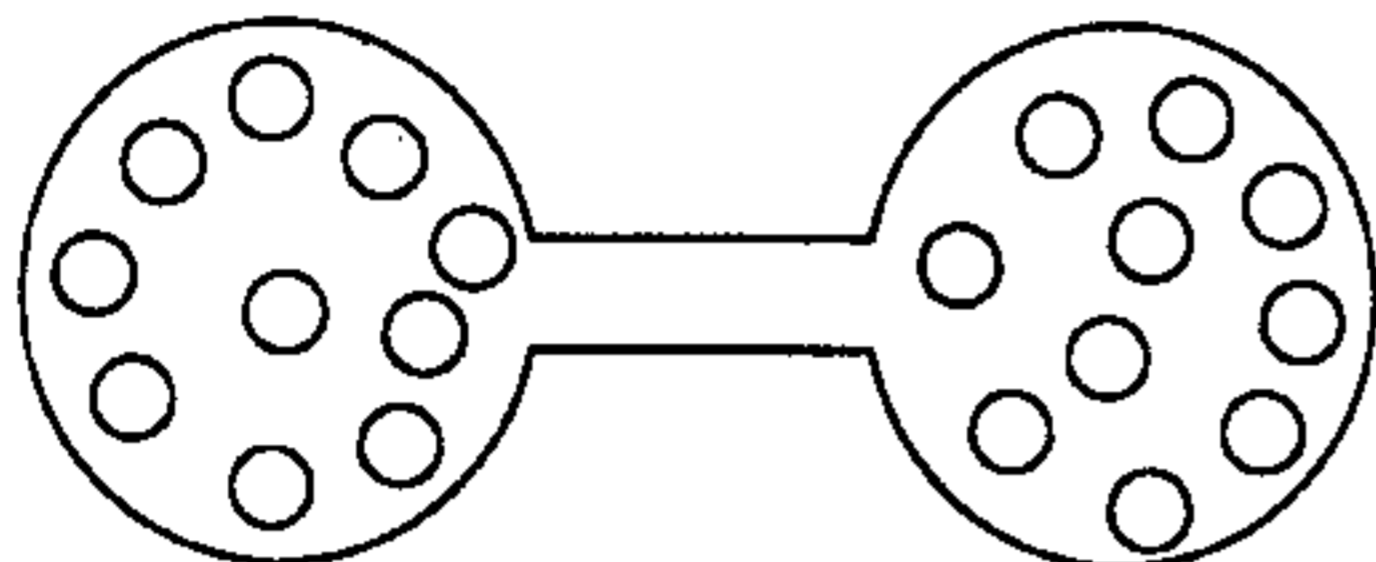


# 19 Chemistry Thermodynamics

## Visualizing Concepts

19.1

(a)



- (b)  $\Delta S$  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  $\Delta H$  for the mixing of ideal gases is zero, assuming heat exchange only between the two bulbs.

- (c) The process is irreversible. It is inconceivable that the gases would recombine.
- (d) The entropy change of the surroundings is related to  $\Delta H$  for the system. Since we are mixing ideal gases and  $\Delta H = 0$ ,  $\Delta H_{\text{surr}}$  is also zero, assuming heat exchange only between the two bulbs.

19.2

(a)

The process depicted is a change of state from a solid to a gas.  $\Delta S$  increases because of the greater motional freedom of the particles.  $\Delta H$  increases because both melting and boiling are endothermic processes. Since  $\Delta G = \Delta H - T\Delta S$ , and both  $\Delta H$  and  $\Delta S$  are positive, the sign of  $\Delta G$  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  $\Delta G$  is negative. If the temperature is lower than the boiling point, the process is not spontaneous and  $\Delta G$  is positive.

- (b) If the process is spontaneous, the second law states that  $\Delta S_{\text{univ}} \geq 0$ . Since  $\Delta S_{\text{sys}}$  increases,  $\Delta S_{\text{surr}}$  must decrease. 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  $\Delta S_{\text{sys}}$  is greater than the magnitude of  $\Delta S_{\text{surr}}$ , but the sign of  $\Delta S_{\text{surr}}$  is still negative.

19.3

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  $\Delta S$  is positive for this reaction.

19.4

(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  $\Delta G$  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.

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

*Plan.* Box 1 is an equilibrium mixture. By definition,  $\Delta G = 0$  for box 1. Calculate  $K$  and  $\Delta G^\circ$  for the reaction from box 1. Boxes 2 and 3 are nonequilibrium mixtures. Calculate  $Q$  and  $\Delta G$  for boxes 2 and 3.

*Solve.*  $K = \frac{[AB]^2}{[A][B]}$ . Use number of molecules as a measure of concentration.

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

$$\Delta G = \Delta G^\circ + RT \ln K; 0 = \Delta G^\circ - RT \ln(1), 0 = \Delta G^\circ - 0; \Delta G^\circ = 0$$

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

$$\Delta G = \Delta G^\circ + RT \ln Q = 0 - RT \ln(0.0625) = 2.77 RT = 3RT$$

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

$$\Delta G = \Delta G^\circ + RT \ln Q = 0 - RT \ln(49) = -3.89 RT = -4RT$$

- (b) The magnitudes of  $\Delta G$  (ignoring sign) are: box 1, 0; box 2, 2.8 RT; box 3, 3.9 RT. The order of increasing *magnitude* of  $\Delta G$  is: box 1 < box 2 < box 3.

The signs on  $\Delta G$  indicate in which direction the reaction is spontaneous. The mixture in box 2 will react spontaneously in the forward direction, toward products. The mixture in box 3 will react spontaneously in the reverse direction, toward reactants. The driving force for the reverse reaction in box 3, the *magnitude* of  $\Delta G$ , is greater than the driving force for the forward reaction in box 2.

