

19.8: Free Energy Changes for Nonstandard States - The Relationship between and

Learning Objectives

- To know the relationship between free energy and the equilibrium constant.

We have identified three criteria for whether a given reaction will occur spontaneously:

1. $\Delta S_{univ} > 0$,
2. $\Delta G_{sys} < 0$ (applicable under constant temperature and constant pressure conditions), and
3. the relative magnitude of the reaction quotient Q versus the equilibrium constant K .

Recall that if $Q < K$, then the reaction proceeds spontaneously to the right as written, resulting in the net conversion of reactants to products. Conversely, if $Q > K$, then the reaction proceeds spontaneously to the left as written, resulting in the net conversion of products to reactants. If $Q = K$, then the system is at equilibrium, and no net reaction occurs. Table 19.8.1 summarizes these criteria and their relative values for spontaneous, nonspontaneous, and equilibrium processes.

Table 19.8.1: Criteria for the Spontaneity of a Process as Written

Spontaneous	Equilibrium	Nonspontaneous*
$\Delta S_{univ} > 0$	$\Delta S_{univ} = 0$	$\Delta S_{univ} < 0$
$\Delta G_{sys} < 0$	$\Delta G_{sys} = 0$	$\Delta G_{sys} > 0$
$Q < K$	$Q = K$	$Q > K$
*Spontaneous in the reverse direction.		

Because all three criteria are assessing the same thing—the spontaneity of the process—it would be most surprising indeed if they were not related. In this section, we explore the relationship between the standard free energy of reaction (ΔG°) and the equilibrium constant (K).

Free Energy and the Equilibrium Constant

Because ΔH° and ΔS° determine the magnitude and sign of ΔG° and also because K is a measure of the ratio of the concentrations of products to the concentrations of reactants, we should be able to express K in terms of ΔG° and vice versa. "Free Energy", ΔG is equal to the maximum amount of work a system can perform on its surroundings while undergoing a spontaneous change. For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature, thereby eliminating ΔH from the equation for ΔG . The general relationship can be shown as follows (derivation not shown):

$$\Delta G = V\Delta P - S\Delta T \quad (19.8.1)$$

If a reaction is carried out at constant temperature ($\Delta T = 0$), then Equation 19.8.1 simplifies to

$$\Delta G = V\Delta P \quad (19.8.2)$$

Under normal conditions, the pressure dependence of free energy is not important for solids and liquids because of their small molar volumes. For reactions that involve gases, however, the effect of pressure on free energy is very important.

Assuming ideal gas behavior, we can replace the V in Equation 19.8.2 by nRT/P (where n is the number of moles of gas and R is the ideal gas constant) and express ΔG in terms of the initial and final pressures (P_i and P_f , respectively):

$$\Delta G = \left(\frac{nRT}{P} \right) \Delta P \quad (19.8.3)$$

$$= nRT \frac{\Delta P}{P} \quad (19.8.4)$$

$$= nRT \ln \left(\frac{P_f}{P_i} \right) \quad (19.8.5)$$

If the initial state is the standard state with $P_i = 1 \text{ atm}$, then the change in free energy of a substance when going from the standard state to any other state with a pressure P can be written as follows:

$$G - G^\circ = nRT \ln P$$

This can be rearranged as follows:

$$G = G^\circ + nRT \ln P \quad (19.8.6)$$

As you will soon discover, Equation 19.8.6 allows us to relate ΔG° and K_p . Any relationship that is true for K_p must also be true for K because K_p and K are simply different ways of expressing the equilibrium constant using different units.

