Sample Exercise 19.1 Identifying Spontaneous Processes

Predict whether the following processes are spontaneous as described, spontaneous in the reverse direction, or in equilibrium: (a) When a piece of metal heated to 150 °C is added to water at 40 °C, the water gets hotter. (b) Water at room temperature decomposes into H₂(g) and O₂(g). (c) Benzene vapor, C₆H₆(g), at a pressure of 1 atm condenses to liquid benzene at the normal boiling point of benzene, 80.1 °C.

Solution

Analyse: We are asked to judge whether each process will proceed spontaneously in the direction indicated, in the reverse direction, or in neither direction.

Plan: We need to think about whether each process is consistent with our experience about the natural direction of events or whether we expect the reverse process to occur.

Solve: (a) This process is spontaneous. Whenever two objects at different temperatures are brought into contact, heat is transferred from the hotter object to the colder one. Thus, heat is transferred from the hot metal to the cooler water. The final temperature, after the metal and water achieve the same temperature (thermal equilibrium), will be somewhere between the initial temperatures of the metal and the water.

(b) Experience tells us that this process is not spontaneous—we certainly have never seen hydrogen and oxygen gases spontaneously bubbling up out of water! Rather, the reverse process—the reaction of H₂ and O₂ to form H₂O—is spontaneous.

(c) By definition, the normal boiling point is the temperature at which a vapor at 1 atm is in equilibrium with its liquid. Thus, this is an equilibrium situation. If the temperature were below 80.1 °C, condensation would be spontaneous.

Practice Exercise

Under 1 atm pressure CO₂(s) sublimes at −78 °C. Is the transformation of CO₂(s) to CO₂(g) a spontaneous process at −100 °C and 1 atm pressure?

Answer: No, the reverse process is spontaneous at this temperature.
Sample Exercise 19.2 Calculating $\Delta S$ for a Phase Change

The element mercury, Hg, is a silvery liquid at room temperature. The normal freezing point of mercury is $-38.9 \, ^\circ C$, and its molar enthalpy of fusion is $\Delta H_{\text{fusion}} = 2.29 \, \text{kJ/mol}$. What is the entropy change of the system when 50.0 g of Hg($l$) freezes at the normal freezing point?

Solution

Analyze: We first recognize that freezing is an exothermic process; heat is transferred from the system to the surroundings when a liquid freezes ($q < 0$). The enthalpy of fusion is $\Delta H$ for the melting process. Because freezing is the reverse of melting, the enthalpy change that accompanies the freezing of 1 mol of Hg is $-\Delta H_{\text{fusion}} = -2.29 \, \text{kJ/mol}$.

Plan: We can use $-\Delta H_{\text{fusion}}$ and the atomic weight of Hg to calculate $q$ for freezing 50.0 g of Hg:

\[
q = (50.0 \, \text{g Hg}) \left( \frac{1 \, \text{mol Hg}}{200.59 \, \text{g Hg}} \right) \left( \frac{-2.29 \, \text{kJ}}{1 \, \text{mol Hg}} \right) \left( \frac{1000 \, \text{J}}{1 \, \text{kJ}} \right) = -571 \, \text{J}
\]

We can use this value of $q$ as $q_{\text{rev}}$ in Equation 19.2. We must first, however, convert the temperature to K:

\[-38.9 \, ^\circ C = (-38.9 + 273.15) \, \text{K} = 234.3 \, \text{K}\]

Solve: We can now calculate the value of $\Delta S_{\text{sys}}$:

\[
\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T} = \frac{-571 \, \text{J}}{234.3 \, \text{K}} = -2.44 \, \text{J/K}
\]

Check: The entropy change is negative because heat flows from the system, making $q_{\text{rev}}$ negative.

Comment: The procedure we have used here can be used to calculate $\Delta S$ for other isothermal phase changes, such as the vaporization of a liquid at its boiling point.
Sample Exercise 19.2 Calculating $\Delta S$ for a Phase Change

Practice Exercise

The normal boiling point of ethanol, $\text{C}_2\text{H}_5\text{OH}$, is 78.3 °C, and its molar enthalpy of vaporization is 38.56 kJ/mol. What is the change in entropy in the system when 68.3 g of $\text{C}_2\text{H}_5\text{OH}(g)$ at 1 atm condenses to liquid at the normal boiling point?

*Answer:* $-163 \text{ J/K}$
Sample Exercise 19.3 Predicting the Sign of $\Delta S$

Predict whether $\Delta S$ is positive or negative for each of the following processes, assuming each occurs at constant temperature:

(a) $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$
(b) $\text{Ag}^+(aq) + \text{Cl}^-(aq) \rightarrow \text{AgCl}(s)$
(c) $4\text{Fe}(s) + 3\text{O}_2(g) \rightarrow 2\text{Fe}_2\text{O}_3(s)$
(d) $\text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g)$

Solution

Analyze: We are given four equations and asked to predict the sign of $\Delta S$ for each chemical reaction.

