Date: 25/10/24

Relationship between Entropy and EMF:

$$\Delta G = \Delta H + T\left[\frac{d\Delta G}{dT}\right]_P$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta S = -\left(\frac{d\Delta G}{dT}\right)_P \qquad (\Delta G = -nFE_{cell})$$

$$\boxed{\Delta S = nF\left(\frac{dE_{cell}}{dT}\right)_P}$$

At standard rate,

$$\boxed{\Delta S^\circ = nF\left(\frac{dE^\circ_{cell}}{dT}\right)_P}$$

5M

NERNST EQUATION:

It gives the idea about the effect of concentration of an electrolyte on electrode potential.

$$\boxed{E_{cell} = E^o_{cell} - \frac{2.303RT}{nF} \log \frac{[P]}{[R]}}$$

where E_{cell} = EMF of the cell.

E^o_{cell} = Standard EMF of the cell.

n = no. of electrone transfer

R = gas constant (8.314 J/mol)

F = 1 Faraday (96500 C)

$[P]$ = molar concentration of product

$[R]$ = molar concentration of Reactant

T = Temprature (298 K)

$$E_{cell} = E^o_{cell} - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[P]}{[R]}$$

$$* \boxed{E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}}$$

Let us consider as a hypothetical reaction.

1) $\underbrace{aA + bB}_{R} \longrightarrow \underbrace{cC + dD}_{P}$

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

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

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log \frac{[Zn]^{2+}[Cu]}{[Zn][Cu]^{2+}}$$

Q1) Calculate EMF of the cell $Zn/Zn^{2+}(0.1m) // Ag^+(0.1m)/Ag$ add 298K. Given that $E^o_{Zn/Zn^{2+}} = 0.76V$, $E^o_{Ag/Ag} = 0.8V$ (cathod)

$E^o_{Zn^{2+}/Zn} = -0.76V$ (anode)

Ans:

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

$Ag^+ + 1e^- \longrightarrow Ag \;] \times 2$

$Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$

$E^\circ_{cell} = E^\circ_{R.P\ cathod} - E^\circ_{R.P\ anode}$

$= 0.8 - (-0.76V)$

$= 1.56\ V$

$E_{cell} = 1.56V - \frac{0.0591}{2} \log \frac{[Zn^{2+}][Ag]^2}{[Zn][Ag^+]^2}$

$= 1.56V - \frac{0.0591}{2} \log \frac{0.1}{(0.1)^2}$

$= 1.56V - \frac{0.0591}{2} \log [10]$ $[\because \log 10 = 1$

$E_{cell} = 1.56 - \frac{0.0591}{2}$

$E_{cell} = 1.53045.$

Q2) Calculate the EMF of the cell $Zn/Zn^{2+}(0.1m) // Cu^{2+}(0$ $/C$. at 298k temprature.

$E^\circ_{Zn/Zn^{2+}} = 0.76V$, $E^\circ_{Cu^{2+}/Cu} = 0.34V$.

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

Ans:-

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

$Cu^{2+} - 2e^- \longrightarrow Cu$

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

$E^\circ_{cell} = E^\circ_{R.P(cathod)} - E^\circ_{R.P(anode)}$

$= 0.34 - (-0.76)$

$= 1.1V.$

$E_{cell} = 1.1 - \frac{0.0591}{2} \log \frac{(0.1)}{(0.01)}$

$= 1.1 - \frac{0.0591}{2} \log [10]$

$= 1.1 - \frac{0.0591}{2}$

$E_{cell} = 1.07$

* Ionic product of water:

Based on the fact that water can act as an acid as well as base it can be easily understand by the reaction.

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$
(base) (acid)

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

[H_2O is a constant due to high amount H_2O is neglect]

$$\boxed{K_W = [H^+][OH^-]} \quad -(1)$$

[K_W = ionic product of water]

→ Ionic product of water is defined as the product of concentration of $[H^+]$ & $[OH^-]$ ions.

