

Thermodynamics and Equilibrium Chemistry

Thermodynamics is the study of thermal, electrical, chemical, and mechanical forms of energy. The study of thermodynamics crosses many disciplines, including physics, engineering, and chemistry. Of the various branches of thermodynamics, the most important to chemistry is the study of the change in energy during a chemical reaction.

Consider, for example, the general equilibrium reaction shown in equation 6.1, involving the species A, B, C, and D, with stoichiometric coefficients a , b , c , and d .



For obvious reasons, we call the double arrow, \rightleftharpoons , an equilibrium arrow.

By convention, we identify species on the left side of the equilibrium arrow as reactants, and those on the right side of the equilibrium arrow as products. As Berthollet discovered, writing a reaction in this fashion does not guarantee that the reaction of A and B to produce C and D is favorable. Depending on initial conditions, the reaction may move to the left, move to the right, or be in a state of equilibrium. Understanding the factors that determine the reaction's final, equilibrium position is one of the goals of chemical thermodynamics.

The direction of a reaction is that which lowers the overall free energy. At a constant temperature and pressure, typical of many bench-top chemical reactions, a reaction's free energy is given by the **Gibb's free energy** function

$$\Delta G = \Delta H - T\Delta S \quad (6.2)$$

where T is the temperature in kelvin, and ΔG , ΔH , and ΔS are the differences in the Gibb's free energy, the enthalpy, and the entropy between the products and the reactants.

Enthalpy is a measure of the flow of energy, as heat, during a chemical reaction. Reactions releasing heat have a negative ΔH and are called exothermic. Endothermic reactions absorb heat from their surroundings and have a positive ΔH . **Entropy** is a measure of energy that is unavailable for useful, chemical work. The entropy of an individual species is always positive and tends to be larger for gases than for solids, and for more complex molecules than for simpler molecules. Reactions producing a large number of simple, gaseous products usually have a positive ΔS .

For many students, entropy is the most difficult topic in thermodynamics to understand. For a rich resource on entropy, visit the following web site: <http://www.entropysite.com/>.

The sign of ΔG indicates the direction in which a reaction moves to reach its equilibrium position. A reaction is thermodynamically favorable when its enthalpy, ΔH , decreases and its entropy, ΔS , increases. Substituting the inequalities $\Delta H < 0$ and $\Delta S > 0$ into equation 6.2 shows that a reaction is thermodynamically favorable when ΔG is negative. When ΔG is positive the reaction is unfavorable as written (although the reverse reaction is favorable). A reaction at equilibrium has a ΔG of zero.

Equation 6.2 shows that the sign of ΔG depends on the signs of ΔH and ΔS , and the temperature, T . The following table summarizes the possibilities.

ΔH	ΔS	ΔG
-	+	$\Delta G < 0$ at all temperatures
-	-	$\Delta G < 0$ at low temperatures
+	+	$\Delta G < 0$ at low temperatures
+	-	$\Delta G > 0$ at all temperatures

As a reaction moves from its initial, non-equilibrium condition to its equilibrium position, the value of ΔG approaches zero. At the same time, the chemical species in the reaction experience a change in their concentrations. The Gibb's free energy, therefore, must be a function of the concentrations of reactants and products.

As shown in equation 6.3, we can split the Gibb's free energy into two terms.

$$\Delta G = \Delta G^\circ + RT \ln Q \quad (6.3)$$

The first term, ΔG° , is the change in Gibb's free energy when each species in the reaction is in its **standard state**, which we define as follows: gases with partial pressures of 1 atm, solutes with concentrations of 1 mol/L, and pure solids and pure liquids. The second term, which includes the reaction quotient, Q , accounts for non-standard state pressures or concentrations. For reaction 6.1 the reaction quotient is

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad (6.4)$$

where the terms in brackets are the concentrations of the reactants and products. Note that we define the reaction quotient with the products are in the numerator and the reactants are in the denominator. In addition, we raise the concentration of each species to a power equivalent to its stoichiometry in the balanced chemical reaction. For a gas, we use partial pressure in place of concentration. Pure solids and pure liquids do not appear in the reaction quotient.

Although not shown here, each concentration term in equation 6.4 is divided by the corresponding standard state concentration; thus, the term $[C]^c$ really means

$$\left\{ \frac{[C]}{[C]^\circ} \right\}^c$$

where $[C]^\circ$ is the standard state concentration for C. There are two important consequences of this: (1) the value of Q is unitless; and (2) the ratio has a value of 1 for a pure solid or a pure liquid. This is the reason that pure solids and pure liquids do not appear in the reaction quotient.

At equilibrium the Gibb's free energy is zero, and equation 6.3 simplifies to

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

where K is an **equilibrium constant** that defines the reaction's equilibrium position. The equilibrium constant is just the numerical value of the reaction quotient, Q , when substituting equilibrium concentrations into equation 6.4.

$$K = \frac{[C]_{\text{ceq}} [D]_{\text{deq}}}{[A]_{\text{aeq}} [B]_{\text{beq}}} \quad (6.5)$$

Here we include the subscript "eq" to indicate a concentration at equilibrium. Although we usually will omit the "eq" when writing equilibrium constant expressions, it is important to remember that the value of K is determined by equilibrium concentrations.