

Factors affecting electrode potential

The rate of the above reactions depend on

i) The nature of the metal.

ii) The temperature.

iii) The concentration of metal ions in solution.

Single electrode potential (E)

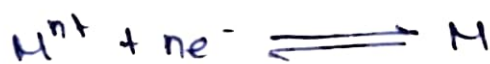
It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

Standard electrode potential (E°)

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1 molar concentration at 25°C .

Nernst equation for electrode potential:

Consider the following redox reaction.



For such a redox reversible reaction, the free energy change (ΔG) and its equilibrium

constant (k) are inter related as,

$$\Delta G = -RT \ln k + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]} \quad \text{--- (1)}$$

where,

ΔG° = standard free energy change

The above equation (1) is known as van't Hoff isotherm.
(equilibrium constant of chemical rxn to the change in temp)

The decrease in free energy ($-\Delta G$) in the above reaction will produce electrical energy. In the cell, if the reaction involves transfer of 'n' number of electrons, then 'n' faraday of electricity will flow. If E is the emf of the cell, then the total electrical energy (nEF) produced in the cell is,

$$-\Delta G = nEF$$

(or)

(Faraday - changing magnetic field induces a voltage in circuit)

$$-\Delta G^\circ = nE^\circ F \quad \text{--- (2)}$$

where,

$-\Delta G$: decrease in free energy change.

(or) $-\Delta G^\circ$ = decrease in standard free energy change.

Comparing equation 1 and 2, it becomes

$$-nEF = -nE^{\circ}F + RT \ln \frac{[M]}{[M^{n+}]} \quad \text{--- (3)}$$

Dividing the above equation (3) by $-nF$

\therefore the activity of solid metal $[M] = 1$

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]}$$

E = reduction Potential
 E° = Standard Potential

In general, $E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Product}]}{[\text{Reactant}]}$

R = universal gas constant
 T = Temp in kelvin

(or)

$$E = E^{\circ} + \frac{RT}{nF} \ln [M^{n+}]$$

n = ion charge (moles of e^{-})
 F = Faraday constant

(or)

$$E = E^{\circ} + \frac{2.303 RT}{nF} \log [M^{n+}] \quad \text{--- (4)}$$

When, $R = 8.314 \text{ J/K/mole}$; $F = 96500 \text{ coulombs}$
 $T = 298 \text{ K (25}^{\circ}\text{C)}$, the above equation becomes,

$$E = E^{\circ}_{\text{red}} + \frac{0.0591}{n} \log [M^{n+}] \quad \text{--- (5)}$$

In general, $E = E^{\circ}_{\text{red}} + \frac{0.0591}{n} \log c$

Similarly for oxidation Potential

$$E = E^{\circ}_{\text{oxi}} - \frac{0.0591}{n} \log [M^{n+}] \quad \text{--- (6)}$$

The above equation 5 & 6 are known as "Nernst equation for single electrode potential".