

Nernst equation

Using thermodynamics of equilibrium for the given rxn



From law of mass action,

$Q < K$; rxn shift to right

$Q > K$; rxn shift to left

$Q = K$; no reaction

$$K_{eq} = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b}$$

At equilibrium

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Not equilibrium

Using this Q for above reaction, we can write

Change in Gibbs free energy for any reaction, thermodynamically

$$\Delta G = \Delta G^0 + RT \ln Q \dots\dots\dots(1)$$

For galvanic cell work is done by the cell
And this work done is electrical work done
which can be given by

$$\begin{aligned} W_{\max} &= - \text{charge} \times V \\ &= - nFE \end{aligned}$$

This work done is equal to ΔG of reaction
ie., $\Delta G = -nFE_{\text{Cell}}$

Also, $\Delta G^0 = -nFE_{\text{Cell}}^0 \dots\dots\dots(2)$

Putting this value in eq 1,

$$-nFE_{\text{Cell}} = -nFE_{\text{Cell}}^0 + RT \ln Q$$

Dividing this equation by $-nF$

$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q \dots\dots\dots(3)$$

E_{Cell} = EMF of cell (or electrode potential) at non standard condition

E_{Cell}^0 = EMF of cell (or electrode potential) at standard condition

R = Universal gas constant = 8.314 J/mol-K

T = Absolute Temperature in Kelvin

N = Number of electron take part in redox reaction

F = Faraday constant = 96500 C/mol

Q = reaction quotient similar to equilibrium constant in reversible reaction

Temperature is generally taken 25°C (298K)

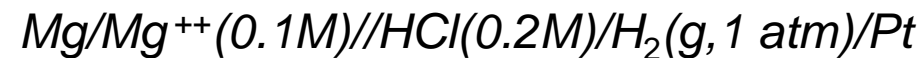
$$\boxed{E_{cell} = E_{cell}^o - \frac{0.0257}{n} \ln Q} \dots\dots\dots(4)$$

In chemistry common log is used and Since; $\ln(x) = 2.303 \log(x)$

We have,

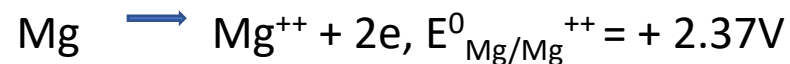
$$\boxed{E_{cell} = E_{cell}^o - \frac{0.0592}{n} \log Q} \dots\dots\dots(5)$$

Q1. Calculate the emf of given cell at 30°C

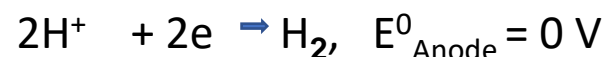


Given, $E^0_{\text{Mg}^{++}/\text{Mg}} = -2.37 \text{ V}$

Solution; At anode (oxidation)



At cathode (reduction)



Net rxn, $\text{Mg} + 2\text{H}^+ \longrightarrow \text{Mg}^{++} + \text{H}_2, E^0_{\text{cell}} = 2.37 \text{ V}$

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT}{nF} \ln Q$$

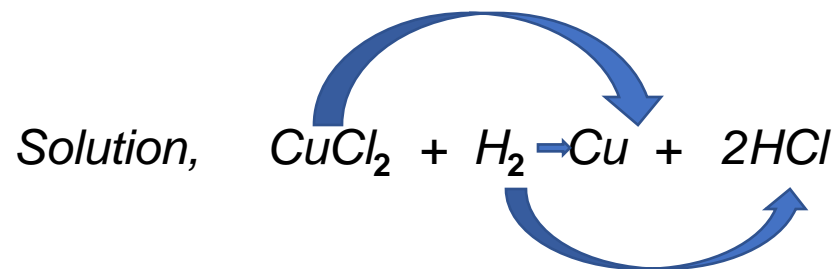
$$= 2.37 - (8.314 \times 303 / 2 \times 96500) \ln ([\text{Mg}^{++}][\text{H}_2]) / [\text{Mg}][\text{H}^+]^2$$

$$= 2.37 - 0.01305 \ln 0.1 / (0.2)^2$$

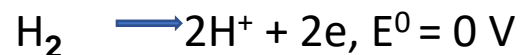
$$= 2.37 - 0.012$$

$$= 2.35 \text{ V}$$

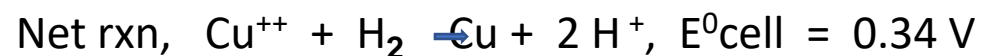
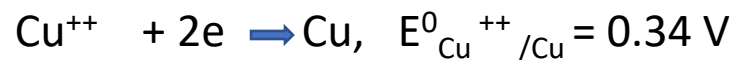
Q2. From the given reaction, calculate the emf of cell at 25° C



