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 $H_2(g)$ and $O_2(g)$, **(c)** Benzene vapor, $C_6H_6(g)$, at a pressure of 1 atm condenses to liquid benzene at the normal boiling point of benzene, 80.1 °C.

Solution

Analyze: 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 H_2 and O_2 to form H_2O—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 $CO_2(s)$ sublimes at –78 °C. Is the transformation of $CO_2(s)$ to $CO_2(g)$ 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 ΔS for a Phase Change

The element mercury, Hg, is a silvery liquid at room temperature. The normal freezing point of mercury is –38.9 °C, and its molar enthalpy of fusion is $\Delta H_{fusion} = 2.29$ 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 ΔH for the melting process. Because freezing is the reverse of melting, the enthalpy change that accompanies the freezing of 1 mol of Hg is $-\Delta H_{fusion} = -2.29$ kJ/mol.

Plan: We can use $-\Delta H_{fusion}$ 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_{rev} in Equation 19.2. We must first, however, convert the temperature to K:

$$-38.9 \text{ °C} = (-38.9 + 273.15) \text{ K} = 234.3 \text{ K}$$

Solve: We can now calculate the value of ΔS_{sys}

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

Check: The entropy change is negative because heat flows from the system, making q_{rev} negative.
Comment: The procedure we have used here can be used to calculate ΔS for other isothermal phase changes, such as the vaporization of a liquid at its boiling point.

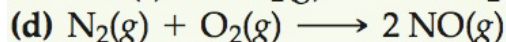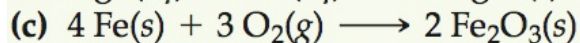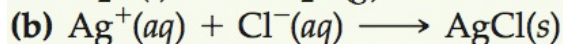# Sample Exercise 19.2 Calculating ΔS for a Phase Change
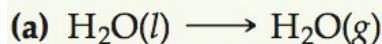
Practice Exercise

The normal boiling point of ethanol, C_2H_5OH, 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 $C_2H_5OH(g)$ at 1 atm condenses to liquid at the normal boiling point?

Answer: –163 J/K

Sample Exercise 19.3 Predicting the Sign of ΔS

Predict whether ΔS is positive or negative for each of the following processes, assuming each occurs at constant temperature:

(a) $H_2O(l) \longrightarrow H_2O(g)$
(b) $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$
(c) $4\,Fe(s) + 3\,O_2(g) \longrightarrow 2\,Fe_2O_3(s)$
(d) $N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$

Solution

Analyze: We are given four equations and asked to predict the sign of ΔS for each chemical reaction.

Plan: The sign of ΔS 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, ΔS 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, ΔS is negative.
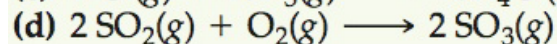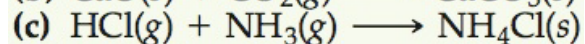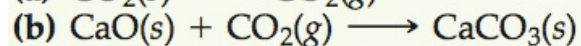
(c) The particles of a solid are confined to specific locations and have fewer ways to move (fewer microstates) than do the molecules of a gas. Because O_2 gas is converted into part of the solid product Fe_2O_3, ΔS is negative.

(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 ΔS is impossible to predict based on our discussions thus far, but we can predict that ΔS 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) $CO_2(s) \longrightarrow CO_2(g)$
(b) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$
(c) $HCl(g) + NH_3(g) \longrightarrow NH_4Cl(s)$
(d) $2 SO_2(g) + O_2(g) \longrightarrow 2 SO_3(g)$
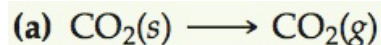
Answer: (a) increase, (b) decrease, (c) decrease, (d) decrease