Plan: The sign of $\Delta S$ will be positive if there is an increase in temperature, an increase in the volume in which the molecules move, or an increase in the number of gas particles in the reaction. The question states that the temperature is constant. Thus, we need to evaluate each equation with the other two factors in mind.

Solve:
(a) The evaporation of a liquid is accompanied by a large increase in volume. One mole of water (18 g) occupies about 18 mL as a liquid and if it could exist as a gas at STP it would occupy 22.4 L. Because the molecules are distributed throughout a much larger volume in the gaseous state than in the liquid state, an increase in motional freedom accompanies vaporization. Therefore, $\Delta S$ is positive.
(b) In this process the ions, which are free to move throughout the volume of the solution, form a solid in which they are confined to a smaller volume and restricted to more highly constrained positions. Thus, $\Delta S$ is negative.
(c) The particles of a solid are confined to specific locations and have fewer ways to move (fewer microstates) than do the molecules of a gas. Because $\text{O}_2$ gas is converted into part of the solid product $\text{Fe}_2\text{O}_3$, $\Delta S$ is negative.
(d) The number of moles of gases is the same on both sides of the equation, and so the entropy change will be small. The sign of $\Delta S$ is impossible to predict based on our discussions thus far, but we can predict that $\Delta S$ will be close to zero.
Sample Exercise 19.3 Predicting the Sign of ΔS

Practice Exercise

Indicate whether each of the following processes produces an increase or decrease in the entropy of the system:

(a) CO₂(s) → CO₂(g)
(b) CaO(s) + CO₂(g) → CaCO₃(s)
(c) HCl(g) + NH₃(g) → NH₄Cl(s)
(d) 2 SO₂(g) + O₂(g) → 2 SO₃(g)

Answer: (a) increase, (b) decrease, (c) decrease, (d) decrease
Sample Exercise 19.4 Predicting Which Sample of Matter Has the Higher Entropy

Choose the sample of matter that has greater entropy in each pair, and explain your choice: (a) 1 mol of NaCl(s) or 1 mol of HCl(g) at 25 °C, (b) 2 mol of HCl(g) or 1 mol of HCl(g) at 25 °C, (c) 1 mol of HCl(g) or 1 mol of Ar(g) at 298 K.

Solution

Analyze: We need to select the system in each pair that has the greater entropy.
Plan: To do this, we examine the state of the system and the complexity of the molecules it contains.
Solve: (a) Gaseous HCl has the higher entropy because gases have more available motions than solids. (b) The sample containing 2 mol of HCl has twice the number of molecules as the sample containing 1 mol. Thus, the 2-mol sample has twice the number of microstates and twice the entropy when they are at the same pressure. (c) The HCl sample has the higher entropy because the HCl molecule is capable of storing energy in more ways than is Ar. HCl molecules can rotate and vibrate; Ar atoms cannot.

Practice Exercise

Choose the substance with the greater entropy in each case: (a) 1 mol of H₂(g) at STP or 1 mol of H₂(g) at 100 °C and 0.5 atm, (b) 1 mol of H₂O(s) at 0 °C or 1 mol of H₂O(l) at 25 °C, (c) 1 mol of H₂(g) at STP or 1 mol of SO₂(g) at STP, (d) 1 mol of N₂O₄(g) at STP or 2 mol of NO₂(g) at STP.

Answers: (a) 1 mol of H₂(g) at 100 °C and 0.5 atm, (b) 1 mol of H₂O(l) at 25 °C, (c) 1 mol of SO₂(g) at STP, (d) 2 mol of NO₂(g) at STP.
Sample Exercise 19.5 Calculating $\Delta S$ from Tabulated Entropies

Calculate $\Delta S^\circ$ for the synthesis of ammonia from $\text{N}_2(g)$ and $\text{H}_2(g)$ at 298 K:

$$\text{N}_2(g) + 3 \text{H}_2(g) \rightarrow 2 \text{NH}_3(g)$$

**Solution**

**Analyze:** We are asked to calculate the entropy change for the synthesis of $\text{NH}_3(g)$ from its constituent elements.

**Plan:** We can make this calculation using Equation 19.8 and the standard molar entropy values for the reactants and the products that are given in Table 19.2 and in Appendix C.

**Solve:** Using Equation 19.8, we have

$$\Delta S^\circ = 2S^\circ(\text{NH}_3) - [S^\circ(\text{N}_2) + 3S^\circ(\text{H}_2)]$$

Substituting the appropriate $S^\circ$ values from Table 19.2 yields

$$\Delta S^\circ = (2 \text{ mol})(192.5 \text{ J/mol-K}) - [(1 \text{ mol})(191.5 \text{ J/mol-K}) + (3 \text{ mol})(130.6 \text{ J/mol-K})] = -198.3 \text{ J/K}$$

**Check:** The value for $\Delta S^\circ$ is negative, in agreement with our qualitative prediction based on the decrease in the number of molecules of gas during the reaction.

