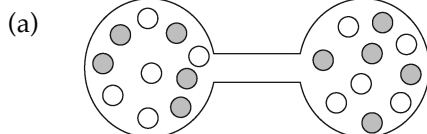# 19 Chemical Thermodynamics

## Visualizing Concepts

19.1    (a)



(b)    ΔS is positive, because the disorder of the system increases. Each gas has greater motional freedom as it expands into the second bulb, and there are many more possible arrangements for the mixed gases.

By definition, ideal gases experience no attractive or repulsive intermolecular interactions, so ΔH for the mixing of ideal gases is zero, assuming heat exchange only between the two bulbs.

(c)    The process is irreversible. It is inconceivable that the gases would reseparate.

(d)    The entropy change of the surroundings is related to ΔH for the system. Since we are mixing ideal gases and ΔH = 0, $\Delta H_{surr}$ is also zero, assuming heat exchange only between the two bulbs.

19.4    *Analyze/Plan.* Consider the physical changes that occur when a substance is heated. How do these changes affect the entropy of the substance?

(a)    Both 1 and 2 represent changes in entropy at constant temperature; these are phase changes. Since 1 happens at lower temperature, it represents melting (fusion), and 2 represents vaporization.

(b)    The substance changes from solid to liquid in 1, from liquid to gas in 2. The larger volume and greater motional freedom of the gas phase causes ΔS for vaporization to (always) be larger than ΔS for fusion.

19.6    (a)    At equilibrium, ΔG = 0.  On the diagram, ΔG = 0 at 250 K.   The system is at equilibrium at 250 K.

(b)    A reaction is spontaneous when ΔG is negative.  The reaction is spontaneous at temperatures greater than 250 K.

(c)    ΔG = ΔH − TΔS, in the form of y = b + mx.  ΔH is the y intercept of the graph and is positive.

(d)    The slope of the graph is −ΔS.  The slope is negative, so ΔS is positive.  [Also, ΔG decreases as T increases, so the TΔS term must become more negative and ΔS is positive.]

# *19* Chemical Thermodynamics      **Solutions to Exercises**

## Spontaneous Processes

19.9    *Analyze/Plan*.  Follow the logic in Sample Exercise 19.1.      *Solve*.

   (a)    Spontaneous; at ambient temperature, ripening happens without intervention.

   (b)    Spontaneous; sugar is soluble in water, and even more soluble in hot coffee.

   (c)    Spontaneous; $N_2$ molecules are stable relative to isolated N atoms.

   (d)    Spontaneous; under certain atmospheric conditions, lightening occurs.

   (e)    Nonspontaneous; $CO_2$ and $H_2O$ are in contact continuously at atmospheric conditions in nature and do not form $CH_4$ and $O_2$.

19.11   (a)    $NH_4NO_3(s)$ dissolves in water, as in a chemical cold pack. Naphthalene (mothballs) sublimes at room temperature.

   (b)    Melting of a solid is spontaneous above its melting point but nonspontaneous below its melting point.

19.13   *Analyze/Plan*. Define the system and surroundings. Use the appropriate definition to answer the specific questions.      *Solve*.

   (a)    Water is the system. Heat must be added to the system to evaporate the water. The process is endothermic.

   (b)    At 1 atm, the reaction is spontaneous at temperatures above 100°C.

   (c)    At 1 atm, the reaction is nonspontaneous at temperatures below 100°C.

   (d)    The two phases are in equilibrium at 100°C.

19.15   *Analyze/Plan*. Define the system and surroundings. Use the appropriate definition to answer the specific questions.      *Solve*.

   (a)    For a *reversible* process, the forward and reverse changes occur by the same path. In a reversible process, both the system and the surroundings are restored to their original condition by exactly reversing the change. A reversible change produces the maximum amount of work.

   (b)    If a system is returned to its original state via a reversible path, the surroundings are also returned to their original state. That is, there is no net change in the surroundings.

   (c)    The vaporization of water to steam is reversible if it occurs at the boiling temperature of water for a specified external (atmospheric) pressure, and if the needed heat is added infinitely slowly.

   (d)    No.  Natural processes, such as a banana ripening or a lightening strike are spontaneous in the direction they occur and nonspontaneous in the opposite direction.  By definition they are irreversible; they do not occur by reversible pathways.  Neither the system nor the surroundings can be returned to their original condition by the same pathway that the change occurred.  It is impossible to imagine a banana unripening.

19.17     *Analyze/Plan.* The related properties of a gas are pressure, volume, temperature and amount.

        (a)     If T decreases while V is unchanged, either P or amount must change. For a closed system (Section 5.1) at constant volume, a decrease in external temperature leads to a decrease in the temperature of the system, in this case an ideal gas, as well as a decrease in pressure of the gas. An example is the decrease in air pressure in a tire or the first cold autumn day.

        (b)     If T decreases while P stays constant, either amount or volume must change. For a closed system at constant pressure, if the temperature of the gas decreases, the volume also decreases.

        (c)     No. $\Delta E$ is a state function. $\Delta E = q + w$; q and w are not state functions. Their values do depend on path, but their sum, $\Delta E$, does not.

19.19     *Analyze/Plan.* Define the system and surroundings. Use the appropriate definition to answer the specific questions.     *Solve.*

        (a)     An ice cube can melt reversibly at the conditions of temperature and pressure where the solid and liquid are in equilibrium. At 1 atm external pressure, the normal melting point of water is 0°C.

        (b)     We know that melting is a process that increases the energy of the system, even though there is no change in temperature. $\Delta E$ is not zero for the process.

