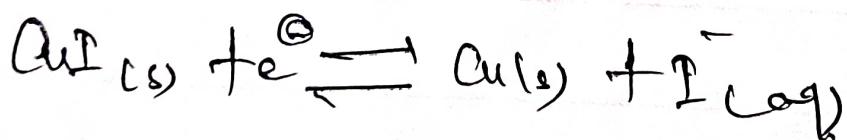
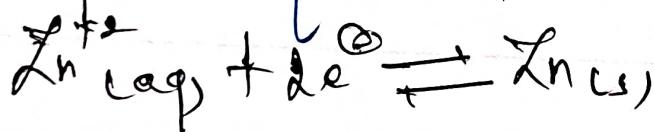
or the feasible cell reaction

$$= 0.34 \text{ V} - (-0.76 \text{ V})$$

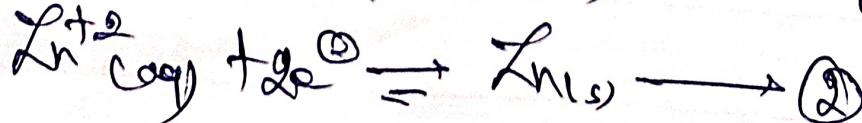
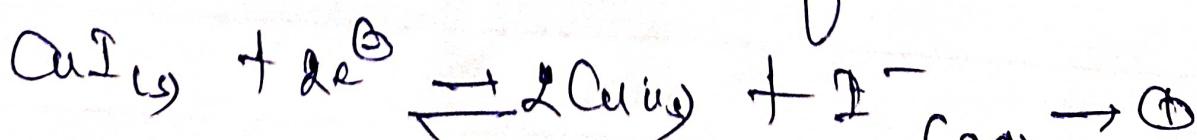
$$\boxed{= 0.34 + 0.76 = 1.10 \text{ V}}$$

example
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Given the following ^{Half} Cell Reaction :-



solution
Balance the reduction formula.



Subtracting equation No. ② from equation No. ①



$$E^\circ = -0.17 - (-0.76)$$

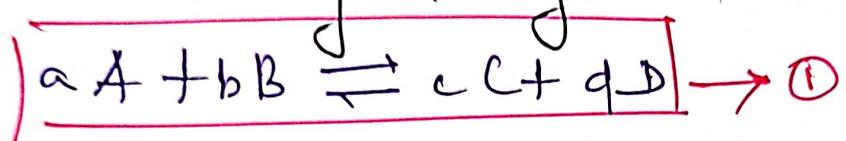
$$= -0.17 + 0.76$$

$$I = 0.59 \times$$

at the 28th cell pattern

Relationship between the cell potential and the free energy.

Suppose the reaction occurring in a reversible cell containing the general reaction



the decrease in free energy - ΔG accompanying in the process is given by well known thermodynamic function

$$-\Delta G = -\Delta G^\circ - RT \ln Q.$$

$-\Delta G$ is the decrease in the free energy when all the reactants and products are in their standard states of unit activity and $\textcircled{1}$ stands for the reaction quotient of the activities of the products and the reactants at any given stage of the reaction.

$$Q = \frac{[a_c]^c [a_d]^d}{[a_A]^a [a_B]^b} \rightarrow \textcircled{1}$$

If E is the EMF of the cell in Volt and the cell reaction involves the passage of n Faraday [Coulomb] the electrical energy produced by the cell is nFE Volt Coulombs (i.e.) Joules.

$$nFE = -\Delta G^\circ - RT \ln K \rightarrow \textcircled{1}$$

$$-\Delta G^\circ = RT \ln K \rightarrow \textcircled{2}$$

Where K is the equilibrium constant of the cell reaction

Substituting in eq $\textcircled{2}$ in $\textcircled{1}$

$$nFE = RT \ln K - RT \ln K \rightarrow \textcircled{3}$$

Substituting eq No $\textcircled{3}$ in eq No $\textcircled{1}$

$$nFE = RT \ln K - RT \ln \frac{[A]^c [B]^d}{[A]^a [B]^b}$$

changing \ln to \log and divided by nFE

$$\frac{E}{nFE} = \frac{2.303 RT}{nFE} \log \frac{[A]^c [B]^d}{[A]^a [B]^b}$$

At 25°C and standard conditions

$$\frac{2.303RT}{nF} = \frac{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{96485 \text{ C mol}^{-1}}$$
$$= 0.0591 \text{ Volt}$$

$$E = \frac{0.0591}{n} \log k - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

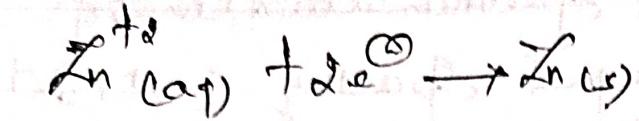
knowing the E_{mfp} of the cell and the concentration of reactants and products of the cell reaction

we can calculate the equilibrium constant of the cell reaction.

