# ENGINEERING CHEMISTRY

Department of Science and Humanities

# ENGINEERING CHEMISTRY
## Electrochemical Equilibria
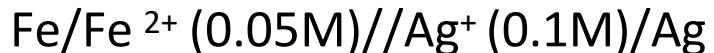
*Class content:*

- *Numericals on electrochemistry*
    - *Nernst equation*
    - *Ion selective electrode*

# ENGINEERING CHEMISTRY

## Electrochemical Equilibria

1. For the given cell:

   $Fe/Fe^{2+} (0.05M)//Ag^+ (0.1M)/Ag$

(i) Write the overall cell reaction

(ii) Calculate $E^0_{cell}$ and $E_{cell}$ at $25^0C$

(Given : $E^0_{Fe+2/ Fe} = - 0.44V$ ; $E^0_{Ag+/Ag} = 0.80V$)

**Sol.** Anode : $Fe \rightarrow Fe^{2+} + 2e^-$

Cathode : $2Ag^+ + 2e^- \rightarrow 2Ag$

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

$E^0_{cell} = E^o_C - E^o_A = 0.80 + 0.44 = $**1.24V**

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

$E_{cell} = 1.24 - \dfrac{0.0591}{2} \log(\dfrac{[0.05]}{[0.1]^2})$

$E_{cell}$ =**1.2193V**

2. For the following concentration cell:
   Pt/$H_2$ (8atm)/HCl(0.3M)/$H_2$(2atm)/Pt
   Calculate  potential of the cell at 25⁰C.

**Sol.**

$$E_{cell} = \frac{0.0591}{n} \log \frac{p_{H2(anode)}}{p_{H2(cathode)}}$$

$$E_{cell} = \frac{0.0591}{n} \log \frac{8}{2}$$

$E_{cell}$ = **0.01779V**

3. A decinormal calomel 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 $25^0C$.

**Sol.**

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

$E_{cell} = E_R-E_L$

$= [E^0 - 0.0591log (0.1)] -[ E^0 - 0.0591log(x)]$
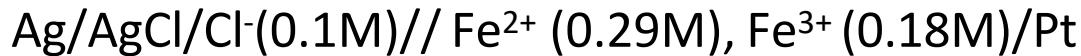
$$\frac{0.0988}{0.0591} = log\frac{x}{0.1}$$

1.6717 - 1= log(x)

x = Antilog(0.6717)

**x = 4.69M**

4. For the following cell:

    $Ag/AgCl/Cl^-(0.1M)// Fe^{2+} (0.29M), Fe^{3+} (0.18M)/Pt$
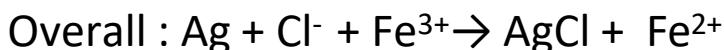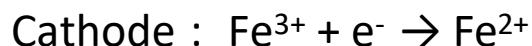
(i) Write the half cell reactions and overall cell reaction.

(ii) Calculate $E^o_{Cell}$ and $E_{Cell}$ at 298 K

(Given: $E^0_{Fe^{3+}/Fe^{2+}} = 0.77$ V , $E^0_{Calomel} = 0.222$ V, R = 8.314 J/K/mol,  F = 96500 C/mol)

**Sol.**   (i) Anode:  $Ag + Cl^- \rightarrow AgCl + e^-$

   Cathode :  $Fe^{3+} + e^- \rightarrow Fe^{2+}$

   Overall : $Ag + Cl^- + Fe^{3+} \rightarrow AgCl + Fe^{2+}$

(ii) $E^0_{cell} = E^o_C - E^o_A = 0.77 - 0.222 =$ **0.548V**

$$E_{cell} = E^o_{cell} - \frac{0.0591}{n} \log[\frac{([Fe^{2+}] ಇ\vec{\delta}}{([Fe^{3+}][Cl ್ಹ}]$$   $$E_{cell} = 0.548 - \frac{0.0591}{1} \log[\frac{[0.29]}{[0.18]x[0.1]}]$$

$E_{Cell=}$ **0.4767V**

5. Calculate the EMF of the following cell at $25^0C$.

$Au/Au^{3+}$ (0.05M) // $Au^{3+}$ (0.12 M)/ Au

(Given :  R = 8.314 J/K/mol, F = 96500 C/mol)