**Practice Exercise**

Using the standard entropies in Appendix C, calculate the standard entropy change, $\Delta S^\circ$, for the following reaction at 298 K:

$$\text{Al}_2\text{O}_3(s) + 3 \text{H}_2(g) \rightarrow 2 \text{Al}(s) + 3 \text{H}_2\text{O}(g)$$

**Answers:** 180.39 J/K
Sample Exercise 19.6 Calculating Free-Energy Change from $\Delta H^\circ$, $T$, $\Delta S^\circ$

Calculate the standard free energy change for the formation of NO(g) from N$_2$(g) and O$_2$(g) at 298 K:

$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{NO}(\text{g})$$

given that $\Delta H^\circ = 180.7 \text{ kJ}$ and $\Delta S^\circ = 24.7 \text{ J/K}$. Is the reaction spontaneous under these circumstances?

**Solution**

**Analyze:** We are asked to calculate $\Delta G^\circ$ for the indicated reaction (given $\Delta H^\circ$, $\Delta S^\circ$ and $T$) and to predict whether the reaction is spontaneous under standard conditions at 298 K.

**Plan:** To calculate $\Delta G^\circ$, we use Equation 19.12, $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$. To determine whether the reaction is spontaneous under standard conditions, we look at the sign of $\Delta G^\circ$.

**Solve:**

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

$$= 180.7 \text{ kJ} - (298 \text{ K})(24.7 \text{ J/K})(1 \text{ kJ})$$

$$= 180.7 \text{ kJ} - 7.4 \text{ kJ}$$

$$= 173.3 \text{ kJ}$$

Because $\Delta G^\circ$ is positive, the reaction is not spontaneous under standard conditions at 298 K.

**Comment:** Notice that we had to convert the units of the $T \Delta S^\circ$ term to kJ so that they could be added to the $\Delta H^\circ$ term, whose units are kJ.

**Practice Exercise**

A particular reaction has $\Delta H^\circ = 24.6 \text{ kJ}$ and $\Delta S^\circ = 132 \text{ J/K}$ at 298 K. Calculate $\Delta G^\circ$.

Is the reaction spontaneous under these conditions?

**Answers:** $\Delta G^\circ = -14.7 \text{ kJ}$; the reaction is spontaneous.
Sample Exercise 19.7 Calculating Standard Free-Energy Change from Free Energies of Formation

(a) Use data from Appendix C to calculate the standard free-energy change for the following reaction at 298 K:

\[ \text{P}_4(\text{g}) + 6 \text{Cl}_2(\text{g}) \rightarrow 4 \text{PCl}_3(\text{g}) \]

(b) What is \( \Delta G^\circ \) for the reverse of the above reaction?

Solution

**Analyze:** We are asked to calculate the free-energy change for the indicated reaction and then to determine the free-energy change of its reverse.

**Plan:** To accomplish our task, we look up the free-energy values for the products and reactants and use Equation 19.14: We multiply the molar quantities by the coefficients in the balanced equation, and subtract the total for the reactants from that for the products.

**Solve:**

(a) \( \text{Cl}_2(\text{g}) \) is in its standard state, so \( \Delta G^\circ_f \) is zero for this reactant. \( \text{P}_4(\text{g}) \), however, is not in its standard state, so \( \Delta G^\circ_f \) is not zero for this reactant. From the balanced equation and using Appendix C, we have:

\[
\Delta G^\circ_{\text{rxn}} = 4 \Delta G^\circ_f[\text{PCl}_3(\text{g})] - \Delta G^\circ_f[\text{P}_4(\text{g})] - 6 \Delta G^\circ_f[\text{Cl}_2(\text{g})] \\
= (4 \text{ mol})(-269.6 \text{ kJ/mol}) - (1 \text{ mol})(24.4 \text{ kJ/mol}) - 0 \\
= -1102.8 \text{ kJ}
\]
Sample Exercise 19.7 Calculating Standard Free-Energy Change from Free Energies of Formation

Solution (continued)

The fact that $\Delta G^\circ$ is negative tells us that a mixture of $P_4(g)$, $Cl_2(g)$, and $PCl_3(g)$ at 25 °C, each present at a partial pressure of 1 atm, would react spontaneously in the forward direction to form more $PCl_3$. Remember, however, that the value of $\Delta G^\circ$ tells us nothing about the rate at which the reaction occurs.

(b) Remember that $\Delta G = G(\text{products}) - G(\text{reactants})$. If we reverse the reaction, we reverse the roles of the reactants and products. Thus, reversing the reaction changes the sign of $\Delta G$, just as reversing the reaction changes the sign of $\Delta H$. (Section 5.4) Hence, using the result from part (a):

$$4 \text{ PCl}_3(g) \rightarrow \text{ P}_4(g) + 6 \text{ Cl}_2(g) \Delta G^\circ = +1102.8 \text{ kJ}$$

Practice Exercise

By using data from Appendix C, calculate $\Delta G^\circ$ at 298 K for the combustion of methane:

$\text{CH}_4(g) + 2 \text{ O}_2(g) \rightarrow \text{CO}_2(g) + 2 \text{ H}_2\text{O}(g)$.

