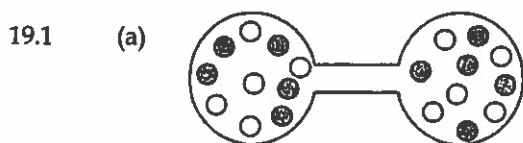


19 Chemical Thermodynamics

Visualizing Concepts



- (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 spontaneous and therefore irreversible. It is inconceivable that the gases would recombine.
- (d) The entropy change of the surroundings is related to ΔH for the system. Since we are mixing ideal gases and $\Delta H = 0$, ΔH_{surr} is also zero, assuming heat exchange only between the two bulbs.
- 19.2 (a) Based on experience, the process is spontaneous. We know that 1,1-difluoroethane is a gas at atmospheric pressure, so the pressure inside the can must be much greater than atmospheric in order for the substance to be liquefied. When the nozzle is pressed and the system is open to the lower pressure of the atmosphere, the liquid vaporizes spontaneously. The 1,1-difluoroethane gas escapes the nozzle without external assistance.
- (b) We expect q_{sys} to be positive. We know that ΔH is positive for the vaporization of a gas. Since the change does not occur at constant pressure, q_{sys} and ΔH are not equal, but the sign of q_{sys} is still positive.
- (c) ΔS is definitely positive for this process, owing to the larger volume occupied and greater motional freedom of the system, the 1,1-difluoroethane molecules.
- (d) The operation of the keyboard cleaner definitely depends more on entropy change than heat flow.
- 19.3 (a) The process depicted is a change of state from a solid to a gas. ΔS is positive because of the greater motional freedom of the particles. ΔH is positive because both melting and boiling are endothermic processes.
- (b) Since $\Delta G = \Delta H - T\Delta S$, and both ΔH and ΔS are positive, the sign of ΔG depends on temperature. This is true for all phase changes. If the temperature of the system is

greater than the boiling point of the substance, the process is spontaneous and ΔG is negative. If the temperature is lower than the boiling point, the process is not spontaneous and ΔG is positive.

- (c) If the process is spontaneous, the second law states that $\Delta S_{\text{univ}} \geq 0$. Since ΔS_{sys} is positive, ΔS_{surr} must be negative. If the change occurs via a reversible pathway, $\Delta S_{\text{univ}} = 0$ and $\Delta S_{\text{surr}} = -\Delta S_{\text{sys}}$. If the pathway is irreversible, the magnitude of ΔS_{sys} is greater than the magnitude of ΔS_{surr} , but the sign of ΔS_{surr} is still negative.
- 19.4 In the depicted reaction, both reactants and products are in the gas phase (they are far apart and randomly placed). There are twice as many molecules (or moles) of gas in the products, so ΔS is positive for this reaction.
- 19.5 *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 a 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) We expect the enthalpy of combustion of the two isomers to be very similar. The molecular formulas of the two molecules are the same, so the balanced chemical equations for the two combustion reactions are identical. In the calculation of combustion enthalpy from standard enthalpies of formation of products and reactants, the only difference will be in the standard enthalpies of formation of the two isomers.
- (b) We expect n-pentane to have the higher standard molar entropy. The rod-shaped n-pentane has more possible vibrational and rotational motions than the almost-spherical neopentane. That is, n-pentane has greater motional energy, which results in a higher standard molar entropy than that of neopentane.
- 19.7 (a) At 300 K, $\Delta H = T\Delta S$. Since $\Delta G = \Delta H - T\Delta S$, $\Delta G = 0$ at this point. When $\Delta G = 0$, the system is at equilibrium.
- (b) The reaction is spontaneous when ΔG is negative. This condition is met when $T\Delta S > \Delta H$. From the diagram, $T\Delta S > \Delta H$ when $T > 300$ K. The reaction is spontaneous at temperatures above 300 K.
- 19.8 (a) At equilibrium, $\Delta G = 0$. On the diagram, $\Delta G = 0$ 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) $\Delta G = \Delta H - T\Delta S$, in the form of $y = b + mx$. ΔH is the y intercept of the graph (where $T = 0$) and is positive.
- (d) The slope of the graph is $-\Delta S$. The slope is negative, so ΔS is positive. [Also, ΔG decreases as T increases, so the $T\Delta S$ term must become more negative and ΔS is positive.]

- 19.9 (a) *Analyze.* The boxes depict three different mixtures of reactants and products for the reaction $A_2 + B_2 \rightleftharpoons 2AB$.

Plan. $K_c = 1 = \frac{[AB]^2}{[A][B]}$. Calculate Q for each box, using number of molecules as a measure of concentration. If $Q = 1$, the system is at equilibrium. *Solve.*

$$\text{Box 1: } K = \frac{(3)^2}{(3)(3)} = 1.$$

$$\text{Box 2: } Q = \frac{(1)^2}{(4)(4)} = \frac{1}{16} = 0.0625 = 0.06$$

$$\text{Box 3: } Q = \frac{(7)^2}{(1)(1)} = \frac{49}{1} = 49$$

Box 1 is at equilibrium.

- (b) All nonequilibrium systems move spontaneously to achieve equilibrium. As the reaction is written, the sign of ΔG indicates the direction in which the reaction is spontaneous. If ΔG is negative, the reaction is spontaneous in the forward direction, toward products. This is the case for Box 2. If ΔG is positive, the reaction is spontaneous in the reverse direction, toward reactants. This is the case for Box 3.
- (c) Qualitatively, Box 3 is farthest from equilibrium, so it has the largest magnitude of ΔG (driving force to reach equilibrium), then Box 2, then Box 1, where $\Delta G = 0$. Box 1 < Box 2 < Box 3.

Quantitatively, $\Delta G = \Delta G^\circ - RT \ln Q$. For Box 1, $\Delta G = 0$ and $K = 1$, so $\Delta G^\circ = 0$.

$$\text{Box 2: } \Delta G = 0 - RT \ln(0.0625) = 2.77 RT$$

$$\text{Box 3: } \Delta G = 0 - RT \ln(49) = -3.89 RT$$

Quantitative treatment confirms the order for magnitude of ΔG as Box 1 < Box 2 < Box 3.

- 19.10 (a) The minimum in the plot is the equilibrium position of the reaction, where $\Delta G = 0$.
- (b) The quantity x is the difference in free energy between reactant and products in their standard states, ΔG° .

Spontaneous Processes (section 19.1)

- 19.11 *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 .
- 19.12 (a) Nonspontaneous; at 1 atm, ice does not melt spontaneously at temperatures below its normal melting point.
- (b) Nonspontaneous; a mixture cannot be separated without outside intervention.
- (c) Spontaneous.
- (d) Spontaneous. The reaction is spontaneous but slow unless encouraged by a catalyst or spark.
- (e) Spontaneous; the very polar HCl molecules readily dissolve in water to form concentrated $\text{HCl}(\text{aq})$.
- 19.13 (a) $\text{NH}_4\text{NO}_3(\text{s})$ dissolves in water, as in a chemical cold pack. Naphthalene (mothballs) sublimates at room temperature.
- (b) Melting of a solid is spontaneous above its melting point but nonspontaneous below its melting point.
- 19.14 Yes. Bertholet postulated that all spontaneous processes are exothermic. The spontaneous endothermic reaction described in this exercise is one of many exceptions to Bertholet's generalization.
- 19.15 *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 .
- 19.16 (a) Exothermic. If melting requires heat and is endothermic, freezing must be exothermic.
- (b) At 1 atm (indicated by the term "normal" freezing point), the freezing of n -octane is spontaneous at temperatures below -57°C .
- (c) At 1 atm, the freezing of n -octane is nonspontaneous at temperatures above -57°C .
- (d) At 1 atm and -57°C , the normal freezing point of n -octane, the solid and liquid phases are in equilibrium. That is, at the freezing point, n -octane molecules escape to the liquid phase at the same rate as liquid n -octane solidifies, assuming no heat is exchanged between n -octane and the surroundings.
- 19.17 *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 required heat is added infinitely slowly.
- (d) No. Natural processes, such as a banana ripening or a lightning 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.
- 19.18 (a) A process is *irreversible* if the system cannot be returned to its original state by the same path that the forward process took place.
- (b) Since the system returned to its initial state via a different path (different q_r and w_r than q_f and w_f), there is a net change in the surroundings.
- (c) The condensation of a liquid will be irreversible if it occurs at any temperature other than the boiling point of the liquid, at a specified pressure.
- 19.19 *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. ΔE is a state function. $\Delta E = q + w$; q and w are not state functions. Their values do depend on path, but their sum, ΔE , does not.
- 19.20 (a) $\Delta E (1 \rightarrow 2) = -\Delta E (2 \rightarrow 1)$
- (b) We can say nothing about the values of q and w because we have no information about the paths.
- (c) If the changes of state are reversible, the two paths are the same and $w (1 \rightarrow 2) = -w (2 \rightarrow 1)$. This is the maximum realizable work from this system.

- 19.21 *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. ΔE is not zero for the process.
- 19.22 (a) The detonation of an explosive is definitely spontaneous, once it is initiated.
- (b) The quantity q is related to ΔH . Since the detonation is highly exothermic, q is large and negative.
- If only PV-work is done and P is constant, $\Delta H = q$. Although these conditions probably do not apply to a detonation, we can still predict the sign of q , based on ΔH , if not its exact magnitude.
- (c) The sign (and magnitude) of w depend on the path of the process, the exact details of how the detonation is carried out. It seems clear, however, that work will be done by the system on the surroundings in almost all circumstances (buildings collapse, earth and air are moved), so the sign of w is probably negative.
- (d) $\Delta E = q + w$. If q and w are both negative, then the sign of ΔE is negative, regardless of the magnitudes of q and w .

Entropy and the Second Law of Thermodynamics (section 19.2)

- 19.23 (a) For a process that occurs at constant temperature, an isothermal process, $\Delta S = q_{\text{rev}}/T$. Here q_{rev} is the heat that would be transferred if the process were reversible. Since ΔS is a state function, it is independent of path, so ΔS for the reversible path must equal ΔS for any path.
- (b) No. ΔS is a state function, so it is independent of path.
- 19.24 Both vaporizations are *isothermal*; they occur at constant temperature. For an isothermal process, $\Delta S = q_{\text{rev}}/T$.
- (a) Assuming that q_{rev} is closely related to enthalpy of vaporization and is about the same at the two temperatures, ΔS is larger at 25°C than at 100°C.
- (b) No. Because ΔS is a state function, it is independent of path. We can calculate ΔS for a reversible pathway, even if the change does not occur that way.
- 19.25 (a) $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$, entropy increases, more mol gas in products, greater motional freedom.
- (b)
$$\Delta S = \frac{\Delta H}{T} = \frac{29.6 \text{ kJ}}{\text{mol Br}_2(\text{l})} \times 1.00 \text{ mol Br}_2(\text{l}) \times \frac{1}{(273.15 + 58.8)\text{K}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 89.2 \text{ J/K}$$

- 19.26 (a) $\text{Ga(l)} \rightarrow \text{Ga(s)}$, ΔS is negative, less motional freedom
- (b) $\Delta H = 60.0 \text{ g Ga} \times \frac{1 \text{ mol Ga}}{69.723 \text{ g Ga}} \times \frac{-5.59 \text{ kJ}}{\text{mol Ga}} = -4.81046 = -4.81 \text{ kJ}$
- $$\Delta S = \frac{\Delta H}{T} = -4.81046 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1}{(273.15 + 29.8)\text{K}} = -15.9 \text{ J/K}$$
- 19.27 (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, $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$. If ΔS_{sys} is positive, ΔS_{surr} must be negative.
- (c) Since ΔS_{univ} must be positive for a spontaneous process, ΔS_{surr} must be greater than -42 J/K .
- 19.28 (a) For a spontaneous process, $\Delta S_{\text{univ}} > 0$. For a reversible process, $\Delta S_{\text{univ}} = 0$.
- (b) ΔS_{surr} is positive and greater than the magnitude of the decrease in ΔS_{sys} .
- (c) $\Delta S_{\text{sys}} = 78 \text{ J/K}$.
- 19.29 *Analyze.* Consider ΔS for the isothermal expansion of 0.200 mol of an ideal gas at 27°C and an initial volume of 10.0 L.
- (a) Whenever an ideal gas expands isothermally, we expect an increase in entropy, or positive ΔS , owing to the greater volume available for motion of the particles.
- (b) *Plan.* Use the relationship $\Delta S_{\text{sys}} = nR \ln(V_2/V_1)$, Equation [19.3].
- Solve.* $\Delta S_{\text{sys}} = 0.200 (8.314 \text{ J/mol}\cdot\text{K})(\ln [18.5 \text{ L}/10.0 \text{ L}]) = 1.02 \text{ J/K}$
- Check.* We expect ΔS to be positive when the motional freedom of a gas increases, and our calculation agrees with this prediction.
- (c) The temperature at which the expansion occurs is not needed to calculate the entropy change, as long as the process is isothermal.
- 19.30 (a) According to Boyle's law, pressure and volume are inversely proportional at constant amount and temperature. If the pressure of an ideal gas increases, volume decreases. We expect a decrease in entropy, or negative ΔS , for the isothermal compression of an ideal gas, owing to the smaller volume available for motion of the particles.
- (b) According to Boyle's law, $P_1 V_1 = P_2 V_2$ at constant n and T .
- $$0.750 \text{ atm} \times V_1 = 1.20 \text{ atm} \times V_2; V_2/V_1 = 0.750 \text{ atm}/1.20 \text{ atm} = 0.62500 = 0.625$$
- $$\Delta S_{\text{sys}} = nR \ln(V_2/V_1) = 0.600 \text{ mol} (8.314 \text{ J/mol}\cdot\text{K})(\ln 0.625) = -2.34 \text{ J/K}$$
- Check.* An increase in pressure results in a decrease in volume at constant T , so we expect ΔS to be negative, and it is.
- (c) The temperature at which the compression (increase in pressure, decrease in volume) occurs is not needed to calculate the entropy change, as long as the process is isothermal.

