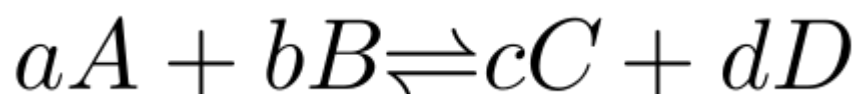


Equilibrium Constant and Free Energy

Chemical equilibrium is the state of a reversible chemical reaction in which the rates of the forward and reverse reactions become equal. At equilibrium, the concentrations of the reactants and products remain constant with time. However, the forward and reverse reactions continue simultaneously, so chemical equilibrium is dynamic in nature.

Equilibrium Constant

Consider the general reversible reaction:



According to the law of mass action, the rate of the forward reaction is proportional to the product of the concentrations of the reactants, each raised to the power of its stoichiometric coefficient. Therefore,

$$r_f = k_f[A]^a[B]^b$$

Similarly, the rate of the reverse reaction is:

$$r_b = k_b[C]^c[D]^d$$

At equilibrium, the rates of the forward and reverse reactions are equal:

$$r_f = r_b$$

Therefore,

$$k_f[A]^a[B]^b = k_b[C]^c[D]^d$$

Rearranging this equation gives:

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

At a fixed temperature, k_f and k_b have constant values. Therefore, their ratio is also constant. This constant is called the equilibrium constant.

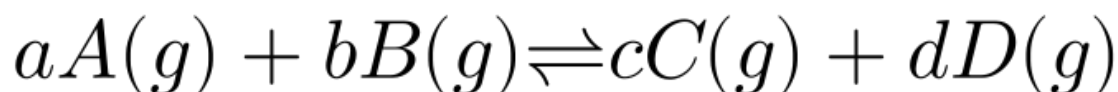
Thus, for the reaction $aA + bB \rightleftharpoons cC + dD$,

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

The subscript **C** indicates that the equilibrium constant is expressed in terms of concentration.

Equilibrium Constant in Terms of Partial Pressure

For gaseous reactions, the equilibrium constant may be expressed in terms of the partial pressures of the reacting gases. For the reaction



the pressure equilibrium constant is:

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Here, P_A , P_B , P_C and P_D are the equilibrium partial pressures of the respective gases.

Relation Between K_p and K_c

The relation between the pressure and concentration equilibrium constants can be derived using the ideal gas equation.

For an ideal gas:

$$PV = nRT$$

Dividing both sides by V :

$$P = \frac{n}{V}RT$$

Since n/V represents molar concentration:

$$P = CRT$$

Therefore, for the individual gases:

$$P_A = [A]RT$$

$$P_B = [B]RT$$

$$P_C = [C]RT$$

$$P_D = [D]RT$$

The expression for K_p is:

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

Substituting the pressure-concentration relation:

$$K_p = \frac{([C]RT)^c ([D]RT)^d}{([A]RT)^a ([B]RT)^b}$$

Expanding the powers:

$$K_p = \frac{[C]^c [D]^d (RT)^{c+d}}{[A]^a [B]^b (RT)^{a+b}}$$

Separating the concentration and temperature terms:

$$K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{c+d-a-b}$$

The concentration term is K_c :

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

Also,

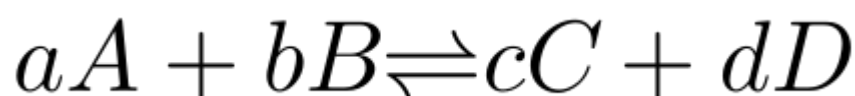
$$\Delta n = (c + d) - (a + b)$$

Therefore:

$$K_p = K_c (RT)^{\Delta n}$$

Thermodynamic Equilibrium Constant

The most fundamental form of the equilibrium constant is expressed in terms of the activities of the reacting species. For the reaction



the thermodynamic equilibrium constant is:

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

Here, a_A , a_B , a_C and a_D represent the activities of the respective species.

For an ideal gas, the activity is defined relative to the standard pressure:

$$a_i = \frac{P_i}{P^\circ}$$

where P° is the standard pressure.

Gibbs Free Energy

The thermodynamic condition for chemical equilibrium is conveniently described using Gibbs free energy. Gibbs free energy is defined as:

$$G = H - TS$$

For a chemical reaction:

$$\Delta G = \Delta H - T\Delta S$$

At constant temperature and pressure, a system tends towards a state of lower Gibbs free energy. The reaction proceeds until the equilibrium state is reached.

At equilibrium, there is no net thermodynamic driving force for the reaction. Therefore:

$$\Delta G = 0$$

Chemical Potential and Gibbs Free Energy

To obtain the thermodynamic relationship between Gibbs free energy and the equilibrium constant, we use the concept of chemical potential.