- 19.6 (a) The minimum in the plot is the equilibrium position of the reaction, where  $\Delta G = 0$ .
- (b)  $X$  is the difference in free energy between reactant and products in their standard states,  $\Delta G^\circ$ .

### Spontaneous Processes

- 19.7 *Analyze/Plan.* Follow the logic in Sample Exercise 19.1. *Solve.*
- (a) Nonspontaneous;  $-5^\circ\text{C}$  is below the melting point of ice, so melting does not happen without continuous intervention.
- (b) Spontaneous; sugar is soluble in water, and even more soluble in hot coffee.
- (c) Spontaneous;  $\text{N}_2$  molecules are stable relative to isolated N atoms.

- (d) Spontaneous; the filings organize in a magnetic field without intervention.
- (e) Nonspontaneous;  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are in contact continuously at atmospheric conditions in nature and do not form  $\text{CH}_4$  and  $\text{O}_2$ .
- 19.8 (a) Spontaneous; a gas, in this case perfume vapor, expands to fill its container, the room.
- (b) Nonspontaneous; a mixture cannot be separated without outside intervention.
- (c) Nonspontaneous; an inflated balloon doesn't burst without external stress, such as a pin prick, a squeeze, or adding more gas.
- (d) Spontaneous; see Figure 8.2.
- (e) Spontaneous; the very polar  $\text{HCl}$  molecules readily dissolve in water to form concentrated  $\text{HCl}(\text{aq})$ .
- 19.9 (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.
- 19.10 Berthelot's suggestion is incorrect. Some examples of nonexothermic spontaneous processes are expansion of certain pressurized gases, dissolving of one liquid in another, and dissolving of many salts in water.
- 19.11 *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  $100^\circ\text{C}$ .
- (c) At 1 atm, the reaction is nonspontaneous at temperatures below  $100^\circ\text{C}$ .
- (d) The two phases are in equilibrium at  $100^\circ\text{C}$ .
- 19.12 (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 1-propanol is spontaneous at temperatures below  $-127^\circ\text{C}$ .
- (c) At 1 atm, the freezing of 1-propanol is nonspontaneous at temperatures above  $-127^\circ\text{C}$ .
- (d) At 1 atm and  $-127^\circ\text{C}$ , the normal freezing point of 1-propanol, the solid and liquid phases are in equilibrium. That is, at the freezing point, 1-propanol molecules escape to the liquid phase at the same rate as liquid 1-propanol solidifies, assuming no heat is exchanged between 1-propanol and the surroundings.
- 19.13 *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 only if the needed heat is added infinitely slowly.
- 19.14. (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.
- 19.15. No.  $\Delta E$  is a state function.  $\Delta E = q + w$ ;  $q$  and  $w$  are not state functions. Their values do depend on path, but their sum,  $\Delta E$ , does not.
- 19.16 (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.
- 19.17 *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  $0^\circ\text{C}$ .
- (b) We know that melting is a process that increases the energy of the system, even though there is no change in temperature.  $\Delta E$  is not zero for the process.
- 19.18 (a) The detonation of an explosive is definitely spontaneous, once it is initiated.
- (b) The quantity  $q$  is related to  $\Delta H$ . 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  $\Delta H$ , 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

# 19 Chemistry Thermodynamics Solutions to Exercises

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  $\Delta E$  is negative, regardless of the magnitudes of  $q$  and  $w$ .

## Entropy and the Second Law of Thermodynamics

- 19.19 (a) For a process that occurs at constant temperature, an isothermal process,  $\Delta S = q_{\text{rev}}/T$ . Here  $q_{\text{rev}}$  is the heat that would be transferred if the process were reversible. Since  $\Delta S$  is a state function, it is independent of path, so  $\Delta S$  for the reversible path must equal  $\Delta S$  for any path.
- (b) No.  $\Delta S$  is a state function, so it is independent of path.
- 19.20 (a) When a liquid freezes, the entropy of the system decreases.
- (b)  $\Delta S$  is negative.
- (c) Entropy being a state function means that  $\Delta S$  is independent of the path of the process.  $\Delta S$  defined in terms of a reversible path must equal  $\Delta S$  for any path.
- 19.21 (a)  $\text{CH}_3\text{OH}(\text{l}) \rightarrow \text{CH}_3\text{OH}(\text{g})$ , entropy increases, more mol gas in products, greater motional freedom.
- (b) 
$$\Delta S = \frac{\Delta H}{T} = \frac{71.8 \text{ kJ}}{\text{mol CH}_3\text{OH}(\text{l})} \times 1.00 \text{ mol CH}_3\text{OH}(\text{l}) \times \frac{1}{(273.15 + 64.7)\text{K}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 213 \text{ J/K}$$
- 19.22 (a)  $\text{Cs}(\text{l}) \rightarrow \text{Cs}(\text{s})$ ,  $\Delta S$  is negative
- (b) 
$$\Delta H = 15.0 \text{ g Cs} \times \frac{1 \text{ mol Cs}}{132.9 \text{ g Cs}} \times \frac{2.09 \text{ kJ}}{\text{mol Cs}} = 0.2359 = 0.236 \text{ kJ}$$

$$\Delta S = \frac{\Delta H}{T} = 0.2359 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1}{(273.15 + 28.4)\text{K}} = 0.782 \text{ J/K}$$
- 19.23 (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,  $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$ . If  $\Delta S_{\text{system}}$  is positive,  $\Delta S_{\text{surroundings}}$  must be negative.
- (c) Since  $\Delta S_{\text{universe}}$  must be positive for a spontaneous process,  $\Delta S_{\text{surroundings}}$  must be greater than  $-42 \text{ J/K}$ .
- 19.24 (a) For a spontaneous process,  $\Delta S_{\text{universe}} > 0$ . For a reversible process,  $\Delta S_{\text{universe}} = 0$ .
- (b)  $\Delta S_{\text{surroundings}}$  is positive and greater than the magnitude of the decrease in  $\Delta S_{\text{system}}$ .
- (c)  $\Delta S_{\text{system}} = 78 \text{ J/K}$ .
- 19.25 *Analyze.* Calculate  $\Delta S$  for the isothermal expansion of 0.100 mol He from 2.00 L to 5.00 L at 27°C.
- Plan.* Use the relationship  $\Delta S_{\text{sys}} = nR \ln(V_2/V_1)$ .