The Molecular Interpretation of Entropy (section 19.3)

- 19.31 (a) Yes, the expansion is spontaneous.
- (b) The ideal gas is the system, and everything else, including the vessel containing the vacuum, is the surroundings. There is literally nothing inside the vessel containing the vacuum, no gas molecules and no physical barriers. As the ideal gas expands into the vacuum, there is nothing for it to "push back", so no work is done. Mathematically, $w = -P_{\text{ext}}\Delta V$. Since the gas expands into a vacuum, $P_{\text{ext}} = 0$ and $w = 0$.
- (c) The "driving force" for the expansion of the gas is the increase in entropy associated with greater volume, more motional freedom and more possible positions for the gas particles.
- 19.32 (a) A thermodynamic *state* is a set of conditions, usually temperature and pressure, that defines the properties of a bulk material. A *microstate* is a single possibility for all the positions and kinetic energies of all the molecules in a sample; it is a snapshot of positions and speeds at a particular instant.
- (b) According to Equation [19.5] (Boltzman's Law), the more possible microstates for a macroscopic state, the greater the entropy of the state. If S decreases going from A to B, then A has more microstates than B. Or, if ΔS is negative, the number of microstates decreases.
- (c) According to part (b), if the number of microstates available to a system decreases, ΔS_{sys} is negative. For a spontaneous process, ΔS_{univ} is positive, so ΔS_{surr} is positive (and the magnitude is greater than that of ΔS_{sys}).
- 19.33 (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.
- 19.34 (a) ΔH_{vap} for H_2O at $25^\circ\text{C} = 44.02 \text{ kJ/mol}$; at $100^\circ\text{C} = 40.67 \text{ kJ/mol}$
- $$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{44.02 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1}{298 \text{ K}} = 148 \text{ J/mol} \cdot \text{K}$$
- $$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{40.67 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1}{373 \text{ K}} = 109 \text{ J/mol} \cdot \text{K}$$
- (b) At both temperatures, the liquid \rightarrow gas phase transition is accompanied by an increase in entropy, as expected. That the magnitude of the increase is greater at the lower temperature requires some explanation.

In the liquid state, there are significant hydrogen bonding interactions between H_2O molecules. This reduces the number of possible molecular positions and the

number of microstates. Liquid water at 100° has sufficient kinetic energy to have broken many hydrogen bonds, so the number of microstates for $\text{H}_2\text{O}(\text{l})$ at 100° is greater than the number of microstates for $\text{H}_2\text{O}(\text{l})$ at 25°C. The difference in the number of microstates upon vaporization at 100°C is smaller, and the magnitude of ΔS is smaller.

19.35 *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; ΔS is positive.

(b) S_{sys} may increase slightly in 19.11 (a), where the sample softens; this is not definitive.

S_{sys} clearly increases in Exercise 19.11 (b), where there is an increase in volume and possible arrangements for the sample.

In 19.11 (c), the system goes from two moles of gaseous reactants to one mole of gaseous products, and S_{sys} decreases.

In 19.11 (d), the entropy of the universe clearly increases, but the definition of the system in a lightning strike is more problematic.

In 19.11 (e), the state is specified as room temperature and 1 atm pressure. This means that H_2O is present as a liquid; there is then one mol of gaseous reactants (CO_2) and three mol of gaseous products (CH_4 and 2 O_2), so S_{sys} increases. (The reaction is not spontaneous because of the very large positive ΔH_{sys} for the reaction as written.)

19.36 (a) Solids are much more ordered than gases, so ΔS is negative.

(b) The entropy of the system increases in Exercise 19.12 (a) and (e). There is more motional freedom for the system in both cases. In (b), (c) and (d), there is less motional freedom after the change and the entropy of the system decreases.

19.37 *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.

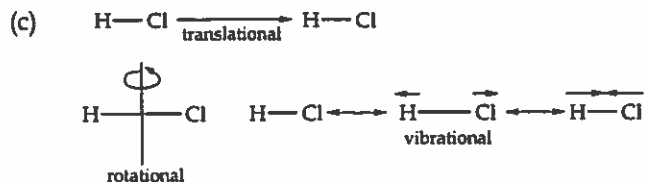
(c) S increases; volume and translational motion are greater in the gas than the solid.

19.38 (a) When temperature increases, the range of accessible molecular speeds and kinetic energies increases. This produces more microstates and an increase in entropy.

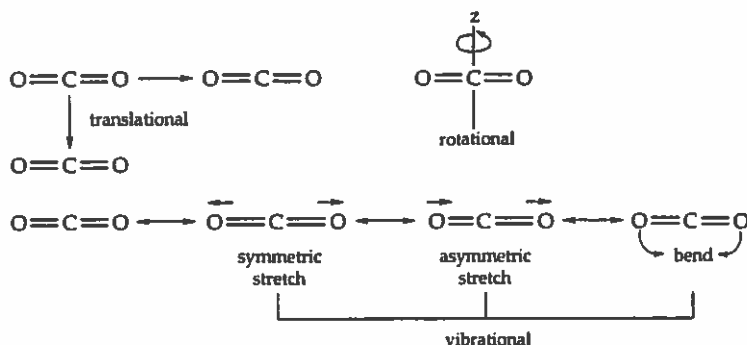
(b) When the volume of a gas increases (even at constant T), there are more possible positions for the particles, more microstates, and greater entropy.

- (c) When equal volumes of two miscible liquids are mixed, the volume of the sample and therefore the number of possible arrangements increases. This produces more microstates and an increase in entropy.

- 19.39 (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.



- 19.40 (a) In order for the entropy of a system to be zero, the system must be a pure crystalline (exactly ordered in three dimensions) solid, and the temperature must be absolute zero.
- (b) Since CO_2 has more than one atom, the thermal energy can be distributed as translational, vibrational, or rotational motion.



- (c) At a given temperature, $\text{CO}_2(\text{g})$ has more microstates and thus greater entropy than $\text{Ar}(\text{g})$. Because $\text{CO}_2(\text{g})$ is a triatomic molecule, it has multiple rotational and vibrational microstates not available to monatomic $\text{Ar}(\text{g})$.

- 19.41 *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) $\text{Ar}(\text{g})$ (gases have higher entropy due primarily to much larger volume)
- (b) $\text{He}(\text{g})$ at 1.5 atm (larger volume and more motional freedom)
- (c) 1 mol of $\text{Ne}(\text{g})$ in 15.0 L (larger volume provides more motional freedom)
- (d) $\text{CO}_2(\text{g})$ (more motional freedom)

- 19.42 (a) 1 mol of $\text{As}_4(\text{g})$ at 300°C , 0.01 atm (As_4 has more massive atoms in a comparable system at the same temperature.)

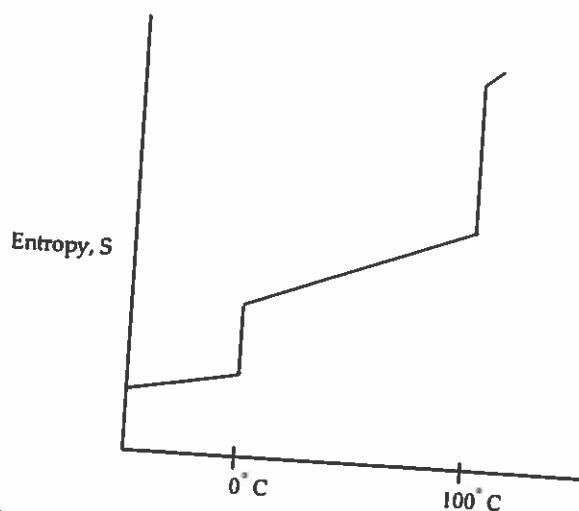
- (b) 1 mol $\text{H}_2\text{O}(\text{g})$ at 100°C , 1 atm (larger volume occupied by $\text{H}_2\text{O}(\text{g})$)
 (c) 0.5 mol $\text{CH}_4(\text{g})$ at 298 K, 20-L volume (more complex molecule, more rotational and vibrational degrees of freedom)
 (d) 100 g of $\text{Na}_2\text{SO}_4(\text{aq})$ at 30°C (more motional freedom in aqueous solution)

19.43 *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 is small and probably positive (moles of gas same in reactants and products, $\text{H}_2\text{O}(\text{g})$ is more structurally complex than $\text{H}_2(\text{g})$)
- 19.44 (a) $\text{Au}(\text{l}) \rightarrow \text{Au}(\text{s})$; negative ΔS , less motional freedom in the solid
 (b) $\text{Cl}_2(\text{g}) \rightarrow 2\text{Cl}(\text{g})$; positive ΔS , moles of gas increase
 (c) $\text{CO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$; negative ΔS , moles of gas decrease
 (d) $3\text{Ca}(\text{NO}_3)_2(\text{aq}) + 2(\text{NH}_4)_3\text{PO}_4(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s}) + 6\text{NH}_4\text{NO}_3(\text{aq})$; ΔS is negative, less motional freedom, fewer moles of ions in aqueous solution.

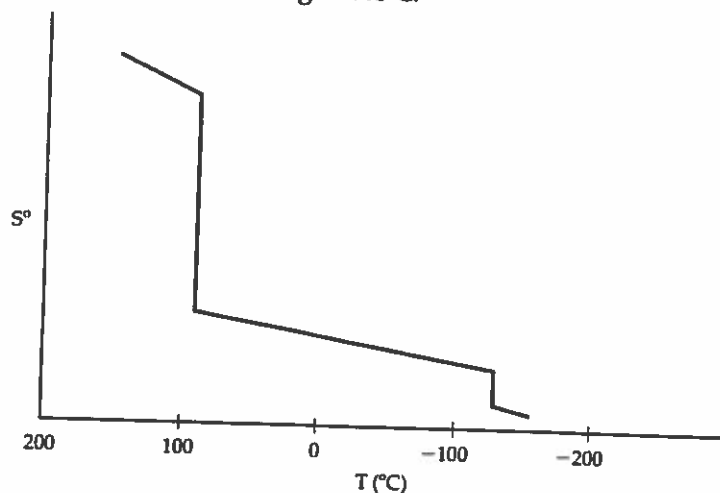
Entropy Changes in Chemical Reactions (section 19.4)

19.45 (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.

19.46 Melting = -126.5°C ; boiling = 97.4°C .



19.47 *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) $\text{C}_2\text{H}_6(\text{g})$ has more degrees of freedom and larger S° .
 (b) $\text{CO}_2(\text{g})$ has more degrees of freedom and larger S° .

19.48 Propylene will have a higher S° at 25°C . At this temperature, both are gases, so there are no lattice effects. Since they have the same molecular formula, only the details of their structures are different. In propylene, there is free rotation around the C—C single bond, while in cyclopropane the 3-membered ring severely limits rotation. The greater motional freedom of the propylene molecule leads to a higher absolute entropy.

19.49 *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) $\text{Sc}(\text{s})$, $34.6 \text{ J/mol}\cdot\text{K}$; $\text{Sc}(\text{g})$, $174.7 \text{ J/mol}\cdot\text{K}$. 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) $\text{NH}_3(\text{g})$, $192.5 \text{ J/mol}\cdot\text{K}$; $\text{NH}_3(\text{aq})$, $111.3 \text{ J/mol}\cdot\text{K}$. Molecules in the gas phase have more motional freedom than molecules in solution.
 (c) 1 mol of $\text{P}_4(\text{g})$, 280 J/K ; 2 mol of $\text{P}_2(\text{g})$, $2(218.1) = 436.2 \text{ J/K}$. More particles have greater motional energy (more available microstates).
 (d) $\text{C}(\text{diamond})$, $2.43 \text{ J/mol}\cdot\text{K}$; $\text{C}(\text{graphite})$ $5.69 \text{ J/mol}\cdot\text{K}$. 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.

