
19. THERMODYNAMICS AND EQUILIBRIUM

■ Solutions to Exercises

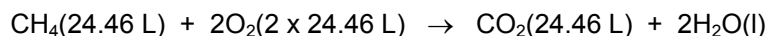
Note on units and significant figures: The mol unit is omitted from all thermodynamic parameters such as S° , ΔS° , etc. If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

- 19.1 Calculate the work, w , done using $w = F \times d = (mg) \times d$. Then, use w to calculate ΔE .

$$w = (mg) \times d = (2.20 \text{ kg} \times 9.80 \text{ m/s}^2) \times 0.250 \text{ m} = 5.390 \text{ kg}\cdot\text{m}^2/\text{s}^2 = 5.39 \text{ J}$$

$$\Delta U = q + w = (-1.50 \text{ J}) + (5.390 \text{ J}) = 3.890 = 3.89 \text{ J}$$

- 19.2 At 1.00 atm and 25 °C, the volume occupied by 1.00 mol of any of the gases in the equation is 22.41 L $\times (298/273) = 24.46 \text{ L}$. Find the change in volume:



$$\Delta V = 24.46 \text{ L} - (3 \times 24.46 \text{ L}) = -48.92 \text{ L}$$

Next, calculate the work, w , done on the system (its value decreases) using 1.00 atm = $1.013 \times 10^5 \text{ Pa}$ and $1.00 \text{ L} = 1.00 \times 10^{-3} \text{ m}^3$. Add this to the heat, q_p , at constant P:

$$w = -P\Delta V = -(1.013 \times 10^5 \text{ Pa}) \times (-48.92 \times 10^{-3} \text{ m}^3) = 4.9556 \times 10^3 \text{ J} = 4.96 \text{ kJ}$$

$$\Delta U = q_p + w = (-890.2 \text{ kJ}) + (+4.9556 \text{ kJ}) = -885.24 = -885.2 \text{ kJ}$$

- 19.3 When the liquid evaporates, it absorbs heat: $\Delta H_{\text{vap}} = 42.6 \text{ kJ/mol}$ ($42.6 \times 10^3 \text{ J/mol}$) at 25°C , or 298 K . The entropy change, ΔS , is

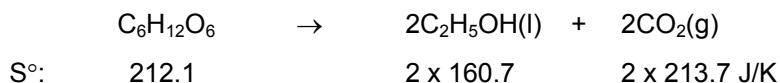
$$\Delta S = \frac{\Delta H_{\text{vap}}}{T} = \frac{42.6 \times 10^3 \text{ J/mol}}{298 \text{ K}} = 142.9 \text{ J/(mol}\cdot\text{K)}$$

The entropy of one mol of the vapor equals the entropy of one mol of liquid (161 J/K) plus 142.9 J/K .

$$S^\circ = (161 + 142.9) \text{ J/(mol}\cdot\text{K)} = 303.9 = 304 \text{ J/(mol}\cdot\text{K)}$$

- 19.4 a. ΔS° is positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +1$) from a solid reactant forming a mole of gas. (Entropy increases.)
- b. ΔS° is positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +1$) from a liquid reactant forming a mole of gas. (Entropy increases.)
- c. ΔS° is negative because there is a decrease in moles of gas ($\Delta n_{\text{gas}} = -1$) from liquid and gaseous reactants forming two moles of solid. (Entropy decreases.)
- d. ΔS° is positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +1$) from solid and liquid reactants forming a mole of gas and four moles of an ionic compound. (Entropy increases.)

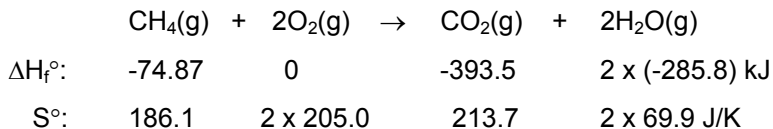
- 19.5 The reaction and standard entropies are given below. Multiply the S° values by their stoichiometric coefficients, and subtract the entropy of the reactant from the sum of the product entropies.



$$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$

$$[(2 \times 160.7 + 2 \times 213.7) - 212.1] \text{ J/K} = 536.7 \text{ J/K}$$

- 19.6 The reaction, standard enthalpy changes, and standard entropies are as follows:



(continued)

Calculate ΔH° and ΔS° for the reaction by taking the values for products and subtracting the values for reactants.

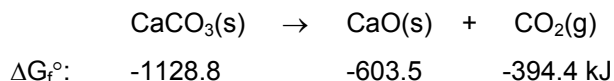
$$\begin{aligned}\Delta H^\circ &= \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants}) = \\ &[(-393.5 + 2 \times -285.8) - (-74.87)] \text{ kJ} = -890.\underline{23} \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants}) = \\ &[(213.7 + 2 \times 69.9) - (186.1 + 2 \times 205.0)] \text{ J/K} = -242.6 \text{ J/K}\end{aligned}$$

Now, substitute into the equation for ΔG° in terms of ΔH° and ΔS° ($= -242.6 \times 10^{-3} \text{ kJ/K}$):

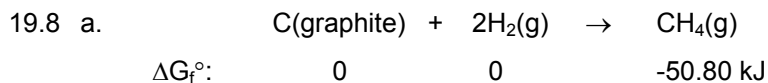
$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -890.23 \text{ kJ} - (298 \text{ K})(-242.6 \times 10^{-3} \text{ kJ/K}) \\ &= -817.\underline{93} = -817.9 \text{ kJ}\end{aligned}$$

- 19.7 Write the values of ΔG_f° multiplied by their stoichiometric coefficients below each formula:

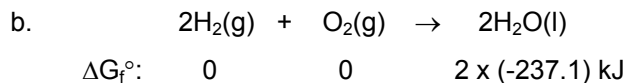


The calculation is

$$\begin{aligned}\Delta G^\circ &= \sum nG_f^\circ(\text{products}) - \sum mG_f^\circ(\text{reactants}) = \\ &[(-603.5) + (-394.4) - (-1128.8)] \text{ kJ} = 130.\underline{9} \text{ kJ}\end{aligned}$$

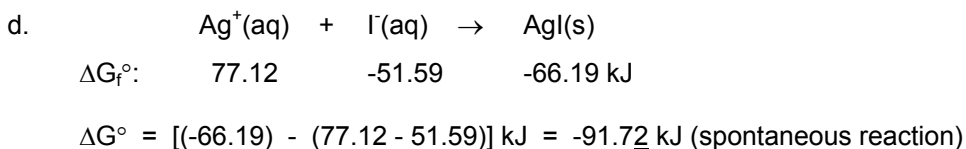
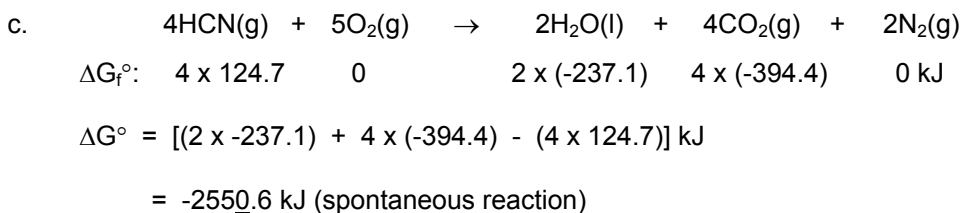


$$\Delta G^\circ = [(-50.80) - (0)] \text{ kJ} = -50.80 \text{ kJ (spontaneous reaction)}$$



$$\Delta G^\circ = [(2 \times -237.1) - (0)] \text{ kJ} = -474.\underline{2} \text{ kJ (spontaneous reaction)}$$

(continued)



19.9 a. $K = K_p = P_{\text{CO}_2}$

b. $K = K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2$

c. $K = \frac{P_{\text{CO}_2}}{[\text{H}^+][\text{HCO}_3^-]}$

19.10 First, calculate ΔG° using the ΔG_f° values from Table 19.2.



Subtract ΔG_f° of reactant from that of the products:

$$\Delta G_f^\circ = \sum n G_f^\circ(\text{products}) - \sum m G_f^\circ(\text{reactants}) =$$

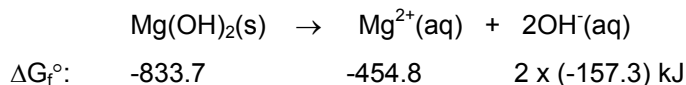
$$[(-603.5) + (-394.4) - (-1128.8)] \text{ kJ} = 130.9 \text{ kJ}$$

Use the rearranged form of the equation, $\Delta G^\circ = -RT \ln K$, to solve for $\ln K$. To get compatible units, express ΔG° in joules, and set R equal to $8.31 \text{ J/(mol}\cdot\text{K)}$. Substituting the numerical values into the expression gives

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{130.9 \times 10^3}{-8.31 \times 298} = -52.859$$

$$K = K_p = e^{-52.859} = 1.10 \times 10^{-23} = 1 \times 10^{-23}$$

19.11 First, calculate ΔG° using the ΔG_f° values in the exercise.



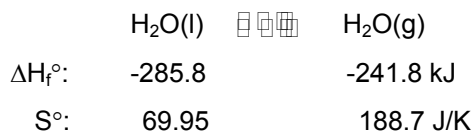
Hence, ΔG° for the reaction is

$$\Delta G^\circ = [2 \times (-157.3) + (-454.8) - (-833.7)] \text{ kJ} = 64.3 \text{ kJ}$$

Now, substitute numerical values into the equation relating $\ln K$ and ΔG° .

$$\begin{aligned} \ln K &= \frac{\Delta G^\circ}{-RT} = \frac{64.3 \times 10^3}{-8.31 \times 298} = -25.965 \\ K &= K_{\text{sp}} = e^{-25.965} = 5.289 \times 10^{-12} = 5 \times 10^{-12} \end{aligned}$$

19.12 From Appendix C, you have



Calculate ΔH° and ΔS° from these values.

$$\Delta H^\circ = [-241.8 - (-285.8)] \text{ kJ} = 44.0 \text{ kJ}$$

$$\Delta S^\circ = [188.7 - 69.95] \text{ J/K} = 118.75 \text{ J/K}$$

Substitute ΔH° , ΔS° ($= 0.11875 \text{ kJ/K}$) and T ($= 318 \text{ K}$) into the equation for ΔG_T° :

$$\Delta G_T^\circ = \Delta H^\circ - T\Delta S^\circ = 44.0 \text{ kJ} - (318 \text{ K})(0.11875 \text{ kJ/K}) = 6.23 \text{ kJ}$$

Substitute the value of ΔG° ($6.23 \times 10^3 \text{ J}$) at 318 K into the equation relating $\ln K$ and ΔG° .

$$\begin{aligned} \ln K &= \frac{\Delta G^\circ}{-RT} = \frac{6.23 \times 10^3}{-8.31 \times 318} = -2.360 \\ K &= K_p = e^{-2.360} = 0.0943 = 0.09 \end{aligned}$$

$K_p = P_{\text{H}_2\text{O}}$, so the vapor pressure of H_2O is 0.09 atm (71.7 mmHg).

The value is 0.0946 atm in Table 5.6.

19.13 First, calculate ΔH° and ΔS° using the given ΔH_f° and S° values.

	$\text{MgCO}_3(\text{s})$	\rightleftharpoons	$\text{MgO}(\text{s})$	+	$\text{CO}_2(\text{g})$
ΔH_f° :	-1111.7		-601.2		-393.5 kJ
ΔS° :	65.85		26.92		213.7 J/K

$$\Delta H^\circ = [-601.2 + (-393.5) - (-1111.7)] \text{ kJ} = 117.0 \text{ kJ}$$

$$\Delta S^\circ = [(26.92 + 213.7) - 65.85] \text{ J/K} = 174.77 \text{ J/K}$$

Substitute these values into the expression relating T , ΔH° , and ΔS° ($= 0.17477 \text{ kJ/K}$).

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{117.0 \text{ kJ}}{0.17477 \text{ kJ/K}} = 669.45 \text{ K (lower than that for CaCO}_3\text{)}$$

■ Answers to Concept Checks

- 19.1 The process is $\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})$. The iodine atoms have gone from a state of some order (crystalline iodine) to one that is more disordered (gas). The entropy will have increased.
- 19.2 The standard free energy of formation for $\text{NO}(\text{g})$ is 86.60 kJ/mol. This rather large positive value means the equilibrium constant is small. At equilibrium, the NO concentration is low.
- 19.3 a. The standard free-energy change, ΔG° , is independent of concentration, so it will not change.
- b. The relationship between ΔG and ΔG° is given by $\Delta G = \Delta G^\circ + RT \ln Q$, where Q is the reaction quotient. If the concentration of C is increased, it will cause the value of Q to increase, and in turn ΔG to increase.
- 19.4 You must break a chemical bond when N_2O_4 goes to 2NO_2 . It will take energy to do that, so you expect ΔH to be positive (the reaction is endothermic). Also, when you break a molecule in two, you generally increase the entropy (ΔS is positive). According to Table 19.3, the reaction should be nonspontaneous at relatively low temperature, but spontaneous at some higher temperature. That is, the concentration of NO_2 increases with temperature.

