

Numericals on Electrochemistry

Nernst equation to determine emf of the cell

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

Where $Q = [\text{products}] / [\text{reactants}]$

$$E = E^{\circ} - \frac{RT}{nF} \ln [\text{products}] / [\text{reactants}]$$

E = $E^{\circ} - 2.303 \frac{RT}{nF} \log_{10} [\text{products}] / [\text{reactants}]$

Where, E° = 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⁻¹mol⁻¹

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

At 25°C, $2.303 \frac{RT}{nF} = 0.0592$ (by substituting values of R,T,F) Therefore ,at 25°C, the Nernst equation becomes

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

Q.1 A zinc rod is placed in a 0.1M solution of zinc sulphate at 25°C. Calculate the potential of the electrode at this temperature , assuming 96% dissociation of ZnSO₄ & E° Zn²⁺/Zn = 0.76 V.

Solution:

Given data:

$$E^\circ \text{ Zn}^{2+}/\text{Zn} = 0.76 \text{ V.}$$

$$T = 25 + 273 = 298^\circ\text{K}$$

$$[\text{ZnSO}_4] = 0.1 \text{ M}$$

96% dissociation

$$\begin{aligned} E \text{ Zn}^{2+}/\text{Zn} &= E^\circ \text{ Zn}^{2+}/\text{Zn} - 2.303RT/nF * \log_{10} [\text{Zn}]/[\text{Zn}^{2+}] \\ &= 0.76 - 2.303 * 8.314 * 298 / 2 * 96500 * \log_{10} 0.096 \\ &= 0.76 - (0.0592/2) * \log_{10} 0.096 \end{aligned}$$

(since 96% dissociation, [Zn/Zn²⁺] = 96/100 * 0.1 = 0.096
where [ZnSO₄] = 0.1 M)

$$= 0.76 - (0.0296 * 1.0177)$$

$$= 0.76 - 0.0301$$

$$= \underline{\underline{0.7299 \text{ V}}}$$

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

Solution: Given data:

$$T = 23.1^\circ\text{C} = 23.1 + 273 = 296.1^\circ\text{K}$$

$$[\text{CuSO}_4] = 0.206\text{M}$$

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

The reaction taking place



$$E = E^\circ - \frac{2.303RT}{nF} \log_{10} [\text{products}]/[\text{reactants}]$$

$$\begin{aligned} E &= +0.34 - \frac{2.303 * 8.314 * 296.1 / 2 * 96500}{2 * 96500} \log_{10} [\text{Cu}] / [\text{Cu}^{2+}] \\ &= +0.34 - (2.303 * 8.314 * 296.1 / 2 * 96500) * \log_{10} 1 / 0.206 \\ &= 0.31984\text{V} \end{aligned}$$

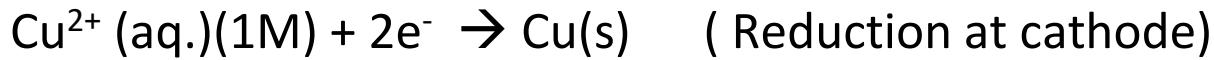
Q.3 Construct a cell from Ni^{2+}/Ni & Cu^{2+}/Cu half cells .
Write the cell reaction & calculate the standard potential of the cell.

Given: $E^\circ \text{Ni} = -0.257\text{V}$, $E^\circ \text{Cu} = 0.337\text{V}$

Solution:



Electrode Reaction:



Adding equation 1) & 2)

Overall reaction is



Standard electrode potential of the cell is

$$E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{anode}}$$

$$= 0.337 - (-0.257)$$

$$= 0.337 + 0.257$$

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

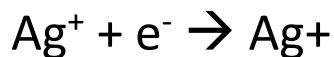
Q.4 Calculate the emf of the following cell



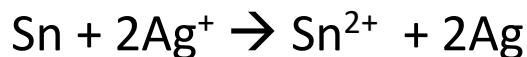
$$E^\circ_{\text{Sn}} = -0.14 \text{ V}, \quad E^\circ_{\text{Ag}} = 0.80$$

Solution:

Electrode reactions



Net reaction:



Standard electrode potential of the cell

$$E^\circ \text{ Cell} = E^\circ \text{Cathode} - E^\circ \text{anode}$$

$$= 0.8 - (-0.14)$$

$$= 0.94 \text{V}$$

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

$$= E^\circ \text{ cell} - 0.0592/n \log_{10} [\text{Sn}^{2+}]/[\text{Ag}^+]^2$$

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

$$= \underline{\underline{0.9725 \text{V}}}$$

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 $E^\circ \text{ Ni}^{2+}/\text{Ni} = -0.14 \text{ V}$.

- **Solution:**

- Given data: $E \text{ Ni}^{2+}/\text{Ni} = -0.16942 \text{ V}$
- $T = 24.9 + 273 = 297.9 \text{ K}$
- $E^\circ \text{ Ni}^{2+}/\text{Ni} = -0.14 \text{ V}$.
- $n=2$, $[\text{Ni}^{2+}] = [\text{NiCl}_2] = ?$
- $E \text{ Ni}^{2+}/\text{Ni} = E^\circ \text{ Ni}^{2+}/\text{Ni} - \frac{2.303RT}{nF} \log_{10} \frac{[\text{Ni}]}{[\text{Ni}^{2+}]}$
- $-0.16942 = -0.14 + \frac{2.303 \times 8.314 \times 297.9}{2 \times 96500} \log_{10} \frac{[\text{Ni}]}{[\text{Ni}^{2+}]}$
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- 2×96500
- $[\text{Ni}^{2+}] = 0.1010 \text{ M}$
- $[\text{NiCl}_2] = 0.1010 \text{ M}$
- **Ans : Concentration of $\text{NiCl}_2 = 0.1010 \text{ M}$**
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- 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:
- $E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{anode}}$
- $= E^\circ_{\text{Ag}} - E^\circ_{\text{Cu}}$
- $0.462 = E^\circ_{\text{Ag}} - 0.337$
- $E^\circ_{\text{Ag}} = 0.462 + 0.337$
- $= \underline{\underline{0.799 \text{ V}}}$