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 $H_2(g)$ at STP or 1 mol of $H_2(g)$ at 100 °C and 0.5 atm, **(b)** 1 mol of $H_2O(s)$ at 0 °C or 1 mol of $H_2O(l)$ at 25 °C, **(c)** 1 mol of $H_2(g)$ at STP or 1 mol of $SO_2(g)$ at STP, **(d)** 1 mol of $N_2O_4(g)$ at STP or 2 mol of $NO_2(g)$ at STP.
Answers: **(a)** 1 mol of $H_2(g)$ at 100 °C and 0.5 atm, **(b)** 1 mol of $H_2O(l)$ at 25 °C, **(c)** 1 mol of $SO_2(g)$ at STP, **(d)** 2 mol of $NO_2(g)$ at STP

Sample Exercise 19.5 Calculating ΔS from Tabulated Entropies

Calculate $\Delta S°$ for the synthesis of ammonia from $N_2(g)$ and $H_2(g)$ at 298 K:

$$N_2(g) + 3 H_2(g) \rightarrow 2 NH_3(g)$$
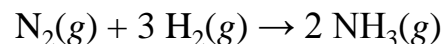
Solution

Analyze: We are asked to calculate the entropy change for the synthesis of $NH_3(g)$ 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.
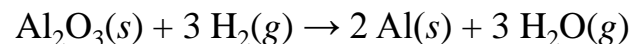
Solve: Using Equation 19.8, we have $\Delta S° = 2S°(NH_3) - [S°(N_2) + 3S°(H_2)]$

Substituting the appropriate $S°$ values from Table 19.2 yields

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

Check: The value for $\Delta S°$ 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, $\Delta S°$, for the following reaction at 298 K:

$$Al_2O_3(s) + 3 H_2(g) \rightarrow 2 Al(s) + 3 H_2O(g)$$

Answers: 180.39 J/K

PEARSON Education

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By Theodore E. Brown, H. Eugene LeMay, Bruce E. Bursten, and Catherine J. Murphy
With contributions from Patrick Woodward

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Sample Exercise 19.6 Calculating Free-Energy Change from $\Delta H°$, T, $\Delta S°$

Calculate the standard free energy change for the formation of $NO(g)$ from $N_2(g)$ and $O_2(g)$ at 298 K:

$$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$$
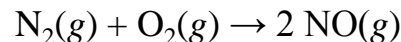
given that $\Delta H° = 180.7$ kJ and $\Delta S° = 24.7$ J/K. Is the reaction spontaneous under these circumstances?

Solution

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

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

Solve:
$$\Delta G° = \Delta H° - T\Delta S°$$
$$= 180.7\ \text{kJ} - (298\ \text{K})(24.7\ \text{J/K})\left(\frac{1\ \text{kJ}}{10^3\ \text{J}}\right)$$
$$= 180.7\ \text{kJ} - 7.4\ \text{kJ}$$
$$= 173.3\ \text{kJ}$$

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

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

Practice Exercise

A particular reaction has $\Delta H° = 24.6$ kJ and $\Delta S° = 132$ J/K at 298 K. Calculate $\Delta G°$.
Is the reaction spontaneous under these conditions?
Answers: $\Delta G° = -14.7$ kJ; the reaction is spontaneous.

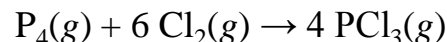# Sample Exercise 19.7 Calculating Standard Free-Energy Change from Free Energies of Formation

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

$$P_4(g) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g)$$

(b) What is $\Delta G°$ 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) $Cl_2(g)$ is in its standard state, so $\Delta G°_f$ is zero for this reactant. $P_4(g)$, however, is not in its standard state, so $\Delta G°_f$ is not zero for this reactant. From the balanced equation and using Appendix C, we have:

$$
\begin{aligned}
\Delta G°_{rxn} &= 4\ \Delta G°_f[PCl_3(g)] - \Delta G°_f[P_4(g)] - 6\ \Delta G°_f[Cl_2(g)] \\
&= (4\ mol)(-269.6\ kJ/mol) - (1\ mol)(24.4\ kJ/mol) - 0 \\
&= -1102.8\ kJ
\end{aligned}
$$

Sample Exercise 19.7 Calculating Standard Free-Energy Change from Free Energies of Formation
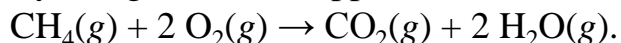
Solution (continued)

The fact that $\Delta G°$ 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 $\Delta G°$ tells us nothing about the rate at which the reaction occurs.

