Numericals on Electrode Potential

- Do you know all equations and terms used for solving the problems

- Do you know what all important to write or solve the problems ?

E_{cell} n E^0 $[M^{n+}]$ $E_{M^{n+}/M}$ $E^0_{M^{n+}/M}$ $\triangle G = -nFE$

E^0_{cell} $E_{cell} = E_{cathode} - E_{anode}$ E^0_G

anode / anode electrolyte // cathode electrolyte / cathode

Less reduction potential

More reduction potential

For concentration cell

anode / anode electrolyte // cathode electrolyte / cathode

Less concentration

More concentration

For complete cell

$$E^0_{cell} = E^0_{cathode} - E^0_{anode}$$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]} \quad \text{Or} \quad E_{cell} = E^0_{cell} + \frac{0.0591}{n} \log \frac{[R]}{[P]}$$

Anodic ion

Cathodic ion

For half cell

$$E_{Mn+/M} = E^0_{Mn+/M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \quad \text{Or} \quad E_{Mn+/M} = E^0_{Mn+/M} + \frac{0.0591}{n} \log [M^{n+}]$$

For concentration cell

$$E_{cell} = \frac{0.0591}{n} \log \frac{[M_2]}{[M_1]} \qquad M_2 > M_1$$

Determination of pH

$$P^H = \frac{E^0_G - E_{cal} - E_{cell}}{0.0591}$$

Numerical for Electrode Potential

1. Calculate the electrode potential of Zinc electrode when the standard potential of Zinc electrode is -0.76 V and concentration of Zn^{2+} ion is 0.1M.

$E^0_{Zn2+/Zn} = -0.76V,$

$[Zn^{2+}] = 0.1M$

$E_{Zn2+/Zn} = \ ?$

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

$$E_{Mn+/M} = E^0_{Mn+/M} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

$$E_{Zn2+/Zn} = E^0_{Zn2+/Zn} + \frac{0.0591}{n} \log [Zn^{2+}]$$

$$= -0.76V + \frac{0.0591}{2} \log (0.1)$$

$$= -0.7895 \text{ V}$$

2. Calculate at 25^0C the electrode potential of Fe^{2+}(0.1M)/ Fe given $E^0_{Fe2+/Fe} = -0.44$ V.

$E^0_{Fe2+/Fe} = -0.76V$,

$[Fe^{2+}] = 0.1M$

$E_{Fe2+/Fe} = \ ?$

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

$$E_{Fe2+/Fe} = E^0_{Fe2+/Fe} + \frac{0.0591}{n} \log [Fe^{2+}]$$

$$= -0.44 + \frac{0.0591}{2} \log [0.1]$$

$$= -0.44 + \frac{0.0591}{2} \log [10]$$

$$= -44 - \frac{0.0591 (1)}{2}$$

$$= -0.4695 \text{ V}$$

3. Calculate the reduction potential of copper when it is in contact with 5M CuSO4 solution at 298K. The E^0 value of copper electrode is 0.34 V.

$E^0_{Cu2+/Cu} = 0.34$

$[Cu^{2+}] = 5M$

$E_{Cu2+/Cu} = ?$

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

$$E_{Cu2+/Cu} = E^0_{Cu2+/Cu} + \frac{0.0591}{n} \log [Cu^{2+}]$$

$$E_{Cu2+/Cu} = 0.34 + \frac{0.0591}{2} \log [5]$$

$$E_{Cu2+/Cu} = 0.36 \text{ Volts}$$

4. Calculate the electrode potential of copper its electrode potential at 25 ^{0}C is 0.292V when $[Cu^{2+}] = 0.015M$.

$E^0_{Cu2+/Cu} = 0.292$

$[Cu^{2+}] = 0.015M$

$E_{Cu2+/Cu} = ?$

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

$$E_{Cu2+/Cu} = E^0_{Cu2+/Cu} + \frac{0.0591}{n} \log [Cu^{2+}]$$

$$E_{Cu2+/Cu} = 0.292 + \frac{0.0591}{2} \log [0.015]$$

$$E_{Cu2+/Cu} = 0.23810 \text{ V}$$

5. Write the cell representation and calculate the emf of a cell containing Copper and Silver electrode given that the electrode potentials of copper and silver are 0.34 V and 0.8 V respectively.