The chemical potential of a component is defined as its partial molar Gibbs free energy:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_j}$$

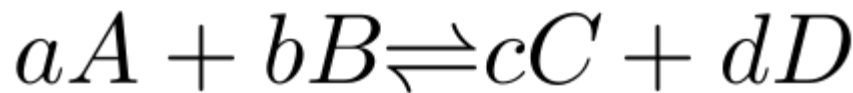
For an ideal system, the chemical potential is related to activity by:

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

Here, μ_i° is the standard chemical potential and a_i is the activity of the component.

Thermodynamic Derivation

Consider the reaction:



The Gibbs free-energy change of the reaction is equal to the sum of the chemical potentials of the products minus the sum of the chemical potentials of the reactants:

$$\Delta G = c\mu_C + d\mu_D - a\mu_A - b\mu_B$$

Substituting

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

for each species:

$$\Delta G = c(\mu_C^\circ + RT \ln a_C) + d(\mu_D^\circ + RT \ln a_D) - a(\mu_A^\circ + RT \ln a_A) - b(\mu_B^\circ + RT \ln a_B)$$

Expanding the terms:

$$\Delta G = c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ + RT(c \ln a_C + d \ln a_D - a \ln a_A - b \ln a_B)$$

The standard chemical-potential terms represent the standard Gibbs free-energy change:

$$\Delta G^\circ = c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ$$

Therefore:

$$\Delta G = \Delta G^\circ + RT(c \ln a_C + d \ln a_D - a \ln a_A - b \ln a_B)$$

Using the logarithmic relation

$$n \ln x = \ln x^n$$

the logarithmic terms can be combined:

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right)$$

The expression inside the logarithm is the reaction quotient Q . Therefore:

$$\boxed{\Delta G = \Delta G^\circ + RT \ln Q}$$

Derivation of the Relation Between ΔG° and K

At equilibrium, the activities of the reactants and products have their equilibrium values. Therefore, the reaction quotient becomes equal to the equilibrium constant:

$$Q = K$$

At equilibrium, the Gibbs free-energy change of the net reaction is zero:

$$\Delta G = 0$$

Starting from:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

and putting $Q = K$:

$$0 = \Delta G^\circ + RT \ln K$$

Rearranging:

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

Therefore:

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

Since:

$$\ln K = 2.303 \log K$$

the equation can also be written as:

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

Significance of the Relation

The equation

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

shows that the equilibrium constant has a direct thermodynamic significance.

When:

$$K > 1$$

then:

$$\Delta G^{\circ} < 0$$

and the equilibrium composition is relatively product-rich.

When:

$$K < 1$$

then:

$$\Delta G^{\circ} > 0$$

and the equilibrium composition is relatively reactant-rich.

When:

$$K = 1$$

then:

$$\Delta G^{\circ} = 0$$

Relation Between ΔG , Q and K

The actual Gibbs free-energy change can be related directly to the reaction quotient and equilibrium constant.

We have:

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

and:

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

Substituting:

$$\Delta G = -RT \ln K + RT \ln Q$$

Therefore:

$$\Delta G = RT(\ln Q - \ln K)$$

Using:

$$\ln Q - \ln K = \ln \left(\frac{Q}{K} \right)$$

we obtain:

$$\Delta G = RT \ln \left(\frac{Q}{K} \right)$$

If:

$$Q < K$$

then:

$$\Delta G < 0$$

and the forward reaction is thermodynamically favoured.

If:

$$Q > K$$

then:

$$\Delta G > 0$$

for the forward reaction, and the reverse direction is favoured.

If:

$$Q = K$$

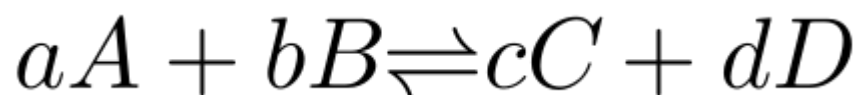
then:

$$\Delta G = 0$$

and the system is at equilibrium.

Important Equations

For the general reaction:



the important equations are:

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

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_p = K_c (RT)^{\Delta n}$$

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

$$\Delta G = \Delta G^\circ + RT \ln Q$$

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

$$\Delta G = RT \ln \left(\frac{Q}{K} \right)$$

Summary

The equilibrium constant describes the composition of a reversible chemical system at equilibrium. For gaseous reactions, the concentration and pressure equilibrium constants are related through the ideal gas equation. The thermodynamic treatment is based on chemical potential and activity. From the relation between chemical potential and activity, the Gibbs free-energy equation is obtained as

$$\Delta G = \Delta G^\circ + RT \ln Q.$$

At equilibrium, $Q = K$ and $\Delta G = 0$, giving the important thermodynamic relation

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

Thus, the equilibrium constant and Gibbs free energy are directly related.