■ Answers to Review Questions

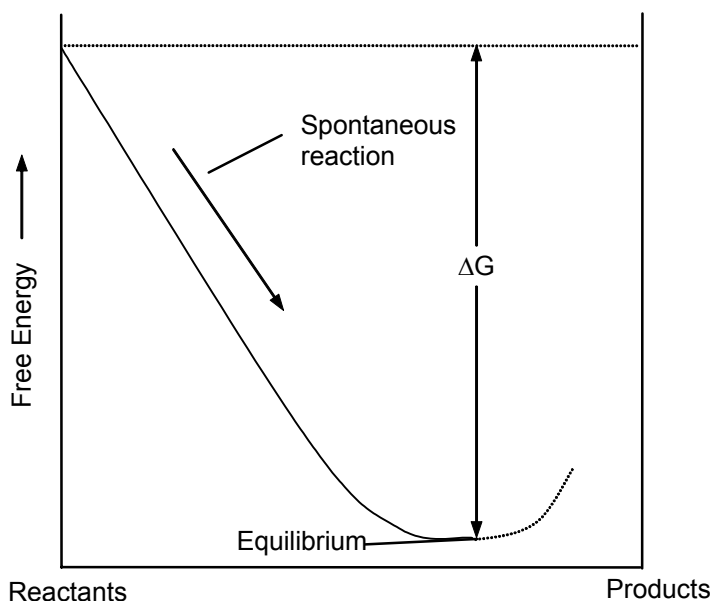
- 19.1 A spontaneous process is a chemical and/or a physical change that occurs by itself without the continuing intervention of an outside agency. Three examples are (1) a rock on a hilltop rolls down, (2) heat flows from a hot object to a cold one, and (3) iron rusts in moist air. Three examples of nonspontaneous processes are (1) a rock rolls uphill by itself, (2) heat flows from a cold object to a hot one, and (3) rust is converted to iron and oxygen.
- 19.2 Because the energy is more dispersed in liquids than in solids, liquid benzene contains more entropy than does the same quantity of frozen benzene.
- 19.3 The second law of thermodynamics states that, for a spontaneous process, the total entropy of a system and its surroundings always increases. As stated in Section 19.2, a spontaneous process actually creates energy dispersal, or entropy.
- 19.4 The relationship between entropy and enthalpy can be expressed in terms of the following equation

$$\Delta S = \frac{\Delta H - \Delta G}{T}$$

At equilibrium, ΔG equals 0, so the equation reduces to $\Delta H/T$ whereas, when not at equilibrium, $\Delta G \neq 0$, so this is not the case. In contrast to a phase change at equilibrium, the entropy change for a spontaneous chemical reaction (at constant pressure) does not equal $\Delta H/T$ because entropy is created by the spontaneous reaction. This can be an increase in the entropy of the surroundings or of the system. An example of the latter is the reaction $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$, where one reactant molecule forms two product molecules, thus increasing the randomness.

- 19.5 The standard entropy of hydrogen gas at 25 °C can be obtained by starting near 0.0 K as a reference point, where the entropy of perfect crystals of hydrogen is almost zero. Then, warm to room temperature in small increments, and calculate ΔS° for each incremental temperature change (say, 2 K) by dividing the heat absorbed by the average temperature (1 K is used as the average for 0 K to 2 K), and also take into account the entropy increases that accompany a phase change.
- 19.6 To predict the sign of ΔS° , look for a change, Δn_{gas} , in the number of moles of gas. If there is an increase in moles of gas in the products (Δn_{gas} is positive), then ΔS° should be positive. A decrease in moles of gas in the products suggests ΔS° should be negative.
- 19.7 Free energy, G , equals $H - TS$; that is, it is the difference between the enthalpy of a system and the product of temperature and entropy. The free-energy change, ΔG , equals $\Delta H - T\Delta S$.

- 19.8 The standard free-energy change, ΔG° , equals $\Delta H^\circ - T\Delta S^\circ$; that is, it is the difference between the standard enthalpy change of a system and the product of temperature and the standard entropy change of a system. The standard free-energy change of formation is the free-energy change when one mole of a substance is formed from its elements in their stable states at one atm and at a standard temperature, usually 25 °C.
- 19.9 If ΔG° for a reaction is negative, the equation for the reaction is spontaneous in the direction written; that is, the reactants form the products as written. If it is positive, then the equation as written is nonspontaneous.
- 19.10 In principle, if a reaction is carried out so that no entropy is produced, the useful work obtained is the maximum useful work, w_{\max} , and is equal to ΔG of the reaction.
- 19.11 When gasoline burns in an automobile engine, the change in free energy shows up as useful work. Gasoline, a mixture of hydrocarbons such as C_8H_{18} or octane, burns to yield energy, gaseous CO_2 , and gaseous H_2O .
- 19.12 A nonspontaneous reaction can be made to occur by coupling it with a spontaneous reaction having a sufficiently negative ΔG° to furnish the required energy. (The net ΔG° of the coupled reactions must be negative.)
- 19.13 As a spontaneous reaction proceeds, the free energy decreases until equilibrium is reached at a minimum ΔG . See the diagram below.



- 19.14 Because the equilibrium constant is related to ΔH° and ΔS° by $-RT \ln K = \Delta H^\circ - T\Delta S^\circ$, heat measurements alone can be used to obtain it. The standard enthalpy, ΔH° , is the heat of reaction measured at constant pressure. The standard entropy change, ΔS° , can be calculated from standard entropies, which are obtained from heat-capacity data.
- 19.15 The four combinations are as follows: (1) A negative ΔH° and a positive ΔS° always give a negative ΔG° and a spontaneous reaction. (2) A positive ΔH° and a negative ΔS° always give a positive ΔG° and a nonspontaneous reaction. (3) A negative ΔH° and a negative ΔS° may give a negative or a positive ΔG° . At low temperatures, ΔG° will usually be negative and the reaction spontaneous; at high temperatures, ΔG° will usually be positive and the reaction nonspontaneous. (4) A positive ΔH° and a positive ΔS° may give a negative or a positive ΔG° . At low temperatures, ΔG° will usually be positive and the reaction nonspontaneous; at high temperatures, ΔG° will usually be negative and the reaction spontaneous.
- 19.16 You can estimate the temperature at which a nonspontaneous reaction becomes spontaneous by substituting zero for ΔG° into the equation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and then solving for T using the form $T = \Delta H^\circ/\Delta S^\circ$.

■ Answers to Conceptual Problems

- 19.17 a. False. The enthalpy change (heat of reaction) has no direct relation to spontaneity.
b. False. The rate of a reaction has nothing to do with the spontaneity (thermodynamics) of a reaction.
c. False. The entropy may increase or decrease during a spontaneous reaction.
d. True. The entropy of the system plus its surroundings always increases during a spontaneous change.
e. False. The energy may increase or decrease during a spontaneous reaction.
- 19.18 a. Spontaneous. Sugar dissolves spontaneously in hot water.
b. Nonspontaneous. Rust does not spontaneously change to iron; rather, iron spontaneously rusts in air.
c. Spontaneous. The burning of butane in air is a spontaneous reaction.
d. Nonspontaneous. A pendulum, once stopped, will not spontaneously begin to move again.
e. Nonspontaneous. Water will not spontaneously decompose into its elements.

- 19.19 a. The 2.0 mol of CO_2 at 20°C and one atm has a greater entropy; two moles of substance have more entropy than one mole.
- b. The 1.0 mol of butane gas at 20°C and ten atm has the higher entropy; the gaseous state has more entropy than the liquid state of the same substance under the same conditions.
- c. The 1.0 mol of $\text{CO}_2(\text{s})$ at -80°C and one atm has the higher entropy; a solid substance has more entropy at the higher temperature.
- d. The twenty five grams of bromine vapor at -7°C and twelve atm has the higher entropy; the gaseous (vapor) state has more entropy than the liquid state of the same substance under the same conditions.
- 19.20 a. Entropy increases; ΔS is positive; energy dispersal increases when the food coloring disperses throughout the water.
- b. Entropy decreases; ΔS is negative; as a tree leafs out, energy dispersal decreases, and entropy decreases.
- c. Entropy increases; ΔS is positive; as flowers wilt and stems decompose, energy dispersal increases and entropy increases.
- d. Entropy decreases; ΔS is negative; as a liquid changes to a solid, there is a decrease in energy dispersal and a decrease of entropy.
- e. Entropy increases; ΔS is positive; as a liquid changes to a vapor, energy dispersal increases and entropy increases.
- 19.21 a. Since this is a gas phase reaction, calculate the change in the number of moles of gas molecules, $\Delta n = 1 - 3 = -2$. This corresponds to a decrease in entropy, so ΔS is negative for this reaction.
- b. Since this is an equilibrium state, $\Delta G = 0$, so $\Delta H - T\Delta S = 0$ also. This gives $\Delta H = T\Delta S$ and, since ΔS is positive, so is ΔH .
- c. The reaction spontaneously reestablishes equilibrium, so ΔG is negative prior to equilibrium.
- d. At equilibrium, $\Delta G = 0$.
- 19.22 The process is not spontaneous; you have to stretch the rubber band (the opposite process, a stretched rubber band snapping to its normal shorter shape, is spontaneous). Thus, ΔG is positive. The fact that the stretched rubber band feels warm means that ΔH is negative (exothermic). Note that $\Delta G = \Delta H - T\Delta S$; so $\Delta S = -(\Delta G - \Delta H)/T$. This implies that ΔS is negative, which is consistent with an increase in order.

- 19.23 a. Changes in volume will affect the position of the equilibrium, but will not change the value of the equilibrium constant for a reaction.
- b. The increase in volume of the container corresponds to a decrease in the pressure. According to Le Chatelier's principle, the reaction will shift towards the side with more gas molecules to reestablish the pressure. This means the reaction will shift toward the left side, $X(g) + Y(g)$. A reaction that shifts to the left has a Q value larger than the equilibrium constant.
- c. Immediately after the volume change, the value of ΔS for the forward reaction will still be the same, negative. Since the reaction is now spontaneous in the reverse reaction, ΔG for the forward reaction must be positive.
- 19.24 a. ΔH° is positive for this reaction (you need energy to break bonds), and ΔS° is also positive (breaking a molecule into two increases energy dispersal and entropy). Referring to Table 19.3, you see the reaction is nonspontaneous at low T and spontaneous at high T . Therefore, the spontaneity (ΔG°) of the reaction increases with temperature.
- b. ΔS° for this reaction is negative (two molecules form one, so there is a decrease in energy dispersal, and a decrease in entropy), and ΔH° is also negative (energy is released when bonds form). Referring to Table 19.3, you see the reaction is spontaneous at low T and nonspontaneous at high T . Therefore, the spontaneity (ΔG°) of the reaction decreases with temperature.

■ Solutions to Practice Problems

Note on significant figures: The mol unit is omitted from all thermodynamic parameters such as S° , ΔS° , etc. If the final answer to a solution needs to be rounded off, it is given first with one nonsignificant figure, and the last significant figure is underlined. The final answer is then rounded to the correct number of significant figures. In multiple-step problems, intermediate answers are given with at least one nonsignificant figure; however, only the final answer has been rounded off.