Answer: $-800.7$ kJ
Sample Exercise 19.8 Estimating and Calculating $\Delta G^\circ$

In Section 5.7 we used Hess’s law to calculate $\Delta H^\circ$ for the combustion of propane gas at 298 K:

$$\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(l) \quad \Delta H^\circ = -2220 \text{ kJ}$$

(a) Without using data from Appendix C, predict whether $\Delta G^\circ$ for this reaction is more negative or less negative than $\Delta H^\circ$. (b) Use data from Appendix C to calculate the standard free-energy change for the reaction at 298 K. Is your prediction from part (a) correct?

Solution

Analyze: In part (a) we must predict the value for $\Delta G^\circ$ relative to that for $\Delta H^\circ$ on the basis of the balanced equation for the reaction. In part (b) we must calculate the value for $\Delta G^\circ$ and compare with our qualitative prediction.

Plan: The free-energy change incorporates both the change in enthalpy and the change in entropy for the reaction (Equation 19.11), so under standard conditions:

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

To determine whether $\Delta G^\circ$ is more negative or less negative than $\Delta H^\circ$, we need to determine the sign of the term $T \Delta S^\circ$. $T$ is the absolute temperature, 298 K, so it is a positive number. We can predict the sign of $\Delta S^\circ$ by looking at the reaction.
Sample Exercise 19.8 Estimating and Calculating $\Delta G^\circ$

Solution (continued)

Solve:

(a) We see that the reactants consist of six molecules of gas, and the products consist of three molecules of gas and four molecules of liquid. Thus, the number of molecules of gas has decreased significantly during the reaction. By using the general rules we discussed in Section 19.3, we would expect a decrease in the number of gas molecules to lead to a decrease in the entropy of the system—the products have fewer accessible microstates than the reactants. We therefore expect $\Delta S^\circ$ and therefore $T \Delta S^\circ$ to be negative numbers. Because we are subtracting $T \Delta S^\circ$, which is a negative number, we would predict that $\Delta G^\circ$ is less negative than $\Delta H^\circ$.

(b) Using Equation 19.14 and values from Appendix C, we can calculate the value of $\Delta G^\circ$

\[
\Delta G^\circ = 3 \Delta G_f^\circ[CO_2(g)] + 4 \Delta G_f^\circ[H_2O(l)] - \Delta G_f^\circ[C_3H_8(g)] - 5 \Delta G_f^\circ[O_2(g)]
\]

\[
= 3 \text{ mol}(-394.4 \text{ kJ/mol}) + 4 \text{ mol}(-237.13 \text{ kJ/mol}) - 1 \text{ mol}(-23.47 \text{ kJ/mol}) - 5 \text{ mol}(0 \text{ kJ/mol}) = -2108 \text{ kJ}
\]

Notice that we have been careful to use the value of $\Delta G_f^\circ$ for H$_2$O(l), as in the calculation of $\Delta H$ values, the phases of the reactants and products are important. As we predicted, $\Delta G^\circ$ is less negative than $\Delta H^\circ$ because of the decrease in entropy during the reaction.

Practice Exercise

Consider the combustion of propane to form $CO_2(g)$ and $H_2O(g)$ at 298 K: $C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(g)$. Would you expect $\Delta G^\circ$ to be more negative or less negative than $\Delta H^\circ$?

Answer: more negative
Sample Exercise 19.9 Determining the Effect of Temperature on Spontaneity

The Haber process for the production of ammonia involves the equilibrium

\[ \text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]

Assume that \( \Delta H^\circ \) and \( \Delta S^\circ \) for this reaction do not change with temperature. (a) Predict the direction in which \( \Delta G^\circ \) for this reaction changes with increasing temperature. (b) Calculate the values \( \Delta G^\circ \) of for the reaction at 25 °C and 500 °C.

Solution

**Analyze:** In part (a) we are asked to predict the direction in which \( \Delta G^\circ \) for the ammonia synthesis reaction changes as temperature increases. In part (b) we need to determine \( \Delta G^\circ \) for the reaction at two different temperatures.

**Plan:** In part (a) we can make this prediction by determining the sign of \( \Delta S^\circ \) for the reaction and then using that information to analyze Equation 19.12. In part (b) we need to calculate \( \Delta H^\circ \) and \( \Delta S^\circ \) for the reaction by using the data in Appendix C. We can then use Equation 19.12 to calculate \( \Delta G^\circ \).

**Solve:**

(a) Equation 19.12 tells us that \( \Delta G^\circ \) is the sum of the enthalpy term \( \Delta H^\circ \) and the entropy term \(-T \Delta S^\circ\). The temperature dependence of \( \Delta G^\circ \) comes from the entropy term. We expect \( \Delta S^\circ \) for this reaction to be negative because the number of molecules of gas is smaller in the products. Because \( \Delta S^\circ \) is negative, the term \(-T \Delta S^\circ\) is positive and grows larger with increasing temperature. As a result, \( \Delta G^\circ \) becomes less negative (or more positive) with increasing temperature. Thus, the driving force for the production of \( \text{NH}_3 \) becomes smaller with increasing temperature.