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

$$4 \text{ PCl}_3(g) \rightarrow P_4(g) + 6 \text{ Cl}_2(g) \ \Delta G° = +1102.8 \text{ kJ}$$

Practice Exercise

By using data from Appendix C, calculate $\Delta G°$ at 298 K for the combustion of methane:
$CH_4(g) + 2 \text{ O}_2(g) \rightarrow CO_2(g) + 2 \text{ H}_2O(g)$.
Answer: –800.7 kJ

Sample Exercise 19.8 Estimating and Calculating $\Delta G°$

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

$$C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l) \quad \Delta H° = -2220\ kJ$$
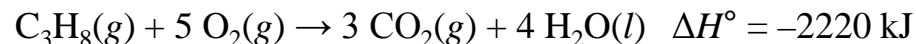
(a) *Without using data from Appendix C*, predict whether $\Delta G°$ for this reaction is more negative or less negative than $\Delta H°$. **(b)** Use data from Appendix C to calculate the standard free-energy change for the reaction at 298 K. Is your prediction from part (a) correct?

Solution

Analyze: In part (a) we must predict the value for $\Delta G°$ relative to that for $\Delta H°$ on the basis of the balanced equation for the reaction. In part (b) we must calculate the value for $\Delta G°$ 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:

$$\Delta G° = \Delta H° - T\,\Delta S°$$

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

Sample Exercise 19.8 Estimating and Calculating $\Delta G°$

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 $\Delta S°$ and therefore $T\Delta S°$ to be negative numbers. Because we are subtracting , which is a negative number, we would predict that $\Delta G°$ is *less negative* than $\Delta H°$.

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

$$\Delta G° = 3\Delta G_f°[CO_2(g)] + 4\Delta G_f°[H_2O(l)] - \Delta G_f°[C_3H_8(g)] - 5\Delta G_f°[O_2(g)]$$
$$= 3 \text{ mol}(-394.4 \text{ kJ/mol}) + 4 \text{ mol}(-237.13 \text{ kJ/mol}) -$$
$$1 \text{ mol}(-23.47 \text{ kJ/mol}) - 5 \text{ mol}(0 \text{ kJ/mol}) = -2108 \text{ kJ}$$

Notice that we have been careful to use the value of $\Delta G°_f$ for $H_2O(l)$, as in the calculation of ΔH values, the phases of the reactants and products are important. As we predicted, $\Delta G°$ is less negative than $\Delta H°$ because of the decrease in entropy during the reaction.

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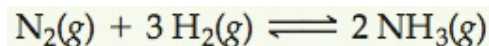
Consider the combustion of propane to form $CO_2(g)$ and $H_2O(g)$ at 298 K:
$C_3H_8(g) + 5 O_2(g) \rightarrow 3 CO_2(g) + 4 H_2O(g)$. Would you expect $\Delta G°$ to be more negative or less negative than $\Delta H°$?

Answer: more negative

The Haber process for the production of ammonia involves the equilibrium

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

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

Solution

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

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

Solve:

(a) Equation 19.12 tells us that $\Delta G°$ is the sum of the enthalpy term $\Delta H°$ and the entropy term $-T\,\Delta S°$. The temperature dependence of $\Delta G°$ comes from the entropy term. We expect $\Delta S°$ for this reaction to be negative because the number of molecules of gas is smaller in the products. Because $\Delta S°$ is negative, the term $-T\,\Delta S°$ is positive and grows larger with increasing temperature. As a result, $\Delta G°$ becomes less negative (or more positive) with increasing temperature. Thus, the driving force for the production of NH_3 becomes smaller with increasing temperature.