Derivation of the Nernst equation:

Consider an electrode consisting of a metal in contact with a solution of its cation for example.

The rod is in contact with a solution of zinc sulphate furnishing Zn^{2+} from the following equilibrium will be established



the decrease in free energy is accompanied with the electrode reaction is given by.

$$NFE_{el} = NFE_{el}^{\circ} - RT \ln \left(\frac{a_{\text{Zn}}}{a_{\text{Zn}^{+2}}} \right) \rightarrow ①$$

$$E_{el} = E_{el}^{\circ} - \frac{RT}{2F} \ln \frac{a_{\text{Zn}}}{a_{\text{Zn}^{+2}}} \rightarrow ② [a_{\text{Zn}} = 1]$$

$$E_{el} = E_{el}^{\circ} - \frac{RT}{2F} \ln \left[\frac{1}{a_{\text{Zn}^{+2}}} \right] \rightarrow ③$$

solids concentrate
in Unity.

$$E_{el} = E_{el}^{\circ} + \frac{RT}{2F} \ln [\text{Zn}^{+2}] \rightarrow ④$$

Where E_{el} is the electrode potential of Zinc electrode under the operating condition.

E_{el}° is the standard electrode potential of Zinc electrode (Zn°) potential developed on the Zinc rod when it is contact with its own ion in solution.

equation No ⑤ can be written as

$$E_{eq} = E_{eq}^{\circ} + \frac{RT}{nF} \ln [x_n^{+2}] \rightarrow ⑥$$

$$E_{eq} = E_{eq}^{\circ} + \frac{0.0591}{n} \log [x_n^{+2}] \text{ at } 25^{\circ}$$

In General

$$E_{eq} = E_{eq}^{\circ} + \frac{0.0591}{n} \log [M_n^{+2}] \text{ at } 25^{\circ}$$

equation No ⑥ gives the Nernst equation shows the effect of Concentration of M_n^{+2} .

Nernst equation Application

* It is very important application of E_{mgf} measurement in potentiometric titration.

Acid-Base Titration

* In Acid-Base titration PbO_2 electrode is employed as the Indicator electrode.

Reference electrode is the saturated Calomel electrode.

Half cell reaction for acid base titration will be



Oxidation-Reduction reaction

Titration involving oxidizing agents ($\text{K}_2\text{Cr}_2\text{O}_7$ or KMnO_4) and reducing agents like ferrous salt can be followed potentiometrically by using platinum indicator electrode.

On adding KMnO_4 first the emf of the cell will increase first slowly, but at the equivalence point there will be sudden jump in the potential.

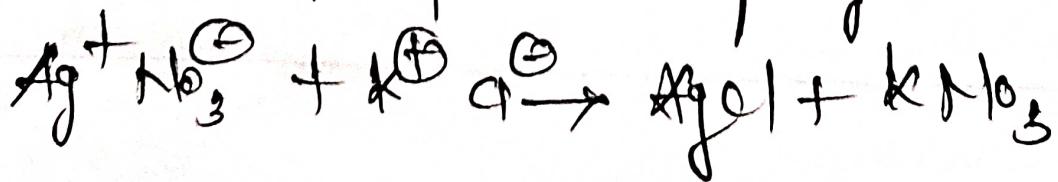
$$E = E_{\text{cell}}^{\circ} + \frac{RT}{F} \ln \left[\frac{[\text{Fe}^{+2}]}{[\text{Fe}^{+3}]} \right]$$

rapid at the equivalence point

Precipitation Titration

Titration involving precipitation e.g. AgNO_3 & KCl (or KI) can also be followed by potentiometrically by the use of indicator electrode.

As the titration proceeds Ag^+ ion decreases due to the precipitation of Ag^+ ion as AgI



Reduction potential of Indicator electrode (Ag) goes on decreasing progressively on the addition of KCl .

At the end point of the concentration change of Ag^+ is zero rapidly at the end point.

The Ag^+ concentration becomes very small on account of slight solubility of AgCl .

If addition of KCl is continued the Ag^+ concentration is not affected except a very small decrease due to decrease in the solubility of AgCl on the account of Common Ion effect formation.

On plotting the value $\left| \frac{\Delta E}{\Delta x} \right|$ versus x the point of maxima gives the end point.