- 19.50 (a) CuO(s) , 42.59 J/mol-K; $\text{Cu}_2\text{O(s)}$, 92.36 J/mol-K. Molecules in the solid state have only vibrational motion available to them. The more complex Cu_2O molecule has more vibrational degrees of freedom and a larger standard entropy.
- (b) 1 mol $\text{N}_2\text{O}_4(\text{g})$, 304.3 J/K; 2 mol $\text{NO}_2(\text{g})$, $2(240.45) = 480.90$ J/K. More particles have a greater number of arrangements.
- (c) $\text{SiO}_2(\text{s})$, 41.84 J/mol-K; $\text{CO}_2(\text{g})$, 213.6 J/mol-K. Molecules in the gas phase have a larger volume and more motional freedom than molecules in the solid state. SiO_2 is a covalent network solid so its molecular motion is even more restrained than a typical molecular solid.
- (d) CO(g) , 197.9 J/mol-K; $\text{CO}_2(\text{g})$, 213.6 J/mol-K. The more complex CO_2 molecule has more vibrational degrees of freedom and a slightly higher entropy.
- 19.51 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.
- 19.52 (a) C(diamond) , $S^\circ = 2.43$ J/mol-K; C(graphite) , $S^\circ = 5.69$ 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 translational or vibrational freedom within the covalent-network diamond lattice.
- (b) S° for buckminsterfullerene will be ≥ 10 J/mol-K. S° for graphite is twice S° for diamond, and S° for the fullerene should be higher than that of graphite. The 60-atom "bucky" balls have more flexibility than graphite sheets. Also, the balls have translational freedom in three dimensions, while graphite sheets have it in only two directions. Because of the ball structure, there is more empty space in the fullerene lattice than in graphite or diamond; essentially, 60 C-atoms in fullerene occupy a larger volume than 60 C-atoms in graphite or diamond. Thus, the fullerene has additional "molecular" complexity, more degrees of translational freedom, and occupies a larger volume, all features that point to a higher absolute entropy.
- 19.53 *Analyze/Plan.* Follow the logic in Sample Exercise 19.5. *Solve.*
- (a) $\Delta S^\circ = S^\circ \text{C}_2\text{H}_6(\text{g}) - S^\circ \text{C}_2\text{H}_4(\text{g}) - S^\circ \text{H}_2(\text{g})$
 $= 229.5 - 219.4 - 130.58 = -120.5$ J/K
 ΔS° is negative because there are fewer moles of gas in the products.
- (b) $\Delta S^\circ = 2S^\circ \text{NO}_2(\text{g}) - \Delta S^\circ \text{N}_2\text{O}_4(\text{g}) = 2(240.45) - 304.3 = +176.6$ J/K
 ΔS° is positive because there are more moles of gas in the products.
- (c) $\Delta S^\circ = \Delta S^\circ \text{BeO(s)} + \Delta S^\circ \text{H}_2\text{O(g)} - \Delta S^\circ \text{Be(OH)}_2(\text{s})$
 $= 13.77 + 188.83 - 50.21 = +152.39$ J/K
 ΔS° is positive because the product contains more total particles and more moles of gas.

$$(d) \quad \Delta S^\circ = 2S^\circ \text{CO}_2(\text{g}) + 4S^\circ \text{H}_2\text{O}(\text{g}) - 2S^\circ \text{CH}_3\text{OH}(\text{g}) - 3S^\circ \text{O}_2(\text{g}) \\ = 2(213.6) + 4(188.83) - 2(237.6) - 3(205.0) = +92.3 \text{ J/K}$$

ΔS° is positive because the product contains more total particles and more moles of gas.

$$19.54 \quad (a) \quad \Delta S^\circ = S^\circ \text{NH}_4\text{NO}_3(\text{s}) - S^\circ \text{HNO}_3(\text{g}) - S^\circ \text{NH}_3(\text{g}) \\ = 151 - 266.4 - 192.5 = -307.9 = -308 \text{ J/K}$$

ΔS° is large and negative because all reactants are gases (2 moles) and the product is a solid.

$$(b) \quad \Delta S^\circ = 4S^\circ \text{Fe}(\text{s}) + 3S^\circ \text{O}_2(\text{g}) - 2S^\circ \text{Fe}_2\text{O}_3(\text{s}) \\ = 4(27.15) + 3(205.0) - 2(89.96) = 543.68 = 543.7 \text{ J/K}$$

ΔS° is large and positive because the reaction produces 3 moles of gas and the reactant is a solid.

$$(c) \quad \Delta S^\circ = S^\circ \text{CaCl}_2(\text{s}) + S^\circ \text{CO}_2(\text{g}) + S^\circ \text{H}_2\text{O}(\text{l}) - S^\circ \text{CaCO}_3(\text{s}) - 2S^\circ \text{HCl}(\text{g}) \\ = 104.6 + 213.6 + 69.91 - 92.88 - 2(186.69) = -78.15 \text{ J/K}$$

ΔS° is small and negative because the products contain one fewer mole of gas, but one more mole of liquid. Note the very small standard entropy for $\text{H}_2\text{O}(\text{l})$, owing to its strength of hydrogen bonding. If the products included one mole of a different liquid, the magnitude of the entropy change would be even smaller.

$$(d) \quad \Delta S^\circ = S^\circ \text{C}_6\text{H}_6(\text{l}) + 6S^\circ \text{H}_2(\text{g}) - 3S^\circ \text{C}_2\text{H}_6(\text{g}) \\ = 172.8 + 6(130.58) - 3(229.5) = 267.78 = 267.8 \text{ J/K}$$

ΔS° is positive because there are more moles of gas in the products.

Gibbs Free Energy (sections 19.5 and 19.6)

$$19.55 \quad (a) \quad \Delta G = \Delta H - T\Delta S$$

(b) If ΔG is positive, the process is nonspontaneous, but the reverse process is spontaneous.

(c) There is no relationship between ΔG and rate of reaction. A spontaneous reaction, one with a $-\Delta G$, may occur at a very slow rate. For example: $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$, $\Delta G = -457 \text{ kJ}$ is very slow if not initiated by a spark.

19.56 (a) The *standard* free energy change, ΔG° , represents the free energy change for the process when all reactants and products are in their standard states. When any or all reactants or products are not in their standard states, the free energy is represented simply as ΔG . The value for ΔG thus depends on the specific states of all reactants and products.

(b) When $\Delta G = 0$, the system is at equilibrium.

(c) The sign and magnitude of ΔG give no information about rate; we cannot predict whether the reaction will occur rapidly.

19.57 *Analyze/Plan.* Consider the definitions of ΔH° , ΔS° and ΔG° , along with sign conventions. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. *Solve.*

- (a) ΔH° is negative; the reaction is exothermic.
 (b) ΔS° is negative; the reaction leads to decrease in disorder (increase in order) of the system.
 (c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -35.4 \text{ kJ} - 298 \text{ K} (-0.0855 \text{ kJ/K}) = -9.921 = -9.9 \text{ kJ}$
 (d) At 298 K, ΔG° is negative. If all reactants and products are present in their standard states, the reaction is spontaneous (in the forward direction) at this temperature.

- 19.58 (a) ΔH° is positive; the reaction is endothermic.
 (b) ΔS° is positive; the reaction leads to an increase in disorder.
 (c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 23.7 \text{ kJ} - 298 \text{ K} (0.0524 \text{ kJ/K}) = 8.0848 = 8.08 \text{ kJ}$
 (d) At 298 K, ΔG° is positive. If all reactants and products are present in their standard states, the reaction is spontaneous in the reverse direction at this temperature; it is nonspontaneous in the forward direction.

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

- (a) $\Delta H^\circ = 2(-268.61) - [0 + 0] = -537.22 \text{ kJ}$
 $\Delta S^\circ = 2(173.51) - [130.58 + 202.7] = 13.74 = 13.7 \text{ J/K}$
 $\Delta G^\circ = 2(-270.70) - [0 + 0] = -541.40 \text{ kJ}$
 $\Delta G^\circ = -537.22 \text{ kJ} - 298(0.01374) \text{ kJ} = -541.31 \text{ kJ}$
 (b) $\Delta H^\circ = -106.7 - [0 + 2(0)] = -106.7 \text{ kJ}$
 $\Delta S^\circ = 309.4 - [5.69 + 2(222.96)] = -142.21 = -142.2 \text{ J/K}$
 $\Delta G^\circ = -64.0 - [0 + 2(0)] = -64.0 \text{ kJ}$
 $\Delta G^\circ = -106.7 \text{ kJ} - 298(-0.14221) \text{ kJ} = -64.3 \text{ kJ}$
 (c) $\Delta H^\circ = 2(-542.2) - [2(-288.07) + 0] = -508.26 = -508.3 \text{ kJ}$
 $\Delta S^\circ = 2(325) - [2(311.7) + 205.0] = -178.4 = -178 \text{ J/K}$
 $\Delta G^\circ = 2(-502.5) - [2(-269.6) + 0] = -465.8 \text{ kJ}$
 $\Delta G^\circ = -508.26 \text{ kJ} - 298(-0.1784) \text{ kJ} = -455.097 = -455.1 \text{ kJ}$

(The discrepancy in ΔG° values is due to experimental uncertainties in the tabulated thermodynamic data.)

- (d) $\Delta H^\circ = -84.68 + 2(-241.82) - [2(-201.2) + 0] = -165.92 = -165.9 \text{ kJ}$
 $\Delta S^\circ = 229.5 + 2(188.83) - [2(237.6) + 130.58] = 1.38 = 1.4 \text{ J/K}$
 $\Delta G^\circ = -32.89 + 2(-228.57) - [2(-161.9) + 0] = -166.23 = -166.2 \text{ kJ}$
 $\Delta G^\circ = -165.92 \text{ kJ} - 298(0.00138) \text{ kJ} = -166.33 = -166.3 \text{ kJ}$

- 19.60 (a) There is no thermodynamic data in Appendix C for Cr_2O_3 ; we will substitute Cr_2O_3 . $4\text{Cr}(s) + 3\text{O}_2(g) \rightarrow 2\text{Cr}_2\text{O}_3(s)$

$$\Delta H^\circ = 2(-1139.7) - 4(0) + 3(0) = -2279.4 \text{ kJ}$$

$$\Delta S^\circ = 2(81.2) - 4(23.6) - 3(205.0) = -547.0 \text{ J/K}$$

$$\Delta G^\circ = 2(-1058.1) - 4(0) - 3(0) = -2116.2 \text{ kJ}$$

$$\Delta G^\circ = -2279.4 \text{ kJ} - 298 \text{ K}(-0.5470 \text{ kJ/K}) = -2116.4 \text{ kJ}$$

- (b) $\Delta H^\circ = -553.5 - 393.5 - (-1216.3) = 269.3 \text{ kJ}$

$$\Delta S^\circ = 70.42 + 213.6 - 112.1 = 171.92 = 171.9 \text{ J/K}$$

$$\Delta G^\circ = -525.1 - 394.4 - (-1137.6) = 218.1 \text{ kJ}$$

$$\Delta G^\circ = 269.3 \text{ kJ} - 298 \text{ K}(0.1719 \text{ kJ/K}) = 218.1 \text{ kJ}$$

- (c) Assume the reactant is $\text{P}(g)$, not $\text{P}(s)$.

$$\Delta H^\circ = 2(-1594.4) + 5(0) - 2(316.4) - 10(-268.61) = -1135.5 \text{ kJ}$$

$$\Delta S^\circ = 2(300.8) + 5(130.58) - 2(163.2) - 10(173.51) = -807.0 \text{ J/K}$$

$$\Delta G^\circ = 2(-1520.7) + 5(0) - 2(280.0) - 10(-270.70) = -894.4 \text{ kJ}$$

$$\Delta G^\circ = -1135.5 \text{ kJ} - 298 \text{ K}(-0.8070 \text{ kJ/K}) = -895.014 = -895.0 \text{ kJ}$$

(The small discrepancy in ΔG° values is due to experimental uncertainties in tabulated thermodynamic data.)

- (d) $\Delta H^\circ = -284.5 - (0) - (0) = -284.5 \text{ kJ}$

$$\Delta S^\circ = 122.5 - 64.67 - 205.0 = -147.2 \text{ J/K}$$

$$\Delta G^\circ = -240.6 - (0) - (0) = -240.6 \text{ kJ}$$

$$\Delta G^\circ = -284.5 \text{ kJ} - 298 \text{ K}(-0.1472 \text{ kJ/K}) = -240.634 = -240.6 \text{ kJ}$$

- 19.61 Analyze/Plan. Follow the logic in Sample Exercise 19.7. Solve.