Let's consider the following hypothetical reaction, in which all the reactants and the products are ideal gases and the lowercase letters correspond to the stoichiometric coefficients for the various species:



Because the free-energy change for a reaction is the difference between the sum of the free energies of the products and the reactants, we can write the following expression for ΔG :

$$\Delta G = \sum_m G_{\text{products}} - \sum_n G_{\text{reactants}} \quad (19.8.8)$$

$$= (cG_C + dG_D) - (aG_A + bG_B) \quad (19.8.9)$$

Substituting Equation 19.8.6 for each term into Equation 19.8.9

$$\Delta G = [(cG_C^\circ + cRT \ln P_C) + (dG_D^\circ + dRT \ln P_D)] - [(aG_A^\circ + aRT \ln P_A) + (bG_B^\circ + bRT \ln P_B)]$$

Combining terms gives the following relationship between ΔG and the reaction quotient Q :

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{P_C^c P_D^d}{P_A^a P_B^b} \right) \quad (19.8.10)$$

$$= \Delta G^\circ + RT \ln Q \quad (19.8.11)$$

where ΔG° indicates that all reactants and products are in their standard states. For gases at equilibrium ($Q = K_p$), and as you've learned in this chapter, $\Delta G = 0$ for a system at equilibrium. Therefore, we can describe the relationship between ΔG° and K_p for gases as follows:

$$0 = \Delta G^\circ + RT \ln K_p \quad (19.8.12)$$

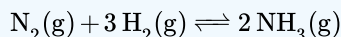
$$\Delta G^\circ = -RT \ln K_p \quad (19.8.13)$$

If the products and reactants are in their standard states and $\Delta G^\circ < 0$, then $K_p > 1$, and products are favored over reactants when the reaction is at equilibrium. Conversely, if $\Delta G^\circ > 0$, then $K_p < 1$, and reactants are favored over products when the reaction is at equilibrium. If $\Delta G^\circ = 0$, then $K_p = 1$, and neither reactants nor products are favored when the reaction is at equilibrium.

For a spontaneous process under standard conditions, K_{eq} and K_p are greater than 1.

✓ Example 19.8.1

ΔG° is -32.7 kJ/mol of N_2 for the reaction



This calculation was for the reaction under standard conditions—that is, with all gases present at a partial pressure of 1 atm and a temperature of 25°C . Calculate ΔG for the same reaction under the following nonstandard conditions:

- $P_{\text{N}_2} = 2.00 \text{ atm}$,
- $P_{\text{H}_2} = 7.00 \text{ atm}$,
- $P_{\text{NH}_3} = 0.021 \text{ atm}$, and
- $T = 100^\circ\text{C}$.

Does the reaction proceed to the right, as written, or to the left to reach equilibrium?

Given: balanced chemical equation, partial pressure of each species, temperature, and ΔG°

Asked for: whether the reaction proceeds to the right or to the left to reach equilibrium

Strategy:

- Using the values given and Equation 19.8.11, calculate Q .
- Determine if Q is $>$, $<$, or $=$ to K
- Substitute the values of ΔG° and Q into Equation 19.8.11 to obtain ΔG for the reaction under nonstandard conditions.

Solution:

A The relationship between ΔG° and ΔG under nonstandard conditions is given in Equation 19.8.11. Substituting the partial pressures given, we can calculate Q :

$$Q = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = \frac{(0.021)^2}{(2.00)(7.00)^3} = 6.4 \times 10^{-7}$$

B Because ΔG° is $-$, K must be a number greater than 1

C Substituting the values of ΔG° and Q into Equation 19.8.11,

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ &= -32.7 \text{ kJ} + \left[(8.314 \text{ J/K})(373 \text{ K}) \left(\frac{1 \text{ kJ}}{1000 \text{ J}} \right) \ln(6.4 \times 10^{-7}) \right] \\ &= -32.7 \text{ kJ} + (-44 \text{ kJ}) \\ &= -77 \text{ kJ/mol of N}_2 \end{aligned}$$

Because $\Delta G < 0$ and $Q < K$ (because $Q < 1$), the reaction proceeds spontaneously to the right, as written, in order to reach equilibrium.

? Exercise 19.8.1

Calculate ΔG for the reaction of nitric oxide with oxygen to give nitrogen dioxide under these conditions: $T = 50^\circ\text{C}$, $P_{\text{NO}} = 0.0100 \text{ atm}$, $P_{\text{O}_2} = 0.200 \text{ atm}$, and $P_{\text{NO}_2} = 1.00 \times 10^{-4} \text{ atm}$. The value of ΔG° for this reaction is $-72.5 \text{ kJ/mol of O}_2$. Are products or reactants favored?