→ A 25°C or 298K K_W of pure water is

$$\boxed{K_W = 1 \times 10^{-14} \frac{mol^2}{lit^2}}$$

In pure water, $[H^+] = [OH^-]$

In equation (1), we get

$$K_W = [H^+][OH^-]$$
$$= [H^+][H^+]$$
$$= [H^+]^2$$
$$H^+ = \sqrt{K_W}$$
$$H^+ = \sqrt{1 \times 10^{-14} \frac{mol^2}{lit^2}}$$
$$\boxed{[H^+] = 1 \times 10^{-7} \frac{mol}{lit}}$$

* pH is equal to negative logarithem of H^+ ion.

$$pH = -\log [H^+]$$
$$= -\log 10^{-7}$$
$$pH = \boxed{pH = +7}$$

NOTE:

→ For a neutral solution $[H^+] = [OH^-]$ [$pH = 7$]

→ For an acidic solution $[H^+] > [OH^-]$ [$pH < 7$]

→ For a basic solution $[H^+] < [OH^-]$ [$pH > 7$]

Date: 26/10/24

Q1) Add 32k Temprature. what is the p^H of water if K_w is $4 \times 10^{-14} \frac{mol^2}{lit^2}$.

Ans:- $K_w = 4 \times 10^{-14} \frac{mol^2}{lit^2}$

$$[H^+] = \sqrt{K_w}$$

$$[H^+] = \sqrt{4 \times 10^{-14} \frac{mol^2}{lit^2}}$$

$$[H^+] = 2 \times 10^{-7}\ mol/lit$$

Taking log both side

$$\log [H^+] = \log 2 \times 10^{-7}\ mol/lit \qquad \boxed{p^H = -\log [H^+]}$$

$$p^H = -\log 2 \times 10^{-7}\ mol/lit$$

$$p^H = -(\log 2 - 7 \log 10)$$

$$p^H = -(0.3010 - 7)$$

$$\boxed{p^H = 6.70}\ (\text{Acid})$$

Q2) calculate the p^H of 0.1m KOH at 298K calculate the p^H of KOH.

Ans:-

$$[OH^-] = 0.1m$$

$$K_w = [H^+][OH^-]$$

$$[H^+] = \frac{K_w}{[OH^-]} \qquad \left[K_w = 1 \times 10^{-14} \frac{mol^2}{lit^2}\right]$$

$$[H^+] = \frac{1 \times 10^{-14}\ mol^2/lit^2}{0.1}$$

$$[H^+] = 1 \times 10^{-13}\ mol/lit.$$

Taking log both side

$$\log [H^+] = \log 1 \times 10^{-13}\ mol/lit \qquad \boxed{p^H = -\log [H^+]}$$

$$p^H = -\log 10^{-13}\ mol/lit$$

$$p^H = +13 \log 10$$

$$\boxed{p^H = 13}\ (\text{Basic})$$

Concept of p^H:

→ p means power and H means hydrogen. so p^H is simply defined as the power of hydrogen.

→ p^H is defined the negative logarithem of hydrogen ion concentration.

$$\boxed{pH = -\log H^+}$$

→ The concentration of H^+ ion is a measure of acidity and basicity of a aqueous solution at a specific solution. Acidic solution have higher relative number of H^+ ion.

→ Basic or alkaline solution have higher relative number of OH^- ion.

→ pH scale help to measure the acidity and basicity of any solution.

→ pH ranges from 0 to 14.

→ The scale starts with 0 pH indicate that solution is strongly acidic.

☆ IMPORTANCE OF pH IN EVERY DAY LIFE :

* pH in our digestive system :

• Stomach produces HCL of pH about 1.4 which help indigestion. Some time excess acid produces due to various reason. Then we take Antaacid to cure it.

* pH cause tooth decay :

• Sugar convert latic acid tooth decay starts when the pH of acid form in mouth falls below 5. Then we use tooth paste to cure it.

* plants and animal are sensitive to pH :

• plant grows when if pH is about 7.

• Animals body work well if pH is about 7.0 to 7.8.

• Rain water pH is below 5.6. (acid).

☆ Buffer :

Any solution which resists any change in pH on addition of small amount of acid and base.