At anode (oxidation)

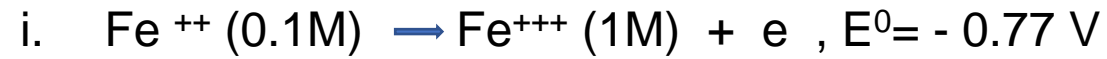


At cathode (reduction)



$$\begin{aligned}
 E_{\text{cell}} &= E^0_{\text{cell}} - \frac{RT}{nF} \ln Q \\
 &= 0.34 - (0.0592/2) \log_{10} ([\text{H}^+]^2 / [\text{Cu}^{++}]) \\
 &= 0.34 - 0.0296 \log_{10} (0.5)^2 / 0.2 \\
 &= 0.34 - 0.0028 \\
 &= 0.312 \text{ V}
 \end{aligned}$$

Q3. From the given data (I and ii) at 25° C, answer the following questions



- Write down electrode reactions
- What is net cell reaction?
- Calculate EMF of cell
- Reaction is spontaneous or not
- Write down the cell notation

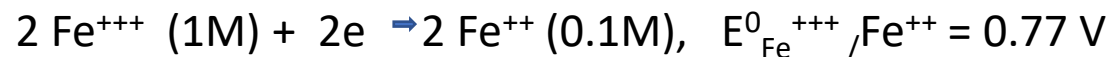
Solution; to find out anode and cathode, the electrode potential should be in terms of reduction

- i. $\text{Fe}^{++} (0.1\text{M}) \rightarrow \text{Fe}^{+++} (1\text{M}) + e^-$, $E^0_{\text{Fe}^{++}/\text{Fe}^{+++}} = -0.77 \text{ V}$, $E^0_{\text{Fe}^{+++}/\text{Fe}^{++}} = +0.77 \text{ V}$
 ii. $\text{Cu}^{++} (0.2\text{M}) + 2e^- \rightarrow \text{Cu}$, $E^0_{\text{Cu}^{++}/\text{Cu}} = 0.34 \text{ V}$

At anode (oxidation)



At cathode (reduction)



Net cell rxn, $\text{Cu} + 2 \text{Fe}^{+++} (1\text{M}) \rightarrow \text{Cu}^{++} + 2 \text{Fe}^{++} (0.1\text{M})$, $E^0_{\text{cell}} = 0.43 \text{ V}$

$$E_{\text{cell}} = E^0_{\text{cell}} - \frac{RT}{nF} \ln Q$$

$$\begin{aligned} &= 0.43 - (0.0591/2) \log_{10} ([\text{Fe}^{++}]^2 [\text{Cu}^{++}]/[\text{Fe}^{+++}]^2) \\ &= 0.43 - 0.0296 \log_{10} (0.1)^2 \times 0.2 / (1)^2 \\ &= 0.43 - (-0.079) \\ &= 0.50 \text{ V} \end{aligned}$$

Since, emf of cell is +ve, the redox reaction towards forward direction is spontaneous

Cell notation; $\text{Cu}/\text{Cu}^{++} (0.2\text{M}) // \text{Fe}^{+++} (1\text{M}) / \text{Fe}^{++} (0.1\text{M}) / \text{Pt}$

Will give you TUTORIAL next week

1) The following reaction takes place in a cell.

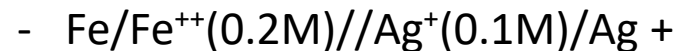


$$E^0_{\text{Zn}/\text{Zn}^{+2}} = 0.76\text{V}$$

$$E^0_{\text{Co}/\text{Co}^{+2}} = 0.18\text{V}$$

Write the cell notation and calculate the EMF of the cell.

2) From the given cell notation at 20°C



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

$$E^0_{\text{Ag}^{+}/\text{Ag}} = 0.8\text{V}$$

3) What is non-standard electrode potential? Calculate the emf of cell obtained from given electrode reactions.



4) What is single electrode potential? Calculate the emf of cell obtained by following electrode reactions at 30°C