- 19.25 The values of q and w are -82 J and 29 J , respectively.

$$\Delta U = q + w = (-82 \text{ J}) + 29 \text{ J} = -53 \text{ J}$$

- 19.26 $\Delta U = 0 = q + w$

$$0 = (-76 \text{ J}) + w$$

$$w = 76 \text{ J}$$

- 19.27 At 100 °C (373 K) and one atm (1.013×10^5 Pa), 1.00 mol of $\text{H}_2\text{O}(\text{g})$ occupies

$$22.41 \text{ L} \times \frac{373 \text{ K}}{273 \text{ K}} = 30.619 \text{ L} \quad (30.619 \times 10^{-3} \text{ m}^3)$$

The work done by the chemical system in pushing back the atmosphere is

$$\begin{aligned} w &= -P\Delta V = -(1.013 \times 10^5 \text{ Pa}) \times (30.619 \times 10^{-3} \text{ m}^3) = -3.1017 \times 10^3 \text{ J} \\ &= -3.1017 \text{ kJ} \end{aligned}$$

$$\Delta U = q_p + w = (40.66 \text{ kJ}) + (-3.1017 \text{ kJ}) = 37.583 = 37.58 \text{ kJ}$$

- 19.28 At 25 °C (298 K) and one atm (1.013×10^5 Pa), the decrease in volume going from four mol to two mol of gas is

$$-2 \times 2.41 \text{ L} \times \frac{298 \text{ K}}{273 \text{ K}} = -48.924 \text{ L} \quad (-48.924 \times 10^{-3} \text{ m}^3)$$

The work done on the chemical system by the atmosphere is

$$\begin{aligned} w &= -P\Delta V = -(1.013 \times 10^5 \text{ Pa}) \times (-48.924 \times 10^{-3} \text{ m}^3) \\ &= 4.9560 \times 10^3 \text{ J} = 4.9560 \text{ kJ} \end{aligned}$$

$$\Delta U = q_p + w = (-91.8 \text{ kJ}) + 4.956 \text{ kJ} = -86.844 = -8.68 \text{ kJ}$$

- 19.29 First, determine the enthalpy change for the reaction of 1.20 mol of CHCl_3 .

$$\Delta H = 1.20 \text{ mol} \times \frac{29.6 \text{ kJ}}{1 \text{ mol}} = 35.52 \text{ kJ} = 3.552 \times 10^4 \text{ J}$$

Use the equilibrium relation between ΔS and ΔH_{vap} at the boiling point (61.2 °C = 334.4 K):

$$\Delta S = \frac{\Delta H}{T} = \frac{3.552 \times 10^4 \text{ J}}{334.4 \text{ K}} = 106.2 = 106 \text{ J/K}$$

19.30 First, determine the enthalpy change for 1.34 mol of $(\text{C}_2\text{H}_5)_2\text{O}$.

$$\Delta H = 1.34 \text{ mol} \times \frac{26.7 \text{ kJ}}{1 \text{ mol}} = 35.778 \text{ kJ} = 3.5778 \times 10^4 \text{ J}$$

Use the equilibrium relation between ΔS and ΔH_{vap} at the boiling point ($35.6^\circ\text{C} = 308.8 \text{ K}$):

$$\Delta S = \frac{\Delta H}{T} = \frac{3.5778 \times 10^4 \text{ J}}{308.8 \text{ K}} = 115.86 = 116 \text{ J/K}$$

19.31 First, determine the enthalpy change for the condensation of 1.00 mol of $\text{CH}_3\text{OH}(\text{l})$.
 $\Delta H_{\text{cond}} = -\Delta H_{\text{vap}} = -38.0 \text{ kJ/mol}$.

The entropy change for this condensation at 25°C (298 K) is

$$\Delta S = \frac{\Delta H_{\text{cond}}}{T} = \frac{-3.80 \times 10^4 \text{ J}}{298 \text{ K}} = -127.51 \text{ J/K}$$

The entropy of one mole of liquid is calculated using the entropy of one mole of vapor, $255 \text{ J/(mol}\cdot\text{K)}$.

$$S_{\text{liq}} = S_{\text{vap}} + \Delta S_{\text{cond}} = 255 \text{ J/K} + (-127.51 \text{ J/K}) = 127.48 = 127 \text{ J/K}$$

19.32 First, determine the enthalpy change for the vaporization of 1.00 mol of $\text{CS}_2(\text{l})$.
 $\Delta H_{\text{cond}} = -\Delta H_{\text{vap}} = -27.2 \text{ kJ/mol}$.

The entropy change for this condensation at 25°C (298 K) is

$$\Delta S = \frac{\Delta H_{\text{cond}}}{T} = \frac{-2.72 \times 10^4 \text{ J}}{298 \text{ K}} = -91.27 \text{ J/K}$$

The entropy of one mole of liquid is calculated using the entropy of one mole of vapor, $243 \text{ J/(mol}\cdot\text{K)}$.

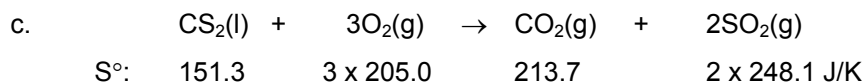
$$S_{\text{liq}} = S_{\text{vap}} + \Delta S_{\text{cond}} = 243 \text{ J/K} + (-91.27 \text{ J/K}) = 151.7 = 152 \text{ J/K}$$

19.33 a. ΔS° is negative because there is a decrease in moles of gas ($\Delta n_{\text{gas}} = -2$) from three moles of gaseous reactants forming one mole of gaseous product. (Entropy decreases.)

(continued)

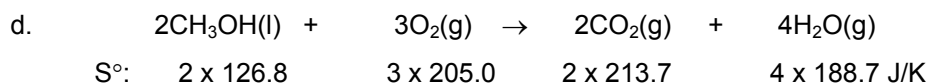
- b. ΔS° is not predictable from the rules given. The molecules N_2 , O_2 and NO are of similar size and present in equal number. There is no change in moles of gas ($\Delta n_{\text{gas}} = 0$), since two moles of gaseous reactants form two moles of gaseous products. Also, there is no phase change occurring.
- c. ΔS° is positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +1$) from five moles of gaseous reactants forming six moles of gaseous products. (Entropy increases.)
- d. ΔS° is positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +1$) from a solid reactant and one mole of gaseous reactant forming two moles of gaseous products. (Entropy increases.)
- 19.34 a. ΔS° is positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +1$) from two moles of gaseous reactant forming three moles of gaseous products. (Entropy increases.)
- b. ΔS° is negative because there is a decrease in moles of gas ($\Delta n_{\text{gas}} = -1$) from a liquid reactant and three moles of gaseous reactant forming two moles of gaseous product and liquid product. (Entropy decreases.)
- c. ΔS° is negative because there is a decrease in moles of gas ($\Delta n_{\text{gas}} = -1$) from one mole of gaseous reactant forming one mole of solid product. (Entropy decreases.)
- d. ΔS° is positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +2$) from a solid reactant forming two moles of gaseous product plus solid product. (Entropy increases.)
- 19.35 The reaction and standard entropies are given below. Multiply the S° values by their stoichiometric coefficients, and subtract the entropy of the reactant from the sum of the product entropies.
- a.
- | | | | | |
|----------------------|---|-------------------------|---------------|-------------------|
| 2Na(s) | + | $\text{Cl}_2\text{(g)}$ | \rightarrow | 2NaCl(s) |
| $S^\circ:$ 2 x 51.46 | | 223.0 | | 2 x 72.12 J/K |
- $$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$
- $$[(2 \times 72.12) - (2 \times 51.46 + 223.0)] \text{ J/K} = -181.68 = -181.7 \text{ J/K}$$
- b.
- | | | | | |
|------------------|---|-----------------------------|---------------|------------------|
| Ag(s) | + | $1/2 \text{Cl}_2\text{(g)}$ | \rightarrow | AgCl(s) |
| $S^\circ:$ 172.9 | | $1/2 \times 223.0$ | | 96.2 J/K |
- $$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$
- $$[(96.2) - (172.9 + 1/2 \times 223.0)] \text{ J/K} = -188.13 = -188.1 \text{ J/K}$$

(continued)



$$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$

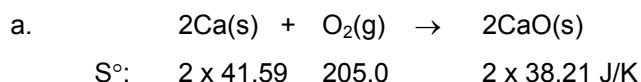
$$[(213.7 + 2 \times 248.1) - (151.3 + 3 \times 205.0)] \text{ J/K} = -56.4 \text{ J/K}$$



$$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$

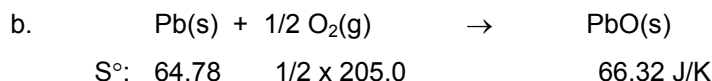
$$[(2 \times 213.7 + 4 \times 188.7) - (2 \times 126.8 + 3 \times 205.0)] \text{ J/K} = 313.6 = 314 \text{ J/K}$$

19.36 The reaction and standard entropies are given below. Multiply the S° values by their stoichiometric coefficients, and subtract the entropy of the reactant from the sum of the product entropies. In part b, note that aqueous CaCl_2 exists as $\text{Ca}^+(\text{aq})$ and $2\text{Cl}^-(\text{aq})$ ions.



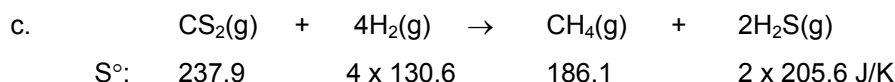
$$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$

$$[(2 \times 38.21) - (2 \times 41.59 + 205.0)] \text{ J/K} = -211.76 = -211.8 \text{ J/K}$$



$$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$

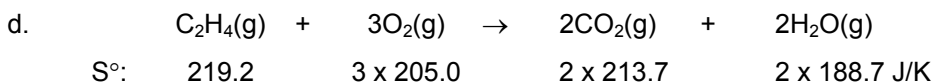
$$[66.32 - 64.78 - 1/2 \times 205.0] \text{ J/K} = -100.96 = -101.0 \text{ J/K}$$



$$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$

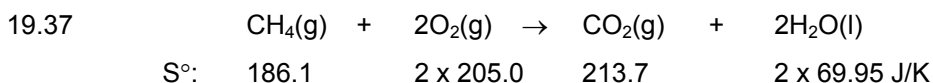
$$[(186.1 + 2 \times 205.6) - (237.9 + 4 \times 130.6)] \text{ J/K} = -163.0 \text{ J/K}$$

(continued)



$$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$

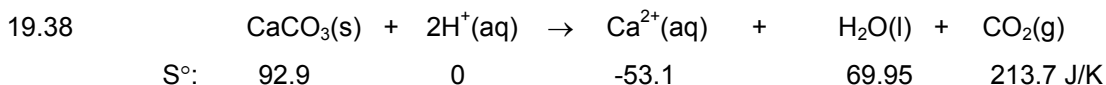
$$[(2 \times 213.7 + 2 \times 188.7) - (219.2 + 3 \times 205.0)] \text{ J/K} = -29.4 \text{ J/K}$$



$$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$

$$[(213.7 + 2 \times 69.95) - (186.1 + 2 \times 205.0)] \text{ J/K} = -242.50 \text{ J/K}$$

S decreases as expected from the decrease in moles of gas.

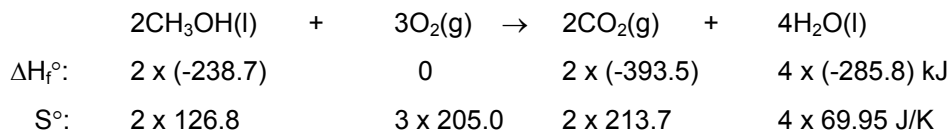


$$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$

$$[(-53.1 + 69.95 + 213.7) - (92.9)] \text{ J/K} = 137.65 \text{ J/K}$$

S increases as expected from the increase in moles of gas.

19.39 The reaction, with standard enthalpies of formation and standard entropies written underneath, is



Calculate ΔH° and ΔS° for the reaction.

$$\Delta H^\circ = \Sigma n\Delta H_f^\circ(\text{products}) - \Sigma m\Delta H_f^\circ(\text{reactants}) =$$

$$[2 \times (-393.5) + 4 \times (-285.8) - 2 \times (-238.7)] \text{ kJ} = -1452.8 \text{ kJ}$$

$$\Delta S^\circ = \Sigma nS^\circ(\text{products}) - \Sigma mS^\circ(\text{reactants}) =$$

$$[(2 \times 213.7 + 4 \times 69.95) - (2 \times 126.8 + 3 \times 205.0)] \text{ J/K}$$

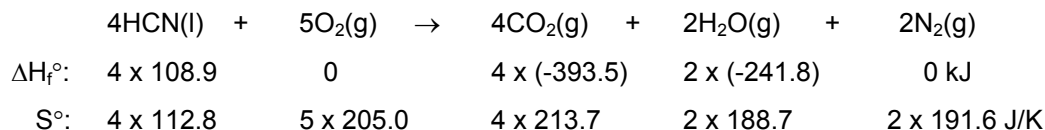
$$= -161.40 = -161.4 \text{ J/K}$$

(continued)

Now, substitute into the equation for ΔG° in terms of ΔH° and ΔS° ($= -0.16140$ kJ/K).