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

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

19.26 According to Boyle's law,  $P_1 V_1 = P_2 V_2$  at constant  $n$  and  $T$ .

$$0.900 \text{ atm} \times V_1 = 3.00 \text{ atm} \times V_2; V_2/V_1 = 0.900 \text{ atm}/3.00 \text{ atm} = 0.300$$

$$\Delta S_{\text{sys}} = nR \ln (V_2/V_1) = 0.500 \text{ mol} (8.314 \text{ J/mol}\cdot\text{K})(\ln 0.300) = -5.0049 = -5.00 \text{ J/K}$$

*Check.* An increase in pressure results in a decrease in volume at constant  $T$ , so we expect  $\Delta S$  to be negative, and it is.

### The Molecular Interpretation of Entropy

- 19.27 (a) The higher the temperature, the broader the distribution of molecular speeds and kinetic energies available to the particles. This wider range of accessible kinetic energies leads to more microstates for the system.
- (b) An increase in volume generates more possible positions for the particles and leads to more microstates for the system.
- (c) Going from solid to 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.

19.28 (a)  $\Delta H_{\text{vap}}$  for  $\text{H}_2\text{O}$  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  $\text{H}_2\text{O}$  molecules. This reduces the number of possible molecular positions and the number of microstates. Liquid water at  $100^\circ$  has sufficient kinetic energy to have broken many hydrogen bonds, so the number of microstates for  $\text{H}_2\text{O}(\text{l})$  at  $100^\circ$  is greater than the number of microstates for  $\text{H}_2\text{O}(\text{l})$  at  $25^\circ\text{C}$ . The difference in the number of microstates upon vaporization at  $100^\circ\text{C}$  is smaller, and the magnitude of  $\Delta S$  is smaller.

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

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

- (b)  $\Delta S$  is positive for Exercise 19.8 (a) and (c). Both processes represent an increase in volume and possible arrangements for the sample. [In (e), even though  $\text{HCl}(\text{aq})$  is a mixture, there are fewer moles of gas in the product, so  $\Delta S$  is not positive.]

19.30 (a) Solids are much more ordered than gases, so  $\Delta S$  is negative.

- (b)  $\Delta S$  is positive for Exercise 19.7 (a), (b), and (e). [At room temperature and 1 atm pressure,  $\text{H}_2\text{O}$  is a liquid, so there are more moles of gas in the products in part (e) and  $\Delta S > 0$ .]

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

- (a)  $S$  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.

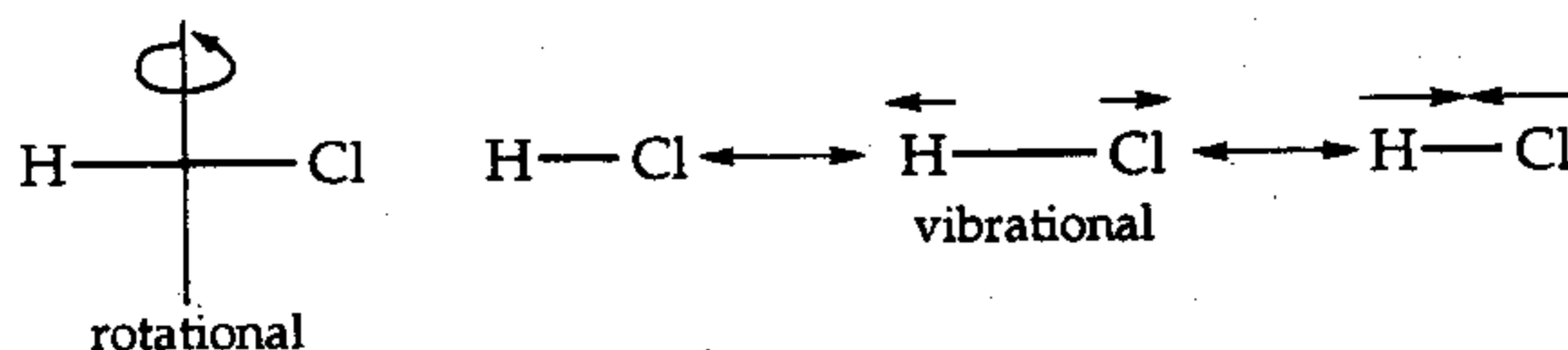
19.32 (a) When temperature increases, the range of accessible molecular speeds and kinetic energies increases. This produces more microstates and an increase in entropy.

- (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.