Answer

$-92.9 \text{ kJ/mol of O}_2$; the reaction is spontaneous to the right as written. The reaction will proceed in the forward direction to reach equilibrium.

✓ Example 19.8.2

Calculate K_p for the reaction of H_2 with N_2 to give NH_3 at 25°C . ΔG° for this reaction is $-32.7 \text{ kJ/mol of N}_2$.

Given: balanced chemical equation from Example 19.8.1, ΔG° , and temperature

Asked for: K_p

Strategy:

Substitute values for ΔG° and T (in kelvin) into Equation 19.8.13 to calculate K_p , the equilibrium constant for the formation of ammonia.

Solution

In Example 19.8.1, we used tabulated values of ΔG°_f to calculate ΔG° for this reaction (-32.7 kJ/mol of N_2). For equilibrium conditions, rearranging Equation 19.8.13

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

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

Inserting the value of ΔG° and the temperature ($25^\circ\text{C} = 298$ K) into this equation,

$$\ln K_p = -\frac{(-32.7 \text{ kJ})(1000 \text{ J/kJ})}{(8.314 \text{ J/K})(298 \text{ K})} = 13.2$$

$$K_p = 5.4 \times 10^5$$

Thus the equilibrium constant for the formation of ammonia at room temperature is product-favored. However, the rate at which the reaction occurs at room temperature is too slow to be useful.

? Exercise 19.8.3

Calculate K_p for the reaction of NO with O_2 to give NO_2 at 25°C . ΔG° for this reaction is -70.5 kJ/mol of O_2 .

Answer

$$2.3 \times 10^{12}$$

Although K_p is defined in terms of the partial pressures of the reactants and the products, the equilibrium constant K is defined in terms of the concentrations of the reactants and the products. The numerical magnitude of K_p and K are related:

$$K_p = K(RT)^{\Delta n} \quad (19.8.14)$$

where Δn is the number of moles of gaseous product minus the number of moles of gaseous reactant. For reactions that involve only solutions, liquids, and solids, $\Delta n = 0$, so $K_p = K$. For all reactions that do not involve a change in the number of moles of gas present, the relationship in Equation 19.8.13 can be written in a more general form:

$$\Delta G^\circ = -RT \ln K \quad (19.8.15)$$

Only when a reaction results in a net production or consumption of gases is it necessary to correct Equation 19.8.15 for the difference between K_p and K .

📌 Non-Ideal Behavior

Although we typically use concentrations or pressures in our equilibrium calculations, recall that equilibrium constants are generally expressed as unitless numbers because of the use of **activities** or **fugacities** in precise thermodynamic work. Systems that contain gases at high pressures or concentrated solutions that deviate substantially from ideal behavior require the use of fugacities or activities, respectively.

Combining Equation 19.8.15 with $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ provides insight into how the components of ΔG° influence the magnitude of the equilibrium constant:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (19.8.16)$$

$$= -RT \ln K \quad (19.8.17)$$

Notice that K becomes larger as ΔS° becomes more positive, indicating that the magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum disorder. Moreover, K increases as ΔH° decreases. Thus the magnitude of the equilibrium constant is also directly influenced by the tendency of a system to seek the lowest energy state possible.

The magnitude of the equilibrium constant is directly influenced by the tendency of a system to move toward maximum entropy and seek the lowest energy state possible.



Relating Grxn and Kp: [Relating Grxn and Kp\(opens in new window\)](#) [youtu.be]

Temperature Dependence of the Equilibrium Constant

The fact that ΔG° and K are related provides us with another explanation of why equilibrium constants are temperature dependent. This relationship is shown explicitly in Equation 19.8.17, which can be rearranged as follows:

$$\ln K = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (19.8.18)$$

Assuming ΔH° and ΔS° are temperature independent, for an exothermic reaction ($\Delta H^\circ < 0$), the magnitude of K decreases with increasing temperature, whereas for an endothermic reaction ($\Delta H^\circ > 0$), the magnitude of K increases with increasing temperature. The quantitative relationship expressed in Equation 19.8.18 agrees with the qualitative predictions made by applying Le Chatelier's principle. Because heat is produced in an exothermic reaction, adding heat (by increasing the temperature) will shift the equilibrium to the left, favoring the reactants and decreasing the magnitude of K . Conversely, because heat is consumed in an endothermic reaction, adding heat will shift the equilibrium to the right, favoring the products and increasing the magnitude of K . Equation 19.8.18 also shows that the magnitude of ΔH° dictates how rapidly K changes as a function of temperature. In contrast, the magnitude and sign of ΔS° affect the magnitude of K but not its temperature dependence.