- (a) $\Delta G^\circ = 2\Delta G^\circ \text{SO}_3(g) - [2\Delta G^\circ \text{SO}_2(g) + \Delta G^\circ \text{O}_2(g)]$

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

- (b) $\Delta G^\circ = 3\Delta G^\circ \text{NO}(g) - [\Delta G^\circ \text{NO}_2(g) + \Delta G^\circ \text{N}_2\text{O}(g)]$

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

- (c) $\Delta G^\circ = 4\Delta G^\circ \text{FeCl}_3(s) + 3\Delta G^\circ \text{O}_2(g) - [6\Delta G^\circ \text{Cl}_2(g) + 2\Delta G^\circ \text{Fe}_2\text{O}_3(s)]$

$$= 4(-334) + 3(0) - [6(0) + 2(-740.98)] = +146 \text{ kJ, nonspontaneous}$$

- (d) $\Delta G^\circ = \Delta G^\circ \text{S}(s) + 2\Delta G^\circ \text{H}_2\text{O}(g) - [\Delta G^\circ \text{SO}_2(g) + 2\Delta G^\circ \text{H}_2(g)]$

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

- 19.62 (a) $\Delta G^\circ = 2\Delta G^\circ \text{AgCl}(s) - [2\Delta G^\circ \text{Ag}(s) + \Delta G^\circ \text{Cl}_2(g)]$

$$= 2(-109.7) - 2(0) - 0 = -219.4 \text{ kJ, spontaneous}$$

- (b) There is no thermodynamic data in Appendix C for $\text{P}_4\text{O}_6(s)$; we will substitute $\text{P}_4\text{O}_{10}(s)$. $\text{P}_4\text{O}_{10}(s) + 16\text{H}_2(g) \rightarrow 4\text{PH}_3(g) + 10\text{H}_2\text{O}(g)$

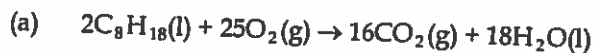
$$\Delta G^\circ = 4\Delta G^\circ \text{PH}_3(g) + 10\Delta G^\circ \text{H}_2\text{O}(g) - [\Delta G^\circ \text{P}_4\text{O}_{10}(s) + 16\Delta G^\circ \text{H}_2(g)]$$

$$= 4(13.4) + 10(-228.57) - [-2675.2] - 16(0) = 443.1 \text{ kJ, nonspontaneous}$$

$$\begin{aligned} \text{(c)} \quad \Delta G^\circ &= \Delta G^\circ \text{CF}_4(\text{g}) + 4\Delta G^\circ \text{HF}(\text{g}) - [\Delta G^\circ \text{CH}_4(\text{g}) + 4\Delta G^\circ \text{F}_2(\text{g})] \\ &= -635.1 + 4(-270.70) - (-50.8) - 4(0) = -1667.1 \text{ kJ, spontaneous} \end{aligned}$$

$$\begin{aligned} \text{(d)} \quad \Delta G^\circ &= 2\Delta G^\circ \text{H}_2\text{O}(\text{l}) + \Delta G^\circ \text{O}_2(\text{g}) - 2\Delta G^\circ \text{H}_2\text{O}_2(\text{l}) \\ &= 2(-237.13) + 0 - 2(-120.4) = -233.5 \text{ kJ, spontaneous} \end{aligned}$$

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



(b) Because there are more moles of gas in the reactants, ΔS° is negative, which makes $-\Delta S$ positive. ΔG° is less negative than ΔH° . (This argument is true for the reaction as written. If the products are all in the gas phase, there are more moles of gas in the products and ΔG° is more negative than ΔH° .)

19.64 (a) ΔG° should be less negative than ΔH° . Products contain fewer moles of gas, so ΔS° is negative. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$; $-T\Delta S^\circ$ is positive so ΔG° is less negative than ΔH° .

(b) We can estimate ΔS° using a similar reaction and then use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ (estimate) to get a ballpark figure. There are no sulfite salts listed in Appendix C, so use a reaction such as $\text{CO}_2(\text{g}) + \text{CaO}(\text{s}) \rightarrow \text{CaCO}_3(\text{s})$ or $\text{CO}_2(\text{g}) + \text{BaO}(\text{s}) \rightarrow \text{BaCO}_3(\text{s})$. Or calculate both ΔS° values and use the average as your estimate.

19.65 *Analyze/Plan.* Based on the signs of ΔH and ΔS for a particular reaction, assign a category from Table 19.3 to each reaction. *Solve.*

(a) ΔG 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) ΔG is positive at all temperatures. The reaction is nonspontaneous in the forward direction at all temperatures.

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

$$19.66 \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\text{(a)} \quad \Delta G^\circ = -844 \text{ kJ} - 298 \text{ K}(-0.165 \text{ kJ/K}) = -795 \text{ kJ, spontaneous}$$

$$\text{(b)} \quad \Delta G^\circ = +572 \text{ kJ} - 298 \text{ K}(0.179 \text{ kJ/K}) = +519 \text{ kJ, nonspontaneous}$$

To be spontaneous, ΔG must be negative ($\Delta G < 0$).

$$\text{Thus, } \Delta H^\circ - T\Delta S^\circ < 0; \Delta H^\circ < T\Delta S^\circ; T > \Delta H^\circ / \Delta S^\circ; T > \frac{572 \text{ kJ}}{0.179 \text{ kJ/K}} = 3.20 \times 10^3 \text{ K}$$

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

$$\text{At } 390 \text{ K, } \Delta G < 0; \Delta G = \Delta H - T\Delta S < 0$$

$$23.7 \text{ kJ} - 390 \text{ K}(\Delta S) < 0; 23.7 \text{ kJ} < 390 \text{ K}(\Delta S); \Delta S > 23.7 \text{ kJ}/390 \text{ K}$$

$$\Delta S > 0.06077 \text{ kJ/K or } \Delta S > 60.8 \text{ J/K}$$

19.68 At 45°C or 318 K, $\Delta G > 0$. $\Delta G = \Delta H - T\Delta S > 0$

$$\Delta H - 318 \text{ K} (72 \text{ J/K}) > 0; \Delta H > +2.3 \times 10^4 \text{ J}; \Delta H > +23 \text{ kJ}$$

19.69 *Analyze/Plan.* Use Equation [19.11] to calculate T when $\Delta G = 0$. This is similar to calculating the temperature of a phase transition in Sample Exercise 19.10. Use Table 19.3 to determine whether the reaction is spontaneous or non-spontaneous above this temperature. *Solve.*

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

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

(b) Nonspontaneous. The sign of ΔS is negative, so as T increases, ΔG becomes more positive.

19.70 ΔG is negative when $T\Delta S > \Delta H$ or $T > \Delta H/\Delta S$.

$$\Delta H^\circ = \Delta H^\circ \text{CH}_3\text{OH} + \Delta H^\circ \text{CO(g)} - \Delta H^\circ \text{CH}_3\text{COOH(l)}$$

$$= -201.2 - 110.5 - (-487.0) = 175.3 \text{ kJ}$$

$$\Delta S^\circ = S^\circ \text{CH}_3\text{OH} + S^\circ \text{CO(g)} - S^\circ \text{CH}_3\text{COOH(l)} = 237.6 + 197.9 - 159.8 = 275.7 \text{ J/K}$$

$$T > \frac{175.3 \text{ kJ}}{0.2757 \text{ kJ/K}} = 635.8 \text{ K}$$

The reaction is spontaneous above 635.8 K (363°C)

19.71 *Analyze/Plan.* Given a chemical equation and thermodynamic data (values of ΔH_f° , ΔG_f° 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 $T\Delta S^\circ$.

$$\begin{aligned} \Delta H^\circ &= 3\Delta H^\circ \text{NO(g)} - \Delta H^\circ \text{NO}_2\text{(g)} - \Delta H^\circ \text{N}_2\text{O(g)} \\ &= 3(90.37) - 33.84 - 81.6 = 155.7 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= 3S^\circ \text{NO(g)} - S^\circ \text{NO}_2\text{(g)} - S^\circ \text{N}_2\text{O(g)} \\ &= 3(210.62) - 240.45 - 220.0 = 171.4 \text{ J/K} \end{aligned}$$

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Since ΔS° is positive, $-T\Delta S^\circ$ becomes more negative as T increases and ΔG° becomes more negative.

(b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 155.7 \text{ kJ} - (800 \text{ K})(0.1714 \text{ kJ/K})$

$$\Delta G^\circ = 155.7 \text{ kJ} - 137 \text{ kJ} = 19 \text{ kJ}$$

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

(c) $\Delta G^\circ = 155.7 \text{ kJ} - (1000 \text{ K})(0.1714 \text{ kJ/K}) = 155.7 \text{ kJ} - 171.4 \text{ kJ} = -15.7 \text{ kJ}$

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

$$19.72 \quad (a) \quad \Delta H^\circ = \Delta H_f^\circ \text{CH}_3\text{OH}(g) - \Delta H_f^\circ \text{CH}_4(g) - 1/2 \Delta H_f^\circ \text{O}_2(g)$$

$$= -201.2 - (-74.8) - (1/2)(0) = -126.4 \text{ kJ}$$

$$\Delta S^\circ = S^\circ \text{CH}_3\text{OH}(g) - S^\circ \text{CH}_4(g) - 1/2 S^\circ \text{O}_2(g)$$

$$= 237.6 - 186.3 - 1/2(205.0) = -51.2 \text{ J/K} = -0.0512 \text{ kJ/K}$$

(b) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. $-T\Delta S^\circ$ is positive, so ΔG° becomes more positive as temperature increases.

$$(c) \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -126.4 \text{ kJ} - 298 \text{ K}(-0.0512 \text{ kJ/K}) = -111.1 \text{ kJ}$$

The reaction is spontaneous at 298 K because ΔG° is negative at this temperature. In this case, ΔG° could have been calculated from ΔG_f° values in Appendix C, since these values are tabulated at 298 K.

(d) The reaction is at equilibrium when $\Delta G^\circ = 0$.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 0. \quad \Delta H^\circ = T\Delta S^\circ, \quad T = \Delta H^\circ / \Delta S^\circ$$

$$T = -126.4 \text{ kJ} / -0.0512 \text{ kJ/K} = 2469 = 2470 \text{ K.}$$

This temperature is so high that the reactants and products are likely to decompose. At standard conditions, equilibrium is functionally unattainable for this reaction.

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

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

$$\Delta H_{\text{vap}}^\circ = \Delta H^\circ \text{C}_6\text{H}_6(g) - \Delta H^\circ \text{C}_6\text{H}_6(l) = 82.9 - 49.0 = 33.9 \text{ kJ}$$

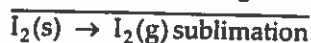
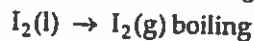
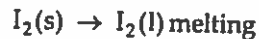
$$\Delta S_{\text{vap}}^\circ = S^\circ \text{C}_6\text{H}_6(g) - S^\circ \text{C}_6\text{H}_6(l) = 269.2 - 172.8 = 96.4 \text{ J/K}$$

$$T_b = 33.9 \times 10^3 \text{ J} / 96.4 \text{ J/K} = 351.66 = 352 \text{ K} = 79^\circ\text{C}$$

(b) From the *Handbook of Chemistry and Physics*, 74th Edition, $T_b = 80.1^\circ\text{C}$. The values are remarkably close; the small difference is due to deviation from ideal behavior by $\text{C}_6\text{H}_6(g)$ and experimental uncertainty in the boiling point measurement and the thermodynamic data.

$$19.74 \quad (a) \quad \text{As in Sample Exercise 19.10, } T_{\text{sub}} = \Delta H_{\text{sub}}^\circ / \Delta S_{\text{sub}}^\circ$$

Use Data from Appendix C to calculate $\Delta H_{\text{sub}}^\circ$ and $\Delta S_{\text{sub}}^\circ$ for $\text{I}_2(s)$.



$$\Delta H_{\text{sub}}^\circ = \Delta H_f^\circ \text{I}_2(g) - \Delta H_f^\circ \text{I}_2(s) = 62.25 - 0 = 62.25 \text{ kJ}$$

$$\Delta S_{\text{sub}}^\circ = S^\circ \text{I}_2(g) - S^\circ \text{I}_2(s) = 260.57 - 116.73 = 143.84 \text{ J/K} = 0.14384 \text{ kJ/K}$$

$$T_{\text{sub}} = \frac{\Delta H_{\text{sub}}^\circ}{\Delta S_{\text{sub}}^\circ} = \frac{62.25 \text{ kJ}}{0.14384 \text{ kJ/K}} = 432.8 \text{ K} = 159.6^\circ\text{C}$$

In making this estimate, we assume that at equilibrium, both $\text{I}_2(s)$ and $\text{I}_2(g)$ are present in their standard state of pure solid and vapor at 1 atm and consequently,

$\Delta G_{\text{sub}} = \Delta G_{\text{sub}}^{\circ} = 0$. We also assume that the values of $\Delta H_{\text{sub}}^{\circ}$ and $\Delta S_{\text{sub}}^{\circ}$ are the same at 298 K and at the sublimation temperature.