$E_{Cu2+/Cu} = 0.34\ V$

$E_{Ag+/Ag} = 0.8\ V$

$E_{\ cell} = ?$

Cell Representation $Cu_{(s)} / Cu^{2+}{}_{(1M)} // Ag^{+}{}_{(1M)} / Ag_{(s)}$

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

$E_{\ cell} = 0.8 - 0.34$

$E_{\ cell} = 0.46V$

6. A galvanic cell formed by immersing Cd rod in 1M $CdSO_4$ and Cu rod in 1M CuSO4 solution. The standard E^0 valves of Cu and Cd electrodes are +0.34V and -0.40V respectively.

a. How the cell is represented?

b. Write the electrode reactions and cell reaction

c. Calculate the standard emf of the cell at 298K.

$E_{Cu2+/Cu} = 0.34$ V

$E_{Cd2+/Cd} = -0.40$ V

$[Cu^{2+}] = 1M$

$[Cd^{2+}] = 1M$

a. Cell representation $Cd_{(s)} / Cd^{2+}{}_{(1M)} // Cu^{2+}{}_{(1M)} / Cu_{(s)}$

b. Electrode reactions

At anode : $Cd \longrightarrow Cd^{2+} + 2e^-$

At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$

Cell reaction : $Cd + Cu^{2+} \longrightarrow Cd^{2+} + Cu$

c. EMF of cell.

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

$$= E_{Cu} - E_{Cd}$$

$$= 0.34-(-0.4)$$

$$E_{cell} = 0.74 \text{ Volts}$$

7. Write the cell representation, electrode reactions, cell reaction and calculate the emf of the cell at 298K for the cell formed by Fe^{2+}/ Fe, E^0 = -0.44 and Zn^{2+}/Zn E^0 = -0.76V respectively.

$E^0_{Fe2+/Fe}$ = -0.44 V

$E^0_{Zn2+/Zn}$ = -0.76 V

a. Cell representation Zn / Zn^{2+} // Fe^{2+} / Fe

b. Electrode reactions are

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

At cathode : $Fe^{2+} + 2e^- \longrightarrow Fe$

Cell reaction : $Zn + Fe^{2+} \longrightarrow Zn^{2+} + Fe$

c. EMF of cell.

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

$$= -0.44-(-0.76)$$

$$= 0.32\ V$$

8. Calculate the potential of Ag-Zn cell at 298K if the concentration of Ag^+ and Zn^{2+} are 5.2×10^{-6}M and 1.3×10^{-3}M respectively E^0 of the cell at 298K is 1.5V. Calculate the change in free energy △G for the reduction of 1 mole of Ag+. Given that 1 Faraday = 96.5k $JV^{-1}mol^{-1}$ (KJ per volt gram equivalent)

Electrode reactions

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

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

Cell reaction : $Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$

$E^0_{cell} = 1.5$ V

$[Ag^+] = 5.2 \times 10^{-6}$M

$[Zn^{2+}] = 1.3 \times 10^{-3}$M

E_{Cell}

$$E_{Cell} = E^0_{Cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$E_{Cell} = E^0_{Cell} - \frac{0.0591}{n} \log \frac{[Zn^{2+}]}{[Ag^+]^2}$$

$$E_{Cell} = 1.5 - 0.0591 \log \frac{[1.3 \times 10^{-3}]}{[5.2 \times 10^{-6}]^2}$$

$$E_{Cell} = 1.5 - \frac{0.0591}{2} \log 0.048 \times 10^9$$

$$E_{Cell} = 1.5 - \frac{0.0591}{2} \times 7.68$$

$$= 1.5 - 0.226944$$

$$= 1.27 \text{ V.}$$

Change in free energy for the reduction 1 mole of Ag^+

$\triangle G = -nFE$

$= -1 \times 96.5 \times 1.27$

$\triangle G = -122$ KJ

9. An electrochemical cell consists of ion electrode dipped in 0.1M FeSO4 and Silver electrode dipped in 0.05M AgNO3. Write the cell representation, cell reaction and calculate the electrode potential of the cell at 298 K. Given that the standard reduction potential of iron and silver electrodes are -0.44 and +0.80V respectively.

