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Mo Tu We Th Fr Sa Su

* Free energy and emf of the cell.

The cell potential is related to the free energy change (ΔG) for the reaction, is written as -

$\Delta G = -n F E_{cell}$

In standard state -

$\Delta G^\circ = -n F E_{cell}^\circ$

where, n = no. of electrons lost or gain in a chemical reaction.

F = Faraday Constant.

= 96500 Coulomb.

E_{cell} = emf of the cell.

Conditions -

① When $\Delta G = -ve$
 $E_{cell} = +ve$

The cell resp is spontaneous.

② When $\Delta G = 0$
 $E_{cell} = 0$ (at equilibrium)

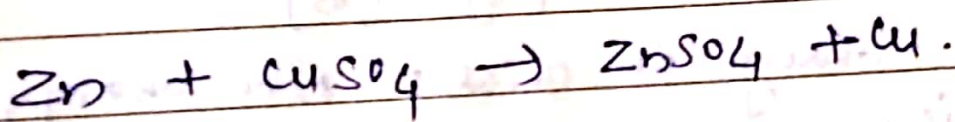


$$\textcircled{3} \quad \Delta G^\circ = +ve.$$

$$E_{\text{cell}}^\circ = -ve.$$

The given cell reaction is non-spontaneous but the reverse reaction is spontaneous.

Q. Does the given cell reaction is feasible?



Given: $E_{\text{Zn}|\text{Zn}^{2+}}^\circ = 0.76 \text{ V}.$

$$E_{\text{Cu}|\text{Cu}^{2+}}^\circ = -0.34 \text{ V}.$$

What is the value of ΔG° for the given reaction?

$$E_{\text{cell}}^\circ = 1.10 \text{ V}.$$

$$\Delta G^\circ = -nFE^\circ$$

$$= -2 \times 96500 \text{ C} \times 1.10 \text{ V}$$

$$= -212300 \text{ J} \quad (\text{C} \cdot \text{V} = \text{J})$$

$$\Delta G^\circ = -212 \text{ KJ}.$$

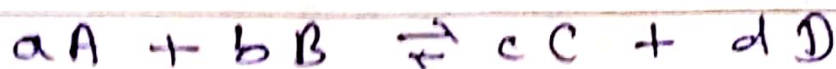
Here $E_{\text{cell}}^\circ = +ve$ value

& $\Delta G^\circ = -ve$ value

Hence, the given cell reaction is feasible.

Relationship between ΔG° and Equilibrium constant K_c .

Let us consider a ~~reversible~~ reversible reaction



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{--- (1)}$$

The change in Gibbs free energy is —

$$\Delta G = \Delta G^\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

At equilibrium, —

$$\Delta G = 0.$$

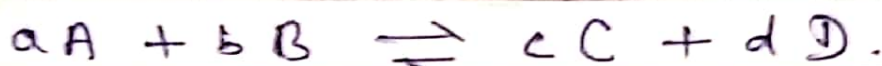
$$\therefore \Delta G^\circ = -RT \ln K_c$$

$$\therefore \Delta G^\circ = -2.303 RT \log K_c$$



*. Tu Nernst Eqⁿ -

Let us consider a general cell respⁿ -



In Thermodynamics, the change in free energy (ΔG) is given as -

$$\Delta G = \Delta G^\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Since,

$$\Delta G = -nFE$$

or

$$\Delta G^\circ = -nFE^\circ \quad (\text{In standard state})$$

from eqⁿ - ①

$$-nFE = -nFE^\circ + RT \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\Rightarrow E = E^\circ - \frac{RT}{nF} \ln \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

$$\Rightarrow E = E^\circ - \frac{2.303RT}{nF} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

→ ②



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At 298 K -

$$T = 298 \text{ K}$$

$$F = 96500 \text{ C}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\frac{2.303 RT}{F} = 0.0591 \text{ V}$$

Then, Eq^a - (2) becomes -

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

(2)

Eq^b - (2) is called Nernst Eqⁿ -