Applications of Nernst Equation:

(1.) Criteria of Spontaneity of cell Reaction:

Connection between sign of EMF of a cell & the nature of associated cell reaction may be derived thermodynamically.

Electron flow spontaneously from left to right electrode, provided the reduction potential of right electrode is greater than that of left electrode. Amount of electrical work involved in moving amount 'n' amount of electron from left to right is given by: $w = qdE$.

ΔG = positive, E_{cell} = negative (Reaction is Non-spontaneous in given direction & spontaneous in opposite direction)

ΔG = negative, E_{cell} = positive (Reaction is spontaneous)

$\Delta G = 0$, $E_{cell} = 0$ (At equilibrium).

(2.) Standard Potentials:

Standard state → gases at 1 atm & solution at 1M. Also activity of pure liquid/solid is unity.

All species are in standard state at 25°C & 1 bar pressure.

We use Nernst equation for cases where reactants & products are not in standard state.

Absolute value for reduction potential of any single half-reaction cannot be determined experimentally or theoretically since the activity of single ionic species like H^+, Cl^- can never be known exactly. However, difference between two reduction potentials can be determined by constructing a suitable cell & then determining its EMF experimentally.

$$E_{cell} = E_R - E_L$$

$H_2 - H^+$ half cell has been adopted as reference half cell & its standard potential has been assigned the name '0' at all temperatures.

Standard potential → $H^+(aq.) | H_2(g) | Pt$.

H^+ & H_2 gas involved are present in their standard state of unit activity & unit fugacity (taken as 1 bar pressure for gas), respectively.

$E_R = E_{cell} + 0$ (E_L = Reference hydrogen cell).

$H^+_{(aq.)} + e^- \rightleftharpoons \frac{1}{2} H_2(g)$ Standard potential = 0

Positive potential means M^{n+} can be more easily reduced to M relative to that of H^+ to H_2.
Negative potential means M^{n+} is more difficult to reduce compared to H^+.

Active metals such as Zn, Na & Mg have highly negative standard potential (lies above $H^+ + e^- \rightleftharpoons \frac{1}{2} H_2$ in electrochemical series) indicating that their compounds are not reduced by H_2 but rather the metal itself can be oxidized by H^+ to yield H_2.

Noble metals such as Cu, Ag & Au have positive E^0 values & hence their compounds are readily reduced by H_2 gas.

Electrochemical series has E^0 values of ions in increasing order of E^0 values. (Reduction potential). Those metals that lie above $H_2 - H^+$ electrode in electrochemical series forms left half cell & those stands lower than $H_2 - H^+$ electrode forms right half cell.

→ Electrode potential vary with concentration of electroactive species in solution. It is not possible to tabulate EMF of all possible electrolyte concentration & combination of electrodes. It is convenient to

measure electron accepting powers (reduction potential) of individual electrodes under standard condition relative to that of standard hydrogen electrode.

Calculation of Standard Potential for an unknown half cell:

A given reaction may be obtained from other reactions by carrying out the simple mathematical manipulations. Since G° is state function, ΔG° of given reaction may be obtained by carrying out corresponding manipulations on ΔG°'s values of the reactions. This procedure cannot be adopted while calculating E° of a half cell reaction from the values of other half cell reaction.

E° can be calculated from ΔG° on whom manipulations have been done.

This is because E° depends on overall makeup of the cell i.e. path followed. If path to find out E° of relevant reaction changes, value of E° changes but ΔG° is a state function which remains same if initial & final state remains same.

e.g. $Fe^{2+} + e^- \rightleftharpoons Fe^{+}$ $\quad E^\circ = ?$

known values:

$Fe^{3+} + 3e^- \rightleftharpoons Fe$ ① $\quad E^\circ_{Fe^{3+}/Fe} = -0.036V$

$Fe^{2+} + 2e^- \rightleftharpoons Fe$ ② $\quad E^\circ_{Fe^{2+}/Fe} = -0.440V$

For ①, $\Delta G_1^\circ = -nFE^\circ = -3F(-0.036) = 0.108F$

For ②, $\Delta G_2^\circ = -nFE^\circ = -2F(-0.440) = 0.880F$

① − ②

$Fe^{3+} + e^- \rightleftharpoons Fe$ $\quad \Delta G^\circ = \Delta G_1^\circ - \Delta G_2^\circ = (-0.772F)V$

$= -nFE^\circ$

$= -FE^\circ_{Fe^{3+}, Fe^{2+}/Pt}$

$E^\circ = 0.772\ V.$

(3) Determination of Thermodynamic Data

$$\boxed{\Delta G = -nFE_{cell}} \quad -(1.)$$

Gibbs-Helmholtz equation:

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \quad -(2.)$$

Differentiate (1.) with respect to Temperature

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = -nF\left(\frac{\partial E}{\partial T}\right)_P \quad -(3.)$$

In (2.) using (1.) & (3.) in (2.)

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

$$\boxed{\Delta H = -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right]} \quad -(4.)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

$$\boxed{\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P}$$

(4.) Determination of equilibrium constant from standard cell potential:

$$\Delta G^\circ = -RT\ln K_{eq}^\circ$$

$$-nFE^\circ_{cell} = -RT\ln K_{eq}^\circ$$

$$\boxed{E^\circ_{cell} = \frac{2.303RT}{nF}\log K_{eq}^\circ}$$

$$\boxed{w = -\Delta G = nFE_{cell}} \quad -(5.)$$

Work done

$$\Delta H = \Delta E + P\Delta V$$

$P\Delta V$ is ignored here as mechanical work is not involved. Only electrochemical work is involved here.

$\therefore \Delta H \approx \Delta E$

$$\Delta E = q + w, \quad \Delta H = q + w$$

$$q = \Delta H - w = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P + nFE \text{ (using (4.) \& (5.))}$$