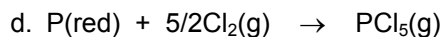
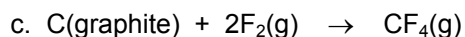
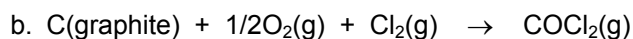
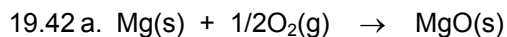
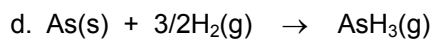
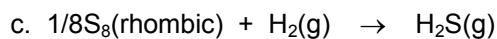
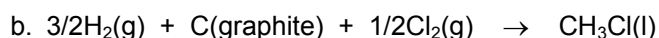
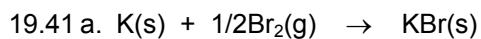
$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -1452.8 \text{ kJ} - (298 \text{ K}) \times (-0.16140 \text{ kJ/K}) \\ &= -1404.\underline{70} = -1404.7 \text{ kJ}\end{aligned}$$

19.40 The reaction, standard enthalpy changes, and standard entropies are as follows:

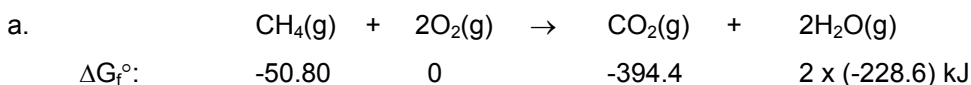


Calculate ΔH° and ΔS° for the reaction.

$$\begin{aligned}\Delta H^\circ &= \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants}) = \\ &[4 \times (-393.5) + 2 \times (-241.8) - 4 \times 108.9] \text{ kJ} = -2493.\underline{2} \text{ kJ} \\ \Delta S^\circ &= \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants}) = \\ &[(4 \times 213.7 + 2 \times 188.7 + 2 \times 191.6) - (4 \times 112.8 + 5 \times 205.0)] \text{ J/K} \\ &= 139.\underline{2} \text{ (0.13920 kJ/K)} \\ \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = -2493.2 \text{ kJ} - (298 \text{ K})(0.13920 \text{ kJ/K}) \\ &= -2534.\underline{6} = -2535 \text{ kJ}\end{aligned}$$

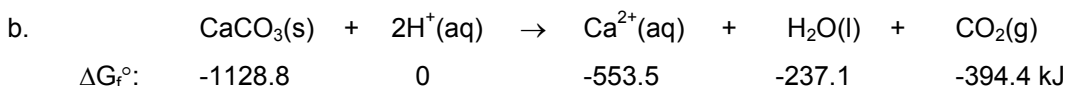


19.43 Write the values of ΔG_f° multiplied by their stoichiometric coefficients below each formula; then subtract ΔG_f° of the reactant from that of the products.



$$\Delta G^\circ = \Sigma n\Delta G_f^\circ(\text{products}) - \Sigma m\Delta G_f^\circ(\text{reactants}) =$$

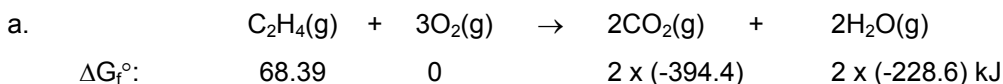
$$[(-394.4) + 2(-228.6) - (-50.80)] \text{ kJ} = -800.8 \text{ kJ}$$



$$\Delta G^\circ = \Sigma n\Delta G_f^\circ(\text{products}) - \Sigma m\Delta G_f^\circ(\text{reactants}) =$$

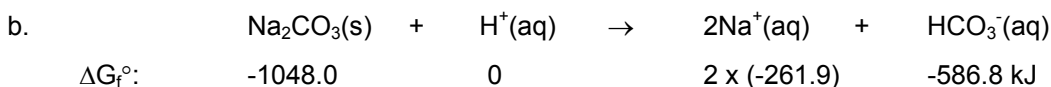
$$[(-553.5) + (-237.1) + (-394.4) - (-1128.8)] \text{ kJ} = -56.2 \text{ kJ}$$

19.44 Write the values of ΔG_f° below each formula; then subtract ΔG_f° values.



$$\Delta G^\circ = \Sigma n\Delta G_f^\circ(\text{products}) - \Sigma m\Delta G_f^\circ(\text{reactants}) =$$

$$[2(-394.4) + 2(-228.6) - (68.39)] \text{ kJ} = -1314.39 = -1314.4 \text{ kJ}$$



$$\Delta G^\circ = \Sigma n\Delta G_f^\circ(\text{products}) - \Sigma m\Delta G_f^\circ(\text{reactants}) =$$

$$[2(-261.9) + (-586.8) - (-1048.0)] \text{ kJ} = -62.6 \text{ kJ}$$

19.45 a. Spontaneous reaction

b. Spontaneous reaction

c. Nonspontaneous reaction

d. Equilibrium mixture; significant amounts of both

e. Nonspontaneous reaction

19.46 a. Spontaneous reaction

b. Nonspontaneous reaction

c. Nonspontaneous reaction

d. Spontaneous reaction

e. Equilibrium mixture; significant amounts of both

19.47 Calculate ΔH° and ΔG° using the given ΔH_f° and ΔG_f° values.

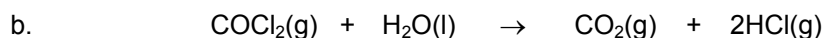
$$\Delta H_f^\circ: \quad -1675.7 \quad 0 \quad -825.5 \quad 0 \text{ kJ}$$

$$\Delta G_f^\circ: \quad -1582.3 \quad 0 \quad -743.5 \quad 0 \text{ kJ}$$

$$\Delta H^\circ = [(-825.5) - (-1675.7)] \text{ kJ} = 850.2 \text{ kJ}$$

$$\Delta G^\circ = [(-743.5) - (-1582.3)] \text{ kJ} = 838.8 \text{ kJ}$$

The reaction is endothermic, absorbing 850.2 kJ of heat. The large positive value for ΔG° indicates the equilibrium composition is mainly reactants.



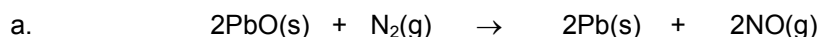
$$\Delta H_f^\circ: \quad -220.1 \quad -285.8 \quad -393.5 \quad 2 \times (-92.31) \text{ kJ}$$

$$\Delta G_f^\circ: \quad -205.9 \quad -237.1 \quad -394.4 \quad 2 \times (-95.30) \text{ kJ}$$

$$\Delta H^\circ = [-393.5 + (2)(-92.31) - (-220.1) - (-285.8)] \text{ kJ} = -72.22 = -72.2 \text{ kJ}$$

$$\Delta G^\circ = [-394.4 + (2)(-95.30) - (-205.9) - (-237.1)] \text{ kJ} = -142.00 = -142.0 \text{ kJ}$$

The reaction is exothermic; the ΔG° value indicates mainly products at equilibrium.

19.48 Calculate ΔH° and ΔG° using the given ΔH_f° and ΔG_f° values.

$$\Delta H_f^\circ: \quad 2(-219.4) \quad 0 \quad 0 \quad 2 \times 90.29 \text{ kJ}$$

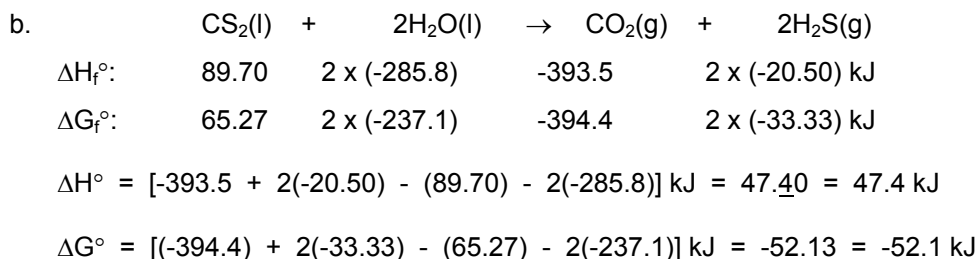
$$\Delta G_f^\circ: \quad 2(-189.3) \quad 0 \quad 0 \quad 2 \times 86.60 \text{ kJ}$$

$$\Delta H^\circ = [2(90.29) - 2(-219.4)] \text{ kJ} = 619.38 = 619.4 \text{ kJ}$$

$$\Delta G^\circ = [2(86.60) - 2(-189.3)] \text{ kJ} = 551.80 = 551.8 \text{ kJ}$$

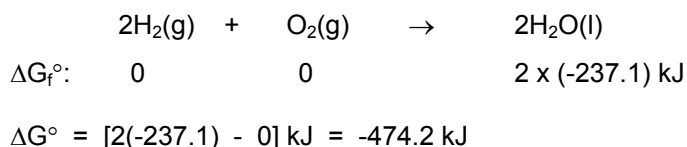
The reaction is endothermic, absorbing 619.4 kJ of heat. The large positive value for ΔG° indicates the equilibrium composition is mainly reactants.

(continued)



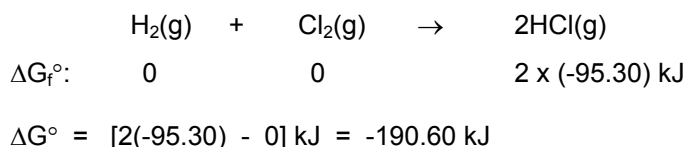
The reaction is endothermic; ΔG° indicates the equilibrium composition is mainly products.

19.49 Calculate ΔG° using the given ΔG_f° values.



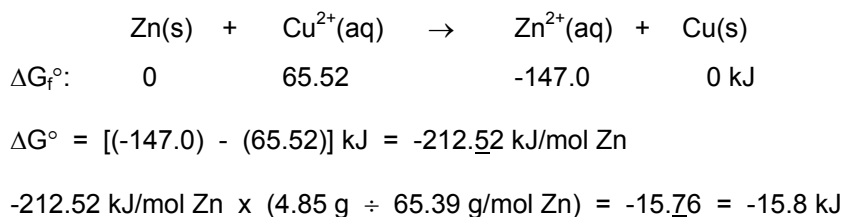
Maximum work equals ΔG° equals -474.2 kJ. Because maximum work is stipulated, no entropy is produced.

19.50 Calculate ΔG° using the given ΔG_f° values.



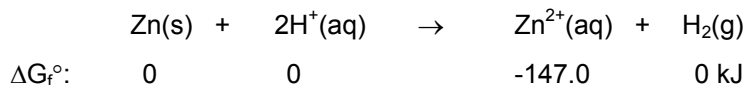
Maximum work equals ΔG° equals -190.60 kJ. Because maximum work is stipulated, no entropy is produced.

19.51 Calculate ΔG° per one mol Zn(s) using the given ΔG_f° values.



Maximum work equals ΔG° equals -15.8 kJ. Because maximum work is stipulated, no entropy is produced.

19.52 Calculate ΔG° per one mol Zn(s) using the given ΔG_f° values.



$$\Delta G^\circ = [(-147.0) - 0] \text{ kJ} = -147.0 \text{ kJ/mol Zn}$$

$$-147.0 \text{ kJ/mol Zn} \times (3.65 \text{ g} \div 65.39 \text{ g/mol Zn}) = -8.205 = -8.21 \text{ kJ}$$

Maximum work equals ΔG° equals -8.21 kJ. Because maximum work is stipulated, no entropy is produced.

$$19.53 \text{ a. } K = K_p = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{CO}} P_{\text{H}_2\text{O}}}$$

$$\text{b. } K = K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2$$

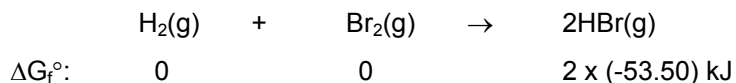
$$\text{c. } K = [\text{Li}^+]^2[\text{OH}^-]^2 P_{\text{H}_2}$$

$$19.54 \text{ a. } K = K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} P_{\text{H}_2}^2}$$

$$\text{b. } K = \frac{1}{K_{\text{sp}}} = \frac{1}{[\text{Ag}^+]^2 [\text{CrO}_4^{2-}]}$$

$$\text{c. } K = \frac{[\text{Ca}^{2+}] P_{\text{CO}_2}}{[\text{H}^+]^2}$$

19.55 First, calculate ΔG° using the ΔG_f° values from Appendix C.



$$\Delta G^\circ = [2(-53.50) - 0] \text{ kJ} = -107.00 \text{ kJ}$$

Use the rearranged form of the equation, $\Delta G^\circ = -RT \ln K$, to solve for $\ln K$. To get compatible units, express ΔG° in joules, and set R equal to $8.31 \text{ J/(mol}\cdot\text{K)}$.

