THERMODYNAMICS OF CHEMICAL EQUILIBRIUM

Spontaneous Chemical Reaction

At a constant temperature and pressure, the spontaneous change occurs in the direction that leads to lower values of the Gibbs free energy, G.

The Gibbs Free Energy Minimum

The determination of the equilibrium composition of a reaction mixture involves assessing the Gibbs energy of the mixture and pinpointing the composition that corresponds to the minimum G.

The relationship between ΔG° (change in Gibbs free energy under standard conditions) and the equilibrium constant, K, is established through the equation:

$$\Delta G = \Delta G^\circ + 2.303RT\ \log Q$$

Under equilibrium conditions, $Q = K$ and $= 0\Delta G^\circ = 0$, leading to the simplified expression:

$$\Delta G^\circ = -2.303RT\log(K)$$

The thermodynamic equilibrium constant, K, for a general reaction $aA + bB \rightleftharpoons cC + dD$ is defined as:

$$K = \frac{[a_C]^c[a_D]^d}{[a_A]^a[a_B]^b}.$$

Here, [a] denotes the activity of reactants and products, representing the ratio of the equilibrium activity to the activity in its standard state ($f = \frac{P}{P^o}$) where f is the activity or fugacity of gas and P^o is the standard pressure). The resulting activity or fugacity is dimensionless, rendering the thermodynamic equilibrium constant a unitless quantity.

(i) For pure solids and liquids, $[a] = 1$.

(ii) For gases, ideal behavior is assumed, and the activity of a gas equals its pressure in atm.

(iii) For components in a solution, [a] corresponds to molar concentration.