## Entropy and the Second Law of Thermodynamics

19.21     (a)     For a process that occurs at constant temperature, an isothermal process, $\Delta S = q_{rev}/T$. Here $q_{rev}$ is the heat that would be transferred if the process were reversible. Since $\Delta S$ is a state function, it is independent of path, so $\Delta S$ for the reversible path must equal $\Delta S$ for any path.

        (b)     No. $\Delta S$ is a state function, so it is independent of path.

19.23     (a)     $CH_3OH(l) \rightarrow CH_3OH(g)$, entropy increases, more mol gas in products, greater motional freedom.

        (b)     $\Delta S = \dfrac{\Delta H}{T} = \dfrac{71.8 \text{ kJ}}{\text{mol } CH_3OH(l)} \times 1.00 \text{ mol } CH_3OH(l) \times \dfrac{1}{(273.15 + 64.7)\text{K}} \times \dfrac{1000 \text{ J}}{1 \text{ kJ}} = 213 \text{ J/K}$

19.25     (a)     For a spontaneous process, the entropy of the universe increases; for a reversible process, the entropy of the universe does not change.

        (b)     In a reversible process, $\Delta S_{system} + \Delta S_{surroundings} = 0$. If $\Delta S_{system}$ is positive, $\Delta S_{surroundings}$ must be negative.

        (c)     Since $\Delta S_{universe}$ must be positive for a spontaneous process, $\Delta S_{surroundings}$ must be greater than –42 J/K.

19.27     *Analyze.* Calculate $\Delta S$ for the isothermal expansion of 0.100 mol He from 2.00 L to 5.00 L at 27°C.

        *Plan.* Use the relationship $\Delta S_{sys} = nR \ln(V_2/V_1)$, Equation [19.3].

*Solve*.   $\Delta S_{sys} = 0.100$ (8.314 J/mol-K)(ln [5.00 L/2.00 L]) = 0.762 J/K.

*Check*. We expect $\Delta S$ to be positive when the motional freedom of a gas increases, and our calculation agrees with this prediction.

## The Molecular Interpretation of Entropy

19.29   (a)   The higher the temperature, the broader the distribution of molecular speeds and kinetic energies available to the particles. At higher temperature, the wider range of accessible kinetic energies leads to more microstates for the system.

(b)   A decrease in volume reduces the number of possible positions for the particles and leads to fewer microstates for the system.

(c)   Going from liquid to gas, particles have greater translational motion, which increases the number of positions available to the particles and the number of microstates for the system.

19.31   *Analyze/Plan*. Consider the conditions that lead to an increase in entropy: more mol gas in products than reactants, increase in volume of sample and, therefore, number of possible arrangements, more motional freedom of molecules, etc.     *Solve*.

(a)   More gaseous particles means more possible arrangements and greater disorder; $\Delta S$ is positive.

(b)   $\Delta S$ is positive for Exercise 19.9 (b), where there is an increase in volume and possible arrangements for the sample. It may be slightly positive in (a), where the sample softens.
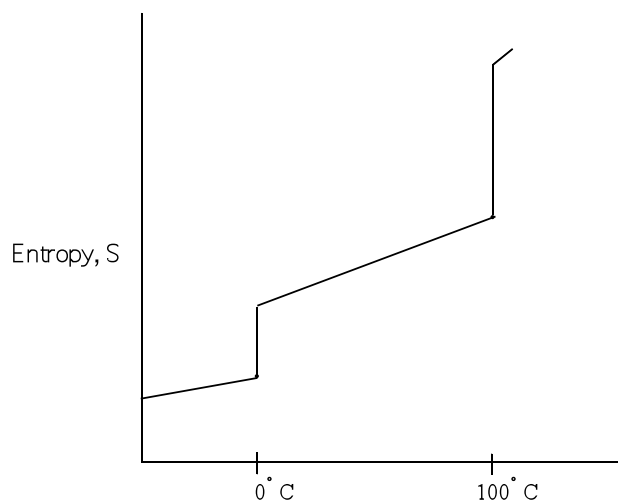
19.33   *Analyze/Plan*. Consider the conditions that lead to an increase in entropy: more mol gas in products than reactants, increase in volume of sample and, therefore, number of possible arrangements, more motional freedom of molecules, etc.     *Solve*.

(a)   S increases; translational motion is greater in the liquid than the solid.

(b)   S decreases; volume and translational motion decrease going from the gas to the liquid.

(c)   S increases; volume and translational motion are greater in the gas than the solid.

19.35   (a)   The entropy of a pure crystalline substance at absolute zero is zero.

(b)   In *translational* motion, the entire molecule moves in a single direction; in *rotational* motion, the molecule rotates or spins around a fixed axis. *Vibrational* motion is reciprocating motion. The bonds within a molecule stretch and bend, but the average position of the atoms does not change.

(c)
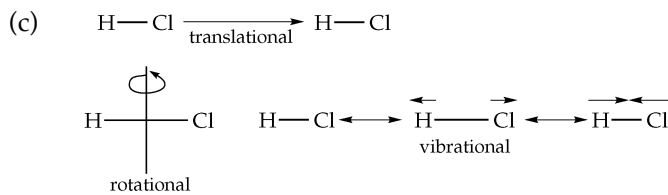
19.37    (a)



    (b)      Boiling water, at 100 °C, has a much larger entropy change than melting ice at 0 °C. Before and after melting, $H_2O$ molecules are touching. And there is actually a small decrease in volume going from solid to liquid water. Boiling drastically increases the distance between molecules and the volume of the sample. The increase in available molecular positions is much greater for boiling than melting, so the entropy change is also greater.

