Q1. Calculate the standard cell potential for the following cells.

(i) $Zn_{(s)}/Zn^{2+}_{(aq,\ 1M)}||Fe^{3+}_{(aq,\ 1M)}/Fe^{2+}_{(aq,\ 1M)}$

Ans: $E^o_{cell} = E^o_{red} - E^o_{ox} = E^o_{Fe3+/Fe2+} - E^o_{Zn2+/Zn} = 0.77 - (-0.76)\ V = 1.53\ V$

(ii) $Na_{(s)}/Na^{+}_{(aq)}||Zn^{2+}_{(aq)}/Zn_{(s)}$

(iii) $Sn^{2+}_{(aq)}/Sn^{4+}_{(aq)}\ ||\ Cr_2O_7{}^{2-}_{(aq)}/Cr^{3+}_{(aq)}$

Thermodynamics of Electrochemical Cells

For an electrochemical cell to function, chemical reaction should occur at the respective electrodes. The chemical reactions at the respective electrodes will spontaneously happen only when Gibbs free energy $\Delta G<0$.

The relationship between Gibbs free energy (**ΔG**) at temperature **T** and standard Gibbs free energy (**ΔG^o**) is given by:

$$\mathbf{\Delta G = \Delta G^o + R.T.\ln Q_c}$$

Where Q_c is the reaction quotient

$aA + bB \rightarrow cC + dD$, $\quad Q_c = ([C]^c.[D]^d)/([A]^a.[B]^b)$ -----(1)

At equilibrium $Q_c = K_c$

The Gibbs free energy is related to the cell potential as: $\Delta G = -nFE_{cell}$ -----(2)

Similarly, the standard GFE is related to the standard cell potential as: $\Delta G^o = -nFE^o_{cell}$ ----(3)

From (1), (2) and (3), $-nFE_{cell} = -nFE^o_{cell} + R.T.\ln Q_c$

$$\Rightarrow E_{cell} = E^o_{cell} - (RT/nF)\ln Q_c$$

$$\mathbf{\Rightarrow E_{cell} = E^o_{cell} - (2.303RT/nF)\log Q_c}$$

This equation is called the Nernst equation and is it gives a variation of cell potential with temperature, concentration and electrons transferred.

e.g., For the net cell reaction of the Daniel cell is: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$.

$E^o_{Zn2+/Zn} = -0.76V$, $E^o_{Cu2+/Cu} = +0.34V$

Nernst equation can be applied on the above cell as follows:

$$\mathbf{E_{cell} = E^o_{cell} - (2.303RT/nF)logQ_c}$$

$$\mathbf{E_{cell} = (E^o_{red} - E^o_{ox}) - (2.303RT/nF)log\frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

$$\mathbf{E_{cell} = (0.34-(-0.76)) - (2.303RT/nF)log\frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

$$\mathbf{E_{cell} = 1.1 - (2.303RT/nF)log\frac{[Zn^{2+}]}{[Cu^{2+}]}}$$

Upon reaching equilibrium, the cell no longer generates emf, so that **at equilibrium $E_{cell} = 0V$**

At equilibrium, from the Nernst equation,

$$\mathbf{E_{cell} = E^o_{cell} - (2.303RT/nF)logQ_c}$$

$$\mathbf{=> 0 = E^o_{cell} - (2.303RT/nF)logK_c} \qquad (Q_c = K_c \text{ at equilibrium})$$

$$=> E^o_{cell} = (2.303RT/nF)logK_c$$

$$=> \log K_c = (nFE^o_{cell})/2.303RT \quad => K_c = \text{antilog}\{(nFE^o_{cell})/2.303RT\} = 10^{\frac{\text{antilog}\{(nFEocell)}{2.303RT}}$$

Q2. Calculate the equilibrium constant for the process at 25 ^{o}C, if $E^{o}_{Fe3+/Fe2+}$ = 0.771V.

Ans: Here, H_2 is getting oxidized (anode) and Fe^{3+}getting reduced (cathode).

The cell representation can be given as: **Pt, $H_{2\,(g)}/H^{+}_{(aq)}||Fe^{3+}_{(aq)}|Fe^{2+}_{(aq)}$**

From the Nernst equation,

$E_{cell} = E^{o}_{cell} - (2.303RT/nF)\log Q_c$

$0 = E^{o}_{cell} - (2.303RT/nF)\log K_c$ (at equilibrium $Q_c = K_c$ and $E_{cell} = 0$)

=> (0.771-0) = $(2.303RT/nF)\log K_c$

=>

Q2. Calculate the equilibrium constant for the reaction.

$$Fe^{+2} + Ce^{+4} \longrightarrow Fe^{+3} + Ce^{+3}$$

Given: $E^{\circ}_{Ce^{+4}/Ce^{+3}} = 1.44\ V$ and $E^{\circ}_{Fe^{+3}/Fe^{+2}} = 0.68\ V$

- EMF (cell potential) of a cell is intensive and as such non-multiplicative.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad E^0 = 0.771V$$

$$2Fe^{3+} + 2e^- \rightarrow 2Fe^{2+} \qquad E^0 = 0.771V$$

Electrode potentials are additive when, half reactions add up to give an overall cell reaction. However they are not additive/subtractive when half reactions add up to give a third half reaction. However, in such a case, **ΔGs are additive/subtractive**.

Q4. For the redox couples, Fe^{2+}/Fe, Fe^{3+}/Fe^{2+} and Fe^{3+}/Fe respectively are E^o_1, E^o_2 and E^o_3.

Find the relationship between E^o_1, E^o_2 and E^o_3.

A: $Fe^{2+} + 2e^- \rightarrow Fe$, E^o_1 --------(1)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$, E^o_2 --------(2)

$Fe^{3+} + 3e^- \rightarrow Fe$, E^o_3 --------(3)

Eqn. (3) – eqn. (1)

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ ------(2)

As a result of subtraction of (1) from (3), we get another half reaction (2), As such the respective EMFs can't be subtracted.

For eqn. (1), $\Delta G_1 = -n_1FE^o_1 = -2FE_1^o$
For eqn. (2), $\Delta G_2 = -n_2FE^o_2 = -1FE_1^o$
For eqn. (3), $\Delta G_3 = -n_3FE^o_3 = -3FE_1^o$
Since we obtain eqn. (2) by subtracting (1) from (3), as a result
$\Delta G_2 = \Delta G_3 - \Delta G_1$
$\Rightarrow -n_2FE^o_2 = -n_3FE^o_3 - (-n_1FE^o_1)$
$\Rightarrow -1FE_2^o = -3FE^o_3 - (-2FE^o_1)$
$\Rightarrow FE_2^o = 3FE^o_3 - 2FE^o_1$
$\Rightarrow E_2^o = 3E^o_3 - 2E^o_1$
$\Rightarrow 3E^o_3 = E_2^o + 2E^o_1$