Electrochemistry

* Determination of ΔG, ΔH, ΔS and K of a cell reaction :-

Suppose in a particular reaction, 'n' is the number of electrons liberated at one electrode, then ~~accordingly~~ evidently, 'n' Faraday (nF) of electricity will be generated in the complete cell reaction. The EMF of the cell is denoted by E, then –

$$-\Delta G = nFE \quad \text{——} (1)$$

, where, ΔG = free energy change.

From Gibbs - Helmholtz equation, decrease in free energy, $-\Delta G$ of a cell at constant pressure, would be given by –

$$-\Delta G = -\Delta H - T\left(\frac{\partial \Delta G}{\partial T}\right)_P \quad \text{——} (2)$$

Where, $-\Delta H$ = decrease in the enthalpy of the cell reaction at constant pressure

Substituting the value of ΔG from eqn (1) –

~~$\Delta G = \Delta H$~~

$$nFE = -\Delta H - T\left[\frac{\partial}{\partial T}(-nFE)\right]_P$$

$$= -\Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_P \quad \text{——} (3)$$

This equation means, whether electrical energy, viz nFE is equal to or ~~[scribbled]~~ less than the enthalpy of the reaction (ΔH) depend upon the sign of $\left(\frac{\partial E}{\partial T}\right)_P$, ie. upon the sign of the temperature coefficient of the emf of the cell.

If it is zero, the electrical energy will be equal to the enthalpy of the cell reaction.

If it is positive, ie. if the emf of the cell increases with rise in temperature, the electrical energy will be greater than the enthalpy of the cell reaction.

The additional energy will be supplied to the cell by surroundings and if it is not possible, the Temperature of the cell will fall during the working.

If $\left(\frac{\partial E}{\partial T}\right)_P$ is negative, the electrical energy will be smaller than the enthalpy of the cell reaction. The difference between the two values will be given out as heat to the surroundings and if that is not possible, the Temperature of the cell will rise during the operation. In the case of Daniel cell $\left(\frac{\partial E}{\partial T}\right)_P$ is very small. Therefore, the electrical energy is very close to the enthalpy of the cell reaction.

If the heat of reaction and the Temperature coefficient of a cell are known, we can calculate the emf of the cell

$$\therefore \quad E = -\frac{\Delta H}{nF}$$

The entropy change related to the enthalpy change and free energy by the well known thermodynamic expression –

$$\Delta G = \Delta H - T\Delta S$$

$$\text{hence,} \quad -\Delta S = \frac{(\Delta G - \Delta H)}{T} \quad \text{——— (4)}$$