19.39    *Analyze/Plan*. Consider the factors that lead to higher entropy: more mol gas in products than reactants, increase in volume of sample and, therefore, number of possible arrangements, more motional freedom of molecules, etc.     *Solve*.

    (a)      Ar(g) (gases have higher entropy due primarily to much larger volume)

    (b)      He(g) at 1.5 atm (larger volume and more motional freedom)

    (c)      1 mol of Ne(g) in 15.0 L (larger volume provides more motional freedom)

    (d)      $CO_2$(g) (more motional freedom)

19.41    *Analyze/Plan*. Consider the markers of an increase in entropy for a chemical reaction: liquids or solutions formed from solids, gases formed from either solids or liquids, increase in moles gas during reaction.   *Solve*.

    (a)      ΔS negative (moles of gas decrease)

    (b)      ΔS positive (gas produced, increased disorder)

    (c)      ΔS negative (moles of gas decrease)

    (d)      ΔS positive (moles of gas increase)

## Entropy Changes in Chemical Reactions

19.43    *Analyze/Plan*. Given two molecules in the same state, predict which will have the higher molar entropy. In general, for molecules in the same state, the more atoms in the molecule, the more degrees of freedom, the greater the number of microstates and the higher the standard entropy, S°.

(a)    $C_2H_6(g)$ has more degrees of freedom and larger S°.

(b)    $CO_2(g)$ has more degrees of freedom and larger S°.

19.45    *Analyze/Plan*. Consider the conditions that lead to an increase in entropy: more mol gas in products than reactants, increase in volume of sample and, therefore, number of possible arrangements, more motional freedom of molecules, etc. *Solve*.

(a)    Sc(s), 34.6 J/mol-K; Sc(g), 174.7 J/mol-K. In general, the gas phase of a substance has a larger S° than the solid phase because of the greater volume and motional freedom of the molecules.

(b)    $NH_3(g)$, 192.5 J/mol-K; $NH_3(aq)$, 111.3 J/mol-K. Molecules in the gas phase have more motional freedom than molecules in solution.

(c)    1 mol of $P_4(g)$, 280 J/K; 2 mol of $P_2(g)$, 2(218.1) = 436.2 J/K. More particles have greater motional energy (more available microstates).

(d)    C(diamond), 2.43 J/mol-K; C(graphite) 5.69 J/mol-K. Diamond is a network covalent solid with each C atom tetrahedrally bound to four other C atoms. Graphite consists of sheets of fused planar 6-membered rings with each C atom bound in a trigonal planar arrangement to three other C atoms. The internal entropy in graphite is greater because there is translational freedom among the planar sheets of C atoms while there is very little vibrational freedom within the network covalent diamond lattice.

19.47    For elements with similar structures, the heavier the atoms, the lower the vibrational frequencies at a given temperature. This means that more vibrations can be accessed at a particular temperature resulting in a greater absolute entropy for the heavier elements.

19.49    *Analyze/Plan*. Follow the logic in Sample Exercise 19.5.        *Solve*.

(a)    $\Delta S° = S° \, C_2H_6(g) - S° \, C_2H_4(g) - S° \, H_2(g)$

   $= 229.5 - 219.4 - 130.58 = -120.5 \text{ J/K}$

$\Delta S°$ is negative because there are fewer moles of gas in the products.

(b)    $\Delta S° = 2S° \, NO_2(g) - \Delta S° \, N_2O_4(g) = 2(240.45) - 304.3 = +176.6 \text{ J/K}$

$\Delta S°$ is positive because there are more moles of gas in the products.

(c)    $\Delta S° = \Delta S° \, BeO(s) + \Delta S° \, H_2O(g) - \Delta S° \, Be(OH)_2(s)$

   $= 13.77 + 188.83 - 50.21 = +152.39 \text{ J/K}$

$\Delta S°$ is positive because the product contains more total particles and more moles of gas.

(d)    $\Delta S° = 2S° \, CO_2(g) + 4S° \, H_2O(g) - 2S° \, CH_3OH(g) - 3S° \, O_2(g)$

   $= 2(213.6) + 4(188.83) - 2(237.6) - 3(205.0) = +92.3 \text{ J/K}$

$\Delta S°$ is positive because the product contains more total particles and more moles of gas.

## Gibbs Free Energy

19.51    (a)    $\Delta G = \Delta H - T\Delta S$

       (b)    If $\Delta G$ is positive, the process is nonspontaneous, but the reverse process is spontaneous.

       (c)    There is no relationship between $\Delta G$ and rate of reaction. A spontaneous reaction, one with a $-\Delta G$, may occur at a very slow rate. For example: $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$, $\Delta G = -457$ kJ is very slow if not initiated by a spark.

19.53    *Analyze/Plan*. Consider the definitions of $\Delta H°$, $\Delta S°$ and $\Delta G°$, along with sign conventions. $\Delta G° = \Delta H° - T\Delta S°$.        *Solve*.

       (a)    $\Delta H°$ is negative; the reaction is exothermic.

       (b)    $\Delta S°$ is negative; the reaction leads to decrease in disorder (increase in order) of the system.

       (c)    $\Delta G° = \Delta H° - T\Delta S° = -35.4$ kJ $- 298$ K $(-0.0855$ kJ$/$K$) = -9.921 = -9.9$ kJ

       (d)    At 298 K, $\Delta G°$ is negative. If all reactants and products are present in their standard states, the reaction is spontaneous (in the forward direction) at this temperature.