- (b) T_m for $\text{I}_2(\text{s}) = 386.85 \text{ K} = 113.7^{\circ}\text{C}$; $T_b = 457.4 \text{ K} = 184.3^{\circ}\text{C}$
(from WebElementsTM, 2005)
- (c) The boiling point of I_2 is closer to the sublimation temperature. Both boiling and sublimation begin with molecules in a condensed phase (little space between molecules) and end in the gas phase (large intermolecular distances). Separation of the molecules is the main phenomenon that determines both ΔH and ΔS , so it is not surprising that the ratio of $\Delta H/\Delta S$ is similar for sublimation and boiling.

19.75 *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 [19.18]), which can be calculated from data in Appendix C and Equation [19.14]. *Solve.*

- (a) $\text{C}_2\text{H}_2(\text{g}) + 5/2 \text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$
- (b) $\Delta H^{\circ} = 2\Delta H_f^{\circ} \text{CO}_2(\text{g}) + \Delta H_f^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H_f^{\circ} \text{C}_2\text{H}_2(\text{g}) - 5/2\Delta H_f^{\circ} \text{O}_2(\text{g})$
 $= 2(-393.5) - 285.83 - 226.77 - 5/2(0)$
 $= -1299.6 \text{ kJ produced/mol C}_2\text{H}_2 \text{ burned}$
- (c) $w_{\text{max}} = \Delta G^{\circ} = 2\Delta G_f^{\circ} \text{CO}_2(\text{g}) + \Delta G_f^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta G_f^{\circ} \text{C}_2\text{H}_2(\text{g}) - 5/2 \Delta G_f^{\circ} \text{O}_2(\text{g})$
 $= 2(-394.4) - 237.13 - 209.2 - 5/2(0) = -1235.1 \text{ kJ}$

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.

- 19.76 (a) $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
 $\Delta H^{\circ} = \Delta H_f^{\circ} \text{CO}_2(\text{g}) + 2\Delta H_f^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H_f^{\circ} \text{CH}_4(\text{g}) - 2\Delta H_f^{\circ} \text{O}_2(\text{g})$
 $= (-393.5) + 2(-285.83) - (-74.8) - 2(0) = -890.4 \text{ kJ/mol CH}_4 \text{ burned}$
- (b) $w_{\text{max}} = \Delta G^{\circ} = \Delta G_f^{\circ} \text{CO}_2(\text{g}) + 2\Delta G_f^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta G_f^{\circ} \text{CH}_4(\text{g}) - 2\Delta G_f^{\circ} \text{O}_2(\text{g})$
 $= (-394.4) + 2(-237.13) - (-50.8) - 2(0) = -817.9 \text{ kJ}$

The system can accomplish at most 817.86 kJ of work per mole of CH_4 on the surroundings.

Free Energy and Equilibrium (section 19.6)

19.77 *Analyze/Plan.* We are given a chemical reaction and asked to predict the effect of the partial pressure of $\text{O}_2(\text{g})$ on the value of ΔG for the system. Consider the relationship $\Delta G = \Delta G^{\circ} + RT \ln Q$ where Q is the reaction quotient. *Solve.*

- (a) $\text{O}_2(\text{g})$ appears in the denominator of Q for this reaction. An increase in pressure of O_2 decreases Q and ΔG becomes smaller or more negative. Increasing the concentration or partial pressure 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 ΔG becomes more positive. Increasing the concentration or partial pressure 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 ΔG 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 ΔG for this reaction. Increasing the concentration or partial pressure of a product decreases the tendency for the reaction to occur.

19.78 Consider the relationship $\Delta G = \Delta G^\circ + RT \ln Q$, where Q is the reaction quotient.

- (a) $H_2(g)$ appears in the denominator of Q for this reaction. An increase in pressure of H_2 decreases Q and ΔG becomes smaller or more negative. Increasing the concentration or partial pressure of a reactant increases the tendency for a reaction to occur.
- (b) $H_2(g)$ appears in the numerator of Q for this reaction. Increasing the pressure of H_2 increases Q and ΔG becomes more positive. Increasing the concentration or partial pressure of a product decreases the tendency for the reaction to occur.
- (c) $H_2(g)$ appears in the denominator of Q for this reaction. An increase in pressure of H_2 decreases Q and ΔG becomes smaller or more negative. Increasing the concentration or partial pressure of a reactant increases the tendency for a reaction to occur.

19.79 *Analyze/Plan.* Given a chemical reaction, we are asked to calculate ΔG° from Appendix C data, and ΔG for a given set of initial conditions. Use Equation [19.14] to calculate ΔG° , and Equation [19.19] to calculate ΔG . Follow the logic in Sample Exercise 19.11 when calculating ΔG . *Solve.*

$$(a) \quad \Delta G^\circ = \Delta G^\circ N_2O_4(g) - 2\Delta G^\circ NO_2(g) = 98.28 - 2(51.84) = -5.40 \text{ kJ}$$

$$(b) \quad \Delta G = \Delta G^\circ + RT \ln P_{N_2O_4} / P_{NO_2}^2 \\ = -5.40 \text{ kJ} + \frac{8.314 \times 10^{-3} \text{ kJ}}{\text{mol} \cdot \text{K}} \times 298 \text{ K} \times \ln[1.60/(0.40)^2] = 0.3048 = 0.30 \text{ kJ}$$

$$19.80 \quad (a) \quad \Delta G^\circ = \Delta G^\circ C_3H_8(g) + 2\Delta G^\circ H_2(g) - 3\Delta G^\circ CH_4(g) \\ = -23.47 + 2(0) - 3(-50.8) = 128.9 \text{ kJ}$$

$$(b) \quad \Delta G = \Delta G^\circ + RT \ln [P_{C_3H_8} \times P_{H_2}^2 / P_{CH_4}^3] \\ = 128.9 + \frac{8.314 \times 10^{-3} \text{ kJ}}{\text{mol} \cdot \text{K}} \times 298 \text{ K} \times \ln[(0.0100) \times (0.0180)^2 / (40.0)^3] \\ = 128.9 - 58.735 = 70.165 = 70.2 \text{ kJ}$$

19.81 *Analyze/Plan.* Given a chemical reaction, we are asked to calculate K using ΔG_r° data from Appendix C. Calculate ΔG° using Equation [19.14]. Then $\Delta G^\circ = -RT \ln K$, Equation [19.20]; $\ln K = -\Delta G^\circ / RT$ *Solve.*

$$(a) \quad \Delta G^\circ = 2\Delta G^\circ HI(g) - \Delta G^\circ H_2(g) - \Delta G^\circ I_2(g) \\ = 2(1.30) - 0 - 19.37 = -16.77 \text{ kJ}$$

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

$$\begin{aligned} \text{(b)} \quad \Delta G^\circ &= \Delta G^\circ \text{C}_2\text{H}_4(\text{g}) + \Delta G^\circ \text{H}_2\text{O}(\text{g}) - \Delta G^\circ \text{C}_2\text{H}_5\text{OH}(\text{g}) \\ &= 68.11 - 228.57 - (-168.5) = 8.04 = 8.0 \text{ kJ} \end{aligned}$$

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

$$\text{(c)} \quad \Delta G^\circ = \Delta G^\circ \text{C}_6\text{H}_6(\text{g}) - 3\Delta G^\circ \text{C}_2\text{H}_2(\text{g}) = 129.7 - 3(209.2) = -497.9 \text{ kJ}$$

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

19.82

$$\Delta G^\circ = -RT \ln K; \quad \ln K = -\Delta G^\circ / RT; \quad \text{at } 298 \text{ K, } RT = 2.4776 = 2.478 \text{ kJ}$$

$$\begin{aligned} \text{(a)} \quad \Delta G^\circ &= \Delta G^\circ \text{NaOH}(\text{s}) + \Delta G^\circ \text{CO}_2(\text{g}) - \Delta G^\circ \text{NaHCO}_3(\text{s}) \\ &= -379.5 + (-394.4) - (-851.8) = +77.9 \text{ kJ} \end{aligned}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-77.9 \text{ kJ}}{2.478 \text{ kJ}} = -31.442 = -31.4; \quad K = 2 \times 10^{-14}$$

$$K = P_{\text{CO}_2} = 2 \times 10^{-14}$$

$$\begin{aligned} \text{(b)} \quad \Delta G^\circ &= 2\Delta G^\circ \text{HCl}(\text{g}) + \Delta G^\circ \text{Br}_2(\text{g}) - 2\Delta G^\circ \text{HBr}(\text{g}) - \Delta G^\circ \text{Cl}_2(\text{g}) \\ &= 2(-95.27) + 3.14 - 2(-53.22) - 0 = -80.96 \text{ kJ} \end{aligned}$$

$$\ln K = \frac{-(-80.96)}{2.4776} = +32.68; \quad K = 1.6 \times 10^{14}$$

$$K = \frac{P_{\text{HCl}}^2 \times P_{\text{Br}_2}}{P_{\text{HBr}}^2 \times P_{\text{Cl}_2}} = 1.6 \times 10^{14}$$

$$\text{(c)} \quad \text{From Solution 19.61(a), } \Delta G^\circ \text{ at } 298 \text{ K} = -140.0 \text{ kJ.}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-140.0)}{2.4776} = 56.51; \quad K = 3.5 \times 10^{24}$$

$$K = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} = 3.5 \times 10^{24}$$

19.83

Analyze/Plan. Given a chemical reaction and thermodynamic data in Appendix C, calculate the equilibrium pressure of $\text{CO}_2(\text{g})$ at two temperatures. $K = P_{\text{CO}_2}$. Calculate ΔG° at the two temperatures using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and then calculate K and P_{CO_2} .
Solve.

$$\begin{aligned} \Delta H^\circ &= \Delta H^\circ \text{BaO}(\text{s}) + \Delta H^\circ \text{CO}_2(\text{g}) - \Delta H^\circ \text{BaCO}_3(\text{s}) \\ &= -553.5 + -393.5 - (-1216.3) = +269.3 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= S^\circ \text{BaO}(\text{s}) + S^\circ \text{CO}_2(\text{g}) - S^\circ \text{BaCO}_3(\text{s}) \\ &= 70.42 + 213.6 - 112.1 = 171.92 \text{ J/K} = 0.1719 \text{ kJ/K} \end{aligned}$$

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

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-218.07 \times 10^3 \text{ J}}{8.314 \text{ J/K} \times 298 \text{ K}} = -88.017 = -88.02$$

$$K = 6.0 \times 10^{-39}; \quad P_{\text{CO}_2} = 6.0 \times 10^{-39} \text{ atm}$$

$$(b) \quad \Delta G \text{ at } 1100 \text{ K} = 269.3 \text{ kJ} - 1100 \text{ K} (0.17192 \text{ kJ/K}) = 80.19 = +80.2 \text{ kJ}$$

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

$$K = 1.6 \times 10^{-4}; \quad P_{\text{CO}_2} = 1.6 \times 10^{-4} \text{ atm}$$

19.84 $K = P_{\text{CO}_2}$. Calculate ΔG° at the two temperatures using $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and then calculate K and P_{CO_2} .

$$\begin{aligned} \Delta H^\circ &= \Delta H^\circ \text{ PbO(s)} + \Delta H^\circ \text{ CO}_2\text{(g)} - \Delta H^\circ \text{ PbCO}_3\text{(s)} \\ &= -217.3 - 393.5 + 699.1 = 88.3 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ &= S^\circ \text{ PbO(s)} + S^\circ \text{ CO}_2\text{(g)} - S^\circ \text{ PbCO}_3\text{(s)} \\ &= 68.70 + 213.6 - 131.0 = 151.3 \text{ J/K or } 0.1513 \text{ kJ/K} \end{aligned}$$

$$\begin{aligned} (a) \quad \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ. \text{ At } 673 \text{ K}, \Delta G^\circ = 88.3 \text{ kJ} - 673 \text{ K}(0.1513 \text{ kJ/K}) = -13.525 \\ &= -13.5 \text{ kJ} \end{aligned}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-13.525 \times 10^3 \text{ J})}{8.314 \text{ J/K} \times 673 \text{ K}} = 2.4172 = 2.42$$

$$K = P_{\text{CO}_2} = 11.214 = 11 \text{ atm}$$

$$\begin{aligned} (b) \quad \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ. \text{ At } 453 \text{ K}, \Delta G^\circ = 88.3 \text{ kJ} - 453 \text{ K} (0.1513 \text{ kJ/K}) = 19.7611 \\ &= 19.8 \text{ kJ} \end{aligned}$$

$$\ln K = \frac{-(19.7611 \times 10^3 \text{ J})}{8.314 \text{ J/K} \times 453 \text{ K}} = -5.2469 = -5.25; \quad K = P_{\text{CO}_2} = 5.3 \times 10^{-3} \text{ atm}$$

19.85 *Analyze/Plan.* Given an acid dissociation equilibrium and the corresponding K_a value, calculate ΔG° and ΔG for a given set of concentrations. Use Equation [19.20] to calculate ΔG° and Equation [19.19] to calculate ΔG . *Solve.*

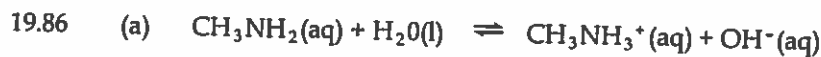


$$(b) \quad \Delta G^\circ = -RT \ln K_a = -(8.314 \times 10^{-3})(298) \ln (4.5 \times 10^{-4}) = 19.0928 = 19.1 \text{ kJ}$$

$$(c) \quad \Delta G = 0 \text{ at equilibrium}$$

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

$$= 19.09 \text{ kJ} + (8.314 \times 10^{-3})(298) \ln \frac{(5.0 \times 10^{-2})(6.0 \times 10^{-4})}{0.20} = -2.725 = -2.7 \text{ kJ}$$



$$(b) \quad \Delta G^\circ = -RT \ln K_b = -(8.314 \times 10^{-3})(298) \ln (4.4 \times 10^{-4}) = 19.148 = 19.1 \text{ kJ}$$

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

(d) $\Delta G = \Delta G^\circ + RT \ln Q$; $[\text{OH}^-] = 1 \times 10^{-14} / 6.7 \times 10^{-9} = 1.4925 \times 10^{-6} = 1.5 \times 10^{-6}$

$$= 19.148 + (8.314 \times 10^{-3})(298) \ln \frac{(2.4 \times 10^{-3})(1.4925 \times 10^{-6})}{0.098} = -23.28 = -23.3 \text{ kJ}$$

Additional Exercises

19.87 (a) The thermodynamic quantities T , E , and S are state functions. T is directly related to the distribution of molecular speeds, which does not depend on the path from one state to another.