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

Solution (continued)

$$\Delta G^\circ = -92.38 \text{ kJ} - (298 \text{ K})(-198.3 \text{ J/K})\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$= -92.38 \text{ kJ} + 59.1 \text{ kJ} = -33.3 \text{ kJ}$$

At $T = 500 + 273 = 773$ K we have

$$\Delta G^\circ = -92.38 \text{ kJ} - (773 \text{ K})\left(-198.3 \frac{\text{J}}{\text{K}}\right)\left(\frac{1 \text{ kJ}}{1000 \text{ J}}\right)$$

$$= -92.38 \text{ kJ} + 153 \text{ kJ} = 61 \text{ kJ}$$

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

Comment: Increasing the temperature from 298 K to 773 K changes ΔG° from –33.3 kJ to +61 kJ. Of course, the result at 773 K depends on the assumption that ΔH° and ΔS° 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 ΔG° 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 ΔG° 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 $\Delta H°$ and $\Delta S°$ at 298 K for the following reaction: $2\ SO_2(g) + O_2(g) \rightarrow 2\ SO_3(g)$. **(b)** Using the values obtained in part (a), estimate $\Delta G°$ at 400 K.

Answers: **(a)** $\Delta H° = -196.6$ kJ, $\Delta S° = -189.6$ J/K; **(b)** $\Delta G° = -120.8$ kJ

# Sample Exercise 19.10 Relating ΔG 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, $CCl_4(l)$. **(b)** What is the value of $\Delta G°$ for the equilibrium in part (a)? **(c)** Use thermodynamic data in Appendix C and Equation 19.12 to estimate the normal boiling point of CCl_4.

Solution

Analyze: (a) We must write a chemical equation that describes the physical equilibrium between liquid and gaseous CCl_4 at the normal boiling point. **(b)** We must determine the value of $\Delta G°$ for CCl_4, in equilibrium with its vapor at the normal boiling point. **(c)** We must estimate the normal boiling point of CCl_4, based on available thermodynamic data.

Plan: (a) The chemical equation will merely show the change of state of CCl_4 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 CCl_4 is the temperature at which pure liquid CCl_4 is in equilibrium with its vapor at a pressure of 1 atm:

$$CCl_4(l) \rightleftharpoons CCl_4\,(g,\ 1\ atm)$$
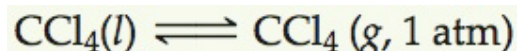
(b) At equilibrium $\Delta G = 0$. In any normal boiling-point equilibrium both the liquid and the vapor are in their standard states (Table 19.2). Consequently, $Q = 1$, $Q = 0$, and $\Delta G = \Delta G°$ for this process. Thus, we conclude that $\Delta G = 0$ for the equilibrium involved in the normal 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 ΔG 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

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

$$T_b = \Delta H^\circ / \Delta S^\circ$$

Solving the equation for T_b, we obtain

Strictly speaking, we would need the values of ΔH° and ΔS° 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 ΔH° and ΔS° for CCl_4 at 298 K, which we can obtain from the data in Appendix C and Equations 5.31 and 19.8:

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

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

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 $CCl_4(l)$:

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

Note also that we have used the conversion factor between J and kJ to make sure that the units of ΔH° and ΔS° match.

Sample Exercise 19.10 Relating ΔG 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 $\Delta H°$ and $\Delta S°$ do not change with temperature.
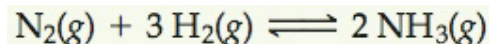
Practice Exercise

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:

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Calculate ΔG 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 ΔG under nonstandard conditions.

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

Solve: Solving for the reaction quotient gives:

$$Q = \frac{P_{NH_3}{}^2}{P_{N_2}\,P_{H_2}{}^3} = \frac{(0.50)^2}{(1.0)(3.0)^3} = 9.3 \times 10^{-3}$$

In Sample Exercise 19.9 we calculated $\Delta G° = -33.3$ 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 $\Delta G°$, where "per mole" means "per mole of the reaction as written." Thus, $\Delta G° = -33.3$ 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 ΔG for these nonstandard conditions:

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

Comment: We see that ΔG becomes more negative, changing from –33.3 kJ/mol to –44.9 kJ/mol, as the pressures of N_2, H_2, and NH_3 are changed from 1.0 atm each (standard conditions, $\Delta G°$) to 1.0 atm, 3.0 atm, and 0.50 atm, respectively. The larger negative value for ΔG indicates a larger "driving force" to produce 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 (H_2) and decreased the pressure of the product (NH_3). Le Châtelier's principle predicts that both of these changes should shift the reaction more to the product side, thereby forming more NH_3.