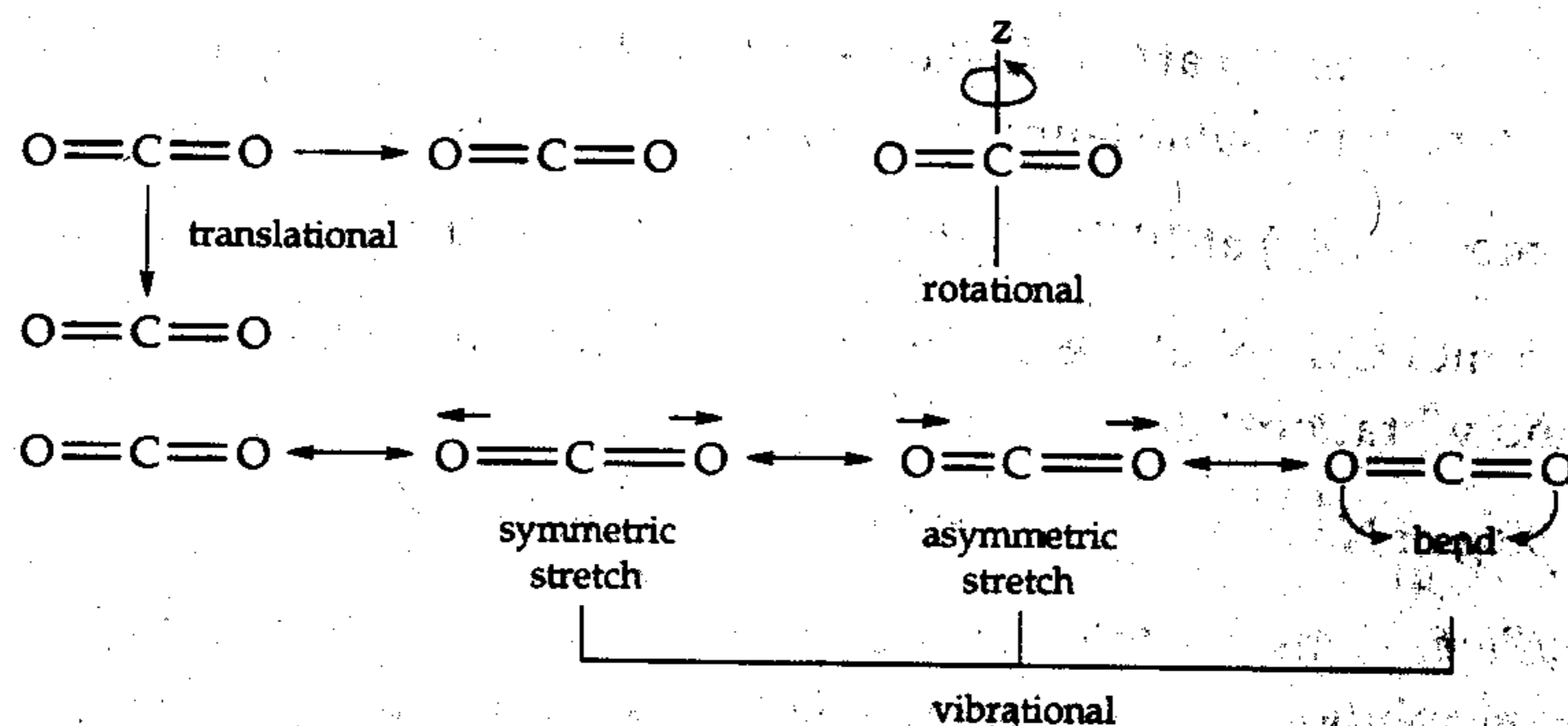
- (c) When a solid dissolves in water, there are both more possible positions for the particles (ions or molecules) and more motional freedom. The number of microstates and entropy increases.

19.33 (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.



19.34 (a) Since  $\text{CO}_2$  has more than one atom, the thermal energy can be distributed as translational, vibrational, or rotational motion.

