Chapter VI :

Enthalpy, Helmholtz Energy, and Gibbs Energy

Helmholtz Energy

In thermodynamics, the Helmholtz free energy (or Helmholtz energy) is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature (isothermal). The change in the Helmholtz energy during a process is equal to the maximum amount of work that the system can perform in a thermodynamic process in which temperature is held constant. At constant temperature, the Helmholtz free energy is minimized at equilibrium.

Reversible process

According to the first law of thermodynamics:

$$dU = \delta Q + \delta W$$

where U is the internal energy, δ Q is the energy added as heat, and δ W is the work done on the system. The second law of thermodynamics for a reversible process yields $\delta Q_{rev} = TdS$

$$V = Cte => \delta W = 0, dU = \delta Q, \qquad \delta Q = TdS \ => \ dU = TdS \ => dU - TdS = 0$$

$$T = cte => dU - Tds = 0 => d(U - TS) = 0$$

U and S: state functions

$$\boldsymbol{\Delta F = \Delta U - T\Delta S}$$

If T and V constant $\boldsymbol{dF = 0 => F_1 = F_2}$

Irreversible process

$$\delta Q_{rev} = TdS$$

$$V = Cte => \delta W = 0, dU = \delta Q, \qquad \delta Q < TdS \ => \ dU < TdS \ => dU - TdS < 0$$

$$T = cte => dU - Tds < 0 => d(U - TS) < 0$$

$$\boldsymbol{\Delta F = \Delta U - T\Delta S < 0}$$

If T and V constant $\boldsymbol{dF < 0 => F_1 < F_2}$

Enthalpy free (Gibbs free energy)

In thermodynamics, the Gibbs free energy (or Gibbs energy as the recommended name; symbol G is a thermodynamic potential that can be used to calculate the maximum amount of work, other than pressure-volume work, that may be performed by a thermodynamically closed system at constant temperature and pressure. It also provides a necessary condition for processes such as chemical reactions that may occur under these conditions.

Reversible process

According to the first law of thermodynamics:

$$dU = \delta Q + \delta W$$

$\delta Q_{rev} = TdS$

$dU = \delta Q - PdV => \delta Q = dU + PdV = TdS => dU + PdV - TdS = 0$

$d(U + PV - TS) = 0 => U + PV = H => d(H - TS) = 0$

S and H: state functions

$G = H - TS => \Delta G = \Delta H - T\Delta S = 0, \quad \boldsymbol{\Delta G = \Delta H - T\Delta S}$

If T and P constant $\boldsymbol{dG = 0 => G_1 = G_2}$

Irreversible process

$\delta Q_{rev} = TdS$

$dU = \delta Q - PdV => \delta Q = dU + PdV < TdS => dU + PdV - TdS < 0$

$d(U + PV - TS) < 0 => U + PV = H => d(H - TS) < 0$

$$\boldsymbol{\Delta G = \Delta H - T\Delta S < 0}$$

If T and P constant $\boldsymbol{dG < 0 => G_1 < G_2}$

Based on the equation $\boldsymbol{\Delta G = \Delta H - T\Delta S}$, we can be predicted if the reaction is spontaneous or not:

	Sign of ΔH	**Sign of ΔS**	**Sign of ΔG**	**remark**
1	Negative (-) Exothermic	Positive (+) Endothermic	Always Negative (-)	Reaction is spontaneous at all temperatures
2	Positive (+) Endothermic	Negative (-) Decrease in entropy	Always Positive (+)	Reaction is non-spontaneous at all temperatures
3	Negative (-) Exothermic	Positive (+) Decrease in entropy	Depends upon temperature: 1) At low temperature $T\Delta S < \Delta H$ 2) At high temperature at $T > T_i$ where, $T_i = \frac{\Delta H}{\Delta S}$	Reaction is spontaneous at low temperature. Reaction is non-spontaneous at high temperature.
4	Positive (+) Endothermic	Negative (-) Decrease in entropy	Depends upon temperature: 1) At low temperature $T\Delta S < \Delta H$ 2) At high temperature $T\Delta S > \Delta H$	Reaction is non-spontaneous at low temperatures Reaction is spontaneous at high temperature

Variation of enthalpy free

$$dG = VdP - SdT$$

- $T = cte$: $dG = VdP$
- $V = cte$: $dG = -SdT$

Variation of energy free

$$dF = -pdV - SdT$$

- $T = cte$: $dF = -PdV$
- $V = cte$: $dF = -SdT$

- **Application in chemical reaction**

- **ΔG_R^0 for the reaction**

We have the following reaction

$$aA + bB \leftrightarrow cC + dD$$

ΔG_R^0 of this reaction

The standard Gibbs free energy for any reaction is just the sum of the standard Gibbs free energies of formation of the products minus the sum of the standard Gibbs free energies of formation of the reactants.

$$\Delta G°_R = \sum n_p \left(\Delta G°_f\right)_p - \sum n_R \left(\Delta G°_f\right)_R$$

$$\Delta G°_{f(N2)} = \Delta G°_{f(O2)} = \Delta G°_{f(H2)} = \Delta G°_{f(C)} = 0$$

Calculate ΔG^0

$\Delta G° = \Delta H° - T\Delta S°$

$$\Delta H°_R = \sum n_p \left(\Delta H°_f\right)_p - \sum n_R \left(\Delta H°_f\right)_R$$

$$\Delta S°_R = \sum n_p \left(S°\right)_p - \sum n_R \left(S°\right)_R$$

Chemical Equilibrium

In a chemical reaction, chemical equilibrium is the state in which both the reactants and products are present in concentrations which have no further tendency to change with time, so that there is no observable change in the properties of the system. This state results when the forward reaction proceeds at the same rate as the reverse reaction. The reaction rates of the forward and backward reactions are generally not zero, but they are equal. Thus, there are no net changes in the concentrations of the reactants and products. Such a state is known as dynamic equilibrium.

For the following reactions:

$$aA + bB \leftrightarrow cC + dD$$

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Relation between Thermodynamics and equilibrium chemical

$$\boldsymbol{\Delta G^0 = -RT\ln Kp}$$

Where: K_p: partial pressure equilibrium

$$K_P = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

$$\boldsymbol{\Delta G^0 = -RT\ln K_c}$$

Relation between k_c and k_p

$$\boldsymbol{Kp = Kc.(RT)^{\Delta n}}$$

Where :

$$\Delta n = \sum(n)_{products(gaz)} - \sum(n)_{Reactants(gaz)}$$

Van’t Hoff Equation

The Van 't Hoff equation relates the change in the equilibrium constant **K**, of a chemical reaction to the change in temperature **T**, given the standard enthalpy change. The Van 't Hoff equation has been widely utilized to explore the changes in state functions in a thermodynamic system. The Van't Hoff plot, which is derived from this equation, is especially effective in estimating the change in enthalpy and entropy of a chemical reaction.

For the **Van 't Hoff** equation, which is:

$$\boldsymbol{\frac{d\ln kp}{dT} = -\frac{1}{R}\frac{\Delta H^0}{T^2}}$$

$$\boldsymbol{=> \ln\frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)}$$