(continued)

Substituting the numerical values into the expression gives

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-107.00 \times 10^3}{-8.31 \times 298} = 43.208$$

$$K = e^{43.208} = 5.82 \times 10^{18} = 6 \times 10^{18}$$

19.56 First, calculate ΔG° using the ΔG_f° values from Appendix C.



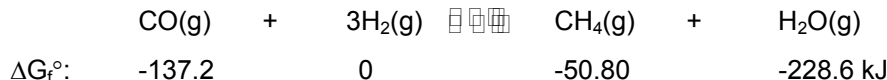
$$\Delta G^\circ = [(-65.27) - 0] \text{ kJ} = -65.27 \text{ kJ}$$

Use the rearranged form of the equation, $\Delta G^\circ = -RT \ln K$, to solve for $\ln K$. To get compatible units, express ΔG° in joules, and set R equal to $8.31 \text{ J/(mol}\cdot\text{K)}$. Substituting the numerical values into the expression gives

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-65.27 \times 10^3}{-8.31 \times 298} = 26.357$$

$$K = e^{26.357} = 2.79 \times 10^{11} = 3 \times 10^{11}$$

19.57 First, calculate ΔG° using the ΔG_f° values from Appendix C.



Subtract ΔG_f° of the reactants from that of the products:

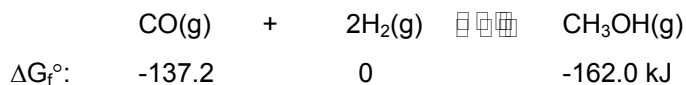
$$\Delta G^\circ = [(-50.80) + (-228.6) - (-137.2)] \text{ kJ} = -142.20 \text{ kJ}$$

Use the rearranged form of the equation, $\Delta G^\circ = -RT \ln K$, to solve for $\ln K$. To get compatible units, express ΔG° in joules, and set R equal to $8.31 \text{ J/(mol}\cdot\text{K)}$. Substituting the numerical values into the expression gives

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-142.20 \times 10^3}{-8.31 \times 298} = 57.422$$

$$K = K_p = e^{57.422} = 8.67 \times 10^{24} = 9 \times 10^{24}$$

19.58 First, calculate ΔG° using the ΔG_f° values from Appendix C.



Subtract ΔG_f° of the reactants from that of the product:

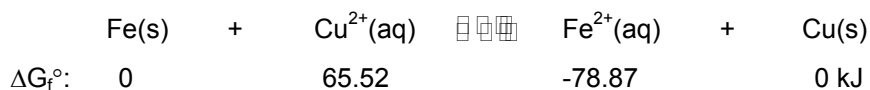
$$\Delta G^\circ = [(-162.0) - (-137.2)] \text{ kJ} = -24.8 \text{ kJ}$$

Use the rearranged form of the equation, $\Delta G^\circ = -RT \ln K$, to solve for $\ln K$. To get compatible units, express ΔG° in joules, and set R equal to $8.31 \text{ J/(mol}\cdot\text{K)}$. Substituting the numerical values into the expression gives

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-24.8 \times 10^3}{-8.31 \times 298} = 10.014$$

$$K = K_p = e^{10.014} = 2.23 \times 10^4 = 2 \times 10^4$$

19.59 First, calculate ΔG° using the ΔG_f° values from Appendix C.



Hence

$$\Delta G^\circ = [(-78.87) - 65.52] \text{ kJ} = -144.38 \text{ kJ}$$

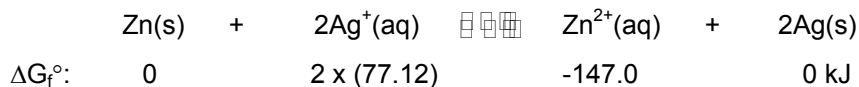
Now, substitute numerical values into the equation relating $\ln K$ and ΔG° .

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-144.38 \times 10^3}{-8.31 \times 298} = 58.306$$

Therefore,

$$K = K_c = e^{58.306} = 2.10 \times 10^{25} = 2 \times 10^{25}$$

19.60 First, calculate ΔG° using the ΔG_f° values from Appendix C.



Hence,

$$\Delta G^\circ = [(-147.0) - 2(77.12)] \text{ kJ} = -301.24 \text{ kJ}$$

(continued)

Now, substitute numerical values into the equation relating $\ln K$ and ΔG° .

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-301.24 \times 10^3}{-8.31 \times 298} = 121.645$$

Therefore,

$$K = K_c = e^{121.645} = 6.75 \times 10^{52} = 7 \times 10^{52}$$

19.61 From Appendix C, you have

	C(graphite)	+	CO ₂ (g)	\rightleftharpoons	2CO(g)
ΔH_f° :	0		-393.5		2 x (-110.5) kJ
S° :	5.740		213.7		2 x (197.5) J/K

Calculate ΔH° and ΔS° from these values.

$$\Delta H^\circ = [2(-110.5) - (-393.5)] \text{ kJ} = 172.5 \text{ kJ}$$

$$\Delta S^\circ = [2(197.5) - (5.740 + 213.7)] \text{ J/K} = 175.56 \text{ J/K}$$

Substitute ΔH° , ΔS° ($= 0.17556 \text{ kJ/K}$), and T ($= 1273 \text{ K}$) into the equation for ΔG_T° .

$$\Delta G_T^\circ = \Delta H^\circ - T\Delta S^\circ = 172.5 \text{ kJ} - (1273 \text{ K})(0.17556 \text{ kJ/K}) = -50.987 \text{ kJ}$$

Substitute the value of ΔG° ($= -50.987 \times 10^3 \text{ J}$) into the equation relating $\ln K$ and ΔG° .

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-50.987 \times 10^3}{-8.31 \times 1273} = 4.8198$$

$$K = K_p = e^{4.8198} = 123.9 = 1.2 \times 10^2$$

Because K_p is greater than one, the data predict combustion of carbon should form significant amounts of CO product at equilibrium.

19.62 From Appendix C, you have

	N ₂ (g)	+	O ₂ (g)	\rightleftharpoons	2NO(g)
ΔH_f° :	0		0		2 x (90.29) kJ
S° :	191.6		205.0		2 x (210.6) J/K

(continued)

Calculate ΔH° and ΔS° from these values.

$$\Delta H^\circ = [2(90.29) - (0)] \text{ kJ} = 180.58 \text{ kJ}$$

$$\Delta S^\circ = [2(210.6) - (191.6 + 205.0)] \text{ J/K} = 24.6 \text{ J/K}$$

Substitute ΔH° , ΔS° ($= 0.0246 \text{ kJ/K}$), and T ($= 2273 \text{ K}$) into the equation for ΔG_T° .

$$\Delta G_T^\circ = \Delta H^\circ - T\Delta S^\circ = 180.58 \text{ kJ} - (2273 \text{ K})(0.0246 \text{ kJ/K}) = 124.664 \text{ kJ}$$

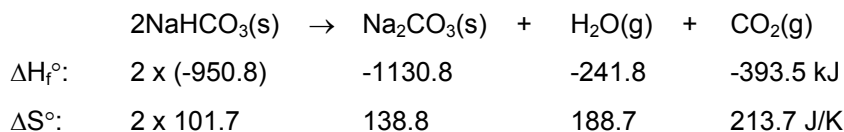
Substitute the value of ΔG° ($= 124.664 \times 10^3 \text{ J}$) into the equation relating $\ln K$ and ΔG° .

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{124.664 \times 10^3}{-8.31 \times 2273} = -6.5999$$

$$K = K_p = e^{-6.5999} = 1.360 \times 10^{-3} = 1.4 \times 10^{-3}$$

Because K_p is slightly less than one but greater than 10^{-4} , the data predict combustion of nitrogen and oxygen should form small (but not significant) amounts of NO product at equilibrium.

19.63 First, calculate ΔH° and ΔS° using the given ΔH_f° and S° values.



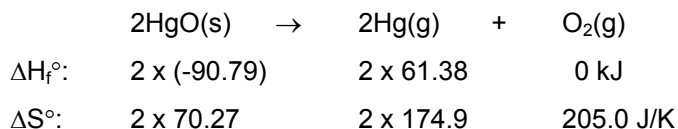
$$\Delta H^\circ = [(-1130.8) + (-241.8) + (-393.5) - 2(-950.8)] \text{ kJ} = 135.5 \text{ kJ}$$

$$\Delta S^\circ = [(138.8 + 188.7 + 213.7) - 2(101.7)] \text{ J/K} = 337.8 \text{ J/K} \quad (0.3378 \text{ kJ/K})$$

Substitute these values into $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; let $\Delta G^\circ = 0$, and rearrange to solve for T .

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{135.5 \text{ kJ}}{0.3378 \text{ kJ/K}} = 401.1 = 401 \text{ K}$$

- 19.64 First, calculate ΔH° and ΔS° using the given ΔH_f° and S° values.



$$\Delta H^\circ = [(2 \times 61.38) - 2(-90.79)] \text{ kJ} = 304.34 \text{ kJ}$$

$$\Delta S^\circ = [(2 \times 174.9 + 205.0) - 2(70.27)] \text{ J/K} = 414.26 \text{ J/K} \quad (0.41426 \text{ kJ/K})$$

Substitute these values into $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$, let $\Delta G^\circ = 0$, and rearrange to solve for T.

$$T = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{304.34 \text{ kJ}}{0.41426 \text{ kJ/K}} = 734.65 = 734.7 \text{ K}$$

■ Solutions to General Problems

- 19.65 The sign of ΔS° should be positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +5$) as the solid reactant forms five moles of gas. The reaction is endothermic, denoting a positive ΔH° . The fact that the reaction is spontaneous implies the product, $T\Delta S^\circ$, is larger than ΔH° , so ΔG° is negative, as required for a spontaneous reaction.
- 19.66 The sign of ΔS° should be negative because there is a decrease in moles of gas ($\Delta n_{\text{gas}} = -3$) as the seven moles of gaseous reactants form four moles of gaseous product plus liquid product. The reaction is exothermic, denoting a negative ΔH° . The fact that the reaction is spontaneous implies the negative ΔH° is larger than the positive value of $-T\Delta S^\circ$, so ΔG° is negative, as required for a spontaneous reaction.
- 19.67 The ΔH value $\sim \text{BE(H-H)} + \text{BE(Cl-Cl)} - \text{BE(H-Cl)} \sim [432 + 240 - 2(428)] \text{ kJ} \sim -184 \text{ kJ}$, and thus the reaction is exothermic. ΔS° should be positive because there is a increase in energy dispersal with the formation of unsymmetrical molecules from symmetrical H_2 and Cl_2 . The reaction should be spontaneous because the contributions of both the ΔH term and the $-T\Delta S$ term are negative.
- 19.68 The ΔH value $\cong \text{BE(HC)} + \text{BE(CN)} + 2\text{BE(HH)} - 3\text{BE(CH)} - 3\text{BE(CN)} - 2\text{BE(NH)} \cong [411 + 887 + 2(432) - 3(411) - 305 - 2(386)] \text{ kJ} \sim -148 \text{ kJ}$. Thus, the reaction is exothermic. ΔS° should be negative because there is a decrease in moles of gas ($\Delta n_{\text{gas}} = -2$) with the formation of one mole of gas from three moles of gas. The reaction is spontaneous because the contributions of the ΔH term dominate the $-T\Delta S$ term.

- 19.69 When the liquid freezes, it releases heat: $\Delta H_{\text{fus}} = -69.0 \text{ J/g}$ at 16.6°C (289.6 K). The entropy change is

$$\Delta S = \frac{\Delta H_{\text{fus}}}{T} = \frac{-69.0 \text{ J/g}}{289.8 \text{ K}} \times \frac{60.05 \text{ g}}{1 \text{ mol}} = -14.\underline{30} = -14.3 \text{ J/(K}\cdot\text{mol)}$$

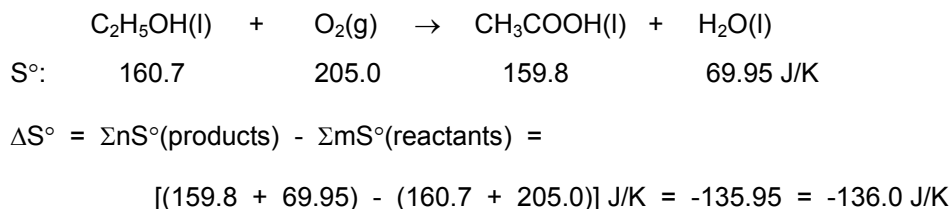
- 19.70 When the liquid evaporates, it absorbs heat: $\Delta H_{\text{vap}} = 29.1 \text{ kJ/mol}$, or $2.91 \times 10^4 \text{ J/mol}$, at 56°C (329 K). The entropy change is:

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T} = \frac{2.91 \times 10^4 \text{ J/g}}{329 \text{ K}} = 88.\underline{45} = 88.4 \text{ J/(K}\cdot\text{mol)}$$

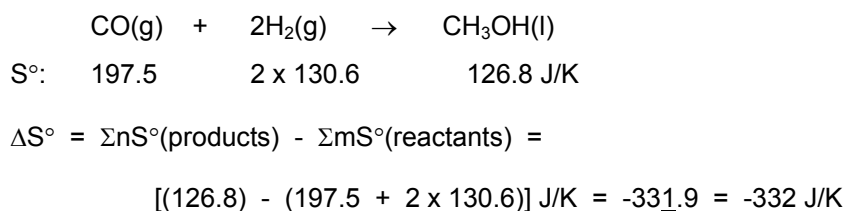
- 19.71 a. ΔS° is negative because there is a decrease in moles of gas ($\Delta n_{\text{gas}} = -1$) from one mole of gaseous reactant forming aqueous and liquid products. (Entropy decreases.)
- b. ΔS° is positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +5$) from a solid reactant forming five moles of gas. (Entropy increases.)
- c. ΔS° is positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +3$) from two moles of gaseous reactant forming five moles of gaseous products. (Entropy increases.)
- d. ΔS° is negative because there is a decrease in moles of gas ($\Delta n_{\text{gas}} = -1$) from three moles of gaseous reactants forming two moles of gaseous products. (Entropy decreases.)
- 19.72 a. Entropy decreases; ΔS° is negative because there is a decrease in the moles of gas ($\Delta n_{\text{gas}} = -2$) from four moles of gaseous reactant forming two moles of gaseous products.
- b. Entropy increases; ΔS° is certainly positive because there is an increase in the moles of gas ($\Delta n_{\text{gas}} = +2$) from a solid reactant forming two moles of gas.
- c. Entropy decreases; ΔS° is negative because there is a decrease in the moles of gas ($\Delta n_{\text{gas}} = -3$) from three moles of gaseous reactant forming a liquid product.
- d. Entropy increases; ΔS° is certainly positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +1$) from solid and liquid reactants forming one mole of gaseous product.
- 19.73 ΔS° is negative because there is a decrease in the moles of gas ($\Delta n_{\text{gas}} = -2$) from three moles of gaseous reactant forming one mole of gaseous product plus liquid product.