(b) We calculated the value of \( \Delta H^\circ \) in Sample Exercise 15.14, and the value of \( \Delta S^\circ \) was determined in Sample Exercise 19.5: \( \Delta H^\circ = -92.38 \text{ kJ} \) and \( \Delta S^\circ = -198.3 \text{ J/K} \). If we assume that these values do not change with temperature, we can calculate \( \Delta G^\circ \) at any temperature by using Equation 19.12. At \( T = 298 \text{ K} \) we have:
Sample Exercise 19.9 Determining the Effect of Temperature on Spontaneity

Solution (continued)

\[
\Delta G^\circ = -92.38 \text{ kJ} - (298 \text{ K})(-198.3 \text{ J/K})(\frac{1 \text{ kJ}}{1000 \text{ J}})
\]
\[
= -92.38 \text{ kJ} + 59.1 \text{ kJ} = -33.3 \text{ kJ}
\]

At \(T = 500 + 273 = 773 \text{ K}\) we have

\[
\Delta G^\circ = -92.38 \text{ kJ} - (773 \text{ K})(-198.3 \frac{\text{ J}}{\text{ K}})(\frac{1 \text{ kJ}}{1000 \text{ J}})
\]
\[
= -92.38 \text{ kJ} + 153 \text{ kJ} = 61 \text{ kJ}
\]

Notice that we have been careful to convert \(-T \Delta S^\circ\) into units of kJ so that it can be added to \(\Delta H^\circ\), which has units of kJ.

Comment: Increasing the temperature from 298 K to 773 K changes \(\Delta G^\circ\) from \(-33.3 \text{ kJ}\) to \(+61 \text{ kJ}\). Of course, the result at 773 K depends on the assumption that \(\Delta H^\circ\) and \(\Delta S^\circ\) do not change with temperature. In fact, these values do change slightly with temperature. Nevertheless, the result at 773 K should be a reasonable approximation. The positive increase in \(\Delta G^\circ\) with increasing \(T\) agrees with our prediction in part (a) of this exercise. Our result indicates that a mixture of \(N_2(g)\), \(H_2(g)\), and \(NH_3(g)\), each present at a partial pressure of 1 atm, will react spontaneously at 298 K to form more \(NH_3(g)\). In contrast, at 773 K the positive value of \(\Delta G^\circ\) tells us that the reverse reaction is spontaneous. Thus, when the mixture of three gases, each at a partial pressure of 1 atm, is heated to 773 K, some of the \(NH_3(g)\) spontaneously decomposes into \(N_2(g)\) and \(H_2(g)\).
Sample Exercise 19.9 Determining the Effect of Temperature on Spontaneity

Practice Exercise

(a) Using standard enthalpies of formation and standard entropies in Appendix C, calculate \( \Delta H^\circ \) and \( \Delta S^\circ \) at 298 K for the following reaction: \( 2 \text{SO}_2(g) + \text{O}_2(g) \rightarrow 2 \text{SO}_3(g) \). (b) Using the values obtained in part (a), estimate \( \Delta G^\circ \) at 400 K.

*Answers: (a) \( \Delta H^\circ = -196.6 \text{ kJ}, \Delta S^\circ = -189.6 \text{ J/K} \); (b) \( \Delta G^\circ = -120.8 \text{ kJ} \)
Sample Exercise 19.10 Relating $\Delta G$ to a Phase change at Equilibrium

As we saw in Section 11.5, the normal boiling point is the temperature at which a pure liquid is in equilibrium with its vapor at a pressure of 1 atm. (a) Write the chemical equation that defines the normal boiling point of liquid carbon tetrachloride, $\text{CCl}_4(l)$. (b) What is the value of $\Delta G^\circ$ for the equilibrium in part (a)? (c) Use thermodynamic data in Appendix C and Equation 19.12 to estimate the normal boiling point of CCl₄.

**Solution**

**Analyze:** (a) We must write a chemical equation that describes the physical equilibrium between liquid and gaseous CCl₄ at the normal boiling point. (b) We must determine the value of $\Delta G^\circ$ for CCl₄, in equilibrium with its vapor at the normal boiling point. (c) We must estimate the normal boiling point of CCl₄, based on available thermodynamic data.

**Plan:** (a) The chemical equation will merely show the change of state of CCl₄ from liquid to solid. (b) We need to analyze Equation 19.16 at equilibrium ($\Delta G = 0$). (c) We can use Equation 19.12 to calculate $T$ when $\Delta G = 0$.