If we know the value of K at a given temperature and the value of ΔH° for a reaction, we can estimate the value of K at any other temperature, even in the absence of information on ΔS° . Suppose, for example, that K_1 and K_2 are the equilibrium constants for a reaction at temperatures T_1 and T_2 , respectively. Applying Equation 19.8.18 gives the following relationship at each temperature:

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + \frac{\Delta S^\circ}{R}$$

and

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + \frac{\Delta S^\circ}{R}$$

Subtracting $\ln K_1$ from $\ln K_2$,

$$\ln K_2 - \ln K_1 = \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (19.8.19)$$

Thus calculating ΔH° from tabulated enthalpies of formation and measuring the equilibrium constant at one temperature (K_1) allow us to calculate the value of the equilibrium constant at any other temperature (K_2), assuming that ΔH° and ΔS° are independent of temperature.

✓ Example 19.8.4

The equilibrium constant for the formation of NH_3 from H_2 and N_2 at 25°C was calculated to be $K_p = 5.4 \times 10^5$ in Example 19.8.3. What is K_p at 500°C ? (Use the data from Example 19.8.1.)

Given: balanced chemical equation, ΔH° , initial and final T , and K_p at 25°C

Asked for: K_p at 500°C

Strategy:

Convert the initial and final temperatures to kelvin. Then substitute appropriate values into Equation 19.8.19 to obtain K_2 , the equilibrium constant at the final temperature.

Solution:

The value of ΔH° for the reaction obtained using Hess's law is -91.8 kJ/mol of N_2 . If we set $T_1 = 25^\circ\text{C} = 298 \text{ K}$ and $T_2 = 500^\circ\text{C} = 773 \text{ K}$, then from Equation 19.8.19 we obtain the following:

$$\begin{aligned}\ln \frac{K_2}{K_1} &= \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ &= \frac{(-91.8 \text{ kJ})(1000 \text{ J/kJ})}{8.314 \text{ J/K}} \left(\frac{1}{298 \text{ K}} - \frac{1}{773 \text{ K}} \right) = -22.8 \\ \frac{K_2}{K_1} &= 1.3 \times 10^{-10} \\ K_2 &= (5.4 \times 10^5)(1.3 \times 10^{-10}) = 7.0 \times 10^{-5}\end{aligned}$$

Thus at 500°C , the equilibrium strongly favors the reactants over the products.

? Exercise 19.8.4

In the exercise in Example 19.8.3 you calculated $K_p = 2.2 \times 10^{12}$ for the reaction of NO with O_2 to give NO_2 at 25°C . Use the ΔH_f° values in the exercise in Example 19.8.1 to calculate K_p for this reaction at 1000°C .

Answer

$$5.6 \times 10^{-4}$$



The Van't Hoff Equation: [The Van't Hoff Equation \(opens in new window\)](#) [youtu.be]

Summary

For a reversible process that does not involve external work, we can express the change in free energy in terms of volume, pressure, entropy, and temperature. If we assume ideal gas behavior, the ideal gas law allows us to express ΔG in terms of the partial

pressures of the reactants and products, which gives us a relationship between ΔG and K_p , the equilibrium constant of a reaction involving gases, or K , the equilibrium constant expressed in terms of concentrations. If $\Delta G^\circ < 0$, then $K > 1$, and products are favored over reactants at equilibrium. Conversely, if $\Delta G^\circ > 0$, then $K < 1$, and reactants are favored over products at equilibrium. If $\Delta G^\circ = 0$, then $K=1$, and neither reactants nor products are favored at equilibrium. We can use the measured equilibrium constant K at one temperature and ΔH° to estimate the equilibrium constant for a reaction at any other temperature.

Contributors and Attributions

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