- 19.74 ΔS° is positive because there is an increase in moles of gas ($\Delta n_{\text{gas}} = +2$) from three moles of gaseous reactant forming five moles of gaseous products.

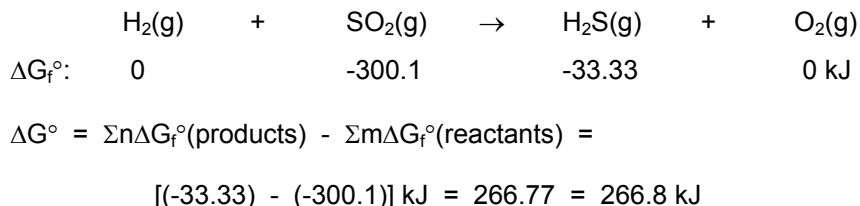
- 19.75 Calculate ΔS° from the individual S° values:



- 19.76 Calculate ΔS° from the individual S° values:

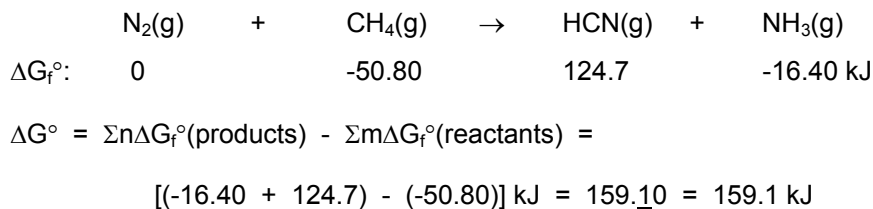


- 19.77 Calculate ΔG° using the ΔG_f° values from Appendix C.



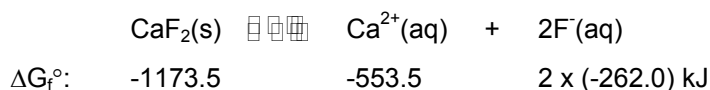
Because ΔG° is positive, the reaction is nonspontaneous, as written, at 25 °C.

- 19.78 Calculate ΔG° using the ΔG_f° values from Appendix C.



Because ΔG° is positive, the reaction is nonspontaneous, as written, at 25 °C.

- 19.79 At low (room) temperature, ΔG° or $(\Delta H^\circ - T\Delta S^\circ)$ must be positive, but at higher temperatures, ΔG° or $(\Delta H^\circ - T\Delta S^\circ)$ must be negative. Thus, at the higher temperatures, the $-T\Delta S^\circ$ term must become more negative than ΔH° . Thus, ΔS° must be positive and so must ΔH° . If either were negative, ΔG° would not become negative at higher temperatures.
- 19.80 At low (room) temperature, ΔG° or $(\Delta H^\circ - T\Delta S^\circ)$ must be negative, but at higher temperatures, ΔG° or $(\Delta H^\circ - T\Delta S^\circ)$ must be positive. Thus, at the higher temperatures, the $-T\Delta S^\circ$ term must become more positive than ΔH° . Thus, ΔS° must be negative and so must ΔH° . If either were positive, ΔG° would not become negative at lower temperatures.
- 19.81 First, calculate ΔG° using the values in Appendix C.



Hence, ΔG° for the reaction is

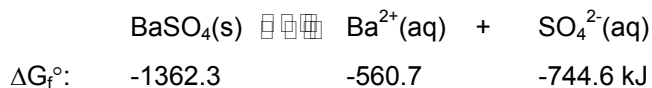
$$\Delta G_f^\circ = [-553.5 + 2(-262.0) - (-1173.5)] \text{ kJ} = 96.0 \text{ kJ}$$

Now, substitute numerical values into the equation relating $\ln K$ and ΔG° .

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{96.0 \times 10^3}{-8.31 \times 298} = -38.766$$

$$K = K_{\text{sp}} = e^{-38.766} = 1.45 \times 10^{-17} = 1 \times 10^{-17}$$

- 19.82 First, calculate ΔG° using the values in Appendix C.



Hence, ΔG° for the reaction is

$$\Delta G^\circ = [-560.7 + (-744.6) - (-1362.3)] \text{ kJ} = 57.0 \text{ kJ}$$

(continued)

Now, substitute numerical values into the equation relating $\ln K$ and ΔG° .

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{57.0 \times 10^3}{-8.31 \times 298} = -22.017$$

$$K = K_{\text{sp}} = e^{-23.017} = 1.00 \times 10^{-10} = 1 \times 10^{-10}$$

19.83 From Appendix C, you have

	$\text{COCl}_2(\text{g})$	\rightarrow	$\text{CO}(\text{g})$	+	$\text{Cl}_2(\text{g})$
ΔH_f° :	-220.1		-110.5		0 kJ
S° :	283.9		197.5		223.0 J/K

Calculate ΔH° and ΔS° from these values.

$$\Delta H^\circ = [(-110.5) - (-220.1)] \text{ kJ} = 109.6 \text{ kJ}$$

$$\Delta S^\circ = [197.5 + 223.0 - 283.9] \text{ J/K} = 136.6 \text{ J/K} \quad (0.1366 \text{ kJ/K})$$

$$\begin{aligned} \text{At } 25^\circ\text{C: } \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 109.6 \text{ kJ} - (298 \text{ K})(0.1366 \text{ kJ/K}) \\ &= 68.89 = 68.9 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \text{At } 800^\circ\text{C: } \Delta G_T^\circ &= \Delta H^\circ - T\Delta S^\circ = 109.6 \text{ kJ} - (1073 \text{ K})(0.1366 \text{ kJ/K}) \\ &= -37.07 = -37.1 \text{ kJ} \end{aligned}$$

Thus, ΔG° changes from a positive value and a nonspontaneous reaction at 25°C to a negative value and a spontaneous reaction at 800°C .

19.84 From Appendix C, you have

	$\text{CS}_2(\text{g})$	+	$4\text{H}_2(\text{g})$	\rightleftharpoons	$\text{CH}_4(\text{g})$	+	$2\text{H}_2\text{S}(\text{g})$
ΔH_f° :	116.9		0		-74.87		$2 \times (-20.50) \text{ kJ}$
S° :	237.9		4×130.6		186.1		2×205.6

Calculate ΔH° and ΔS° from these values.

$$\Delta H^\circ = [(-74.87) + 2(-20.50) - (116.9)] \text{ kJ} = -232.77 \text{ kJ}$$

$$\begin{aligned} \Delta S^\circ &= [186.1 + 2(205.6) - (237.9) - 4(130.6)] \text{ J/K} \\ &= -163.0 \text{ J/K} \quad (-0.1630 \text{ kJ/K}) \end{aligned}$$

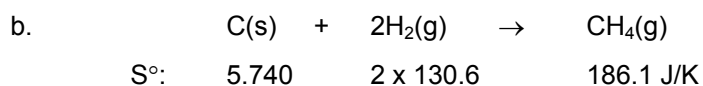
(continued)

$$\begin{aligned}\text{At } 25\text{ }^{\circ}\text{C: } \Delta G^{\circ} &= \Delta H^{\circ} - T\Delta S^{\circ} = -232.77\text{ kJ} - (298\text{ K})(-0.1630\text{ kJ/K}) = -184.\underline{19} \\ &= -184.2\text{ kJ}\end{aligned}$$

$$\begin{aligned}\text{At } 650\text{ }^{\circ}\text{C: } \Delta G_T^{\circ} &= \Delta H^{\circ} - T\Delta S^{\circ} = -232.77\text{ kJ} - (923\text{ K})(-0.1630\text{ kJ/K}) = -82.\underline{32} \\ &= -82.3\text{ kJ}\end{aligned}$$

Thus, ΔG° has a negative value at both temperatures, and the reaction is spontaneous at both temperatures. However, ΔG° is more negative at 25 °C than at 650 °C, and so the relative proportion of the products is greater at 25 °C.

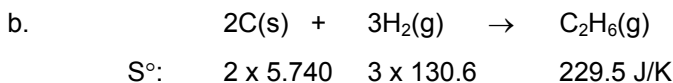
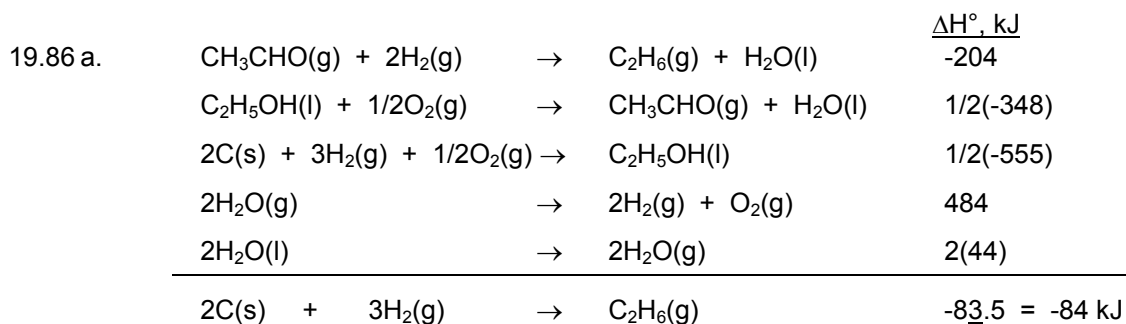
		<u>ΔH°, kJ</u>
19.85 a.	$\text{CO}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{HCHO}(\text{g}) + \text{H}_2\text{O}(\text{g})$	35
	$\text{HCHO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$	-201
	$\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	-393
	$2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$	484
	<hr/>	
	$\text{C}(\text{s}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$	-75 kJ



$$\begin{aligned}\Delta S^{\circ} &= \Sigma nS^{\circ}(\text{products}) - \Sigma mS^{\circ}(\text{reactants}) = \\ &[186.1 - 5.740 - 2(130.6)]\text{ J/K} = -80.\underline{84}\text{ J/K } (-0.08084\text{ kJ/K})\end{aligned}$$

- c. ΔG° for the reaction, which involves one mole of methane, is equal to ΔG_f° for methane, and is obtained as follows.

$$\begin{aligned}\Delta G_f^{\circ} &= \Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \\ &= -75\text{ kJ} - (298\text{ K})(-0.08084\text{ kJ/K}) \\ &= -50.\underline{90} = -51\text{ kJ/mol}\end{aligned}$$



$$\Delta S^\circ = \sum nS^\circ(\text{products}) - \sum mS^\circ(\text{reactants}) =$$

$$[229.5 - 2(5.740) - 3(130.6)] \text{ J/K} = -173.78 \text{ J/K} \quad (-0.17378 \text{ kJ/K})$$

c. ΔG° for the reaction, which involves one mole of ethane, is equal to ΔG_f° for ethane and is obtained as follows.

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

$$= -83.5 \text{ kJ} - (298 \text{ K})(-0.17378 \text{ kJ/K})$$

$$= -31.71 = -31.7 \text{ kJ/mol}$$

19.87 $\Delta H^\circ = [-393.5 + 2(-285.8) - (-238.7)] \text{ kJ} = -726.4 \text{ kJ}$

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

$$-702.2 \text{ kJ} = -726.4 \text{ kJ} - (298 \text{ K})(\Delta S^\circ)$$

$$\Delta S^\circ = -\frac{(-702.2 \text{ kJ}) - (-726.4 \text{ kJ})}{298 \text{ K}} = -0.08120 \text{ kJ/K} = -81.20 \text{ J/K}$$

$$\Delta S^\circ = -81.20 \text{ J/K} = [2(70.0) + 213.7 - (126.8) - (3/2 \text{ mol}) \times S^\circ(\text{O}_2)] \text{ J/K}$$

$$S^\circ(\text{O}_2) = 205.40 = 205.4 \text{ J/mol}\cdot\text{K}$$

$$19.88 \quad \Delta H^\circ = [-241.8 + (-393.5) - (-117.0) - 2/3(142.7)] \text{ kJ} = -613.43 \text{ kJ}$$

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

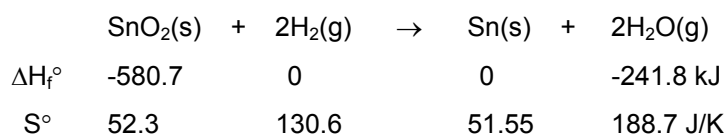
$$-621.7 \text{ kJ} = -613.43 \text{ kJ} - (298 \text{ K})(\Delta S^\circ)$$

$$\Delta S^\circ = -\frac{(-621.7 \text{ kJ}) - (-613.43 \text{ kJ})}{298 \text{ K}} = -0.02774 \text{ kJ/K} = 27.74 \text{ J/K}$$

$$\Delta S^\circ = 27.74 \text{ J/K} = [188.7 + 213.7 - (219.0) - (2/3 \text{ mol}) \times S^\circ(\text{O}_3)] \text{ J/K}$$

$$S^\circ(\text{O}_3) = 233.48 = 233.5 \text{ J/mol}\cdot\text{K}$$

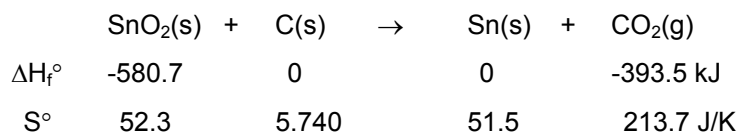
19.89 a. The first reaction is



$$\Delta H^\circ = [2(-241.8) - (-580.7)] \text{ kJ} = 97.1 \text{ kJ} = 97.1 \times 10^3 \text{ J}$$

$$\Delta S^\circ = [2(188.7) + 51.55 - 2(130.6) - 52.3] \text{ J/K} = 115.45 \text{ J/K}$$

The second reaction is



$$\Delta H^\circ = [-393.5 - (-580.7)] \text{ kJ} = 187.2 \text{ kJ} = 187.2 \times 10^3 \text{ J}$$

$$\Delta S^\circ = [213.7 + 51.5 - 5.740 - 52.3] \text{ J/K} = 207.16 \text{ J/K}$$

b. For H_2 , at what temperature does $\Delta G = 0$?

$$0 = \Delta H^\circ - T\Delta S^\circ$$

$$T = \frac{\Delta H}{\Delta S} = \frac{97.1 \times 10^3 \text{ J}}{115.45 \text{ J/K}} = 841.0 = 841 \text{ K}$$

At temperatures greater than 841 K, the reaction will be spontaneous.