**Solve:** (a) The normal boiling point of CCl₄ is the temperature at which pure liquid CCl₄ is in equilibrium with its vapor at a pressure of 1 atm:

(b) At equilibrium $\Delta G = 0$. In any normal boiling-point equilibrium both the liquid and the vapor are in their standard states (Table 19.2). Consequently, $Q = 1$, $Q = 0$, and $\Delta G = \Delta G^\circ$ for this process. Thus, we conclude that $\Delta G = 0$ for the equilibrium involved in the normal boiling point of any liquid. We would also find that $\Delta G = 0$ for the equilibria relevant to normal melting points and normal sublimation points of solids.
Sample Exercise 19.10 Relating $\Delta G$ to a Phase change at Equilibrium

Solution (continued)

(c) Combining Equation 19.12 with the result from part (b), we see that the equality at the normal boiling point, $T_b$, of CCl$_4$(l) or any other pure liquid is

$$\Delta G^\circ = \Delta H^\circ - T_b\Delta S^\circ = 0$$

Solving the equation for $T_b$, we obtain

Strictly speaking, we would need the values of $\Delta H^\circ$ and $\Delta S^\circ$ for the equilibrium between CCl$_4$(l) and CCl$_4$(g) at the normal boiling point to do this calculation. However, we can estimate the boiling point by using the values of $\Delta H^\circ$ and $\Delta S^\circ$ for CCl$_4$ at 298 K, which we can obtain from the data in Appendix C and Equations 5.31 and 19.8:

$$\Delta H^\circ = (1 \text{ mol})(-106.7 \text{ kJ/mol}) - (1 \text{ mol})(-139.3 \text{ kJ/mol}) = +32.6 \text{ kJ}$$

$$\Delta S^\circ = (1 \text{ mol})(309.4 \text{ J/mol-K}) - (1 \text{ mol})(214.4 \text{ J/mol-K}) = +95.0 \text{ J/K}$$

Notice that, as expected, the process is endothermic ($\Delta H > 0$) and produces a gas in which energy can be more spread out ($\Delta S > 0$). We can now use these values to estimate $T_b$ for CCl$_4$(l):

$$T_b = \frac{\Delta H^\circ}{\Delta S^\circ} = \left( \frac{32.6 \text{ kJ}}{95.0 \text{ J/K}} \right) \left( \frac{1000 \text{ J}}{1 \text{ kJ}} \right) = 343 \text{ K} = 70^\circ \text{ C}$$

Note also that we have used the conversion factor between J and kJ to make sure that the units of $\Delta H^\circ$ and $\Delta S^\circ$ match.
Sample Exercise 19.10 Relating $\Delta G$ to a Phase change at Equilibrium

Solution (continued)

Check: The experimental normal boiling point of CCl$_4$(l) is 76.5 °C. The small deviation of our estimate from the experimental value is due to the assumption that $\Delta H^\circ$ and $\Delta S^\circ$ do not change with temperature.

Practice Exercise

Use data in Appendix C to estimate the normal boiling point, in K, for elemental bromine, Br$_2$(l). (The experimental value is given in Table 11.3.)

Answers: 330 K
Sample Exercise 19.11 Calculating the Free-Energy Change under Nonstandard Conditions

We will continue to explore the Haber process for the synthesis of ammonia:

\[
\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g)
\]

Calculate \(\Delta G\) at 298 K for a reaction mixture that consists of 1.0 atm N\(_2\), 3.0 atm H\(_2\), and 0.50 atm NH\(_3\).

**Solution**

**Analyze:** We are asked to calculate \(\Delta G\) under nonstandard conditions.

**Plan:** We can use Equation 19.16 to calculate \(\Delta G\). Doing so requires that we calculate the value of the reaction quotient \(Q\) for the specified partial pressures of the gases and evaluate \(\Delta G^\circ\), using a table of standard free energies of formation.

**Solve:** Solving for the reaction quotient gives:

\[
Q = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = \frac{(0.50)^2}{(1.0)(3.0)^3} = 9.3 \times 10^{-3}
\]

In Sample Exercise 19.9 we calculated \(\Delta G^\circ = -33.3\) kJ for this reaction. We will have to change the units of this quantity in applying Equation 19.16, however. For the units in Equation 19.16 to work out, we will use as our units for \(\Delta G^\circ\), where “per mole” means “per mole of the reaction as written.” Thus, \(\Delta G^\circ = -33.3\) kJ/mol implies per 1 mol of N\(_2\), per 3 mol of H\(_2\), and per 2 mol of NH\(_3\).
Sample Exercise 19.11 Calculating the Free-Energy Change under Nonstandard Conditions

Solution (continued)

We can now use Equation 19.16 to calculate $\Delta G$ for these nonstandard conditions:

$$
\Delta G = \Delta G^\circ + RT \ln Q \\
= (-33.3 \text{ kJ/mol}) + (8.314 \text{ J/mol-K})(298 \text{ K})(1 \text{ kJ/1000 J}) \ln(9.3 \times 10^{-3})
= (-33.3 \text{ kJ/mol}) + (-11.6 \text{ kJ/mol}) = -44.9 \text{ kJ/mol}
$$