19.55    *Analyze/Plan*. Follow the logic in Sample Exercise 19.7. Calculate $\Delta H°$ according to Equation [5.31], $\Delta S°$ by Equation [19.8] and $\Delta G°$ by Equation [19.14]. Then use $\Delta H°$ and $\Delta S°$ to calculate $\Delta G°$ using Equation [19.12], $\Delta G° = \Delta H° - T\Delta S°$.        *Solve*.

       (a)    $\Delta H° = 2(-268.61) - [0 + 0] = -537.22$ kJ

              $\Delta S° = 2(173.51) - [130.58 + 202.7] = 13.74 = 13.7$ J$/$K

              $\Delta G° = 2(-270.70) - [0 + 0] = -541.40$ kJ

              $\Delta G° = -537.22$ kJ $- 298(0.01374)$ kJ $= -541.31$ kJ

       (b)    $\Delta H° = -106.7 - [0 + 2(0)] = -106.7$ kJ

              $\Delta S° = 309.4 - [5.69 + 2(222.96)] = -142.21 = -142.2$ J$/$K

              $\Delta G° = -64.0 - [0 + 2(0)] = -64.0$ kJ

              $\Delta G° = -106.7$ kJ $- 298(-0.14221)$ kJ $= -64.3$ kJ

       (c)    $\Delta H° = 2(-542.2) - [2(-288.07) + 0] = -508.26 = -508.3$ kJ

              $\Delta S° = 2(325) - [2(311.7) + 205.0] = -178.4 = -178$ J$/$K

              $\Delta G° = 2(-502.5) - [2(-269.6) + 0] = -465.8$ kJ

              $\Delta G° = -508.26$ kJ $- 298(-0.1784)$ kJ $= -455.097 = -455.1$ kJ

              (The discrepancy in $\Delta G°$ values is due to experimental uncertainties in the tabulated thermodynamic data.)

       (d)    $\Delta H° = -84.68 + 2(-241.82) - [2(-201.2) + 0] = -165.92 = -165.9$ kJ

              $\Delta S° = 229.5 + 2(188.83) - [2(237.6) + 130.58] = 1.38 = 1.4$ J$/$K

              $\Delta G° = -32.89 + 2(-228.57) - [2(-161.9) + 0] = -166.23 = -166.2$ kJ

              $\Delta G° = -165.92$ kJ $- 298(0.00138)$ kJ $= -166.33 = -166.3$ kJ

19.57    *Analyze/Plan.* Follow the logic in Sample Exercise 19.7.    *Solve.*

     (a)    $\Delta G° = 2\Delta G°\ SO_3(g) - [2\Delta G°\ SO_2(g) + \Delta G°\ O_2(g)]$

           $= 2(-370.4) - [2(-300.4) + 0] = -140.0$ kJ, spontaneous

     (b)    $\Delta G° = 3\Delta G°\ NO(g) - [\Delta G°\ NO_2(g) + \Delta G°\ N_2O(g)]$

           $= 3(86.71) - [51.84 + 103.59] = +104.70$ kJ, nonspontaneous

     (c)    $\Delta G° = 4\Delta G°\ FeCl_3(s) + 3\Delta G°\ O_2(g) - [6\Delta G°\ Cl_2(g) + 2\Delta G°\ Fe_2O_3(s)]$

           $= 4(-334) + 3(0) - [6(0) + 2(-740.98)] = +146$ kJ, nonspontanous

     (d)    $\Delta G° = \Delta G°\ S(s) + 2\Delta G°\ H_2O(g) - [\Delta G°\ SO_2(g) + 2\Delta G°\ H_2(g)]$

           $= 0 + 2(-228.57) - [(-300.4) + 2(0)] = -156.7$ kJ, spontaneous

19.59    *Analyze/Plan.* Follow the logic in Sample Exercise 19.8(a).    *Solve.*

     (a)    $C_6H_{12}(l) + 9O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$

     (b)    Because there are fewer moles of gas in the products, $\Delta S°$ is negative, which makes $-T\Delta S$ positive. $\Delta G°$ is less negative (more positive) than $\Delta H°$.

19.61    *Analyze/Plan.* Based on the signs of $\Delta H$ and $\Delta S$ for a particular reaction, assign a category from Table 19.4 to each reaction.    *Solve.*

     (a)    $\Delta G$ is negative at low temperatures, positive at high temperatures. That is, the reaction proceeds in the forward direction spontaneously at lower temperatures but spontaneously reverses at higher temperatures.

     (b)    $\Delta G$ is positive at all temperatures. The reaction is nonspontaneous in the forward direction at all temperatures.

     (c)    $\Delta G$ is positive at low temperatures, negative at high temperatures. That is, the reaction will proceed spontaneously in the forward direction at high temperature.