* Types of Buffer Solution :-

It is of two types :

(i) Acidic buffer

(ii) Basic buffer.

* Acidic Buffer:

Acid buffer $\longrightarrow$ weak acid + Salt $\begin{cases} \rightarrow \text{weak acid.} \\ \rightarrow \text{strong base} \end{cases}$

$$CH_3-COOH + NaOH \rightleftharpoons CH_3-COONa + H_2O$$
(weak acid) (strong base) (salt)

$$CH_3-COOH \rightleftharpoons CH_3-COO^- + H^+$$

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

$$CH_3-COO^- + Na^+ \longrightarrow CH_3-COONa$$

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

* Basic Buffer:

Basic buffer $\longrightarrow$ weak base $\longrightarrow$ Salt $\begin{cases} \rightarrow \text{weak base} \\ \rightarrow \text{strong acid.} \end{cases}$

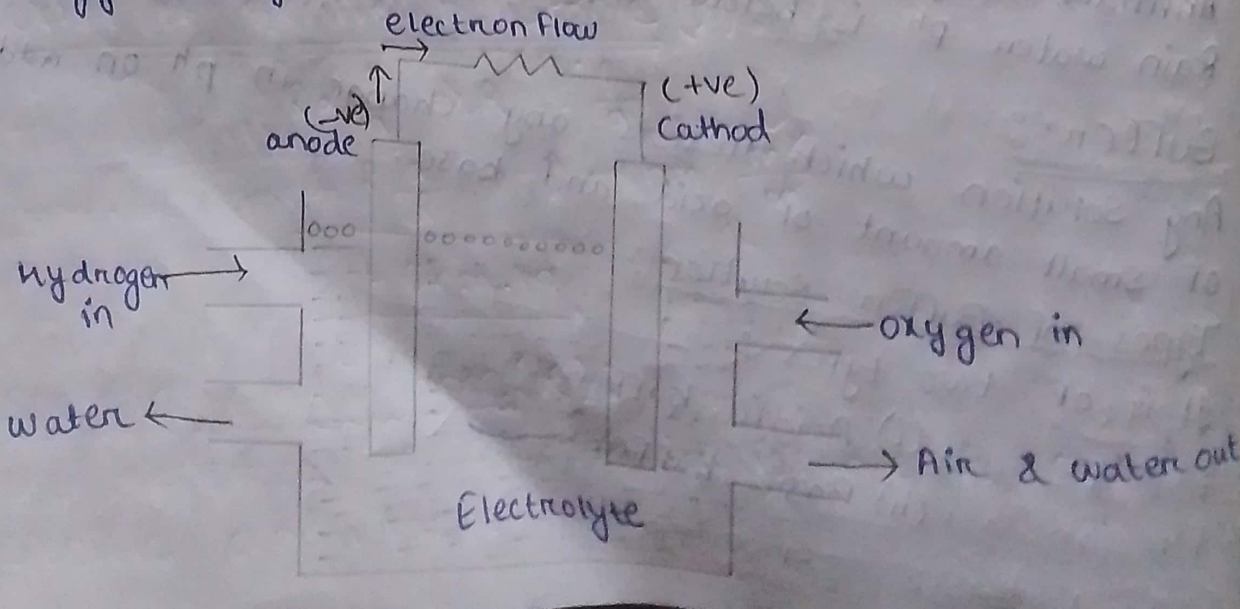
$$NH_4OH + HCl \longrightarrow NH_4 + H_2O$$
(weak base) (strong acid) (salt)

Battery

- Primary Battery (cannot be recharged)
  - Dry cell
  - mercury cell
- Secondary Battery.
  - Li-ion battery
  - lead strong battery
  - Fuel, cell
  - Ni-cd cell.

* FUEL CELL:

A fuel cell is a electrochemical device or cell which convert direct chemical energy of fuel into electrical energy through reaction.



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

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

→ A fuel cell consists of 2 electrodes one is anode and other is cathod which is separated by an electrolyte the organic fuel which can be used in a fuel cell to produce electricity such as Hydrogen.