Comment: We see that $\Delta G$ becomes more negative, changing from $-33.3 \text{ kJ/mol}$ to $-44.9 \text{ kJ/mol}$, as the pressures of $\text{N}_2$, $\text{H}_2$, and $\text{NH}_3$ are changed from 1.0 atm each (standard conditions, $\Delta G^\circ$) to 1.0 atm, 3.0 atm, and 0.50 atm, respectively. The larger negative value for $\Delta G$ indicates a larger “driving force” to produce $\text{NH}_3$. We would have made the same prediction based on Le Châtelier’s principle. (Section 15.7) Relative to standard conditions, we have increased the pressure of a reactant ($\text{H}_2$) and decreased the pressure of the product ($\text{NH}_3$). Le Châtelier’s principle predicts that both of these changes should shift the reaction more to the product side, thereby forming more $\text{NH}_3$.

Practice Exercise

Calculate $\Delta G$ at 298 K for the reaction of nitrogen and hydrogen to form ammonia if the reaction mixture consists of 0.50 atm $\text{N}_2$, 0.75 atm $\text{H}_2$, and 2.0 atm $\text{NH}_3$.

Answers: $-26.0 \text{ kJ/mol}$
Sample Exercise 19.12 Calculating an Equilibrium Constant for $\Delta G^\circ$

Use standard free energies of formation to calculate the equilibrium constant, $K$, at 25 °C for the reaction involved in the Haber process:

$$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$$

The standard free-energy change for this reaction was calculated in Sample Exercise 19.9: $\Delta G^\circ = -33.3 \text{ kJ/mol} = -33,300 \text{ J/mol}$.

**Solution**

**Analyze:** We are asked to calculate $K$ for a reaction, given $\Delta G^\circ$.

**Plan:** We can use Equation 19.18 to evaluate the equilibrium constant, which in this case takes the form

$$K = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

In this expression the gas pressures are expressed in atmospheres. (Remember that we use kJ mol as the units of $\Delta G^\circ$ when using Equations 19.16, 19.17, or 19.18.)

**Solve:** Solving Equation 19.17 for the exponent $-\Delta G^\circ/RT$, we have

$$\frac{-\Delta G^\circ}{RT} = \frac{-(-33,300 \text{ J/mol})}{(8.314 \text{ J/mol-K})(298\text{ K})} = 13.4$$

We insert this value into Equation 19.18 to obtain $K$:

$$K = e^{-\Delta G^\circ/RT} = e^{13.4} \approx 7 \times 10^5$$
Sample Exercise 19.12 Calculating an Equilibrium Constant for $\Delta G^\circ$

Solution (continued)

Comment: This is a large equilibrium constant, which indicates that the product, NH$_3$, is greatly favored in the equilibrium mixture at 25 °C. The equilibrium constants for temperatures in the range of 300 °C to 600 °C, given in Table 15.2, are much smaller than the value at 25 °C. Clearly, a low-temperature equilibrium favors the production of ammonia more than a high-temperature one. Nevertheless, the Haber process is carried out at high temperatures because the reaction is extremely slow at room temperature. Remember: Thermodynamics can tell us the direction and extent of a reaction, but tells us nothing about the rate at which it will occur. If a catalyst were found that would permit the reaction to proceed at a rapid rate at room temperature, high pressures would not be needed to force the equilibrium toward NH$_3$.

Practice Exercise

Use data from Appendix C to calculate the standard free-energy change, $\Delta G^\circ$, and the equilibrium constant, $K$, at 298 K for the reaction

$$\text{H}_2(\text{g}) + \text{Br}_2(\text{l}) \rightleftharpoons 2 \text{HBr}(\text{g})$$

Answers: $\Delta G^\circ = -106.4 \text{ kJ/mol}$, $K = 4 \times 10^{18}$
Sample Integrative Exercise  Putting Concepts Together

Consider the simple salts NaCl(s) and AgCl(s). We will examine the equilibria in which these salts dissolve in water to form aqueous solutions of ions:

\[
\begin{align*}
\text{NaCl}(s) & \rightleftharpoons \text{Na}^+(aq) + \text{Cl}^-(aq) \\
\text{AgCl}(s) & \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)
\end{align*}
\]

(a) Calculate the value of \(\Delta G^\circ\) at 298 K for each of the preceding reactions. (b) The two values from part (a) are very different. Is this difference primarily due to the enthalpy term or the entropy term of the standard free-energy change? (c) Use the values of \(\Delta G^\circ\) to calculate the \(K_{sp}\) values for the two salts at 298 K. (d) Sodium chloride is considered a soluble salt, whereas silver chloride is considered insoluble. Are these descriptions consistent with the answers to part (c)? (e) How will \(\Delta G^\circ\) for the solution process of these salts change with increasing \(T\)? What effect should this change have on the solubility of the salts?

