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Thermodynamics of reversible cells

Standard potential When all the substances taking part in a reaction in a reversible cell are in their standard state i.e. at unit activity the emf is called standard potential E° for the given cell. If the reaction occurs for the passage of n faradays, then the standard free energy ΔG° is equal to $-nFE^\circ$

Let us consider a general reversible reaction as

$$aA + bB \rightleftharpoons lC + mD$$

which occurs in the cell for the passage of n faradays

The decrease in free energy is given by the well known thermodynamic equation

$$-\Delta G = -RT \ln K = -RT \ln \frac{a_C^l \cdot a_D^m}{a_A^a \cdot a_B^b} \quad (1)$$

When all the activities are equal to unity then

$$-\Delta G^\circ = RT \ln K$$

$$\therefore nFE^\circ = RT \ln K \quad (2)$$

$$\therefore nFE = nFE^\circ - RT \ln \frac{a_C^l \cdot a_D^m}{a_A^a \cdot a_B^b}$$

or $$E = E^\circ - \frac{RT}{nF} \ln \frac{a_C^l \cdot a_D^m}{a_A^a \cdot a_B^b} \quad (3)$$

This is the general equation for the emf of any reversible cell in which the reactants and products are at any arbitrary activities a_A, a_B and a_C, a_D respectively. The equation 3 is often referred as Nernst equation.

If a_A, a_B and a_C, a_D are equal to unity, then eq. 3

$$E = E^\circ$$

Where E° is the standard potential of electrode or cell. Thus, the normal or standard potential of electrode may be defined as "the potential of the electrode when the activities or concentrations of the reactant and products are unity".

Sign of the electrode potential

The convention concerning the sign of the emf of a complete cell in conjunction with the interpretation of single electrode potentials just given fixes the convention as to the sign of electrode potential. The emf of cell

$$M \mid M^+(a_{M^+}) \mid H^+(a_{H^+}=1) \mid H_2(1\,Atm)$$ is E

which is equal and opposite to that of the cell

$$H_2(1\,Atm) \mid H^+(a_{M^+}=1) \mid M^+(a_{M^+}) \mid M \; ; -E$$

In accordance with the convention the positive sign represents the tendency for the ions to pass spontaneously from left to right - or of negative ions from right to left through a cell in which the electrode potential is combined with a hydrogen electrode.

Classification of reversible electrodes or half cells

1. Metal-metal ion half cells.
2. Amalgam half cells.
3. Gas ion half cell.
4. Metal-insoluble salt-anion half cells.
5. Oxidation reduction half cells.

1. Metal-Metal ion half cells.

$$M = M^{n+} + ne^-$$

The electrode potential equation is given by

$$E_M = E^\circ_M - \frac{RT}{nF} \ln a_{M^{n+}} \quad \text{---(1)}$$

2 Amalgam half cells

$$Pb(Hg) = Pb^{2+}(a_{Pb^{2+}}) + 2e^-$$

The electrode potential E_a is given by

$$E_a = E^\circ_{Pb} - \frac{RT}{2f} \ln \frac{a_{Pb^{2+}}}{a_{Pb}} \quad -(1)$$

Where as E°_{Pb} = standard electrode potential of pure lead

$a_{Pb^{2+}}$ = activity of plumbous ions in the solution

a_{Pb} = activity of metallic lead in the amalgam

Now eqn (1) as

$$E_a = \left(E^\circ_{Pb} + \frac{RT}{2F} \ln a_{Pb}\right) - \frac{RT}{2F} \ln a_{Pb^{2+}} \quad -(2)$$

$$= E^\circ_a - \frac{RT}{2F} \ln a_{Pb^{2+}}$$

Where as E°_a = standard potential of the given amalgam

Let us evaluate E°_a first

$$E_{Pb} = E^\circ_{Pb} - \frac{RT}{2F} \ln a_{Pb^{2+}} \quad -(3)$$

The difference in potentials E

$$E = E_{Pb} - E_a$$

$$= \left(E^\circ_{Pb} - \frac{RT}{2f} \ln a_{Pb^{2+}}\right) - \left(E^\circ_a - \frac{RT}{2f} \ln a_{Pb^{2+}}\right)$$

$$E = E^\circ_{Pb} - E^\circ_a.$$

If E and E°_a are known E°_{Pb} may be evaluated.

3. Gas - ion half cells -

For hydrogen electrode the half cell reactions

$$\frac{1}{2}H_2(g, P_{H_2}) = H^+(a_{H^+}) + e^-$$

and the potential is expressed by

$$E_{H_2} = E^\circ_{H_2} - \frac{RT}{F} \ln \frac{a_{H^+}}{a_{H_2}^{\frac{1}{2}}} \quad -(1)$$

$$E_{H_2} = -\frac{RT}{F} \ln \frac{a_{H^+}}{P_{H_2}^{1/2}}$$

Rise at moderate and low pressure $a_{H_2(g)} = P_{H_2(g)}$

At $P_{H_2(g)} = 1$ Atm $\quad \ln P_2^{1/2} = 0$ Hence

$$E_{H_2} = -\frac{RT}{F} \ln a_{H^+} \quad -(2)$$

For the chlorine electrode, we may write

$$\frac{1}{2} Cl_2(g, P_{Cl_2}) + e^- = Cl^-(a_{Cl^-})$$

$$E_{Cl_2} = E^\circ_{Cl_2} - \frac{RT}{F} \ln \frac{a_{Cl^-}}{P_{\frac{1}{2}Cl_2}} \quad -(3)$$

4. Metal - insoluble salt - anion half cells.

$$Ag(s) \rightleftharpoons Ag^+ + e^-$$

$$Ag^+ + Cl^- \rightleftharpoons AgCl(s)$$

$$Ag(s) + Cl^- = AgCl(s) + e^-$$

For this reaction the electrode potential is obtained by adding the equations.

$$Ag(s) + Cl^- = AgCl(s) + e^-$$

$$E_{Ag-AgCl} = E^\circ_{Ag-AgCl} - \frac{RT}{F} \ln \frac{1}{a_{Cl^-}} \quad -(1)$$

, and hence this electrode is reversible to chloride ion.

In analogous way for the calomel electrode we derive

$$2Hg(l) + 2Cl^- = Hg_2Cl_2(s) + 2e^-$$

and $$E_{Hg-Hg_2Cl_2} = E^\circ_{Hg-Hg_2Cl_2} - \frac{RT}{F} \ln \frac{1}{a_{Cl^-}}$$

5. Oxidation Reduction half cell.

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

Hence the electrode emf is given by

$$E = E^0 - \frac{RT}{F} \ln \frac{a_{Fe^{2+}}}{a_{Fe^{3+}}} \quad \text{--- (1)}$$

$$M_1^{n_1}(a_1) + ne^- = M^{n_2}(a_2)$$

Where n_1 is the valency in the higher state of oxidation n_2 that is the lower while $n = (n_1 - n_2)$ is the valency change attending the electrode process.

The general e.m.f equation is

$$E = E^0 - \frac{RT}{F} \ln \frac{a_2}{a_1}$$