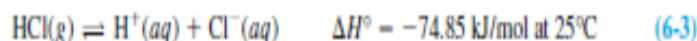


6-2 Equilibrium and Thermodynamics

Equilibrium is controlled by the thermodynamics of a chemical reaction. The heat absorbed or released (*enthalpy*) and the degree of disorder of reactants and products (*entropy*) independently contribute to the degree to which the reaction is favored or disfavored.

Enthalpy

The **enthalpy change**, ΔH , for a reaction is the heat absorbed or released when the reaction takes place under constant applied pressure.⁵ The *standard enthalpy change*, ΔH° , refers to the heat absorbed when all reactants and products are in their standard states:[†]



The negative sign of ΔH° indicates that heat is released by Reaction 6-3—the solution becomes warmer. For other reactions, ΔH is positive, which means that heat is absorbed. Consequently, the solution gets colder during the reaction. A reaction for which ΔH is positive is said to be **endothermic**. Whenever ΔH is negative, the reaction is **exothermic**.

Entropy

The **entropy**, S , of a substance is a measure of its “disorder,” which we will not attempt to define in a quantitative way. The greater the disorder, the greater the entropy. In general, a gas is more disordered (has higher entropy) than a liquid, which is more disordered than a solid. Ions in aqueous solution are normally more disordered than in their solid salt:



ΔS° is the change in entropy (entropy of products minus entropy of reactants) when all species are in their standard states. The positive value of ΔS° indicates that a mole of $\text{K}^+(aq)$ plus a mole of $\text{Cl}^-(aq)$ is more disordered than a mole of $\text{KCl}(s)$. For Reaction 6-3, $\Delta S^\circ = -130.4 \text{ J/(K}\cdot\text{mol)}$ at 25°C . The aqueous ions are less disordered than gaseous HCl.

Free Energy

Systems at constant temperature and pressure, which are common laboratory conditions, have a tendency toward lower enthalpy and higher entropy. A chemical reaction is driven toward the formation of products by a *negative* value of ΔH (heat given off) or a *positive* value of ΔS (more disorder) or both. When ΔH is negative and ΔS is positive, the reaction is clearly favored. When ΔH is positive and ΔS is negative, the reaction is clearly disfavored.

[†]The definition of the standard state contains subtleties beyond the scope of this book. For Reaction 6-3, the standard state of H^+ or Cl^- is the hypothetical state in which each ion is present at a concentration of 1 M but behaves as if it were in an infinitely dilute solution. That is, the standard concentration is 1 M, but the standard behavior is what would be observed in a very dilute solution in which each ion is unaffected by surrounding ions.

$\Delta H = (+)$
Heat is absorbed
Endothermic

$\Delta H = (-)$
Heat is liberated
Exothermic

$\Delta S = (+)$
Products more disordered than reactants

$\Delta S = (-)$
Products less disordered than reactants

When ΔH and ΔS are both positive or both negative, what decides whether a reaction will be favored? The change in **Gibbs free energy**, ΔG , is the arbiter between opposing tendencies of ΔH and ΔS . At constant temperature, T ,

$$\text{Free energy:} \quad \Delta G = \Delta H - T\Delta S \quad (6-5)$$

A reaction is favored if ΔG is negative.

For the dissociation of HCl (Reaction 6-3) when all species are in their standard states, ΔH° favors the reaction and ΔS° disfavors it. To find the net result, we evaluate ΔG° :

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= (-74.85 \times 10^3 \text{ J/mol}) - (298.15 \text{ K})(-130.4 \text{ J/K}\cdot\text{mol}) \\ &= -35.97 \text{ kJ/mol} \end{aligned}$$

ΔG° is negative, so the reaction is favored when all species are in their standard states. The favorable influence of ΔH° is greater than the unfavorable influence of ΔS° in this case.

The point of discussing free energy is to relate the equilibrium constant to the energetics (ΔH° and ΔS°) of a reaction. The equilibrium constant depends on ΔG° in the following manner:

$$\text{Free energy and equilibrium:} \quad K = e^{-\Delta G^\circ/RT} \quad (6-6)$$

where R is the gas constant [$-8.314 \text{ 472 J/(K}\cdot\text{mol)}$] and T is temperature (Kelvin). The more negative the value of ΔG° , the larger is the equilibrium constant. For Reaction 6-3,

$$K = e^{-(-35.97 \times 10^3 \text{ J/mol})/[8.314 \text{ 472 J/(K}\cdot\text{mol)}](298.15 \text{ K})} = 2.00 \times 10^6$$

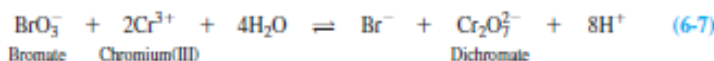
Because the equilibrium constant is large, HCl(g) is very soluble in water and is nearly completely ionized to H^+ and Cl^- when it dissolves.