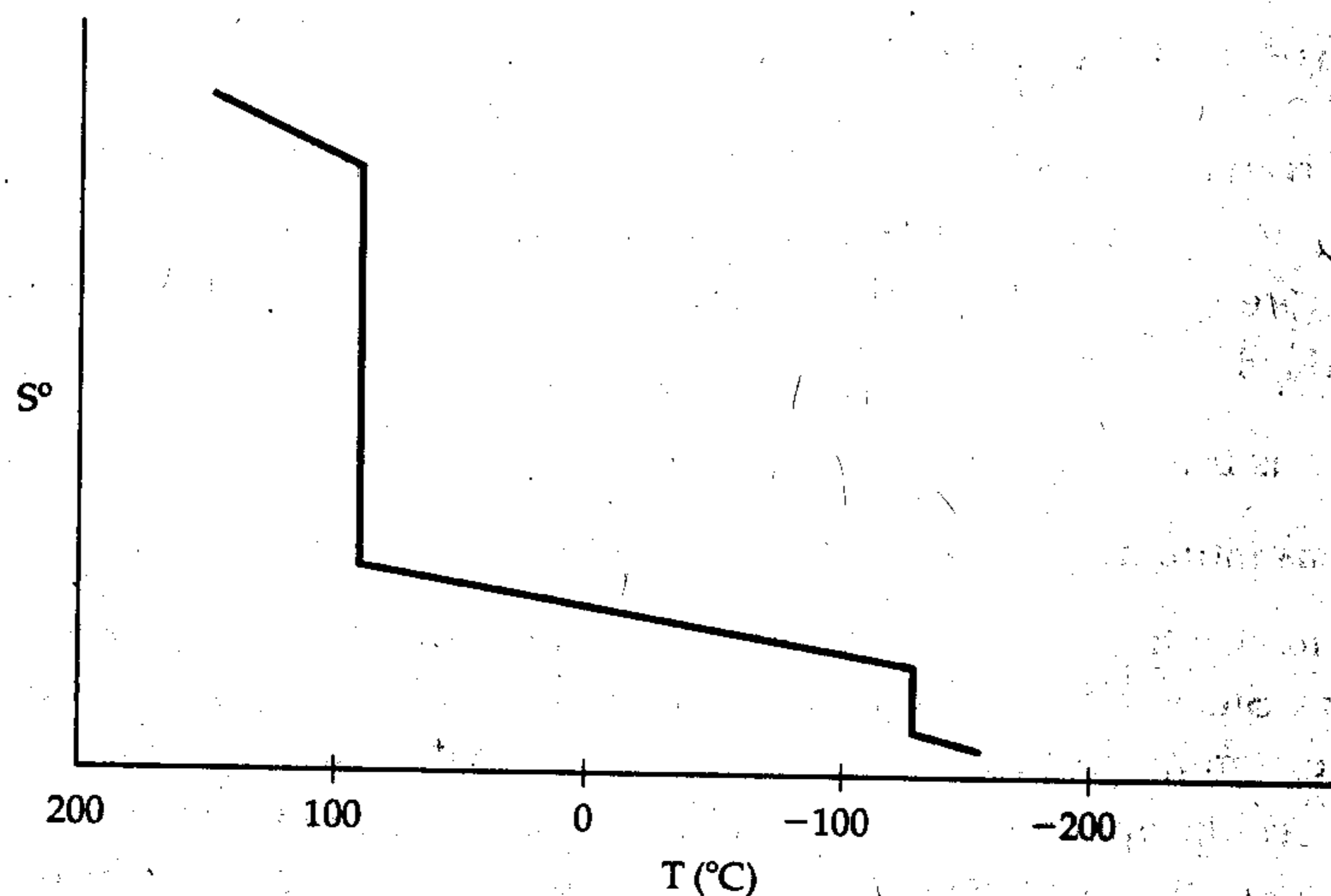


- (b) According to Boltzmann's Law,  $S = k \ln W$ . The number of microstates,  $W$ , is directly proportional to entropy,  $S$ . Thus, if the number of microstates for a system increases, the entropy of the system increases.

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

- (a) Both 1 and 2 represent changes in entropy at constant temperature; these are phase changes. Since 1 happens at lower temperature, it represents melting (fusion), and 2 represents vaporization.
- (b) The substance changes from solid to liquid in 1, from liquid to gas in 2. The larger volume and greater motional freedom of the gas phase causes  $\Delta S$  for vaporization to (always) be larger than  $\Delta S$  for fusion.

19.36 Melting =  $-126.5^\circ\text{C}$ ; boiling =  $97.4^\circ\text{C}$ .



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

- (a) Ar(g) (gases have higher entropy due primarily to much larger volume)
- (b) He(g) at 1.5 atm (larger volume and more motional freedom)
- (c) 1 mol of Ne(g) in 15.0 L (larger volume provides more motional freedom)
- (d) CO<sub>2</sub>(g) (more motional freedom)



- 19.38 (a) 1 mol of  $\text{As}_4(\text{g})$  at  $300^\circ\text{C}$ , 0.01 atm ( $\text{As}_4$  has more massive atoms in a comparable system at the same temperature.)
- (b) 1 mol  $\text{H}_2\text{O}(\text{g})$  at  $100^\circ\text{C}$ , 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  $30^\circ\text{C}$  (more motional freedom in aqueous solution)
- 19.39 *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)  $\Delta S$  negative (moles of gas decrease)
- (b)  $\Delta S$  positive (gas produced, increased disorder)
- (c)  $\Delta S$  negative (moles of gas decrease)
- (d)  $\Delta S$  positive (moles of gas increase)
- 19.40 (a)  $\text{Fe}(\text{l}) \rightarrow \text{Fe}(\text{s})$ ;  $\Delta S$  is negative (less motional freedom)
- (b)  $2\text{Li}(\text{s}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{LiCl}$ ;  $\Delta S$  is negative (moles of gas decrease)
- (c)  $\text{Zn}(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{ZnCl}_2(\text{aq}) + \text{H}_2(\text{g})$ ;  $\Delta S$  is positive (moles of gas increase)
- (d)  $\text{AgNO}_3(\text{aq}) + \text{KBr}(\text{aq}) \rightarrow \text{AgBr}(\text{s}) + \text{KNO}_3(\text{aq})$ ;  $\Delta S$  is negative (less motional freedom)

### Entropy Changes in Chemical Reactions

- 19.41 *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,  $S^\circ$ .
- (a)  $\text{C}_2\text{H}_6(\text{g})$  has more degrees of freedom and larger  $S^\circ$ .
- (b)  $\text{CO}_2(\text{g})$  has more degrees of freedom and larger  $S^\circ$ .
- 19.42 Propylene will have a higher  $S^\circ$  at  $25^\circ\text{C}$ . 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.
- 19.43 *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  $S^\circ$  than the solid phase because of the greater volume and motional freedom of the molecules.

- (b)  $\text{NH}_3(\text{g})$ , 192.5 J/mol·K;  $\text{NH}_3(\text{aq})$ , 111.3 J/mol·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  $\text{P}_2(\text{g})$ ,  $2(218.1) = 436.2$  J/K. More particles have greater motional energy (more available microstates).
- (d)  $\text{C}(\text{diamond})$ , 2.43 J/mol·K;  $\text{C}(\text{graphite})$  5.69 J/mol·K. Diamond is a network covalent solid with each C atom tetrahedrally bound to four other C atoms. Graphite consists of sheets of fused planar 6-membered rings with each C atom bound in a trigonal planar arrangement to three other C atoms. The internal entropy in graphite is greater because there is translational freedom among the planar sheets of C atoms while there is very little vibrational freedom within the network covalent diamond lattice.
- 19.44 (a)  $\text{CuO}(\text{s})$ , 42.59 J/mol·K;  $\text{Cu}_2\text{O}(\text{s})$ , 92.36 J/mol·K. Molecules in the solid state have only vibrational motion available to them. The more complex  $\text{Cu}_2\text{O}$  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)  $\text{CH}_3\text{OH}(\text{g})$ , 237.6 J/mol·K;  $\text{CH}_3\text{OH}(\text{l})$ , 126.8 J/mol·K. Molecules in the gas phase occupy a larger volume and have more motional freedom than molecules in the liquid state.
- (d) 1 mol  $\text{PbCO}_3(\text{s})$ , 131.0 J/K; 1 mol  $\text{PbO}(\text{s}) + 1$  mol  $\text{CO}_2(\text{g})$ ,  $(68.70 + 213.6) = 282.3$  J/K. The second member of the pair has more total particles and half of them are in the gas phase for greater total motional freedom. Note that 1 mol of  $\text{PbCO}_3(\text{s})$  has greater entropy than 1 mol of  $\text{PbO}(\text{s})$ , because of the additional ways to store energy in the more complex  $\text{CO}_3^{2-}$  anion.
- 19.45 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.
- 19.46 (a)  $\text{C}(\text{diamond})$ ,  $S^\circ = 2.43$  J/mol·K;  $\text{C}(\text{graphite})$ ,  $S^\circ = 5.69$  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)  $S^\circ$  for buckminsterfullerene will be  $\geq 10$  J/mol·K.  $S^\circ$  for graphite is twice  $S^\circ$  for diamond, and  $S^\circ$  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.