(continued)

For C, at what temperature does $\Delta G = 0$?

$$T = \frac{\Delta H}{\Delta S} = \frac{187.2 \times 10^3 \text{ J}}{207.16 \text{ J/K}} = 903.6 = 904 \text{ K}$$

At temperatures greater than 904 K, the reaction will be spontaneous.

- c. From a consideration of temperature, the process with hydrogen would be preferred. But hydrogen is very expensive and carbon is cheap. On this basis, carbon would be preferred. Tin is produced commercially using carbon as the reducing agent.

19.90 a. $\Delta G^\circ = [3(-228.6) - (-763.1)] \text{ kJ} = 77.3 \text{ kJ}$

Since ΔG° is positive, K will be less than one.

b. $\Delta H^\circ = [3(-241.8) - (-839.9)] \text{ kJ} = 114.5 \text{ kJ}$

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

$$77.3 \text{ kJ} = 114.5 \text{ kJ} - (298 \text{ K}) \Delta S^\circ$$

$$\Delta S^\circ = 0.1248 \text{ kJ/K} = 125 \text{ J/K}$$

c. $T = \frac{\Delta H}{\Delta S} = \frac{114.5 \times 10^3 \text{ J}}{124.8 \text{ J/K}} = 917.4 = 917 \text{ K}$

- d. The driving force is the change in entropy. At high temperatures, the term $T\Delta S$ becomes very important.

19.91 a. Formic acid is favored as it is of lower energy than CO and H₂O.

- b. The change in entropy for the decomposition of formic acid is positive as a mole of gas is produced. So, the change in entropy would be the driving force for this reaction, favoring the formation of products.

19.92 a. It depends upon whether the products are of lower energy than the reactants (exothermic) or if the products are of higher energy than the reactants (endothermic). If the products have stronger bonds than the reactants, the reaction will be exothermic. If the reactants have stronger bonds than the products, the reaction will be endothermic.

(continued)

- b. i) For a highly exothermic reaction, the driving force is the change in enthalpy. The $T\Delta S$ term under these conditions won't be of great significance.
- ii) The driving force will be the entropy. The change in entropy must be positive, and the $T\Delta S$ must be greater than ΔH .

19.93 a. If ΔG° is negative, then K must be greater than one. Consequently, the products will predominate.

- b. The molecules must have enough energy to react when they collide with each other. So, it depends upon the activation energy for the reaction. Usually it is necessary to heat solids for a reaction to occur as it is difficult to have effective collisions.

19.94 a. Since a gaseous product is produced, ΔS° for the reaction would be positive.

- b. Since ΔH° is negative and S° is positive, this would give a negative value for ΔG° , and K would be greater than one. Products would predominate.
- c. Evidently the reaction doesn't take place at room temperature. Since the reaction requires a catalyst, we must conclude there is a high activation energy without the catalyst. Also, it is necessary to heat the mixture so that a greater fraction of the molecules will have enough energy to react.

19.95 a. $\text{C}_4\text{H}_{10}(\text{g}) + 13/2\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l})$

$$\Delta H^\circ = \frac{-49.50 \text{ kJ}}{1.000 \text{ g}} \times \frac{58.12 \text{ g}}{1 \text{ mol}} = -2876.94 \text{ kJ/mol}$$

$$\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

$$-2876.94 \text{ kJ} = [4(-393.5) + 5(-285.8) - (1 \text{ mol}) \times \Delta H_f^\circ(\text{C}_4\text{H}_{10})] \text{ kJ}$$

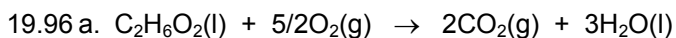
$$\Delta H_f^\circ(\text{C}_4\text{H}_{10}) = -126.06 = -126 \text{ kJ/mol}$$

b. $\Delta G^\circ = [4(-394.4) + 5(-237.1) - (-17.2)] \text{ kJ} = -2745.9 \text{ kJ}$

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

$$-2745.9 \text{ kJ} = -2876.94 \text{ kJ} - (298 \text{ K}) \Delta S^\circ$$

$$\Delta S^\circ = -\frac{(-2745.9 \text{ kJ}) - (-2876.94 \text{ kJ})}{298 \text{ K}} = -0.4397 \text{ kJ/K} = -440. \text{ J/K (for one mole)}$$



$$\Delta H^\circ = \frac{-19.18 \text{ kJ}}{1.000 \text{ g}} \times \frac{62.07 \text{ g}}{1 \text{ mol}} = -1190.4 \text{ kJ/mol}$$

$$\Delta H^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum m\Delta H_f^\circ(\text{reactants})$$

$$-1190.4 \text{ kJ} = [2(-393.5) + 3(-285.8) - (1 \text{ mol}) \times \Delta H_f^\circ(\text{C}_2\text{H}_6\text{O}_2)] \text{ kJ}$$

$$\Delta H_f^\circ[\text{C}_2\text{H}_6\text{O}_2] = -454.0 = -454 \text{ kJ/mol}$$

b. $\Delta G^\circ = [2(-394.4) + 3(-237.1) - (-322.5)] \text{ kJ} = -1177.6 \text{ kJ}$

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

$$-1177.6 \text{ kJ} = -1190.4 \text{ kJ} - (298 \text{ K})(\Delta S^\circ)$$

$$\Delta S^\circ = -\frac{(-1177.6 \text{ kJ}) - (-1190.4 \text{ kJ})}{298 \text{ K}} = -0.04295 \text{ kJ/K} = -43.0 \text{ J/K (for one mole)}$$

19.97 a. $\Delta H^\circ = [-1285 - (-1288.3)] \text{ kJ} = 3.3 \text{ kJ} = 3.3 \times 10^3 \text{ J}$

$$\Delta S^\circ = [89 - 158.2] \text{ J/K} = -69.2 \text{ J/K}$$

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

$$\Delta G^\circ = 3.3 \times 10^3 \text{ J} - (298 \text{ K})(-69.2 \text{ J/K}) = 23.921 \times 10^3 \text{ J}$$

Now, substitute numerical values into the equation relating $\ln K$ and ΔG° .

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{23.921 \times 10^3}{-8.31 \times 298} = -9.6599$$

$$K = e^{-9.6599} = 6.37 \times 10^{-5} = 6 \times 10^{-5}$$

- b. The change in entropy is negative, greater order, so this causes H_3PO_4 to be a weak acid. The enthalpy change hinders the acid strength of H_3PO_4 , and the entropy is a very important term.

(continued)

$$19.98 \text{ a. } \Delta H^\circ = [-626.2 - (-608.8)] \text{ kJ} = -17.4 \text{ kJ} = -17.4 \times 10^3 \text{ J}$$

$$\Delta S^\circ = [139.8 - 232.2] \text{ J/K} = -92.4 \text{ J/K}$$

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

$$\Delta G^\circ = -17.4 \times 10^3 \text{ J} - (298 \text{ K})(-92.4 \text{ J/K}) = 10.135 \times 10^3 \text{ J}$$

Now, substitute numerical values into the equation relating $\ln K$ and ΔG° .

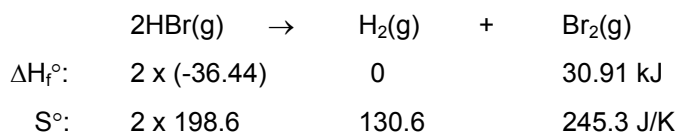
$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{10.135 \times 10^3}{-8.31 \times 298} = -4.092$$

$$K = e^{-4.092} = 0.01669 = 0.017$$

- b. The change in entropy is negative, greater order, so this causes H_2SO_3 to be a weak acid. The enthalpy change hinders the acid strength of H_2SO_3 , and the entropy is a very important term.

■ Solutions to Cumulative-Skills Problems

- 19.99 For the dissociation of HBr , assume ΔH and ΔS are constant over the temperature range from 25°C to 375°C , and calculate the value of each to use to calculate K at 375°C . Start by calculating ΔH° and ΔS° at 25°C , using ΔH_f° and S° values.



Calculate ΔH° and ΔS° from these values.

$$\Delta H^\circ = [30.91 - 2(-36.44)] \text{ kJ} = 103.79 \text{ kJ}$$

$$\Delta S^\circ = [245.3 + 130.6 - 2(198.6)] \text{ J/K} = -21.3 \text{ J/K}$$

Substitute ΔH° , ΔS° ($= -0.02130 \text{ kJ/K}$), and T (648 K) into the equation for ΔG_T° .

$$\begin{aligned} \Delta G_T^\circ &= \Delta H^\circ - T\Delta S^\circ = 103.79 \text{ kJ} - (648 \text{ K})(-0.02130 \text{ kJ/K}) = 117.59 \text{ kJ} \\ &= 117.59 \times 10^3 \text{ J} \end{aligned}$$

(continued)

Now, substitute numerical values into the equation relating $\ln K$ and ΔG° ($= \Delta G_T^\circ$).

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{117.59 \times 10^3}{-8.31 \times 648} = -21.837$$

$$K = e^{-21.837} = 3.28 \times 10^{-10}$$

Assuming x equals $[H_2]$ equals $[Br_2]$ and assuming $[HBr] = (1.00 - 2x) \cong 1.00$ atm, substitute into the equilibrium expression:

$$K = \frac{[H_2][Br_2]}{[HBr]^2} = \frac{(x)(x)}{(1.00)^2} = 3.28 \times 10^{-10}$$

Solve for the approximate pressure of x :

$$x = \sqrt{(3.28 \times 10^{-10})(1.00)^2} = 1.81 \times 10^{-5} \text{ atm}$$

The percent dissociation at 1.00 atm is

$$\text{Percent dissociation} = \frac{2(1.81 \times 10^{-5} \text{ atm})}{1.00 \text{ atm}} \times 100\% = 0.0036 \text{ percent}$$

Based on Le Chatelier's principle, pressure has no effect on equilibrium. Therefore, the percent dissociation is 0.004 percent at 1.00 atm and at 10.0 atm.

- 19.100 For the formation of HI, assume ΔH and ΔS are constant over the temperature range from 25 °C to 205 °C, and calculate the value of each to use to calculate K at 205 °C. Start by calculating ΔH° and ΔS° at 25 °C using ΔH_f° and S° values. From Appendix C, we have

	$H_2(g)$	+	$I_2(g)$	\rightleftharpoons	$2HI(g)$
ΔH_f° :	0		62.42		$2 \times 26.36 \text{ kJ}$
S° :	130.6		260.6		$2 \times 206.36 \text{ J/K}$

Calculate ΔH° and ΔS° from these values.

$$\Delta H^\circ = [2(26.36) - 62.42] \text{ kJ} = -9.70 \text{ kJ}$$

$$\Delta S^\circ = [2(206.36) - 130.6 - 260.6] \text{ J/K} = 21.52 \text{ J/K} = 0.02152 \text{ kJ/K}$$

(continued)

Substitute ΔH° , ΔS° ($= -0.02152 \text{ kJ/K}$), and T (478 K) into the equation for ΔG_T° .

$$\begin{aligned}\Delta G_T^\circ &= \Delta H^\circ - T\Delta S^\circ = -9.70 \text{ kJ} - (478 \text{ K})(0.02152 \text{ kJ/K}) = -19.986 \text{ kJ} \\ &= -19.986 \times 10^3 \text{ J}\end{aligned}$$

Now, substitute numerical values into the equation relating $\ln K$ and ΔG° ($= \Delta G_T^\circ$).

