Numericals on Electrochemistry

Nernst equation to determine emf of the cell

$E = E^o - RT/nF \ln Q$

Where $Q = [products]/[reactants]$

$E = E^o - RT/nF \ln [products]/[reactants]$

$$\boxed{E = E^o - 2.303RT/nF \log_{10} [products]/[reactants]}$$

Where, E^o = standard electrode potential of electrode or cell

n= Number of electrons used in the reaction

F= Faraday = 96500 Coulombs/mole

T= Temperature in Kelvin

R= gas constant = 8.314 $JK^{-1}mol^{-1}$

[products] & [reactants] are the concentration of products & reactants respectively.

At 25^{o}C, $2.303RT/F = 0.0592$ (by substituting values of R,T,F) Therefore ,at 25^{o}C, the Nernst equation becomes

$$\boxed{E = E^o - (0.0592/n) * \log_{10}[products]/[reactants]}$$

Q.1 A zinc rod is placed in a o.1M solution of zinc sulphate at 25°C. Calculate the potential of the electrode at this temperature , assuming 96% dissociation of $ZnSO_4$ & E° Zn2+/Zn = 0.76 V.

Solution:

Given data:

E° Zn2+/Zn = 0.76 V.

T = 25+273 = 298°K

$[ZnSO_4]$ = 0.1 M

96% dissociation

$E\ Zn^{2+}/Zn = E^o\ Zn^{2+}/Zn - 2.303RT/nF * \log_{10} [Zn]/[Zn^{2+}]$

$= 0.76 - 2.303 * 8.314 * 298 / 2 * 96500 * \log_{10} 0.096$

$= 0.76 - (0.0592/2) * \log_{10} 0.096$

(since 96% dissociation, [Zn/Zn2+]= 96/100* 0.1= 0.096 where $[ZnSO_4]$ = 0.1 M)

= o.76 – (0.0296 * 1.0177)

= 0.76-0.0301

= <u>0.7299 V</u>

Q.2 Calculate the electrode potential of copper, if the concentration of copper sulphate is .206 M at 23.1°C. Given that $E^o\ Cu^{2+}/Cu = +.34V$

Solution: Given data:

T= 23.1°C= 23.1+273= 296.1°K

$[CuSO_4]$= 0.206M

$E^o\ Cu^{2+}/Cu = +.34V$

The reaction taking place

$Cu^{2+} + 2e^- \rightarrow Cu$ (n=2)

$$\boxed{E = E^o - 2.303RT/nF \log_{10} [products]/[reactants]}$$

$E= +0.34- 2.303 * 8.314 * 296.1/2*96500 \log_{10}[Cu]/[Cu^{2+}]$

$= +0.34- (2.303 * 8.314 * 296.1/2*96500) * \log_{10} 1/0.206$

= 0.31984V

Q.3 Construct a cell from Ni^{2+}/Ni & Cu^{2+}/Cu half cells . Write the cell reaction & calculate the standard potential of the cell.

Given: E^oNi = -o.257V, E^oCu= 0.337V

Solution:

Ni(S)|Ni^{2+} (aq.) (1M) || cu^{2+} (aq.)(1M) | Cu(S)

Electrode Reaction:

Ni(S) → Ni^{2+} (aq.) (1M) + $2e^-$ (Oxidation at anode)

Cu^{2+} (aq.)(1M) + $2e^-$ → Cu(s) (Reduction at cathode)

Adding equation 1) & 2)

Overall reaction is

Ni (S) + Cu^{2+} (aq.) → Ni^{2+} (aq.) + Cu(S)

Standard electrode potential of the cell is

$E^oCell = E^oCathode - E^oanode$

$= 0.337 – (-0.257)$

$= 0.337 + 0.257$

$\underline{= 0.594 \text{ V}}$

Q.4 Calculate the emf of the following cell

Sn|Sn^{2+}(aq) (0.005M) || Ag^{2+}(aq.) (0.30 M) |Ag

E^oSn= -0.14V, E^oAg= 0.80

Solution:

Electrode reactions

$Sn \rightarrow Sn^{2+} + 2e^-$ Oxidation at anode

$Ag^+ + e^- \rightarrow Ag+$

$2Ag^+ + 2e^- \rightarrow 2\ Ag$ Reduction at cathode

Net reaction:

$Sn + 2Ag^+ \rightarrow Sn^{2+} + 2Ag$

Standard electrode potential of the cell

E^o Cell = E^oCathode-E^oanode

= 0.8 – (-0.14)

= 0.94V

$E\ cell = E^o cell - 2.303RT/nF * \log_{10} [sn^{2+}]/[Ag^+]^2$

$= E^o\ cell - 0.0592/n \log_{10} [sn^{2+}]/[Ag^+]^2$

$= 0.94 - (0.0592/2) \log_{10} [0.005]/[0.3]^2$

= <u>0.9725V</u>

Q.5 Calculate the concentration of $NiCl_2$ in the nickel electrode having a potential of -0.16942 V at 24.9°C, given that E^o Ni^{2+}/Ni = -0.14 V.

- Solution:
- Given data: E Ni^{2+}/Ni = -0.16942 V
- T= 24.9+273 =297.9°K
- E^o Ni^{2+}/Ni = -0.14 V.
- n=2 , $[Ni^{2+}]=[NiCl_2]$= ?
- $E_{Ni^{2+}/Ni} = E^o_{Ni^{2+}/Ni} - 2.303RT/nF * \log_{10} [Ni]/[Ni^{2+}]$
- $- 0.16942 = -0.14 + \dfrac{2.303 * 8.314 * 297.9}{2 * 96500} * \log_{10} [Ni^{2+}]$
- $[Ni^{2+}]$ = 0.1010 M
- $[NiCl_2]$ = 0.1010 M
- Ans : Concentration of $NiCl_2$ = 0.1010 M

- Q.6 **The standard emf of the following cell is 0.462 V.**
- **Cu(s) │Cu2+(aq.) (1M)││Ag+(aq) (1M)│Ag(S)**
- **If the standard electrode potential of Cu electrode is 0.337 V, what is the standard potential of Ag electrode.**
- **Solution:**
- **E^oCell = E^o Cathode – E^o anode**
- **= E^oAg – E^o Cu**
- **0.462 = E^oAg – 0.337**
- **E^o Ag = 0.462 + 0.337**
- **= <u>0.799 V</u>**