19.63    *Analyze/Plan.* We are told that the reaction is spontaneous and endothermic, and asked to estimate the sign and magnitude of $\Delta S$. If a reaction is spontaneous, $\Delta G < 0$. Use this information with Equation [19.11] to solve the problem.    *Solve.*

     At 450 K, $\Delta G < 0$; $\Delta G = \Delta H - T\Delta S < 0$

     34.5 kJ $-$ 450 K $(\Delta S) < 0$; 34.5 kJ $<$ 450 K $(\Delta S)$; $\Delta S >$ 34.5 kJ/450 K

     $\Delta S > 0.0767$ kJ/K or $\Delta S > 76.7$ J/K

19.65    *Analyze/Plan.* Use Equation [19.11] to calculate T when $\Delta G = 0$. This is similar to calculating the temperature of a phase trasition in Sample Exercise 19.10. Use Table 19.4 to determine whether the reaction is spontaneous or non-spontaneous above this temperature.    *Solve.*

     (a)    $\Delta G = \Delta H - T\Delta S$; $0 = -32$ kJ $- T(-98$ J/K$)$; $32 \times 10^3$ J $= T(98$ J/K$)$

           $T = 32 \times 10^3$ J$/(98$ J/K$) = 326.5 = 330$ K

     (b)    Nonspontaneous. The sign of $\Delta S$ is negative, so as T increases, $\Delta G$ becomes more

positive.

19.67     *Analyze/Plan.* Given a chemical equation and thermodynamic data (values of $\Delta H_f^\circ$, $\Delta G_f^\circ$ and S°) for reactants and products, predict the variation of ΔG° with temperature and calculate ΔG° at 800 K and 1000 K. Use Equations [5.31] and [19.8] to calculate ΔH° and ΔS°, respectively; use these values to calculate ΔG° at various temperatures, using Equation [19.12]. The signs of ΔH° and ΔS° determine the variation of ΔG° with temperature.     *Solve.*

(a)     Calculate ΔH° and ΔS° to determine the sign of TΔS°.

ΔH° = 3ΔH° NO(g) – ΔH° $NO_2$(g) – ΔH° $N_2O$(g)

= 3(90.37) – 33.84 – 81.6 = 155.7 kJ

ΔS° = 3S° NO(g) – S° $NO_2$(g) – S° $N_2O$(g)

= 3(210.62) – 240.45 – 220.0 = 171.4 J/K

ΔG° = ΔH° – TΔS°. Since ΔS° is positive, –TΔS° becomes more negative as T increases and ΔG° becomes more negative.

(b)     ΔG° = ΔH° – TΔS° = 155.7 kJ – (800 K)(0.1714 kJ/K)

ΔG° = 155.7 kJ – 137 kJ = 19 kJ

Since ΔG° is positive at 800 K, the reaction is not spontaneous at this temperature.

(c)     ΔG° = 155.7 kJ – (1000 K)(0.1714 kJ/K) = 155.7 kJ – 171.4 kJ = –15.7 kJ

ΔG° is negative at 1000 K and the reaction is spontaneous at this temperature.

19.69     *Analyze/Plan.* Follow the logic in Sample Exercise 19.10.     *Solve.*

(a)     $\Delta S_{vap}^o = \Delta H_{vap}^o / T_b$; $T_b = \Delta H_{vap}^o / \Delta S_{vap}^o$

$\Delta H_{vap}^o = \Delta H° C_6H_6$(g) $- \Delta H° C_6H_6$(l) $= 829 - 490 = 339$ kJ

$\Delta S_{vap}^o = S° C_6H_6$(g) $- S° C_6H_6$(l) $= 269.2 - 172.8 = 96.4$ J/K

$T_b = 33.9 \times 10^3$ J/96.4 J/K = 351.66 = 352 K = 79°C

(b)     From the *Handbook of Chemistry and Physics*, 74th Edition, $T_b$ = 80.1°C. The values are remarkably close; the small difference is due to deviation from ideal behavior by $C_6H_6$(g) and experimental uncertainty in the boiling point measurement and the thermodynamic data.

19.71     *Analyze/Plan.* We are asked to write a balanced equation for the combustion of acetylene, calculate ΔH° for this reaction and calculate maximum useful work possible by the system. Combustion is combination with $O_2$ to produce $CO_2$ and $H_2O$. Calculate ΔH° using data from Appendix C and Equation [5.31]. The maximum obtainable work is ΔG (Equation [19.15]), which can be calculated from data in Appendix C and Equation [19.14].     *Solve.*

(a)     $C_2H_2$(g) + 5/2 $O_2$(g) → 2$CO_2$(g) + $H_2O$(l)

(b)     ΔH° = 2ΔH° $CO_2$(g) + ΔH° $H_2O$(l) – ΔH° $C_2H_2$(g) – 5/2ΔH° $O_2$(g)

= 2(–393.5) – 285.83 – 226.77 – 5/2(0)

= –1299.6 kJ produced/mol $C_2H_2$ burned

(c)     $w_{max} = \Delta G° = 2\Delta G° \, CO_2(g) + \Delta G° \, H_2O(l) - \Delta G° \, C_2H_2(g) - 5/2 \, \Delta G° \, O_2(g)$

           $= 2(-394.4) - 237.13 - 209.2 - 5/2(0) = -1235.1$ kJ

The negative sign indicates that the system does work on the surroundings; the system can accomplish a maximum of 1235.1 kJ of work on its surroundings.

## Free Energy and Equilibrium

19.73    *Analyze/Plan.* We are given a chemical reaction and asked to predict the effect of the partial pressure of $O_2(g)$ on the value of $\Delta G$ for the system. Consider the relationship $\Delta G = \Delta G° + RT \ln Q$ where Q is the reaction quotient.    *Solve.*

(a)    $O_2(g)$ appears in the denominator of Q for this reaction. An increase in pressure of $O_2$ decreases Q and $\Delta G$ becomes smaller or more negative. Increasing the concentration of a reactant increases the tendency for a reaction to occur.

(b)    $O_2(g)$ appears in the numerator of Q for this reaction. Increasing the pressure of $O_2$ increases Q and $\Delta G$ becomes more positive. Increasing the concentration of a product decreases the tendency for the reaction to occur.