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-19.986 \times 10^3}{-8.31 \times 478} = 5.0316$$

$$K = e^{5.0316} = 153.18$$

Letting $[\text{HI}] = 2x$, $[\text{H}_2] = 0.500 \text{ mol} - x$, and $[\text{I}_2] = 1.00 \text{ mol} - x$, substitute into the equilibrium expression:

$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(2x)^2}{(0.500 - x)(1.00 - x)} = 153.18$$

Rearranging gives a quadratic equation: $(149.18)x^2 + (-229.77)x + (76.591) = 0$. Using the quadratic formula, solve for x :

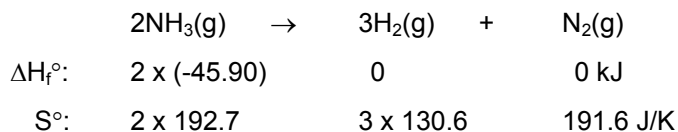
$$\begin{aligned}x &= \frac{-(-229.77) \pm \sqrt{(-229.77)^2 - 4(149.18)(76.591)}}{2 \times 149.18} = \frac{229.777 \pm 84.207}{298.36} \\ &= 0.4878 \text{ mol (negative root)}\end{aligned}$$

$$[\text{HI}] = 2x = 0.9757 \text{ mol}$$

The mol fraction of HI is

$$\begin{aligned}&\frac{0.9757 \text{ mol HI}}{(0.500 - 0.4878) \text{ mol H}_2 + (1.00 - 0.4878) \text{ mol I}_2 + 0.9757 \text{ mol HI}} \\ &= 0.6504 = 0.65\end{aligned}$$

19.101 For the dissociation of NH_3 , assume ΔH and ΔS are constant over the temperature range from 25°C to 345°C , and calculate values of each to calculate K at 345°C .



(continued)

Calculate ΔH° and ΔS° from these values.

$$\Delta H^\circ = [0 - 2(-45.90)] \text{ kJ} = 91.80 \text{ kJ}$$

$$\Delta S^\circ = [3(130.6) + 191.6 - 2(192.7)] \text{ J/K} = 198.0 \text{ J/K}$$

Substitute ΔH° , ΔS° ($= 0.1980 \text{ kJ/K}$), and T (618 K) into the equation for ΔG_T° .

$$\begin{aligned}\Delta G_T^\circ &= \Delta H^\circ - T\Delta S^\circ = 91.8 \text{ kJ} - (618 \text{ K})(0.1980 \text{ kJ/K}) = -30.564 \text{ kJ} \\ &= -30.564 \times 10^3 \text{ J}\end{aligned}$$

Now, substitute numerical values into the equation relating $\ln K$ and ΔG° ($= \Delta G_T^\circ$).

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{-30.564 \times 10^3}{-8.31 \times 618} = 5.951$$

$$K = K_p = e^{5.951} = 384.2$$

Now obtain K_c .

$$\begin{aligned}K_c &= K_p(RT)^{-2} \\ &= (384.2)(0.0821 \times 618)^{-2} = 0.1492\end{aligned}$$

The starting concentration of NH_3 is $1.00 \text{ mol}/20.0\text{L} = 0.0500\text{M}$. You obtain the following table:

	$2\text{NH}_3(\text{g})$	\rightarrow	$3\text{H}_2(\text{g})$	$+$	$\text{N}_2(\text{g})$
Starting	0.0500		0		0
Change	-2x		+3x		+x
Equilibrium	$0.0500 - 2x$		3x		x

The equilibrium equation is

$$K_c = \frac{[\text{H}_2]^3[\text{N}_2]}{[\text{NH}_3]^2}$$

or

$$\frac{(3x)^3 x}{(0.0500 - 2x)^2} = 0.1492$$

(continued)

$$\frac{x^4}{(0.0500 - 2x)^2} = \frac{0.1492}{27} = 5.528 \times 10^{-3}$$

Taking the square root of both sides of this equation gives

$$\frac{x^2}{(0.0500 - 2x)} = 0.07435$$

This can be rearranged into the following quadratic equation.

$$x^2 + (0.1487)x - (3.717 \times 10^{-3}) = 0$$

From the quadratic formula, you obtain

$$x = \frac{-0.1487 \pm \sqrt{(0.1487)^2 + 4(3.717 \times 10^{-3})}}{2}$$

The positive root is

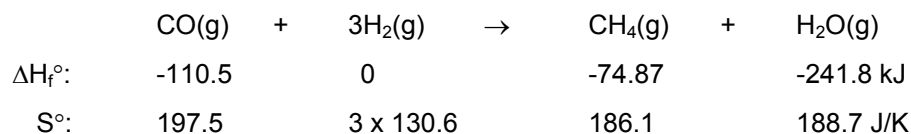
$$x = 0.01942 \text{ M}$$

Hence,

$$[\text{NH}_3] = 0.0500 - 2(0.01942) = 0.01114 \text{ M}$$

$$\begin{aligned} \text{Percent NH}_3 \text{ dissociated} &= \left(1 - \frac{0.01114 \text{ M}}{0.0500 \text{ M}} \right) \times 100\% \\ &= 77.7 = 78 \text{ percent} \end{aligned}$$

19.102 The reaction, with ΔH_f° and S° values underneath the equation, is



Calculate ΔH° and ΔS° from these values.

$$\Delta H^\circ = [(-74.87) + (-241.8) - (-110.5)] \text{ kJ} = -206.17 \text{ kJ}$$

$$\Delta S^\circ = [186.1 + 188.7 - (197.5) - 3(130.6)] \text{ J/K} = -214.5 \text{ J/K}$$

(continued)

Substitute ΔH° , ΔS° ($= 0.21450 \text{ kJ/K}$), and T (1058 K) into the equation for ΔG_T° .

$$\begin{aligned}\Delta G_T^\circ &= \Delta H^\circ - T\Delta S^\circ = -206.17 \text{ kJ} - (1058 \text{ K})(0.21450 \text{ kJ/K}) = 20.771 \text{ kJ} \\ &= 20.771 \times 10^3 \text{ J}\end{aligned}$$

Now, substitute numerical values into the equation relating $\ln K$ and ΔG° ($= \Delta G_T^\circ$).

$$\ln K = \frac{\Delta G^\circ}{-RT} = \frac{20.771 \times 10^3}{-8.31 \times 1058} = -2.362$$

$$K = K_p = e^{-2.362} = 0.09418$$

$$K_c = K_p(RT)^2 = 0.09418(0.0821 \times 1058)^2 = 710.6$$

The starting concentrations of CO and H_2 are

$$[\text{CO}] = \frac{0.0100 \text{ mol}}{25.0 \text{ L}} = 4.00 \times 10^{-4} \text{ M}$$

$$[\text{H}_2] = \frac{0.0300 \text{ mol}}{25.0 \text{ L}} = 1.20 \times 10^{-3} \text{ M}$$

You obtain the following table:

	CO(g)	+	$3\text{H}_2(\text{g})$	\rightarrow	$\text{CH}_4(\text{g})$	+	$\text{H}_2\text{O(g)}$
Starting	4.00×10^{-4}		1.20×10^{-3}		0		0
Change	-x		-3x		+x		+x
Equilibrium	$(4.00 \times 10^{-4}) - x$		$(1.20 \times 10^{-3}) - 3x$		x		x

The equilibrium equation is

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

or

$$\frac{x^2}{[(4.00 \times 10^{-4}) - x][(1.20 \times 10^{-3}) - 3x]^3} = 710.6$$

The denominator can be written as $3^3 [(4.00 \times 10^{-4}) - x]^4$, so this equation can be reduced to a quadratic equation and solved exactly.

(continued)

Multiply both sides of the equation by 27, and then take the square root. This gives

$$\frac{x}{(4.00 \times 10^{-4} - x)^2} = 138.51$$

This can be rearranged into the following quadratic equation:

$$x^2 + (-8.019 \times 10^{-3})x + (1.60 \times 10^{-7}) = 0$$

From the quadratic formula, you obtain

$$\begin{aligned} x &= \frac{-(-8.019 \times 10^{-3}) \pm \sqrt{(-8.019 \times 10^{-3})^2 + 4(1.60 \times 10^{-7})}}{2} \\ &= \frac{8.019 \times 10^{-3} \pm 7.979 \times 10^{-3}}{2} = 1.98 \times 10^{-5} \text{ (negative root)} \end{aligned}$$

$$x = [\text{CH}_4] = [\text{H}_2\text{O}] = 1.98 \times 10^{-5} \text{ M}$$

$$\begin{aligned} \text{Mol CH}_4 &= \text{mol H}_2\text{O} = 25.0 \text{ L} \times (2.00 \times 10^{-5} \text{ mol/L}) \\ &= 4.95 \times 10^{-4} = 5.0 \times 10^{-4} \text{ mol} \end{aligned}$$

19.103 First, calculate ΔG° at each temperature, using $\Delta G^\circ = -RT \ln K$:

$$25.0^\circ\text{C}: \Delta G^\circ = -(0.008314 \text{ kJ/K})(298.2 \text{ K})(\ln 1.754 \times 10^{-5}) = 27.1551 \text{ kJ}$$

$$50.0^\circ\text{C}: \Delta G_T^\circ = -(0.008314 \text{ kJ/K})(323.2 \text{ K})(\ln 1.633 \times 10^{-5}) = 29.6237 \text{ kJ}$$

Next, solve two equations in two unknowns assuming ΔH° and ΔS° are constant over the range of 25.0°C to 50.0°C . Use 0.2982 K(kJ/J) and 0.3232 K(kJ/J) to convert ΔS° in J to $T\Delta S^\circ$ in kJ.

$$1. 27.1551 \text{ kJ} = \Delta H^\circ - [0.2982 \text{ K(kJ/J)}] \Delta S^\circ$$

$$2. 29.6237 \text{ kJ} = \Delta H^\circ - [0.3232 \text{ K(kJ/J)}] \Delta S^\circ$$

(continued)

Then, rearrange equation 2, and substitute for ΔH° into equation 2:

$$3a. \Delta H^\circ = 0.3232 \text{ K(kJ/J)} \Delta S^\circ + 29.6237 \text{ kJ}$$

$$3b. 27.1551 \text{ kJ} = [0.3232 \text{ K(kJ/J)} \Delta S^\circ + 29.6237 \text{ kJ}] - [0.2982 \text{ K(kJ/J)} \Delta S^\circ]$$

Solve for ΔS° :

$$\Delta S^\circ = \frac{(29.6237 - 27.1551) \text{ kJ}}{(0.2982 - 0.3232) \text{ K(kJ/J)}} = -98.\underline{74} = -98.7 \text{ J/K}$$

Substitute this value into equation 3a and solve for ΔH° :

$$\Delta H^\circ = [(0.3232) \text{ K(kJ/J)} \times (-98.74 \text{ J/K})] + 29.6237 \text{ kJ} = -2.289 = -2.29 \text{ kJ}$$

19.104 First, calculate ΔG° at each temperature using $\Delta G^\circ = -RT \ln K$:

$$25.0^\circ\text{C}: \Delta G^\circ = - (0.008314 \text{ kJ/K})(298.2 \text{ K})(\ln 1.782 \times 10^{-10}) = 55.66\underline{42} \text{ kJ}$$

$$35.0^\circ\text{C}: \Delta G_T^\circ = - (0.008314 \text{ kJ/K})(308.2 \text{ K})(\ln 4.159 \times 10^{-10}) = 55.35\underline{87} \text{ kJ}$$

Next, solve two equations in two unknowns assuming ΔH° and ΔS° are constant over the range of 25.0°C to 35.0°C . Use 0.2982 K(kJ/J) and 0.3082 K(kJ/J) to convert ΔS° in J to $T\Delta S^\circ$ in kJ.

$$1. 55.6642 \text{ kJ} = \Delta H^\circ - [0.2982 \text{ K(kJ/J)} \Delta S^\circ]$$

$$2. 55.3587 \text{ kJ} = \Delta H^\circ - [0.3082 \text{ K(kJ/J)} \Delta S^\circ]$$

Then, rearrange equation 2, and substitute for ΔH° into equation 2:

$$3a. \Delta H^\circ = 0.3082 \text{ K(kJ/J)} \Delta S^\circ + 55.3587 \text{ kJ}$$

$$3b. 55.6642 \text{ kJ} = [0.3082 \text{ K(kJ/J)} \Delta S^\circ + 55.3587 \text{ kJ}] - [(0.2982 \text{ K(kJ/J)} \Delta S^\circ)]$$

Solve for ΔS° :

$$\Delta S^\circ = \frac{(55.6642 - 55.3587) \text{ kJ}}{(0.3082 - 0.2982) \text{ K(kJ/J)}} = 30.\underline{55} = 31 \text{ J/K}$$

Substitute this value into equation 3a and solve for ΔH° :

$$\Delta H^\circ = [(0.3082) \text{ K(kJ/J)} \times (30.55 \text{ J/K})] + 55.3587 \text{ kJ} = 64.\underline{77} = 64.8 \text{ kJ}$$

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Number of Characters: 52,027 (approx.)