**Solution**

(a) We will use Equation 19.14 along with \(\Delta G_f^\circ\) values from Appendix C to calculate the \(\Delta G^\circ_{\text{soln}}\) values for each equilibrium. (As we did in Section 13.1, we use the subscript “soln” to indicate that these are thermodynamic quantities for the formation of a solution.) We find

\[
\begin{align*}
\Delta G^\circ_{\text{soln}}(\text{NaCl}) &= (-261.9 \text{ kJ/mol}) + (-131.2 \text{ kJ/mol}) - (-384.0 \text{ kJ/mol}) \\
&= -9.1 \text{ kJ/mol} \\
\Delta G^\circ_{\text{soln}}(\text{AgCl}) &= (+77.11 \text{ kJ/mol}) + (-131.2 \text{ kJ/mol}) - (-109.70 \text{ kJ/mol}) \\
&= +55.6 \text{ kJ/mol}
\end{align*}
\]
Sample Integrative Exercise  Putting Concepts Together

Solution (continued)

(b) We can write $\Delta G^\circ_{\text{soln}}$ as the sum of an enthalpy term, $\Delta H^\circ_{\text{soln}}$, and an entropy term, $-T \Delta S^\circ_{\text{soln}}$: $\Delta G^\circ_{\text{soln}} = \Delta H^\circ_{\text{soln}} + (-T \Delta S^\circ_{\text{soln}})$. We can calculate the values of $\Delta H^\circ_{\text{soln}}$ and $\Delta S^\circ_{\text{soln}}$ by using Equations 5.31 and 19.8. We can then calculate $-T \Delta S^\circ_{\text{soln}}$ at $T = 298$K. All these calculations are now familiar to us. The results are summarized in the following table:

<table>
<thead>
<tr>
<th>Salt</th>
<th>$\Delta H^\circ_{\text{soln}}$</th>
<th>$\Delta S^\circ_{\text{soln}}$</th>
<th>$-T \Delta S^\circ_{\text{soln}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>+3.6 kJ/mol</td>
<td>+43.2 J/mol-K</td>
<td>−12.9 kJ/mol</td>
</tr>
<tr>
<td>AgCl</td>
<td>+65.7 kJ/mol</td>
<td>+34.3 J/mol-K</td>
<td>−10.2 kJ/mol</td>
</tr>
</tbody>
</table>

The entropy terms for the solution of the two salts are very similar. That seems sensible because each solution process should lead to a similar increase in randomness as the salt dissolves, forming hydrated ions. (Section 13.1) In contrast, we see a very large difference in the enthalpy term for the solution of the two salts. The difference in the values of $\Delta G^\circ_{\text{soln}}$ is dominated by the difference in the values of $\Delta H^\circ_{\text{soln}}$.

(c) The solubility product, $K_{sp}$, is the equilibrium constant for the solution process. (Section 17.4) As such, we can relate $K_{sp}$ directly to $\Delta G^\circ_{\text{soln}}$ by using Equation 19.18:

$$K_{sp} = e^{-\Delta G^\circ_{\text{soln}}/RT}$$
Sample Integrative Exercise  Putting Concepts Together

Solution (continued)

We can calculate the $K_{sp}$ values in the same way we applied Equation 19.18 in Sample Exercise 19.12. We use the $\Delta G^{\circ}_{\text{soln}}$ values we obtained in part (a), remembering to convert them from kJ/mol to J/mol:

\[
\text{NaCl: } K_{sp} = [\text{Na}^+ (aq)][\text{Cl}^- (aq)] = e^{-(\Delta G^{\circ}_{\text{soln}})/R/T} = e^{(9100)/(8.314)(298)} = e^{+3.7} = 40
\]
\[
\text{AgCl: } K_{sp} = [\text{Ag}^+ (aq)][\text{Cl}^- (aq)] = e^{-(\Delta G^{\circ}_{\text{soln}})/R/T} = e^{(55600)/(8.314)(298)} = e^{-22.4} = 1.9 \times 10^{-10}
\]

The value calculated for the $K_{sp}$ of AgCl is very close to that listed in Appendix D.

(d) A soluble salt is one that dissolves appreciably in water. (Section 4.2) The $K_{sp}$ value for NaCl is greater than 1, indicating that NaCl dissolves to a great extent. The $K_{sp}$ value for AgCl is very small, indicating that very little dissolves in water. Silver chloride should indeed be considered an insoluble salt.

(e) As we expect, the solution process has a positive value of $\Delta S$ for both salts (see the table in part b). As such, the entropy term of the free-energy change, $-T \Delta S^{\circ}_{\text{soln}}$, is negative. If we assume that $\Delta H^{\circ}_{\text{soln}}$ and $\Delta S^{\circ}_{\text{soln}}$ do not change much with temperature, then an increase in $T$ will serve to make $\Delta G^{\circ}_{\text{soln}}$ more negative. Thus, the driving force for dissolution of the salts will increase with increasing $T$, and we therefore expect the solubility of the salts to increase with increasing $T$. In Figure 13.17 we see that the solubility of NaCl (and that of nearly any salt) increases with increasing temperature. (Section 13.3)