**Sol.**

$$E_{cell} = \frac{0.0591}{n} \, log \, \frac{[M^{n+}(cathode)]}{[M^{n+}(anode)]}$$

$$E_{cell} = \frac{0.0591}{n} log \, [\frac{(0.12)}{0.05}]$$

n = 3 ,

$E_{cell}$ = **0.00749V**

## Electrochemical Equilibria
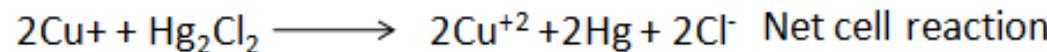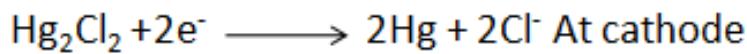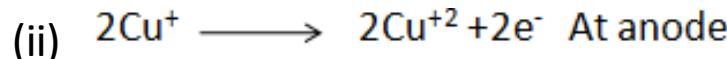
6. A decinormal calomel electrode is used to determine the potential of the following redox electrode : $Pt/Cu^{2+}(0.58\ M), Cu^{+}(0.08M)$

(i) Write cell representation.

(ii) Write the reactions at the electrodes

(iii) Calculate $E^0_{cell}$ and $E_{cell}$ at 298 K.

(Given : $E^o_{Hg/Hg2Cl2/Cl-} = 0.281V$ , $E_{Cu2+/Cu} = 0.153\ V$)

**Sol.** (i) $Pt/Cu^{2+}(0.58\ M), Cu^{+}(0.08M)//Cl^{-}(0.1\ M)/Hg_2Cl_2/Hg$

(ii) $2Cu^{+} \longrightarrow 2Cu^{+2} + 2e^{-}$ At anode

$Hg_2Cl_2 + 2e^{-} \longrightarrow 2Hg + 2Cl^{-}$ At cathode

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$2Cu+ + Hg_2Cl_2 \longrightarrow 2Cu^{+2} + 2Hg + 2Cl^{-}$ Net cell reaction

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(iii) $E^0_{cell} = E^o_C - E^o_A = 0.281 - 0.153 = $ **0.128 V**

$$E_{cell} = E^o{}_{cell} - \frac{0.0591}{n} \log[\frac{([Cl^{-}]^2[Cu^{2+}]^2}{([Cu^{+}]^2}]$$

$$E = E^0{}_{CELL} - \frac{0.0591}{2}\log\frac{0.58^2 \times 0.1^2}{0.08^2}$$

$E_{cell}$ = **0.1362 V**

# ENGINEERING CHEMISTRY

## Electrochemical Equilibria

7. For the following cell:

$Fe/Fe^{+2}(0.1M) || Au^{+3}(0.5M)/Au$

i.   Write the half cell reactions.

ii.  Calculate $E^0_{cell}$ and $E_{cell}$ at 298K .

(Given $E^0_{Au+3/Au} = 1.52V$, $E^0_{Fe+2/Fe} = -0.44V$, R = 8.314 J/K/mol, F = 96500C/mol)

**Sol.**

i) Half cell reactions

$Fe \longrightarrow Fe^{+2} + 2e^-$   x 3   at Anode

$Au^{+3} + 3e^- \longrightarrow Au$ x 2   at Cathode

$3Fe + 2Au^{+3} \longrightarrow 3Fe^{+2} + 2Au$   Net cell reaction

(ii) $E^0_{cell} = E^0_C - E^0_A = 1.52 + 0.44 = $ **1.96 V**

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log\left[\frac{[Fe^{+2}]^3}{[Au^{+3}]^2}\right]$$

$$E_{cell} = 1.96 - \frac{0.0591}{6} \log\left[\frac{[0.1]^3}{[0.5]^2}\right]$$

$E_{cell}$ = **1.9836 V**

# ENGINEERING CHEMISTRY

## Electrochemical Equilibria

8. A glass electrode is coupled with saturated calomel electrode to measure unknown pH. The cell potentials measured are 0.215V and 0.385V in contact with a solution of pH = 7 and with solution of unknown pH respectively. Calculate the pH of unknown solution.
 Given $E_{SCE}$=0.244V

**Sol.**      $E^o_G = E_{cell} + 0.0591pH + E_{SCE}$

       = 0.215 + 0.0591 X 7 + 0.244

       = 0.8727 V

$$pH = \frac{E^0_G - E_{SCE} - E_{Cell}}{0.0591} \qquad pH = \frac{0.8727 - 0.244 - 0.385}{0.0591}$$

**pH = 4.12**

# THANK YOU

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