To summarize, a chemical reaction is favored by the liberation of heat (ΔH negative) and by an increase in disorder (ΔS positive). ΔG takes both effects into account to determine whether or not a reaction is favorable. We say that a reaction is *spontaneous* under standard conditions if ΔG° is negative or, equivalently, if $K > 1$. The reaction is not spontaneous if ΔG° is positive ($K < 1$). You should be able to calculate K from ΔG° and vice versa.

Le Châtelier's Principle

Suppose that a system at equilibrium is subjected to a change that disturbs the system. **Le Châtelier's principle** states that the direction in which the system proceeds back to equilibrium is such that the change is partially offset.

To see what this statement means, let's see what happens when we attempt to change the concentration of one species in the reaction



$$K = \frac{[\text{Br}^-][\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^8}{[\text{BrO}_3^-][\text{Cr}^{3+}]^2} = 1 \times 10^{11} \text{ at } 25^\circ\text{C}$$

In one particular equilibrium state of this system, the following concentrations exist: $[\text{H}^+] = 5.0 \text{ M}$, $[\text{Cr}_2\text{O}_7^{2-}] = 0.10 \text{ M}$, $[\text{Cr}^{3+}] = 0.003 \text{ 0 M}$, $[\text{Br}^-] = 1.0 \text{ M}$, and $[\text{BrO}_3^-] = 0.043 \text{ M}$. Suppose that the equilibrium is disturbed by adding dichromate to the solution to increase the concentration of $[\text{Cr}_2\text{O}_7^{2-}]$ from 0.10 to 0.20 M. In what direction will the reaction proceed to reach equilibrium?

According to the principle of Le Châtelier, the reaction should go back to the left to partially offset the increase in dichromate, which appears on the right side of Reaction 6-7. We can verify this algebraically by setting up the **reaction quotient**, Q , which has the same form as the equilibrium constant. The only difference is that Q is evaluated with whatever concentrations happen to exist, even though the solution is not at equilibrium. When the system reaches equilibrium, $Q = K$. For Reaction 6-7,

$$Q = \frac{(1.0)(0.20)(5.0)^8}{(0.043)(0.003 \text{ 0})^2} = 2 \times 10^{11} > K$$

Note that $25.00^\circ\text{C} = 298.15 \text{ K}$.

Challenge Satisfy yourself that $K > 1$ if ΔG° is negative.

$\Delta G = (+)$
Reaction is disfavored

$\Delta G = (-)$
Reaction is favored

Notice that H_2O is omitted from K because it is the solvent.

The reaction quotient has the same form as the equilibrium constant, but the concentrations are generally not the equilibrium concentrations.

Because $Q > K$, the reaction must go to the left to decrease the numerator and increase the denominator, until $Q = K$.

1. If a reaction is at equilibrium and products are added (or reactants are removed), the reaction goes to the left.
2. If a reaction is at equilibrium and reactants are added (or products are removed), the reaction goes to the right.

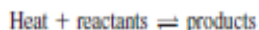
When the temperature of a system is changed, so is the equilibrium constant. Equations 6-5 and 6-6 can be combined to predict the effect of temperature on K :

$$K = e^{-\Delta G^\circ/RT} = e^{-(\Delta H^\circ - T\Delta S^\circ)/RT} = e^{(-\Delta H^\circ/RT + \Delta S^\circ/R)} = e^{-\Delta H^\circ/RT} \cdot e^{\Delta S^\circ/R} \quad (6-8)$$

The term $e^{\Delta S^\circ/R}$ is independent of T (at least over a limited temperature range in which ΔS° is constant). The term $e^{-\Delta H^\circ/RT}$ increases with increasing temperature if ΔH° is positive and decreases if ΔH° is negative. Therefore,

1. The equilibrium constant of an endothermic reaction ($\Delta H^\circ = +$) increases if the temperature is raised.
2. The equilibrium constant of an exothermic reaction ($\Delta H^\circ = -$) decreases if the temperature is raised.

These statements can be understood in terms of Le Châtelier's principle as follows. Consider an endothermic reaction:



If the temperature is raised, then heat is added to the system. The reaction proceeds to the right to partially offset this change.⁶

In dealing with equilibrium problems, we are making *thermodynamic* predictions, not *kinetic* predictions. We are calculating what must happen for a system to reach equilibrium, but not how long it will take. Some reactions are over in an instant; others will not reach equilibrium in a million years. For example, dynamite remains unchanged indefinitely, until a spark sets off the spontaneous, explosive decomposition. The size of an equilibrium constant tells us nothing about the rate (the kinetics) of the reaction. A large equilibrium constant does not imply that a reaction is fast.

if $Q < K$, then the reaction must proceed to the right to reach equilibrium. if $Q > K$, then the reaction must proceed to the left to reach equilibrium.

$$e^{(a+b)} = e^a \cdot e^b$$

Heat can be treated as if it were a reactant in an endothermic reaction and a product in an exothermic reaction.