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

$$\begin{aligned} \text{(a)} \quad \Delta S^\circ &= S^\circ \text{C}_2\text{H}_6(\text{g}) - S^\circ \text{C}_2\text{H}_4(\text{g}) - S^\circ \text{H}_2(\text{g}) \\ &= 229.5 - 219.4 - 130.58 = -120.5 \text{ J/K} \end{aligned}$$

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

$$\text{(b)} \quad \Delta S^\circ = 2S^\circ \text{NO}_2(\text{g}) - \Delta S^\circ \text{N}_2\text{O}_4(\text{g}) = 2(240.45) - 304.3 = +176.6 \text{ J/K}$$

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

$$\begin{aligned} \text{(c)} \quad \Delta S^\circ &= \Delta S^\circ \text{BeO}(\text{s}) + \Delta S^\circ \text{H}_2\text{O}(\text{g}) - \Delta S^\circ \text{Be}(\text{OH})_2(\text{s}) \\ &= 13.77 + 188.83 - 50.21 = +152.39 \text{ J/K} \end{aligned}$$

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

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

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

$$\begin{aligned} \text{19.48 (a)} \quad \Delta S^\circ &= 2S^\circ \text{NH}_3(\text{g}) - S^\circ \text{N}_2\text{H}_4(\text{g}) - S^\circ \text{H}_2(\text{g}) \\ &= 2(192.5) - 238.5 - 130.58 = +15.9 \text{ J/K} \end{aligned}$$

$\Delta S^\circ$  is small because there are the same number of moles of gas in the products as in reactants. The slight increase is due to the relatively small  $S^\circ$  value of  $\text{H}_2(\text{g})$ , which has fewer degrees of freedom than molecules with more than two atoms.

$$\begin{aligned} \text{(b)} \quad \Delta S^\circ &= 2S^\circ \text{AlCl}_3(\text{s}) - 2S^\circ \text{Al}(\text{s}) - 3S^\circ \text{Cl}_2(\text{g}) \\ &= 2(109.3) - 2(28.32) - 3(222.96) = -506.9 \text{ J/K} \end{aligned}$$

$\Delta S^\circ$  is negative because the products contain fewer (no) moles of gas.

$$\begin{aligned} \text{(c)} \quad \Delta S^\circ &= S^\circ \text{MgCl}_2(\text{s}) + 2S^\circ \text{H}_2\text{O}(\text{l}) - S^\circ \text{Mg}(\text{OH})_2(\text{s}) - 2S^\circ \text{HCl}(\text{g}) \\ &= 89.6 + 2(69.91) - 63.24 - 2(186.69) = -207.2 \text{ J/K} \end{aligned}$$

$\Delta S^\circ$  is negative because the products contain fewer (no) moles of gas.

$$\begin{aligned} \text{(d)} \quad \Delta S^\circ &= S^\circ \text{C}_2\text{H}_6(\text{g}) + S^\circ \text{H}_2(\text{g}) - 2S^\circ \text{CH}_4(\text{g}) \\ &= 229.5 + 130.58 - 2(186.3) = -12.5 \text{ J/K} \end{aligned}$$

$\Delta S^\circ$  is very small because there are the same number of moles of gas in the products and reactants. The slight decrease is related to the relatively small  $S^\circ$  value for  $\text{H}_2(\text{g})$ , which has fewer degrees of freedom than molecules with more than two atoms.

## Gibbs Free Energy

- 19.49 (a)  $\Delta G = \Delta H - T\Delta S$
- (b) If  $\Delta G$  is positive, the process is nonspontaneous, but the reverse process is spontaneous.
- (c) There is no relationship between  $\Delta G$  and rate of reaction. A spontaneous reaction, one with a  $-\Delta G$ , may occur at a very slow rate. For example:  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g})$ ,  $\Delta G = -457 \text{ kJ}$  is very slow if not initiated by a spark.
- 19.50 (a) The *standard* free energy change,  $\Delta G^\circ$ , 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  $\Delta G$ . The value for  $\Delta G$  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  $\Delta G$  give no information about rate; we cannot predict whether the reaction will occur rapidly.
- 19.51 *Analyze/Plan.* Consider the definitions of  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$ , along with sign conventions.  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ . *Solve.*
- (a)  $\Delta H^\circ$  is negative; the reaction is exothermic.
- (b)  $\Delta S^\circ$  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,  $\Delta G^\circ$  is negative. If all reactants and products are present in their standard states, the reaction is spontaneous (in the forward direction) at this temperature.
- 19.52 (a)  $\Delta H^\circ$  is negative; the reaction is exothermic.
- (b)  $\Delta S^\circ$  is positive; the reaction leads to an increase in disorder.
- (c)  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -19.5 \text{ kJ} - 298 \text{ K} (0.0427 \text{ kJ/K}) = -32.225 = -32.2 \text{ kJ}$
- (d) At 298 K,  $\Delta G^\circ$  is negative. If all reactants and products are present in their standard states, the reaction is spontaneous (in the forward direction) at this temperature.
- 19.53 *Analyze/Plan.* Follow the logic in Sample Exercise 19.7. Calculate  $\Delta H^\circ$  according to Equation [5.31],  $\Delta S^\circ$  by Equation [19.8] and  $\Delta G^\circ$  by Equation [19.13]. Then use  $\Delta H^\circ$  and  $\Delta S^\circ$  to calculate  $\Delta G^\circ$  using Equation [19.20],  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ . *Solve.*
- (a)  $\Delta H^\circ = 2(-268.61) - [0 + 0] = -537.22 \text{ kJ}$   
 $\Delta S^\circ = 2(173.51) - [130.58 + 202.7] = 13.74 = 13.7 \text{ J/K}$   
 $\Delta G^\circ = 2(-270.70) - [0 + 0] = -541.40 \text{ kJ}$   
 $\Delta G^\circ = -537.22 \text{ kJ} - 298(0.01374) \text{ kJ} = -541.31 \text{ kJ}$