(b) The quantities q and w do depend on the path taken from one state to another.

(c) There is only one *reversible* path between states.

(d) Isothermal processes occur at constant T . Since the process is reversible, q is q_{rev} and w is w_{max} .

$$\Delta E = q_{\text{rev}} + w_{\text{max}} \quad \Delta S = \frac{q_{\text{rev}}}{T}$$

19.88 (a) False. The essential question is whether the reaction proceeds far to the right before arriving at equilibrium. The position of equilibrium, which is the essential aspect, is not only dependent on ΔH but on the entropy change as well.

(b) True.

(c) True.

(d) False. Nonspontaneous processes in general require that work be done to force them to proceed. Spontaneous processes occur without application of work.

(e) False. Such a process might be spontaneous, but would not necessarily be so. Spontaneous processes are those that are exothermic and/or that lead to increased disorder in the system.

19.89	Process	ΔH	ΔS
	(a)	+	+
	(b)	-	-
	(c)	+	+
	(d)	+	+
	(e)	-	+

19.90 There is no inconsistency. The second law states that in any spontaneous process there is an increase in the entropy of the universe. While there may be a decrease in entropy of the system, as in the present case, this decrease is more than offset by an increase in entropy of the surroundings.

19.91 (a) Each of the 4 molecules can be in either the left or the right bulb. Thus, there are $(2)^4 = 16$ arrangements.

(b) Only one arrangement has all 4 molecules in the left flask.

- (c) The gas will spontaneously adopt the state with maximum disorder, the state with the most possible arrangements for the molecules.
- 19.92 (a) Microstates are possible arrangements for the system. For each die, there are six possibilities for the top face, resulting in $(6)(6) = 36$ possible arrangements or microstates. (The face that appears on top of one die is not related to or determined by the face on top of the other die.) The two arrangements of top faces shown in the exercise are two of the 36 possible microstates.
- (b) The left pair of dice belongs to state III; the right pair belongs to state VII.
- (c) There are eleven possible states (II through XII; I is not a possibility)
- (d) The state with the most microstates has the highest entropy. State VII has six microstates and the highest entropy. The microstates are (1+6), (2+5), (3+4), (4+3), (5+2) and (6+1). States VI and VIII, on either side of VII, have five microstates. Moving farther away from VII, the number of microstates decreases until we reach the two extremes, II and XII, which each have one microstate.
- (e) States II and XII, with one microstate each, have the lowest entropy.
- 19.93 If $\text{NH}_4\text{NO}_3(\text{s})$ dissolves spontaneously in water, $\Delta G = \Delta H - T\Delta S$. If ΔG is negative and ΔH is positive, the sign of ΔS must be positive. Furthermore, $T\Delta S > \Delta H$ at room temperature.
- 19.94 (a) The sign of q for expansion is (+). Vaporization is an endothermic process; the enthalpy of the system increases and q is positive. Our system is the refrigerant. Because the expansion does not occur at constant pressure, q is not exactly equal to ΔH , but its sign is positive.
- (b) The sign of q for compression is (-). Compression is the reverse of expansion, and it has the opposite sign.
- (c) The expansion chamber is inside the house and the compression chamber is outside. During expansion, q_{sys} increases and q_{sur} decreases. The air surrounding the expansion chamber is cooled, and then distributed throughout the house to cool it. If expansion occurred outside, the cool air would be wasted. Compression releases heat to the surroundings; it occurs outside so that the released heat can be dissipated by the outside air.
- (d) No. Heat can flow reversibly between a system and its surroundings only if the two have an infinitesimally small difference in temperature and the amount of heat transferred is infinitesimally small. There is no mechanism in our system to regulate the amount of heat transferred. When the liquid flows into the low pressure chamber, all of the liquid vaporizes, not an infinitesimally small amount.
- (e) A spontaneous process occurs without outside intervention. In an air conditioner, expansion (vaporization) of the refrigerant is spontaneous, but compression (condensation) to the liquid state is nonspontaneous. Cooling the house from 31°C to 24°C is nonspontaneous. [Note that all spontaneous processes are irreversible, but not all irreversible processes are spontaneous.]

19.95 At the normal boiling point of a liquid, $\Delta G = 0$ and $\Delta H_{\text{vap}} = T\Delta S_{\text{vap}}$; $T = \Delta H_{\text{vap}}/\Delta S_{\text{vap}}$. By Trouton's rule, $\Delta S_{\text{vap}} = 88 \text{ J/mol}\cdot\text{K}$. The process of vaporization is:

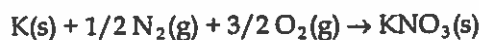
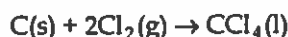
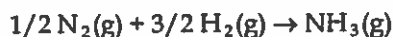


$$\Delta H_{\text{vap}} = \Delta H_f^\circ \text{Br}_2(\text{g}) - \Delta H_f^\circ \text{Br}_2(\text{l}) = 30.71 \text{ kJ} - 0 = 30.71 \text{ kJ}$$

$$T_b = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} = \frac{30.71 \text{ kJ}}{88 \text{ J/mol}\cdot\text{K}} \times \frac{1000 \text{ J}}{\text{kJ}} = 349 = 3.5 \times 10^2 \text{ K}$$

(b) According to WebElements™ 2005, the normal boiling point of $\text{Br}_2(\text{l})$ is 332 K. Trouton's rule provides a good "ballpark" estimate.

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



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



In this reaction, there are more moles of gas in products, ΔS_f° is positive, $-T\Delta S_f^\circ$ is negative and ΔG_f° is more negative than ΔH_f° .



$$\Delta H^\circ = \Delta H^\circ \text{TiCl}_4(\text{g}) - \Delta H^\circ \text{Ti}(\text{s}) - 2\Delta H^\circ \text{Cl}_2(\text{g})$$

$$= -763.2 - 0 - 2(0) = -763.2 \text{ kJ}$$

$$\Delta S^\circ = 354.9 - 30.76 - 2(222.96) = -121.78 = -121.8 \text{ J/K}$$

$$\Delta G^\circ = -726.8 - 0 - 2(0) = -726.8 \text{ kJ}$$



$$\Delta H^\circ = 2\Delta H^\circ \text{CCl}_4(\text{g}) + 6\Delta H^\circ \text{HCl}(\text{g}) - \Delta H^\circ \text{C}_2\text{H}_6(\text{g}) - 7\Delta H^\circ \text{Cl}_2(\text{g})$$

$$= 2(-106.7) + 6(-92.30) - (-84.68) - 7(0) = -682.52 = -682.5 \text{ kJ}$$

$$\Delta S^\circ = 2(309.4) + 6(186.69) - 229.5 - 7(222.96) = -51.28 = -51.4 \text{ J/K}$$

$$\Delta G^\circ = 2(-64.0) + 6(-95.27) - (-32.89) - 7(0) = -666.73 \text{ kJ}$$



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

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

$$\Delta S^\circ = 112.1 - 70.42 - 213.6 = -171.9 \text{ J/K}$$

$$\Delta G^\circ = -1137.6 - (-525.1) - (-394.4) = -218.1 \text{ kJ}$$

- (b) (i), (ii) and (iii) all have negative ΔG° values and are spontaneous at standard conditions and 25°C.
- (c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. All three reactions have negative ΔH° and $-\Delta S^\circ$. They all have negative ΔG° at 25°C, and ΔG° becomes more positive as T increases.

$$19.98 \quad \Delta G = \Delta G^\circ + RT \ln Q$$

$$(a) \quad Q = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3} = \frac{(1.2)^2}{(2.6)(5.9)^3} = 2.697 \times 10^{-3} = 2.7 \times 10^{-3}$$

$$\begin{aligned} \Delta G^\circ &= 2\Delta G^\circ \text{NH}_3(\text{g}) - \Delta G^\circ \text{N}_2(\text{g}) - 3\Delta G^\circ \text{H}_2(\text{g}) \\ &= 2(-16.66) - 0 - 3(0) = -33.32 \text{ kJ} \end{aligned}$$

$$\Delta G = -33.32 \text{ kJ} + \frac{8.314 \times 10^{-3} \text{ kJ}}{\text{mol-K}} \times 298 \text{ K} \times \ln(2.69 \times 10^{-3})$$

$$\Delta G = -33.32 - 14.66 = -47.98 = -48.0 \text{ kJ}$$

$$(b) \quad Q = \frac{P_{\text{N}_2}^3 \times P_{\text{H}_2\text{O}}^4}{P_{\text{N}_2\text{H}_4}^2 \times P_{\text{NO}_2}^2} = \frac{(0.5)^3(0.3)^4}{(5.0 \times 10^{-2})^2(5.0 \times 10^{-2})^2} = 162 = 2 \times 10^2$$

$$\begin{aligned} \Delta G^\circ &= 3\Delta G^\circ \text{N}_2(\text{g}) + 4\Delta G^\circ \text{H}_2\text{O}(\text{g}) - 2\Delta G^\circ \text{N}_2\text{H}_4(\text{g}) - 2\Delta G^\circ \text{NO}_2(\text{g}) \\ &= 3(0) + 4(-228.57) - 2(159.4) - 2(51.84) = -1336.8 \text{ kJ} \end{aligned}$$

$$\Delta G = -1336.8 \text{ kJ} + 2.478 \ln 162 = -1324.2 = -1.32 \times 10^3 \text{ kJ}$$

$$(c) \quad Q = \frac{P_{\text{N}_2} \times P_{\text{H}_2}^2}{P_{\text{N}_2\text{H}_4}} = \frac{(1.5)(2.5)^2}{0.5} = 18.75 = 2 \times 10^1$$

$$\begin{aligned} \Delta G^\circ &= \Delta G^\circ \text{N}_2(\text{g}) + 2\Delta G^\circ \text{H}_2(\text{g}) - \Delta G^\circ \text{N}_2\text{H}_4(\text{g}) \\ &= 0 + 2(0) - 159.4 = -159.4 \text{ kJ} \end{aligned}$$

$$\Delta G = -159.4 \text{ kJ} + 2.478 \ln 18.75 = -152.1 = -152 \text{ kJ}$$

19.99	Reaction	(a) Sign of ΔH°	(a) Sign of ΔS°	(b) $K > 1?$	(c) Variation in K as Temp. Increases
	(i)	-	-	yes	decrease
	(ii)	+	+	no	increase
	(iii)	+	+	no	increase
	(iv)	+	+	no	increase

- (a) Note that at a particular temperature, positive ΔH° leads to a smaller value of K, while positive ΔS° increases the value of K.

$$19.100 \quad (a) \quad K = \frac{\chi_{\text{CH}_3\text{COOH}}}{\chi_{\text{CH}_3\text{OH}} P_{\text{CO}}}$$

$$\Delta G^\circ = -RT \ln K; \ln K = -\Delta G^\circ/RT$$

$$\begin{aligned}\Delta G^\circ &= \Delta G^\circ \text{CH}_3\text{COOH(l)} - \Delta G^\circ \text{CH}_3\text{OH(l)} - \Delta G^\circ \text{CO(g)} \\ &= -392.4 - (-166.23) - (-137.2) = -89.0 \text{ kJ}\end{aligned}$$

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

$$\begin{aligned}\text{(b)} \quad \Delta H^\circ &= \Delta H^\circ \text{CH}_3\text{COOH(l)} - \Delta H^\circ \text{CH}_3\text{OH(l)} - \Delta H^\circ \text{CO(g)} \\ &= -487.0 - (-238.6) - (-110.5) = -137.9 \text{ kJ}\end{aligned}$$

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.