$E^0_{Fe2+/Fe} = -0.44\ V$

$E^0_{Ag+/Ag} = 0.80\ V$

$[Fe^+] = 0.1M$

$[Ag^+] = 0.05M$

Cell representation $Fe_{(s)} / Fe^{2+}_{(0.1M)} // Ag^+_{(0.05M)} / Ag_{(s)}$

Electrode reactions are

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

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

Cell reaction : $Fe + 2Ag^+ \longrightarrow Fe^{2+} + 2Ag$

EMF of cell.

$$E^0_{cell} = E^0_{Ag+/Ag} - E^0_{Fe/Fe2+}$$
$$= 0.80 - (-0.44)$$
$$E^0_{cell} = 1.24\ V$$

E_{cell}

$$E_{Cell} = E^0_{Cell} - \frac{0.0591}{n} \log \frac{[Fe^{2+}]}{[Ag^+]^2}$$

$$E_{Cell} = 1.24 - \frac{0.0591}{2} \log \frac{[0.1]}{[0.05]^2}$$

$$E_{cell} = 1.1927\ V$$

10. Write the electrode reaction and calculate the electrode potential of the following cell at 298K. Given E^0_{cell}=1.3V.

$Cu_{(s)}$ / $Cu^{2+}_{(1 \times 10^{-2} M)}$ // $Ag^{+}_{(1 \times 10^{-1} M)}$ / $Ag_{(s)}$

E^0_{cell}=1.3V.

Electrode reactions are

Electrode reactions

E_{cell}

At anode : $Cu \longrightarrow Cu^{2+} + 2e^-$

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

Cell reaction : $Cu + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag$

E_{cell}

$$E_{Cell} = E^0_{Cell} - \frac{0.0591}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$E_{Cell} = 1.3 - \frac{0.0591}{2} \log \frac{[1 \times 10^{-2}]}{[1 \times 10^{-1}]^2}$$

$$E_{cell} = 1.3 - 0.0591/2 \{\log 10^{-2} - \log 10^{-2}\}$$

$$E_{cell} = 1.3V$$

11. Calculate the electrode potential of the following concentration cell at 298k.

$$Ag_{(s)} / Ag^{+}_{(0.05M)} // Ag^{+}_{(0.5M)} / Ag_{(s)}$$

Electrode reactions are

At anode : $Ag \longrightarrow Ag^{+} + e^{-}$

At cathode : $Ag^{+} + e^{-} \longrightarrow Ag$

$$E_{Cell} = \frac{0.0591}{n} \log \frac{[M_2]}{[M_1]}$$

Where $M_2 > M_1$

$$E_{Cell} = 0.0591 \log \frac{[0.5]}{[0.05]}$$

$$E_{cell} = 0.0591 \text{ V}$$

12. Calculate the pH of a solution in which a glass electrode is placed and connected with a standard calomel electrode. The emf of the cell is found to be 0.034V. Standard calomel electrode potential is 0.2422V and E^0_G =0.8304V.

