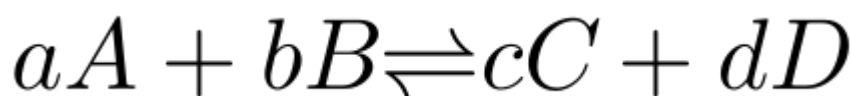


Thermodynamic Derivation of the Law of Mass Action

The law of mass action gives the mathematical relationship between the concentrations or activities of the reactants and products of a chemical reaction at equilibrium. Although the law can be introduced from reaction kinetics, its more fundamental form can be derived from thermodynamic principles using chemical potential and Gibbs free energy.

General Chemical Reaction

Consider a general reversible reaction:



Here, A and B are the reactants, C and D are the products, and a , b , c and d are their respective stoichiometric coefficients.

Chemical Potential

The thermodynamic derivation of the law of mass action is based on the concept of chemical potential. Chemical potential is defined as the partial molar Gibbs free energy of a component.

For a component i , the chemical potential is defined as:

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

where G is Gibbs free energy, n_i is the number of moles of component i , T is temperature and P is pressure.

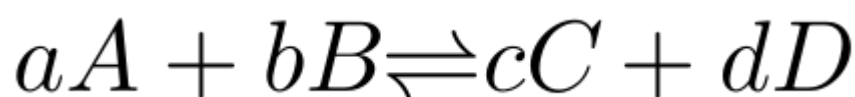
For an ideal system, the chemical potential of a component is related to its activity by:

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

Here, μ_i° is the standard chemical potential of the component, R is the gas constant, T is the absolute temperature and a_i is the activity of the component.

Gibbs Free Energy Change of the Reaction

For 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.

Therefore:

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

Substituting the expression

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

for each component, we get:

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

On expanding:

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

Standard Gibbs Free Energy Change

The first group of terms represents the standard Gibbs free-energy change of the reaction. Thus:

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

Therefore, the Gibbs free-energy change can be written as:

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

Combining the Logarithmic Terms

Using the logarithmic relation:

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

we can write:

$$c \ln a_C = \ln a_C^c$$

$$d \ln a_D = \ln a_D^d$$

Similarly:

$$a \ln a_A = \ln a_A^a$$

and:

$$b \ln a_B = \ln a_B^b$$

Therefore:

$$\Delta_r G = \Delta_r G^\circ + RT[\ln a_C^c + \ln a_D^d - \ln a_A^a - \ln a_B^b]$$

Using the logarithmic relation:

$$\ln x + \ln y = \ln(xy)$$

and:

$$\ln x - \ln y = \ln \left(\frac{x}{y} \right)$$

we obtain:

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

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

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

where:

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

Condition of Equilibrium

At equilibrium, the Gibbs free energy of the system is at its minimum value for the specified temperature and pressure. Consequently, there is no net driving force for the reaction and:

$$\Delta_r G = 0$$

At equilibrium, the reaction quotient becomes constant. This equilibrium value is called the thermodynamic equilibrium constant K .

Therefore:

$$Q = K$$

Hence, at equilibrium:

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

Rearranging:

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

Therefore:

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

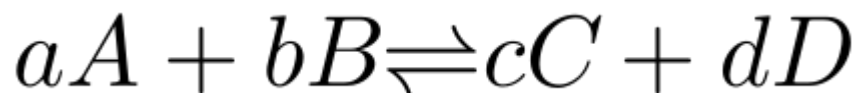
Derivation of the Law of Mass Action

The thermodynamic equilibrium constant is:

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

This is the thermodynamic form of the law of mass action.

Thus, for the general reaction



the equilibrium constant is given by the ratio of the product of the activities of the products to the product of the activities of the reactants, with each activity raised to the corresponding stoichiometric coefficient.

Therefore:

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

This equation represents the law of mass action in its thermodynamically rigorous form.

For Ideal Gases

For an ideal gas, the activity of a gaseous species is defined as the ratio of its partial pressure to the standard pressure:

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

Substituting these activities into the thermodynamic equilibrium expression:

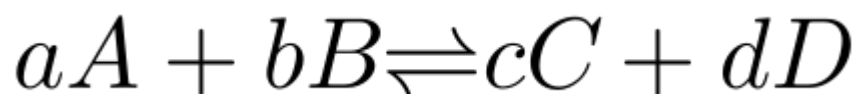
$$K = \frac{\left(\frac{P_C}{P^\circ}\right)^c \left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b}$$

This is the thermodynamic form of the pressure equilibrium constant. Since the standard pressure is fixed, it is commonly represented by the familiar K_p expression.

For Dilute Solutions

For an ideal dilute solution, the activity of a solute can be approximated by its concentration relative to the standard concentration. Therefore, the thermodynamic expression reduces to the concentration form.

For the reaction



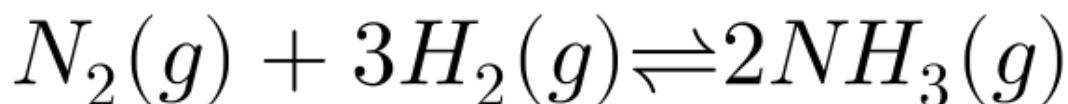
the concentration equilibrium constant is:

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

Thus, the familiar concentration form of the law of mass action is an approximation to the more fundamental activity-based thermodynamic expression when the solution behaves ideally or is sufficiently dilute.

Example

Consider the reaction:



The thermodynamic equilibrium constant is:

$$K = \frac{a_{NH_3}^2}{a_{N_2} a_{H_2}^3}$$

For an ideal dilute or concentration-based treatment, this becomes:

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

For an ideal gaseous system, using activities based on partial pressures:

$$K_p = \frac{(P_{NH_3}/P^\circ)^2}{(P_{N_2}/P^\circ)(P_{H_2}/P^\circ)^3}$$

Significance of the Thermodynamic Derivation

The thermodynamic derivation shows that the law of mass action is not merely an empirical concentration relationship. Its fundamental form arises from the dependence of chemical potential on activity.

The key thermodynamic relation is:

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

which leads to:

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

At equilibrium:

$$\Delta_r G = 0$$

and:

$$Q = K$$

Therefore:

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

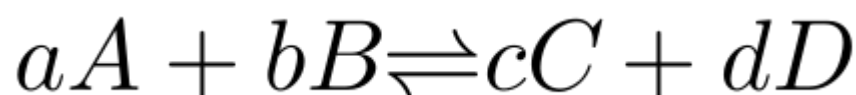
and:

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

Thus, the law of mass action, equilibrium constant and Gibbs free energy are directly connected through thermodynamics.

Important Equations

For the reaction:



the important thermodynamic equations are:

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

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

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

At equilibrium:

$$Q = K$$

and:

$$\Delta_r G = 0$$

Therefore:

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

and:

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

Summary

The thermodynamic derivation of the law of mass action begins with the chemical potential of each component. For an ideal system, the chemical potential is related to activity by

$\mu_i = \mu_i^\circ + RT \ln a_i$. Applying this relation to a general

chemical reaction gives $\Delta_r G = \Delta_r G^\circ + RT \ln Q$.

At equilibrium, $\Delta_r G = 0$ and $Q = K$. Consequently, the equilibrium constant is expressed as the ratio of the activities of the products to those of the reactants, each raised to its stoichiometric coefficient. This is the thermodynamic form of the law of mass action.