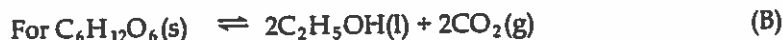
$$\begin{aligned}\text{(c)} \quad \Delta G^\circ &= -RT \ln K; K = 1, \ln K = 0, \Delta G^\circ = 0 \\ \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ; \text{ when } \Delta G^\circ = 0, \Delta H^\circ = T\Delta S^\circ \\ \Delta S^\circ &= S^\circ \text{CH}_3\text{COOH(l)} - S^\circ \text{CH}_3\text{OH(l)} - S^\circ \text{CO(g)} \\ &= 159.8 - 126.8 - 197.9 = -164.9 \text{ J/K} = -0.1649 \text{ kJ/K} \\ -137.9 \text{ kJ} &= T(-0.1649 \text{ kJ/K}), T = 836.3 \text{ K}\end{aligned}$$

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.

19.101 (a) First calculate ΔG° for each reaction:



$$\Delta G^\circ = 6(-237.13) + 6(-394.4) - (-910.4) + 6(0) = -2878.8 \text{ kJ}$$



$$\Delta G^\circ = 2(-394.4) + 2(-174.8) - (-910.4) = -228.0 \text{ kJ}$$

$$\text{For (A), } \ln K = 2879 \times 10^3 / (8.314)(298) = 1162; K = 5 \times 10^{504}$$

$$\text{For (B), } \ln K = 228 \times 10^3 / (8.314)(298) = 92.026 = 92.0; K = 9 \times 10^{39}$$

(b) Both these values for K are unimaginably large. However, K for reaction (A) is larger, because ΔG° is more negative. The magnitude of the work that can be accomplished by coupling a reaction to its surroundings is measured by ΔG . According to the calculations above, considerably more work can in principle be obtained from reaction (A), because ΔG° is more negative.

19.102 (a) $\Delta G^\circ = -RT \ln K$ (Equation [19.20]); $\ln K = -\Delta G^\circ / RT$

Use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ to get ΔG° at the two temperatures. Calculate ΔH° and ΔS° using data in Appendix C.



$$\begin{aligned}\Delta H^\circ &= \Delta H^\circ \text{C}_2\text{H}_6(\text{g}) + \Delta H^\circ \text{H}_2(\text{g}) - 2\Delta H^\circ \text{CH}_4(\text{g}) = -84.68 + 0 - 2(-74.8) = 64.92 \\ &= 64.9 \text{ kJ}\end{aligned}$$

$$\Delta S^\circ = S^\circ \text{C}_2\text{H}_6(\text{g}) + S^\circ \text{H}_2(\text{g}) - 2S^\circ \text{CH}_4(\text{g}) = 229.5 + 130.58 - 2(186.3) = -12.52$$

$$= -12.5 \text{ J/K}$$

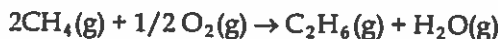
$$\text{at } 298 \text{ K, } \Delta G = 64.92 \text{ kJ} - 298 \text{ K}(-12.52 \times 10^{-3} \text{ kJ/K}) = 68.65 = 68.7 \text{ kJ}$$

$$\ln K = \frac{-68.65 \text{ kJ}}{(8.314 \times 10^{-3} \text{ kJ/K})(298 \text{ K})} = -27.709 = -27.7, K = 9.25 \times 10^{-13} = 9 \times 10^{-13}$$

$$\text{at } 773 \text{ K, } \Delta G = 64.9 \text{ kJ} - 773 \text{ K}(-12.52 \times 10^{-3} \text{ J/K}) = 74.598 = 74.6 \text{ kJ}$$

$$\ln K = \frac{-74.598 \text{ kJ}}{(8.314 \times 10^{-3} \text{ kJ/K})(773 \text{ K})} = -11.607 = -11.6, K = 9.1 \times 10^{-6}$$

Because the reaction is endothermic, the value of K increases with an increase in temperature.



$$\Delta H^\circ = \Delta H^\circ \text{C}_2\text{H}_6(\text{g}) + \Delta H^\circ \text{H}_2\text{O}(\text{g}) - 2\Delta H^\circ \text{CH}_4(\text{g}) - 1/2 \Delta H^\circ \text{O}_2(\text{g})$$

$$= -84.68 + (-241.82) - 2(-74.8) - 1/2(0) = -176.9 \text{ kJ}$$

$$\Delta S^\circ = S^\circ \text{C}_2\text{H}_6(\text{g}) + S^\circ \text{H}_2\text{O}(\text{g}) - 2S^\circ \text{CH}_4(\text{g}) - 1/2 S^\circ \text{O}_2(\text{g})$$

$$= 229.5 + 188.83 - 2(186.3) - 1/2(205.0) = -56.77 = -56.8 \text{ J/K}$$

$$\text{at } 298 \text{ K, } \Delta G = -176.9 \text{ kJ} - 298 \text{ K}(-56.77 \times 10^{-3} \text{ kJ/K}) = -159.98 = -160.0 \text{ kJ}$$

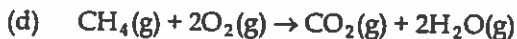
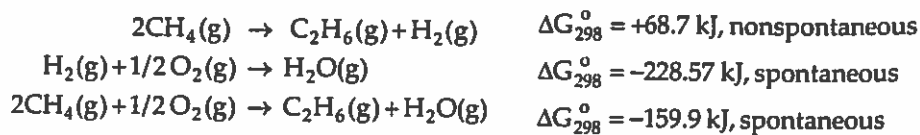
$$\ln K = \frac{-(-159.98 \text{ kJ})}{(8.314 \times 10^{-3} \text{ kJ/K})(298 \text{ K})} = 64.571 = 64.57; K = 1.1 \times 10^{28}$$

$$\text{at } 773 \text{ K, } \Delta G = -176.9 \text{ kJ} - 773 \text{ K}(-56.77 \times 10^{-3} \text{ kJ/K}) = -133.02 = -133.0 \text{ kJ}$$

$$\ln K = \frac{-(-133.02 \text{ kJ})}{(8.314 \times 10^{-3} \text{ kJ/K})(773 \text{ K})} = 20.698 = 20.70; K = 9.750 \times 10^8 = 9.8 \times 10^8$$

Because this reaction is exothermic, the value of K decreases with increasing temperature.

- (b) The difference in ΔG° for the two reactions is primarily enthalpic; the first reaction is endothermic and the second exothermic. Both reactions have $-\Delta S^\circ$, which inhibits spontaneity.
- (c) This is an example of coupling a useful but nonspontaneous reaction with a spontaneous one to spontaneously produce a desired product.



19.103 ΔG° for the metabolism of glucose is:

$$6\Delta G^\circ \text{CO}_2(\text{g}) + 6\Delta G^\circ \text{H}_2\text{O}(\text{l}) - \Delta G^\circ \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) - 6\Delta G^\circ \text{O}_2(\text{g})$$

$$\Delta G^\circ = 6(-394.4) + 6(-237.13) - (-910.4) + 6(0) = -2878.8 \text{ kJ}$$

$$\text{moles ATP} = -2878.8 \text{ kJ} \times 1 \text{ mol ATP} / (-30.5 \text{ kJ}) = 94.4 \text{ mol ATP} / \text{mol glucose}$$

Note that this calculation is done at standard conditions, not metabolic conditions. A more accurate answer would be obtained using ΔG values that reflect actual concentration, partial pressure, and pH in a cell.

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



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

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln \frac{[\text{K}^+ (\text{muscle})]}{[\text{K}^+ (\text{plasma})]} \\ &= 0 + (8.314)(310) \ln \frac{(0.15)}{(5.0 \times 10^{-3})} = 8766 \text{ J} = 8.8 \text{ kJ} \end{aligned}$$

- (b) Note that ΔG 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 ΔG . This value represents the minimum amount of work required to transfer one mole of K^+ ions from the blood plasma at $5 \times 10^{-3} \text{ M}$ to muscle cell fluids at 0.15 M , assuming constancy of concentrations. In practice, a larger than minimum amount of work is required.

- 19.105 (a) To obtain ΔH° from the equilibrium constant data, graph $\ln K$ at various temperatures vs $1/T$, being sure to employ absolute temperature. The slope of the linear relationship that should result is $-\Delta H^\circ/R$; thus, ΔH° is easily calculated.

- (b) Use $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ and $\Delta G^\circ = -RT \ln K$. Substituting the second expression into the first, we obtain

$$-RT \ln K = \Delta H^\circ - T\Delta S^\circ; \quad \ln K = \frac{-\Delta H^\circ}{RT} - \frac{-\Delta S^\circ}{R} = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

Thus, the constant in the equation given in the exercise is $\Delta S^\circ/R$.

- 19.106 $S = k \ln W$ (Equation [19.5]), $k = R/N$, $W \propto V^m$

$$\Delta S = S_2 - S_1; S_1 = k \ln W_1, S_2 = k \ln W_2$$

$$\Delta S = k \ln W_2 - k \ln W_1; W_2 = cV_2^m; W_1 = cV_1^m$$

(The number of particles, m , is the same in both states.)

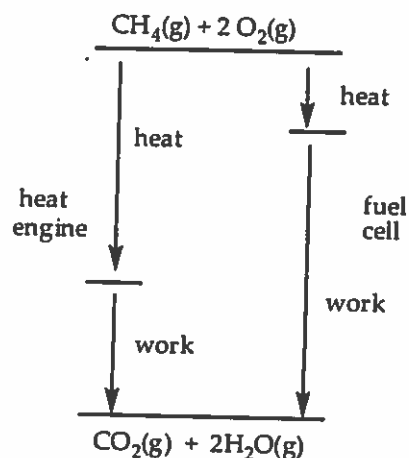
$$\Delta S = k \ln cV_2^m - k \ln cV_1^m; \ln a^b = b \ln a$$

$$\Delta S = k m \ln cV_2 - k m \ln cV_1; \ln a - \ln b = \ln (a/b)$$

$$\Delta S = k m \ln \left(\frac{cV_2}{cV_1} \right) = k m \ln \left(\frac{V_2}{V_1} \right) = \frac{R}{N} m \ln \left(\frac{V_2}{V_1} \right)$$

$$\frac{m}{N} = \frac{\text{particles}}{6.022 \times 10^{23}} = n(\text{mol}); \quad \Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

- 19.107 (a) $(T_{\text{high}} - T_{\text{low}})/T_{\text{high}} = (700 - 288)/700 = 0.58857 = 58.9\%$ efficiency
- (b) The cooler the exit temperature of the engine or generator, the more efficient the engine. If a body of water can be used to naturally reduce the exit temperature, the efficiency of energy production increases.
- (c) The closer the exit temperature to 0 K, the more efficient the heat engine.
- (d) (Refer to Figure 5.10)



Integrative Exercises

- 19.108 (a) At the boiling point, vaporization is a reversible process, so $\Delta S_{\text{vap}}^{\circ} = \Delta H_{\text{vap}}^{\circ} / T$.
- acetone: $\Delta S_{\text{vap}}^{\circ} = \Delta H_{\text{vap}}^{\circ} / T = (29.1 \text{ kJ/mol}) / 329.25 \text{ K} = 88.4 \text{ J/mol-K}$
- dimethyl ether: $\Delta S_{\text{vap}}^{\circ} = (21.5 \text{ kJ/mol}) / 248.35 \text{ K} = 86.6 \text{ J/mol-K}$
- ethanol: $\Delta S_{\text{vap}}^{\circ} = (38.6 \text{ kJ/mol}) / 351.6 \text{ K} = 110 \text{ J/mol-K}$
- octane: $\Delta S_{\text{vap}}^{\circ} = (34.4 \text{ kJ/mol}) / 398.75 \text{ K} = 86.3 \text{ J/mol-K}$
- pyridine: $\Delta S_{\text{vap}}^{\circ} = (35.1 \text{ kJ/mol}) / 388.45 \text{ K} = 90.4 \text{ J/mol-K}$
- (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, $\Delta H_{\text{vap}}^{\circ}$ at $100^{\circ}\text{C} = 40.67 \text{ kJ/mol}$.

$$\Delta S_{\text{vap}}^{\circ} = (40.67 \text{ kJ/mol}) / 373.15 \text{ K} = 109.0 \text{ J/mol-K}$$

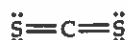
- (d) Use $\Delta S_{\text{vap}}^{\circ} = 88 \text{ J/mol-K}$, the middle of the range for Trouton's rule, to estimate $\Delta H_{\text{vap}}^{\circ}$ for chlorobenzene.

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

- 19.109 The activated complex in Figure 14.15 is a single "particle" or entity that contains four atoms. It is formed from an atom A and a triatomic molecule, ABC, that must collide with exactly the correct energy and orientation to form the single entity. There are many fewer degrees of freedom for the activated complex than the separate reactant particles, so the *entropy of activation* is negative.