→ An Electrolyte material is present between the electrodes fuel is supply to both the rod individually, in a fuel cell the hydrogen is feed to the anode while air is feed to the cathod.

→ Here the catalyst present at the anode side of the cell tends to break the hydrogen molecule into small particles that is proton & electrons. both the element try to move towards the cathod by different path.

→ The electrons reach the cathod and produce the current while the protons travel to the electrolyte membrane and reach the cathod to combine with oxygen molecule and electron to produce water and heat as by product.

→ This cell required a continues input of fuel and oxidizing agent (O_2) in order to substain the reaction that generate the electricity.

* Application of Fuel cell:

→ Transpartation.

→ material handling and stationary.

→ Portable and emergency backup power.

→ Hydrogen can be used in fuel cell to generate power.

Date: 29/10/24

Electrolytic conductance:

→ The flow of electricity through solution of electrolyte is due to the migration of ions when potential difference is applied between the two electrode.

→ The cation which was positively charged moved toward the negatively charged electrode while anion which was negatively charged move towards the positive electrode.

Conductance (G):

→ The easy with which the electricity flows through a Solution is called the conductance of Solution.
→ It is denoted as "G"
→ It is defined as the reciprocal of resistance (R) of the solution.
→ Unit of conductance ohm^{-1} (Ω^{-1}) / mho / simen.

⊛ Specific resistance (ρ):

The resistance of any conductor is

$$R \propto \frac{l}{a}$$

$$\boxed{R = \rho \cdot \frac{l}{a}}$$

where, l = length of conductor.
A = cross section area of conductor.
ρ = constant called specific resistance and it depends upon nature of the material.

* If $l = 1m$, $A = 1m^2$

$$R = \rho \frac{\cancel{1m}}{\cancel{1m^2}}$$

$$\boxed{R = \rho}$$

→ Thus, specific resistance is defined as the resistance of a Specifiment 1m in length $1m^2$ cross section.
→ In other word it the resistance $1m^3$ of the material

* UNIT of specific resistance (ρ):

$$R \propto \frac{l}{a} \Rightarrow R = \rho \frac{l}{a}$$

$$\rho = R \frac{a}{l} \Rightarrow \rho = ohm \frac{m^{\cancel{2}}}{\cancel{m}}$$

$$\boxed{\rho = Ohm.m}$$

⊛ Specific conductance (K):

The reciprocal of specific resistance is called specific conductance.

$$\boxed{k = \frac{1}{\rho}}$$

* **UNIT of specific conductance (k):**

$$k = \frac{1}{\rho} \Rightarrow k = \frac{1}{R\frac{a}{l}}$$

$$k = \frac{1}{R} \cdot \frac{l}{a} \Rightarrow k = G\frac{l}{a}$$

$$\boxed{\Rightarrow k = S\,m^{-1}} \quad \boxed{Ohm^{-1}\,m^{-1}} \quad \boxed{mho\ m^{-1}}$$

* **Equivalent conductance (λ):**

→ Specific conductance is suitable for only metallic conductance.

→ For measuring conductance of electrolyte in solution, equivalent conductance is used.

→ It is defined as the conducting power of the ions produced by 1gr equivalent of an electrolyte in a given solution.

* **Molar conductance (λ_m):**

→ Molar conductance is defined as the conducting power of all the ions produced by 1 mole of electrolyte in a given solution.

→ Later as consider a solution containing "c" moles of an electrolyte in 1 cubic metre of the solution the volume of the solution containing 1 mole of electrolyte would be 1/c cubic metre.

λ_m = conductance of $1m^3$ of the solution $\times$ volume of the solution in m^3 containing one mole of the electrolyte.

λ_m = specific conductance $\times 1/c$

$$\lambda_m = k \times 1/c$$

* **UNIT:**

$$\lambda_m = S\cancel{m^{-1}} \times \frac{1}{mol \cdot \cancel{m^{-3}}}$$

$$\boxed{\lambda_m = S \cdot mol^{-1} \cdot m^2}$$

—x—x—x—x—x—

UNIT-3 Completed

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