1. **For the given cell: Fe/Fe $^{2+}$ (0.05)//Ag$^{+}$ (0.1)/Ag**

i) **Write the overall cell reaction and derive Nernst equation using thermodynamic principles.**

ii) **Calculate $E^0_{cell}$ and $E_{cell}$ at 25$^0$C. (Given$E^0_{Fe2+/Fe}$ = -0.44V ; $E^0_{Ag+/Ag}$ = 0.68V)**

**Sol:** It is a quantitative relationship between electrode potential and concentration of species with which the electrode is reversible.

Let us consider a reversible reaction.

$$M^{n+} + ne^- \rightleftharpoons M.$$

The reaction quotient for this reversible reaction, Q= $[M]/[M^{n+}]$

A thermodynamic equation which relates reaction quotient and decrease in free energy is given by,

$\Delta G = \Delta G^o + RT\ln Q$

where Q is the reaction quotient.

-ΔG represents the maximum work that can be obtainable from the electrochemical reaction. $-\Delta G = W_{max}$

For an electrochemical cell, $W_{max}$ depends on

Number of Coulombs, i.e., No. of moles of electrons exchanged in redox reaction (n), multiplied by no. of coulombs per mole of electrons. F(96,500 e/mol. E) = nF

Energy available per coulomb i.e., emf because volt = energy/Coulomb

Therefore $\Delta G = -nFE$

$-nFE = -nFE^0 + RT\ln(\frac{[M]}{[M+]})$ Where [M] = 1, for pure substances divide throughout by -nF

$$E=E^0 + \frac{RT}{nF}\ln(\frac{[M]}{[M+]})$$

$E^o$ = Standard electrode potential, n = number of electrons exchanged in a redox reaction, R = Gas constant. 8.314 $JK^{-1}\ mol^{-1}$, T = temp in Kelvin, F = Faraday 96500 C $mol^{-1}$.The equation reduces to following form at 298K,

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

Nernst equation may also be used to calculate. emf of electrochemical cells.

Cell reaction: At anode: $Fe \longrightarrow Fe^{2+} + 2e^-$

At Cathode: $2Ag^+ + 2e^- \longrightarrow 2Ag$

Overall reaction: $Fe + 2Ag^+ \rightleftharpoons Fe^{2+} + 2Ag$

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

$E^0_{cell} = E_C - E_A = 1.12V$

$E_{cell} = 1.0994V$

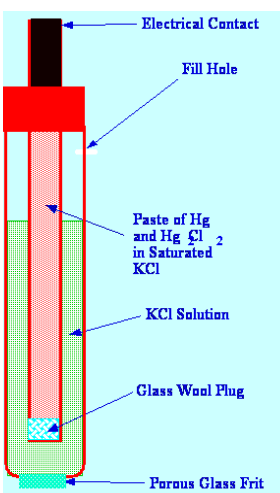
2. **Identify the type of galvanic cell given below and justify your answer. Pt/$H_2$ (8atm)/HCl(0.3M)/$H_2$(2atm)/Pt. Calculate potential of the cell at 25$^0$C.**

**Soln:** The given Galvanic cell is "Electrode concentration cell" Because the same electrodes with different activity are in contact with same electrolyte.

$$E_{cell} = \frac{0.0591}{n}\log\frac{p_1}{p_2}$$

$E_{cell} = 0.01779V$

3. **A decinormal electrode as cathode is coupled with a saturated calomel electrode as anode to form a cell. Write the cell representation and calculate the concentration of $Cl^-$ ion in the saturated calomel electrode, if the cell potential measured is 0.0988 V at 25$^0$C).**




$Pt/Hg/Hg_2Cl_2/Cl^-(x)//Cl^-(0.1M)/Hg_2Cl_2/Hg/Pt$

$E_{cell} = E_R - E_L$

$= E^0 - 0.0591\log(0.1) - E^0 - 0.0591\log(x)$

$$\frac{0.0988}{0.0591} = \log\frac{x}{0.1}$$

$1.6717 - 1 = \log(x)$

$x = \text{Antilog}(0.6717)$

$x = 4.69M$

4. **What are the advnantages and disadvantages of glass electrode?**

**Advantages of glass electrode:**

a) It is very easy to construct and simple to operate.
b) The potential developed remains constant for long time.

c) This electrode can be used with very small amount of the test solution.
d) This electrode can be used even in the presence of oxidized impurities, reducing impurities, poison molecules etc.,
e) The wide pH range from 0 to 14 can be measured using glass electrode.

**Disadvantages:**

- Because of high resistance of glass, a simple potentiometer cannot be used. It requires sensitive potentiometer for emf measurements.
- Alkaline error: It is a phenomenon that occurs at very high pH levels usually pH 9 or over. This is observed when the Sodium ion level is relatively so high that some of the $H^+$ ions in the gel layer around the sensitive electrode membrane are replaced by $Na^+$ ions. The electrode may eventually respond to Sodium ions instead of $H^+$ ions, giving a falsely lower pH value than the real result.

**5. Calculate the potential of concentration cell given by, Fe/$FeSO_4$ (0.09 M)//$FeSO_4$ (2.48 M)/Fe at 298 K.**

**Soln:**

$$Ecell = \frac{0.0591}{2}\log\frac{2.48}{0.09} = 0.04255V$$

**9. Calculate the EMF of the following cell at 25$^0$C. Ag/$Ag^+$ (0.01M) // $Ag^+$ (0,02 M)/ Ag (Given : R = 8.314 J/K/mol, F = 96500 C/mol)**

**Soln:**

$$E_{cell} = \frac{0.0591}{n}\log\left[\frac{M(Cathode)}{M(Anode)}\right]$$

$$E_{cell} = \frac{0.0591}{1}\log\left[\frac{(0.02)}{(0.01)}\right]$$

**$E_{cell}$= 0.01778 V**