- 19.110 (a) $\text{O}_2(\text{g}) \xrightarrow{h\nu} 2\text{O}(\text{g})$; S increases because there are more moles of gas in the products.
- (b) $\text{O}_2(\text{g}) + \text{O}(\text{g}) \rightarrow \text{O}_3(\text{g})$, 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) $\text{NaCl}(\text{aq}) \rightarrow \text{NaCl}(\text{s}) + \text{H}_2\text{O}(\text{l})$; ΔS decreases as the mixture (seawater, greater disorder) is separated into pure substances (fewer possible arrangements, more order).

- 19.111 (a) $16 e^-$, $8 e^-$ pairs. The C-S bond order is approximately 2.



- (b) $2 e^-$ domains around C, linear e^- domain geometry, linear molecular structure
- (c) $\text{CS}_2(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{SO}_2(\text{g})$
- (d) $\Delta H^{\circ} = \Delta H^{\circ} \text{CO}_2(\text{g}) + 2\Delta H^{\circ} \text{SO}_2(\text{g}) - \Delta H^{\circ} \text{CS}_2(\text{l}) - 3\Delta H^{\circ} \text{O}_2(\text{g})$

$$= -393.5 + 2(-296.9) - (89.7) - 3(0) = -1077.0 \text{ kJ}$$

$$\Delta G^{\circ} = \Delta G^{\circ} \text{CO}_2(\text{g}) + 2\Delta G^{\circ} \text{SO}_2(\text{g}) - \Delta G^{\circ} \text{CS}_2(\text{l}) - 3 \Delta G^{\circ} \text{O}_2(\text{g})$$

$$= -394.4 + 2(-300.4) - (65.3) - 3(0) = -1060.5 \text{ kJ}$$

The reaction is exothermic ($-\Delta H^{\circ}$) and spontaneous ($-\Delta G^{\circ}$) at 298 K.

- (e) vaporization:
- $\text{CS}_2(\text{l}) \rightarrow \text{CS}_2(\text{g})$

$$\Delta G_{\text{vap}}^{\circ} = \Delta H_{\text{vap}}^{\circ} - T\Delta S_{\text{vap}}^{\circ}; \quad \Delta S_{\text{vap}}^{\circ} = (\Delta H_{\text{vap}}^{\circ} - \Delta G_{\text{vap}}^{\circ})/T$$

$$\Delta G_{\text{vap}}^{\circ} = \Delta G^{\circ} \text{CS}_2(\text{g}) - \Delta G^{\circ} \text{CS}_2(\text{l}) = 67.2 - 65.3 = 1.9 \text{ kJ}$$

$$\Delta H_{\text{vap}}^{\circ} = \Delta H^{\circ} \text{CS}_2(\text{g}) - \Delta H^{\circ} \text{CS}_2(\text{l}) = 117.4 - 89.7 = 27.7 \text{ kJ}$$

$$\Delta S_{\text{vap}}^{\circ} = (27.7 - 1.9) \text{ kJ}/298 \text{ K} = 0.086577 = 0.0866 \text{ kJ/K} = 86.6 \text{ J/K}$$

ΔS_{vap} is always positive, because the gas phase occupies a greater volume, has more motional freedom and a larger absolute entropy than the liquid.

- (f) At the boiling point,
- $\Delta G = 0$
- and
- $\Delta H_{\text{vap}} = T_b \Delta S_{\text{vap}}$
- .

$$T_b = \Delta H_{\text{vap}} / \Delta S_{\text{vap}} = 27.7 \text{ kJ} / 0.086577 \text{ kJ/K} = 319.9 = 320 \text{ K}$$

$$T_b = 320 \text{ K} = 47^{\circ}\text{C}. \text{CS}_2 \text{ is a liquid at } 298 \text{ K, } 1 \text{ atm}$$

- 19.112 (a)
- $\text{Ag}(\text{s}) + 1/2 \text{N}_2(\text{g}) + 3/2 \text{O}_2(\text{g}) \rightarrow \text{AgNO}_3(\text{s})$
- ;
- S
- decreases because there are fewer moles of gas in the product.

$$(b) \quad \Delta G_f^{\circ} = \Delta H_f^{\circ} - T\Delta S^{\circ}; \quad \Delta S^{\circ} = (\Delta G_f^{\circ} - \Delta H_f^{\circ})/(-T) = (\Delta H_f^{\circ} - \Delta G_f^{\circ})/T$$

$$\Delta S^{\circ} = -124.4 \text{ kJ} - (-33.4 \text{ kJ}) / 298 \text{ K} = -0.305 \text{ kJ/K} = -305 \text{ J/K}$$

ΔS° is relatively large and negative, as anticipated from part (a).

- (c) Dissolving of
- AgNO_3
- can be expressed as



$$\Delta H^{\circ} = \Delta H^{\circ} \text{AgNO}_3(\text{aq}) - \Delta H^{\circ} \text{AgNO}_3(\text{s}) = -101.7 - (-124.4) = +22.7 \text{ kJ}$$

$$\Delta H^{\circ} = \Delta H^{\circ} \text{MgSO}_4(\text{aq}) - \Delta H^{\circ} \text{MgSO}_4(\text{s}) = -1374.8 - (-1283.7) = -91.1 \text{ kJ}$$

Dissolving $\text{AgNO}_3(\text{s})$ is endothermic ($+\Delta H^{\circ}$), but dissolving $\text{MgSO}_4(\text{s})$ is exothermic ($-\Delta H^{\circ}$).

- (d)
- AgNO_3
- :
- $\Delta G^{\circ} = \Delta G_f^{\circ} \text{AgNO}_3(\text{aq}) - \Delta G_f^{\circ} \text{AgNO}_3(\text{s}) = -34.2 - (-33.4) = -0.8 \text{ kJ}$

$$\Delta S^{\circ} = (\Delta H^{\circ} - \Delta G^{\circ}) / T = [22.7 \text{ kJ} - (-0.8 \text{ kJ})] / 298 \text{ K} = 0.0789 \text{ kJ/K} = 78.9 \text{ J/K}$$

$$\text{MgSO}_4: \Delta G^{\circ} = \Delta G_f^{\circ} \text{MgSO}_4(\text{aq}) - \Delta G_f^{\circ} \text{MgSO}_4(\text{s}) = -1198.4 - (-1169.6) = -28.8 \text{ kJ}$$

$$\Delta S^{\circ} = (\Delta H^{\circ} - \Delta G^{\circ}) / T = [-91.1 \text{ kJ} - (-28.8 \text{ kJ})] / 298 \text{ K} = -0.209 \text{ kJ/K} = -209 \text{ J/K}$$

- (e) In general, we expect dissolving a crystalline solid to be accompanied by an increase in positional disorder and an increase in entropy; this is the case for
- AgNO_3
- (
- $\Delta S^{\circ} = +78.9 \text{ J/K}$
-). However, for dissolving
- $\text{MgSO}_4(\text{s})$
- , there is a substantial decrease in entropy (
- $\Delta S = -209 \text{ J/K}$
-). According to Section 13.5, ion-pairing is a significant phenomenon in electrolyte solutions, particularly in concentrated solutions where the charges of the ions are greater than 1. According to Table 13.5, a 0.1
- m*
- MgSO_4
- solution has a van't Hoff factor of 1.21. That is, for each mole of
- MgSO_4
- that dissolves, there are only 1.21 moles of "particles" in solution instead of 2 moles of particles. For a 1
- m*
- solution, the

factor is even smaller. Also, the exothermic enthalpy of mixing indicates substantial interactions between solute and solvent. Substantial ion-pairing coupled with ion-dipole interactions with H_2O molecules lead to a decrease in entropy for $\text{MgSO}_4(\text{aq})$ relative to $\text{MgSO}_4(\text{s})$.

19.113 (a) $K = P_{\text{NO}_2}^2 / P_{\text{N}_2\text{O}_4}$

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 $P_{\text{NO}_2} = P_{\text{N}_2\text{O}_4}$ leads to the expression $K = P_{\text{NO}_2}$. 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, $P_{\text{NO}_2} = P_{\text{N}_2\text{O}_4} = 1.0 \text{ atm}$, $P_t = 2.0 \text{ atm}$.

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

$$\Delta H^\circ = 2\Delta H^\circ \text{NO}_2(\text{g}) - \Delta H^\circ \text{N}_2\text{O}_4(\text{g}) = 2(33.84) - 9.66 = +58.02 \text{ kJ}$$

$$\Delta S^\circ = 2S^\circ \text{NO}_2(\text{g}) - S^\circ \text{N}_2\text{O}_4(\text{g}) = 2(240.45) - 304.3 = 0.1766 \text{ kJ/K}$$

$$T = \frac{58.02 \text{ kJ}}{0.1766 \text{ kJ/K}} = 328.5 \text{ K or } 55.5^\circ \text{C}$$

(b) $P_t = 1.00 \text{ atm}$; $P_{\text{N}_2\text{O}_4} = x$, $P_{\text{NO}_2} = 2x$; $x + 2x = 1.00 \text{ atm}$

$$x = P_{\text{N}_2\text{O}_4} = 0.3333 = 0.333 \text{ atm}; P_{\text{NO}_2} = 0.6667 = 0.667 \text{ atm}$$

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

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

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

$$(0.1742 \text{ kJ/K}) T = 58.02 \text{ kJ}; T = 333.0 \text{ K}$$

(c) $P_t = 10.00 \text{ atm}$; $x + 2x = 10.00 \text{ atm}$

$$x = P_{\text{N}_2\text{O}_4} = 3.3333 = 3.333 \text{ atm}; P_{\text{NO}_2} = 6.6667 = 6.667 \text{ atm}$$

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

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

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

$$(0.15506 \text{ kJ/K}) T = 58.02 \text{ kJ}; T = 374.2 \text{ K}$$

- (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 .

$$19.114 \quad (a) \quad \Delta G^\circ = 3\Delta G_f^\circ \text{S}(s) + 2\Delta G_f^\circ \text{H}_2\text{O}(g) - \Delta G_f^\circ \text{SO}_2(g) - 2\Delta G_f^\circ \text{H}_2\text{S}(g)$$

$$= 3(0) + 2(-228.57) - (-300.4) - 2(-33.01) = -90.72 = -90.7 \text{ kJ}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-90.72 \text{ kJ})}{(8.314 \times 10^{-3} \text{ kJ/K})(298 \text{ K})} = 36.6165 = 36.6; K = 7.99 \times 10^{15}$$

$$= 8 \times 10^{15}$$

(b) The reaction is highly spontaneous at 298 K and feasible in principle. However, use of $\text{H}_2\text{S}(g)$ produces a severe safety hazard for workers and the surrounding community.

$$(c) \quad P_{\text{H}_2\text{O}} = \frac{25 \text{ torr}}{760 \text{ torr/atm}} = 0.033 \text{ atm}$$

$$K = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{SO}_2} \times P_{\text{H}_2\text{S}}^2}; P_{\text{SO}_2} = P_{\text{H}_2\text{S}} = x \text{ atm}$$

$$K = 7.99 \times 10^{15} = \frac{(0.033)^2}{x(x)^2}; x^3 = \frac{(0.033)^2}{7.99 \times 10^{15}}$$

$$x = 5 \times 10^{-7} \text{ atm}$$

$$(d) \quad \Delta H^\circ = 3\Delta H_f^\circ \text{S}(s) + 2\Delta H_f^\circ \text{H}_2\text{O}(g) - \Delta H_f^\circ \text{SO}_2(g) - 2\Delta H_f^\circ \text{H}_2\text{S}(g)$$

$$= 3(0) + 2(-241.82) - (-296.9) - 2(-20.17) = -146.4 \text{ kJ}$$

$$\Delta S^\circ = 3S^\circ \text{S}(s) + 2S^\circ \text{H}_2\text{O}(g) - S^\circ \text{SO}_2(g) - 2S^\circ \text{H}_2\text{S}(g)$$

$$= 3(31.88) + 2(188.83) - 248.5 - 2(205.6) = -186.4 \text{ J/K}$$

The reaction is exothermic ($-\Delta H$), so the value of K_{eq} will decrease with increasing temperature. The negative ΔS° value means that the reaction will become nonspontaneous at some higher temperature. The process will be less effective at elevated temperatures.

19.115 (a) When the rubber band is stretched, the molecules become more ordered, so the entropy of the system decreases, ΔS_{sys} is negative.

(b) $\Delta S_{sys} = q_{rev}/T$. Since ΔS_{sys} is negative, q_{rev} is negative and heat is emitted by the system.

(c) The unstretched rubber band feels cooler. This confirms our answer to (b). If heat is emitted by the system when it is stretched, the surroundings feel warmer. Upon return to the initial state, heat is absorbed by the system (the rubber band) and the surroundings (your lip) feel cooler.