Practice Exercise

Calculate ΔG at 298 K for the reaction of nitrogen and hydrogen to form ammonia if the reaction mixture consists of 0.50 atm N_2, 0.75 atm H_2, and 2.0 atm NH_3.
Answers: –26.0 kJ/mol

Sample Exercise 19.12 Calculating an Equilibrium Constant for ΔG°

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

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$
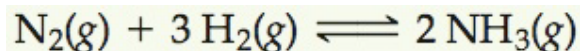
The standard free-energy change for this reaction was calculated in Sample Exercise 19.9:
$\Delta G° = -33.3$ kJ/mol $= -33,300$ J/mol.

Solution

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

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

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

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

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

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

We insert this value into Equation 19.18 to obtain K:

$$K = e^{-\Delta G°/RT} = e^{13.4} = 7 \times 10^5$$

Sample Exercise 19.12 Calculating an Equilibrium Constant for $\Delta G°$

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, $\Delta G°$, and the equilibrium constant, K, at 298 K for the reaction

$$H_2(g) + Br_2(l) \rightleftharpoons 2\,HBr(g).$$

Answers: $\Delta G° = -106.4$ 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:

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$
$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
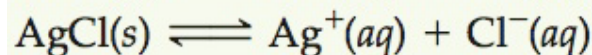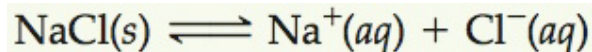
(a) Calculate the value of $\Delta G°$ at 298 K for each of the preceding reactions. **(b)** The two values from part (a) are very different. Is this difference primarily due to the enthalpy term or the entropy term of the standard free-energy change? **(c)** Use the values of $\Delta G°$ to calculate 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 $\Delta G°$ 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 $\Delta G°_f$ values from Appendix C to calculate the $\Delta G°_{soln}$ 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

$$\Delta G°_{soln}(NaCl) = (-261.9 \text{ kJ/mol}) + (-131.2 \text{ kJ/mol}) - (-384.0 \text{ kJ/mol})$$
$$= -9.1 \text{ kJ/mol}$$
$$\Delta G°_{soln}(AgCl) = (+77.11 \text{ kJ/mol}) + (-131.2 \text{ kJ/mol}) - (-109.70 \text{ kJ/mol})$$
$$= +55.6 \text{ kJ/mol}$$

Sample Integrative Exercise Putting Concepts Together

Solution (continued)

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

Salt	$\Delta H°_{soln}$	$\Delta S°_{soln}$	$-T\Delta S°_{soln}$
NaCl	+3.6 kJ/mol	+43.2 J/mol-K	−12.9 kJ/mol
AgCl	+65.7 kJ/mol	+34.3 J/mol-K	−10.2 kJ/mol

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 $\Delta G°_{soln}$ is dominated by the difference in the values of $\Delta H°_{soln}$.
(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 $\Delta G°_{soln}$ by using Equation 19.18:

$$K_{sp} = e^{-\Delta G°_{soln}/RT}$$

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 $\Delta G°_{soln}$ values we obtained in part (a), remembering to convert them from kJ/mol to J/mol:

$$NaCl: K_{sp} = [Na^+(aq)][Cl^-(aq)] = e^{-(-9100)/[(8.314)(298)]} = e^{+3.7} = 40$$

$$AgCl: K_{sp} = [Ag^+(aq)][Cl^-(aq)] = e^{-(+55,600)/[(8.314)(298)]} = e^{-22.4} = 1.9 \times 10^{-10}$$

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 ΔS for both salts (see the table in part b). As such, the entropy term of the free-energy change, $-T\,\Delta S°_{soln}$, is negative. If we assume that $\Delta H°_{soln}$ and $\Delta S°_{soln}$ do not change much with temperature, then an increase in T will serve to make $\Delta G°_{soln}$ 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)