

## Numericals on Electrochemistry

### Nernst equation to determine emf of the cell

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

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

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

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

Where,  $E^{\circ}$  = 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<sup>-1</sup>mol<sup>-1</sup>

$[\text{products}]$  &  $[\text{reactants}]$  are the concentration of products & reactants respectively.

At 25°C,  $2.303RT/F = 0.0592$  (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  $\text{ZnSO}_4$  &  $E^\circ \text{Zn}^{2+}/\text{Zn} = 0.76 \text{ V}$ .

**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

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

(since 96% dissociation,  $[\text{Zn}]/[\text{Zn}^{2+}] = 96/100 \cdot 0.1 = 0.096$   
where  $[\text{ZnSO}_4] = 0.1 \text{ M}$ )

$$\begin{aligned} &= 0.76 - (0.0296 \cdot 1.0177) \\ &= 0.76 - 0.0301 \\ &= \underline{0.7299 \text{ V}} \end{aligned}$$

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



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

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

$$= +0.34 - \left( \frac{2.303 \times 8.314 \times 296.1}{2 \times 96500} \right) \times \log_{10} \frac{1}{0.206}$$

$$= \underline{0.31984\text{V}}$$

Q.3 Construct a cell from  $\text{Ni}^{2+}/\text{Ni}$  &  $\text{Cu}^{2+}/\text{Cu}$  half cells .

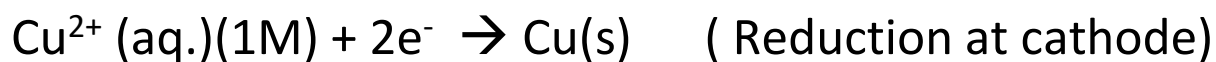
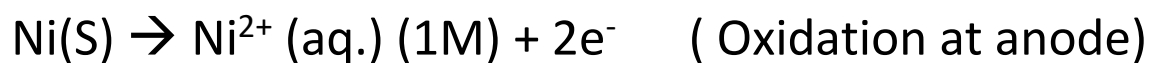
Write the cell reaction & calculate the standard potential of the cell.

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

**Solution:**

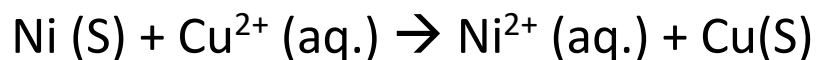


**Electrode Reaction:**



Adding equation 1) & 2)

Overall reaction is



Standard electrode potential of the cell is

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

$$= 0.337 - (-0.257)$$

$$= 0.337 + 0.257$$

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

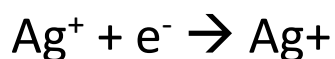
Q.4 Calculate the emf of the following cell



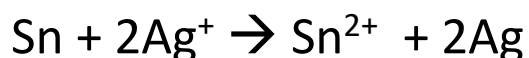
$$E^{\circ}\text{Sn} = -0.14\text{V}, \quad E^{\circ}\text{Ag} = 0.80$$

## Solution:

### Electrode reactions



Net reaction:



Standard electrode potential of the cell

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

$$= 0.8 - (-0.14)$$

$$= 0.94\text{V}$$

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

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

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

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

Q.5 Calculate the concentration of  $\text{NiCl}_2$  in the nickel electrode having a potential of  $-0.16942 \text{ V}$  at  $24.9^\circ\text{C}$ , given that  $E^\circ \text{Ni}^{2+}/\text{Ni} = -0.14 \text{ V}$ .

- **Solution:**

- Given data:  $E \text{Ni}^{2+}/\text{Ni} = -0.16942 \text{ V}$
- $T = 24.9 + 273 = 297.9^\circ\text{K}$
- $E^\circ \text{Ni}^{2+}/\text{Ni} = -0.14 \text{ V}$ .
- $n=2$  ,  $[\text{Ni}^{2+}] = [\text{NiCl}_2] = ?$
- $E \text{Ni}^{2+}/\text{Ni} = E^\circ \text{Ni}^{2+}/\text{Ni} - \frac{2.303RT}{nF} * \log_{10} [\text{Ni}]/[\text{Ni}^{2+}]$
- $-0.16942 = -0.14 + \frac{2.303 * 8.314 * 297.9}{2 * 96500} * \log_{10} [\text{Ni}^{2+}]$
- $$-0.16942 + 0.14 = \frac{2.303 * 8.314 * 297.9}{2 * 96500} * \log_{10} [\text{Ni}^{2+}]$$
- $$-0.02942 = \frac{2.303 * 8.314 * 297.9}{2 * 96500} * \log_{10} [\text{Ni}^{2+}]$$
- $$-0.02942 = 0.0729 * \log_{10} [\text{Ni}^{2+}]$$
- $$\log_{10} [\text{Ni}^{2+}] = \frac{-0.02942}{0.0729}$$
- $$\log_{10} [\text{Ni}^{2+}] = -0.4035$$
- $$[\text{Ni}^{2+}] = 10^{-0.4035}$$
- $$[\text{Ni}^{2+}] = 0.1010 \text{ M}$$
- $$[\text{NiCl}_2] = 0.1010 \text{ M}$$
- **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.
- $\text{Cu(s)} \mid \text{Cu}^{2+}(\text{aq.}) (1\text{M}) \parallel \text{Ag}^{+}(\text{aq}) (1\text{M}) \mid \text{Ag(s)}$
- If the standard electrode potential of Cu electrode is 0.337 V, what is the standard potential of Ag electrode.
- Solution:
- $E^{\circ}\text{Cell} = E^{\circ}\text{Cathode} - E^{\circ}\text{anode}$
- $\quad\quad\quad = E^{\circ}\text{Ag} - E^{\circ}\text{Cu}$
- $0.462 = E^{\circ}\text{Ag} - 0.337$
- $E^{\circ}\text{Ag} = 0.462 + 0.337$
- $\quad\quad\quad = \underline{0.799\text{ V}}$