$$\begin{aligned} \text{(b)} \quad \Delta H^\circ &= -106.7 - [0 + 2(0)] = -106.7 \text{ kJ} \\ \Delta S^\circ &= 309.4 - [5.69 + 2(222.96)] = -142.21 = -142.2 \text{ J/K} \\ \Delta G^\circ &= -64.0 - [0 + 2(0)] = -64.0 \text{ kJ} \\ \Delta G^\circ &= -106.7 \text{ kJ} - 298(-0.14221) \text{ kJ} = -64.3 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad \Delta H^\circ &= 2(-542.2) - [2(-288.07) + 0] = -508.26 = -508.3 \text{ kJ} \\ \Delta S^\circ &= 2(325) - [2(311.7) + 205.0] = -178.4 = -178 \text{ J/K} \\ \Delta G^\circ &= 2(-502.5) - [2(-269.6) + 0] = -465.8 \text{ kJ} \\ \Delta G^\circ &= -508.26 \text{ kJ} - 298(-0.1784) \text{ kJ} = -455.097 = -455.1 \text{ kJ} \end{aligned}$$

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

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

$$\begin{aligned} 19.54 \quad \text{(a)} \quad \Delta H^\circ &= -305.3 - [0 + 0] = -305.3 \text{ kJ} \\ \Delta S^\circ &= 97.65 - [29.9 + 222.96] = -155.21 = -155.2 \text{ J/K} \\ \Delta G^\circ &= -259.0 - [0 + 0] = -259.0 \text{ kJ} \\ \Delta G^\circ &= -305.3 \text{ kJ} - 298(-0.15521) \text{ kJ} = -259.047 = -259.0 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \text{(b)} \quad \Delta H^\circ &= -635.5 + (-393.5) - (-1207.1) = 178.1 \text{ kJ} \\ \Delta S^\circ &= 39.75 + 213.6 - (92.88) = 160.47 = 160.5 \text{ J/K} \\ \Delta G^\circ &= -604.17 + (-394.4) - (-1128.76) = 130.19 = 130.2 \text{ kJ} \\ \Delta G^\circ &= 178.1 \text{ kJ} - 298(0.16047) \text{ kJ} = 130.28 = 130.3 \text{ kJ} \end{aligned}$$

$$\begin{aligned} \text{(c)} \quad \Delta H^\circ &= 4(-1288.3) - [-2940.1 + 6(-285.83)] = -498.12 = -498.1 \text{ kJ} \\ \Delta S^\circ &= 4(158.2) - [228.9 + 6(69.91)] = -15.56 = -15.6 \text{ J/K} \\ \Delta G^\circ &= 4(-1142.6) - [-2675.2 + 6(-237.13)] = -472.42 = -472.4 \text{ kJ} \\ \Delta G^\circ &= -498.12 \text{ kJ} - 298(-0.01556) \text{ kJ} = -493.48 = -493.5 \text{ kJ} \end{aligned}$$

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

$$\begin{aligned} \text{(d)} \quad \Delta H^\circ &= 2(-393.5) + 4(-285.83) - [2(-238.6) + 3(0)] = -1453.1 \text{ kJ} \\ \Delta S^\circ &= 2(213.6) + 4(69.91) - [2(126.8) + 3(205.0)] = -161.76 = -161.8 \text{ J/K} \\ \Delta G^\circ &= 2(-394.4) + 4(-237.13) - [2(-166.23) + 3(0)] = -1404.86 = -1404.9 \text{ kJ} \\ \Delta G^\circ &= -1453.2 \text{ kJ} - 298(-0.16176) \text{ kJ} = -1404.996 = -1405.0 \text{ kJ} \end{aligned}$$

19.55 *Analyze/Plan.* Follow the logic in Sample Exercise 19.6. *Solve.*

$$\begin{aligned} \text{(a)} \quad \Delta G^\circ &= 2\Delta G^\circ \text{SO}_3(\text{g}) - [2\Delta G^\circ \text{SO}_2(\text{g}) + \Delta G^\circ \text{O}_2(\text{g})] \\ &= 2(-370.4) - [2(-300.4) + 0] = -140.0 \text{ kJ, spontaneous} \end{aligned}$$

- (b)  $\Delta G^\circ = 3\Delta G^\circ \text{NO(g)} - [\Delta G^\circ \text{NO}_2\text{(g)} + \Delta G^\circ \text{N}_2\text{O(g)}]$   
 $= 3(86.71) - [51.84 + 103.59] = +104.70 \text{ kJ, nonspontaneous}$
- (c)  $\Delta G^\circ = 4\Delta G^\circ \text{FeCl}_3\text{(s)} + 3\Delta G^\circ \text{O}_2\text{(g)} - [6\Delta G^\circ \text{Cl}_2\text{(g)} + 2\Delta G^\circ \text{Fe}_2\text{O}_3\text{(s)}]$   
 $= 4(-334) + 3(0) - [6(0) + 2(-740.98)] = +146 \text{ kJ, nonspontaneous}$
- (d)  $\Delta G^\circ = \Delta G^\circ \text{S(s)} + 2\Delta G^\circ \text{H}_2\text{O(g)} - [\Delta G^\circ \text{SO}_2\text{(g)} + 2\Delta G^\circ \text{H}_2\text{(g)}]$   
 $= 0 + 2(-228.57) - [(-300.4) + 2(0)] = -156.7 \text{ kJ, spontaneous}$