(c)    $O_2(g)$ appears in the numerator of Q for this reaction. An increase in pressure of $O_2$ increases Q and $\Delta G$ becomes more positive. Since pressure of $O_2$ is raised to the third power in Q, an increase in pressure of $O_2$ will have the largest effect on $\Delta G$ for this reaction.

19.75    *Analyze/Plan.* Given a chemical reaction, we are asked to calculate $\Delta G°$ from Appendix C data, and $\Delta G$ for a given set of initial conditions. Use Equation [19.12] to calculate $\Delta G°$, and Equation [19.16] to calculate $\Delta G$. Follow the logic in Sample Exercise 19.11 when calculating $\Delta G$.    *Solve.*

(a)    $\Delta G° = \Delta G° \, N_2O_4(g) - 2\Delta G° \, NO_2(g) = 98.28 - 2(51.84) = -5.40$ kJ

(b)    $\Delta G = \Delta G° + RT \ln P_{N_2O_4} / P^2_{NO_2}$

       $= -5.40 kJ + \dfrac{8.314 \times 10^{-3} \, kJ}{K\text{-}mol} \times 298 K \times \ln[1.60/(0.40)^2] = 0.3048 = 0.3 kJ$

19.77    *Analyze/Plan.* Given a chemical reaction, we are asked to calculate K using $\Delta G°_f$ data from Appendix C.    Calculate $\Delta G°$ using Equation [19.14].    Then $\Delta G° = -RT \ln K$, Equation [19.17]; $\ln K = -\Delta G°/RT$     *Solve.*

(a)    $\Delta G° = 2\Delta G° \, HI(g) - \Delta G° \, H_2(g) - \Delta G° \, I_2(g)$

       $= 2(1.30) - 0 - 19.37 = -16.77$ kJ

     $\ln K = \dfrac{-(-16.77 kJ) \times 10^3 \, J/kJ}{8.314 J/K \times 298 K} = 6.76876 = 6.769, \; K = 870$

(b)    $\Delta G° = \Delta G° \, C_2H_4(g) + \Delta G° \, H_2O(g) - \Delta G° \, C_2H_5OH(g)$

       $= 68.11 - 228.57 - (-168.5) = 8.04 = 8.0$ kJ

     $\ln K = \dfrac{-(8.04 kJ) \times 10^3 \, J/kJ}{8.314 J/K \times 298 K} = -3.24511 = -3.25, \; K = 0.039$

(c)    $\Delta G° = \Delta G° \, C_6H_6(g) - 3\Delta G° \, C_2H_2(g) = 129.7 - 3(209.2) = -497.9$ kJ

$$\ln K = \frac{-\Delta G^{\circ}}{RT} = \frac{-(-497.9 \text{ kJ}) \times 10^3 \text{ J/KJ}}{8.314 \text{ J/K} \times 298 \text{ K}} = 200.963 = 201.0; \quad K = 2 \times 10^{87}$$

19.79    *Analyze/Plan.* Given a chemical reaction and thermodynamic data in Appendix C, calculate the equilibrium pressure of $CO_2(g)$ at two temperatures. $K = P_{CO_2}$. Calculate $\Delta G^{\circ}$ at the two temperatures using $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ and then calculate K and $P_{CO_2}$. *Solve.*

$\Delta H^{\circ} = \Delta H^{\circ} \text{ BaO(s)} + \Delta H^{\circ} \text{ CO}_2(g) - \Delta H^{\circ} \text{ BaCO}_3(s)$

     $= -553.5 + -393.5 - (-1216.3) = +269.3 \text{ kJ}$

$\Delta S^{\circ} = S^{\circ} \text{ BaO(s)} + S^{\circ} \text{ CO}_2(g) - S^{\circ} \text{ BaCO}_3(s)$

     $= 70.42 + 213.6 - 112.1 = 171.92 \text{ J/K} = 0.1719 \text{ kJ/K}$

(a)     $\Delta G$ at 298 K = 269.3 kJ - 298 K (0.17192 kJ/K) = 218.07 = 218.1 kJ

$$\ln K = \frac{-\Delta G^{\circ}}{RT} = \frac{-218.07 \times 10^3 \text{ J}}{8.314 \text{ J/K} \times 298 \text{ K}} = -88.017 = -88.02$$
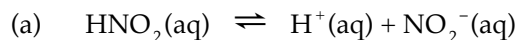
$K = 6.0 \times 10^{-39}; \quad P_{CO_2} = 6.0 \times 10^{-39} \text{ atm}$

(b)     $\Delta G$ at 1100 K = 269.3 kJ - 1100 K (0.17192 kJ) = 80.19 = +80.2 kJ

$$\ln K = \frac{-\Delta G^{\circ}}{RT} = \frac{-80.19 \times 10^3 \text{ J}}{8.314 \text{ J/K} \times 1100 \text{ K}} = -8.768 = -8.77$$

$K = 1.6 \times 10^{-4}; \quad P_{CO_2} = 1.6 \times 10^{-4} \text{ atm}$

19.81    *Analyze/Plan.* Given an acid dissociation equilibrium and the corresponding $K_a$ value, calculate $\Delta G^{\circ}$ and $\Delta G$ for a given set of concentrations. Use Equation [19.17] to calculate $\Delta G^{\circ}$ and Equation [19.16] to calculate $\Delta G$.     *Solve.*