$E^0_G = 0.8304\ V$

$E_{cal} = 0.2422\ V$

$E_{cell} = 0.034\ V$

$$P^H = \frac{E^0_G - E_{cal} - E_{cell}}{0.0591}$$

$$P^H = \frac{0.8304 - 0.2422 - 0.034}{0.0591}$$

$$P^H = 9.3$$

13. Two silver electrodes containing 0.0012M and 0.0137M $AgNO_3$ solution respectively are coupled by salt bridge. Formulate the concentration cell. Calculate the valency of silver ions if the emf of the cell is 0.0627 V at 298 K

Representation of the cell $Ag_{(s)} / AgNO_{3\ (0.0012M)} // AgNO_{3\ (0.0137M)} / Ag_{(s)}$

$[Ag^+] = 0.0012M$

E_{cell}

$[Ag^+] = 0.0137M$

$$E_{Cell} = \frac{2.303RT}{nF} \log \frac{[M_2]}{[M_1]}$$

Where $M_2 > M_1$

$E_{cell} = 0627\ V$

$n = ?$

Here, M_2=0.0137 M; M_1=0.0012 M; T=298 K; R=8.314J/K; F=96500; E_{cell} = 0.0627V

$$n = \frac{2.303 \times 8.31 \times 298}{0.0627 \times 96500} \log \frac{[0.0137]}{[0.0012]}$$

= 0.9972

= 1 Silver in $AgNO_3$ is univalent.

14. Calculate the electrode potential when copper electrode is dipped in a 0.125 M $CuSO_4$ solution which is 80% dissociated into copper ions

$[Cu^{2+}]$ = 0.125 M

Which is 80% dissociated

$E^0_{Cu2+/Cu} = 0.34V$

100 = 0.125
80 = ?

$$[M^{n+}] = \frac{0.125 \times 80}{100}$$

= 0.1

$$E_{Cu2+/Cu} = E^0_{Cu2+/Cu} + \frac{0.0591}{n} \log [Cu^{2+}]$$

$$E_{Cu2+/Cu} = 0.34 + \frac{0.0591}{2} \log [0.1]$$

= 0.31V

15. Two copper electrodes placed in copper sulphate solutions of equal concentration are connected to form a concentration cell. What is the cell voltage if one of the solution is diluted until the concentration of Cu^{2+} ions is 1/5th of its original value. What is the cell voltage after dilution?

$[Cu^{2+}] = 1$ M

$[Cu^{2+}] = 1/5$ M

$$E_{Cell} = \frac{0.0591}{n} \log \frac{[M_2]}{[M_1]}$$

Where $M_2 > M_1$

$$E_{Cell} = \frac{0.0591}{2} \log \frac{[1]}{[1/5]}$$

$$E_{Cell} = \frac{0.0591}{2} \log 5$$

$$= 0.0206\text{V}$$

16. Calculate the cell potential of Ag/Ag^+ coupled with Cu/Cu^{2+} if the concentration of Ag+ and Cu^{2+} are 4.2×10^{-6} M and 1.3×10^{-3}M respectively. $E^0_{Cell} = 0.46$ V . what is the value of delta G for the reduction of 1 mole Ag^+. Given F=96.5k $JV^{-1}mol^{-1}$ (KJ per volt gram equivalent)

$$E^0_{cell} = 0.46 \text{ V}$$

$$[Ag^+] = 4.2 \times 10^{-6} M$$

$$[Cu^{2+}] = 1.3 \times 10^{-3} M$$

$$E_{Cell} = E^0_{Cell} - \frac{0.0591}{n} \log \frac{[\text{Reduced form}]}{[\text{Oxidized form}]}$$

$$E_{Cell} = E^0_{Cell} - \frac{0.0591}{n} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$E_{Cell} = 0.46 - \frac{0.0591}{2} \log \frac{[1.3 \times 10^{-3}]}{[4.2 \times 10^{-6}]^2}$$

$$E_{Cell} = 0.46 - \frac{0.0591}{2} \log 0.0736 \times 10^9$$

$$E_{Cell} = 0.46 - \frac{0.0591}{2} \times 7.86$$

$$= 0.23 \text{ V.}$$

For the reduction of 2 mole of Ag^+ ions 2 equivalent required
For the reduction of 1 mole of Ag^+ ions 1 equivalent required

Change in free energy for the reduction 1 mole of Ag^+

$$\triangle G = -nFE$$

$$= -1 \times 96.5 \times 0.23$$

$$\triangle G = -22 \text{ KJ}$$