(a)     $HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$

(b)     $\Delta G^{\circ} = -RT \ln K_a = -(8.314 \times 10^{-3})(298) \ln (4.5 \times 10^{-4}) = 19.0928 = 19.1 \text{ kJ}$

(c)     $\Delta G = 0$ at equilibrium

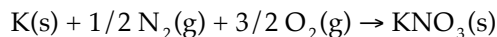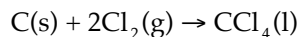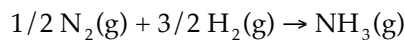(d)     $\Delta G = \Delta G^{\circ} + RT \ln Q$

$$= 19.09 \text{ kJ} + (8.314 \times 10^{-3})(298) \ln \frac{(5.0 \times 10^{-2})(6.0 \times 10^{-4})}{0.20} = -2.72 = -3 \text{ kJ}$$

## Additional Exercises

19.84

| Process | ΔH | ΔS |
|---|---|---|
| (a) | + | + |
| (b) | − | − |
| (c) | + | + |
| (d) | + | + |

(e)                    –              +

19.88   (a)   Formation reactions are the synthesis of 1 mole of compound from elements in their standard states.

$1/2\,N_2(g) + 3/2\,H_2(g) \rightarrow NH_3(g)$

$C(s) + 2Cl_2(g) \rightarrow CCl_4(l)$

$K(s) + 1/2\,N_2(g) + 3/2\,O_2(g) \rightarrow KNO_3(s)$

In each of these formation reactions, there are fewer moles of gas in the products than the reactants, so we expect $\Delta S°$ to be negative. If $\Delta G_f^o = \Delta H_f^o - T\Delta S°$ and $\Delta S°$ is negative, $-T\Delta S°$ is positive and $\Delta G_f^o$ is more positive than $\Delta H_f^o$.

   (b)   $C(s) + 1/2\,O_2(g) \rightarrow CO(g)$

In this reaction, there are more moles of gas in products, $\Delta S°$ is positive, $-T\Delta S°$ is negative and $\Delta G_f^o$ is more negative than $\Delta H_f^o$.

19.92   (a)   $K = \dfrac{\chi_{CH_3COOH}}{\chi_{CH_3OH}\,P_{CO}}$

$\Delta G° = -RT\ln K;\ \ln K = -\Delta G/RT$

$\Delta G° = \Delta G°\ CH_3COOH(l) - \Delta G°\ CH_3OH(l) - \Delta G°\ CO(g)$

   $= -392.4 - (-166.23) - (-137.2) = -89.0\ kJ$

$\ln K = \dfrac{-(-89.0\,kJ)}{(8.314\times 10^{-3}\,kJ/K)(298\,K)} = 35.922 = 35.9;\ K = 4 \times 10^{15}$

   (b)   $\Delta H° = \Delta H°\ CH_3COOH(l) - \Delta H°\ CH_3OH(l) - \Delta H°\ CO(g)$

   $= -487.0 - (-238.6) - (-110.5) = -137.9\ kJ$

The reaction is exothermic, so the value of K will decrease with increasing temperature, and the mole fraction of $CH_3COOH$ will also decrease. Elevated temperatures must be used to increase the speed of the reaction. Thermodynamics cannot predict the rate at which a reaction reaches equilibrium.

   (c)   $\Delta G° = -RT\ln K;\ K = 1,\ \ln K = 0,\ \Delta G° = 0$

$\Delta G° = \Delta H° - T\Delta S°;$ when $\Delta G° = 0,\ \Delta H° = T\Delta S°$

$\Delta S° = S°\ CH_3COOH(l) - S°\ CH_3OH(l) - S°\ CO(g)$

   $= 159.8 - 126.8 - 197.9 = -164.9\ J/K = -0.1649\ kJ/K$

$-137.9\ kJ = T(-0.1649\ kJ/K),\ T = 836.3\ K$

The equilibrium favors products up to 836 K or 563°C, so the elevated temperatures to increase the rate of reaction can be safely employed.

19.96   (a)   The equilibrium of interest here can be written as:

$K^+$ (plasma) $\rightleftharpoons$ $K^+$ (muscle)
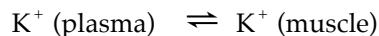
Since an aqueous solution is involved in both cases, assume that the equilibrium constant for the above process is exactly 1, that is, $\Delta G° = 0$. However, $\Delta G$ is not zero because the concentrations are not the same on both sides of the membrane. Use Equation [19.16] to calculate $\Delta G$:

$$\Delta G = \Delta G° + RT \ln \frac{[K^+ (\text{muscle})]}{[K^+ (\text{plasma})]}$$

$$= 0 + (8.314)(310)\ln \frac{(0.15)}{(5.0 \times 10^{-3})} = 8766 J = 8.8 kJ$$

(b)     Note that $\Delta G$ is positive. This means that work must be done on the system (blood plasma plus muscle cells) to move the $K^+$ ions "uphill," as it were. The minimum amount of work possible is given by the value for $\Delta G$. This value represents the minimum amount of work required to transfer one mole of $K^+$ ions from the blood plasma at $5 \times 10^{-3} M$ to muscle cell fluids at 0.15 $M$, assuming constancy of concentrations. In practice, a larger than minimum amount of work is required.

## Integrative Exercises

19.100   (a)     At the boiling point, vaporization is a reversible process, so $\Delta S_{vap}^{o} = \Delta H_{vap}^{o} /T.$

acetone: $\Delta S_{vap}^{o} = \Delta H_{vap}^{o} /T = (29.1 kJ/mol)/329.2 K = 88.4 J/mol\text{-}K$

dimethyl ether: $\Delta S_{vap}^{o} = (21.5 kJ/mol)/248.3 K = 86.6 J/mol\text{-}K$

ethanol: $\Delta S_{vap}^{o} = (38.6 kJ/mol)/351.6 K = 110 J/mol\text{-}K$

octane: $\Delta S_{vap}^{o} = (34.4 kJ/mol)/398.7 K = 86.3 J/mol\text{-}K$

pyridine: $\Delta S_{vap}^{o} = (35.1 kJ/mol)/388.4 K = 90.4 J/mol\text{-}K$

(b)     Ethanol is the only liquid listed that doesn't follow *Trouton's rule* and it is also the only substance that exhibits hydrogen bonding in the pure liquid. Hydrogen bonding leads to more ordering in the liquid state and a greater than usual increase in entropy upon vaporization. The rule appears to hold for liquids with London dispersion forces (octane) and ordinary dipole-dipole forces (acetone, dimethyl ether, pyridine), but not for those with hydrogen bonding.

(c)     Owing to strong hydrogen bonding interactions, water probably does not obey Trouton's rule.

From Appendix B, $\Delta H_{vap}^{o}$ at 100°C = 40.67 kJ/mol.

$\Delta S_{vap}^{o} = (40.67 kJ/mol)/373.1 K = 109.0 J/mol\text{-}K$

(d)     Use $\Delta S_{vap}^{o} = 88 J/mol\text{-}K,$ the middle of the range for Trouton's rule, to estimate $\Delta H_{vap}^{o}$ for chlorobenzene.

$\Delta H_{vap}^{o} = \Delta S_{vap}^{o} \times T = 88 J/mol\text{-}K \times 404.95 K = 36 kJ/mol$

19.103    (a)    $O_2(g) \xrightarrow{h\nu} 2O(g)$ S increases because there are more moles of gas in the products.

        (b)    $O_2(g) + O(g) \rightarrow O_3(g)$, S decreases because there are fewer moles of gas in the products.

        (c)    S increases as the gas molecules diffuse into the larger volume of the stratosphere; there are more possible positions and therefore more motional freedom.

        (d)    $NaCl(aq) \rightarrow NaCl(s) + H_2O(l)$; $\Delta S$ decreases as the mixture (seawater, greater disorder) is separated into pure substances (fewer possible arrangements, more order).

19.106    (a)    $K = P_{NO_2}^2 / P_{N_2O_4}$

           Assume equal amounts means equal number of moles. For gases, $P = n(RT/V)$. In an equilibrium mixture, $RT/V$ is a constant, so moles of gas are directly proportional to partial pressure. Gases with equal partial pressures will have equal moles of gas present. The condition $P_{NO_2} = P_{N_2O_4}$ leads to the expression $K = P_{NO_2}$. The value of K then depends on $P_t$ for the mixture. For any particular value of $P_t$, the condition of equal moles of the two gases can be achieved at some temperature. For example, $P_{NO_2} = P_{N_2O_4} = 1.0\,atm, P_t = 2.0\,atm$.

$$K = \frac{(1.0)^2}{1.0} = 1.0; \quad \ln K = 0; \quad \Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ; \quad T = \Delta H^\circ / \Delta S^\circ$$

$$\Delta H^\circ = 2\Delta H^\circ\, NO_2(g) - \Delta H^\circ\, N_2O_4(g) = 2(33.84) - 9.66 = +58.02\ kJ$$

$$\Delta S^\circ = 2S^\circ\, NO_2(g) - S^\circ\, N_2O_4(g) = 2(240.45) - 304.3 = 0.1766\ kJ/K$$

$$T = \frac{58.02\,kJ}{0.1766\,kJ/K} = 328.5\,K\ or\ 55.3°C$$

        (b)    $P_t = 1.00$ atm; $P_{N_2O_4} = x$, $P_{NO_2} = 2x$; $x + 2x = 1.00$ atm

$$x = P_{N_2O_4} = 0.3333 = 0.333\,atm; \quad P_{NO_2} = 0.6667 = 0.667\,atm$$

$$K = \frac{(0.6667)^2}{0.3333} = 1.334 = 1.33; \quad \Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

$$-(8.314 \times 10^{-3}\ kJ/K)(\ln 1.334)\ T = 58.02\ kJ - (0.1766\ kJ/K)\ T$$

$$(-0.00239\ kJ/K)\ T + (0.1766\ kJ/K)\ T = 58.02\ kJ$$

$$(0.1742\ kJ/K)\ T = 58.02\ kJ; \quad T = 333.0\ K$$

        (c)    $P_t = 10.00$ atm; $x + 2x = 10.00$ atm

$$x = P_{N_2O_4} = 3.3333 = 3.333\,atm; \quad P_{NO_2} = 6.6667 = 6.667\,atm$$

$$K = \frac{(6.6667)^2}{3.3333} = 13.334 = 13.33; \quad -RT \ln K = \Delta H^\circ - T\Delta S^\circ$$

$$-(8.314 \times 10^{-3}\ kJ/K)(\ln 13.334)\ T = 58.02\ kJ - (0.1766\ kJ/K)\ T$$

$$(-0.02154\ kJ/K)\ T + (0.1766\ kJ/K)\ T = 58.02\ kJ$$

(0.15506 kJ/K) T = 58.02 kJ; T = 374.2 K

(d)    The reaction is endothermic, so an increase in the value of K as calculated in parts (b) and (c) should be accompanied by an increase in T.