- 19.56 (a)  $\Delta G^\circ = 2\Delta G^\circ \text{HCl(g)} - [\Delta G^\circ \text{H}_2\text{(g)} + \Delta G^\circ \text{Cl}_2\text{(g)}]$   
 $= 2(-95.27 \text{ kJ}) - 0 - 0 = -190.5 \text{ kJ, spontaneous}$
- (b)  $\Delta G^\circ = \Delta G^\circ \text{MgO(s)} + 2\Delta G^\circ \text{HCl(g)} - [\Delta G^\circ \text{MgCl}_2\text{(s)} + \Delta G^\circ \text{H}_2\text{O(l)}]$   
 $= -569.6 + 2(-95.27) - [-592.1 + (-237.13)] = +69.1 \text{ kJ, nonspontaneous}$
- (c)  $\Delta G^\circ = \Delta G^\circ \text{N}_2\text{H}_4\text{(g)} + \Delta G^\circ \text{H}_2\text{(g)} - 2\Delta G^\circ \text{NH}_3\text{(g)}$   
 $= 159.4 + 0 - 2(-16.66) = +192.7 \text{ kJ, nonspontaneous}$
- (d)  $\Delta G^\circ = 2\Delta G^\circ \text{NO(g)} + \Delta G^\circ \text{Cl}_2\text{(g)} - 2\Delta G^\circ \text{NOCl(g)}$   
 $= 2(86.71) + 0 - 2(66.3) = +40.8 \text{ kJ, nonspontaneous}$

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

- (a)  $\text{C}_6\text{H}_{12}\text{(l)} + 9\text{O}_2\text{(g)} \rightarrow 6\text{CO}_2\text{(g)} + 6\text{H}_2\text{O(l)}$
- (b) Because there are fewer moles of gas in the products,  $\Delta S^\circ$  is negative, which makes  $-T\Delta S$  positive.  $\Delta G^\circ$  is less negative (more positive) than  $\Delta H^\circ$ .

- 19.58 (a)  $\Delta G^\circ$  should be less negative than  $\Delta H^\circ$ . Products contain fewer moles of gas, so  $\Delta S^\circ$  is negative.  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ ;  $-T\Delta S^\circ$  is positive so  $\Delta G^\circ$  is less negative than  $\Delta H^\circ$ .
- (b) We can estimate  $\Delta S^\circ$  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  $\text{CO}_2\text{(g)} + \text{CaO(s)} \rightarrow \text{CaCO}_3\text{(s)}$  or  $\text{CO}_2\text{(g)} + \text{BaO(s)} \rightarrow \text{BaCO}_3\text{(s)}$ . Or calculate both  $\Delta S^\circ$  values and use the average as your estimate.

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

- (a)  $\Delta G$  is negative at low temperatures, positive at high temperatures. That is, the reaction proceeds in the forward direction spontaneously at lower temperatures but spontaneously reverses at higher temperatures.
- (b)  $\Delta G$  is positive at all temperatures. The reaction is nonspontaneous in the forward direction at all temperatures.
- (c)  $\Delta G$  is positive at low temperatures, negative at high temperatures. That is, the reaction will proceed spontaneously in the forward direction at high temperature.

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

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

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

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

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

19.61 *Analyze/Plan.* We are told that the reaction is spontaneous and endothermic, and asked to estimate the sign and magnitude of  $\Delta S$ . If a reaction is spontaneous,  $\Delta G < 0$ . Use this information with Equation [19.20] to solve the problem. *Solve.*

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

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

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

19.62 At  $-25^\circ\text{C}$  or 248 K,  $\Delta G > 0$ .  $\Delta G = \Delta H - T\Delta S > 0$

$\Delta H - 248 \text{ K}(95 \text{ J/K}) > 0$ ;  $\Delta H > +2.4 \times 10^4 \text{ J}$ ;  $\Delta H > +24 \text{ kJ}$

19.63 *Analyze/Plan.* Use Equation [19.20] to calculate  $T$  when  $\Delta G = 0$ . This is similar to calculating the temperature of a phase transition in Sample Exercise 19.9. Use Table 19.4 to determine whether the reaction is spontaneous or non-spontaneous above this temperature. *Solve.*

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

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

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

19.64  $\Delta G$  is negative when  $T\Delta S > \Delta H$  or  $T > \Delta H/\Delta S$ .

$\Delta H^\circ = \Delta H^\circ \text{CH}_4(\text{g}) + \Delta H^\circ \text{CO}_2(\text{g}) - \Delta H^\circ \text{CH}_3\text{COOH}(\text{l})$

$= -74.8 + (-393.5) - (-487.0) = +18.7 \text{ kJ}$

$\Delta S^\circ = S^\circ \text{CH}_4(\text{g}) + S^\circ \text{CO}_2(\text{g}) - S^\circ \text{CH}_3\text{COOH}(\text{l}) = +186.3 + 213.6 - 159.8 = +240.1 \text{ J/K}$

$T > \frac{18.7 \text{ kJ}}{0.2401 \text{ kJ/K}} = 77.9 \text{ K}$

The reaction is spontaneous above 77.9 K ( $-195^\circ\text{C}$ ).

19.65 *Analyze/Plan.* Given a chemical equation and thermodynamic data (values of  $\Delta H_f^\circ$ ,  $\Delta G_f^\circ$  and  $S^\circ$ ) for reactants and products, predict the variation of  $\Delta G^\circ$  with temperature and calculate  $\Delta G^\circ$  at 800 K and 1000 K. Use Equations [5.31] and [19.8] to calculate  $\Delta H^\circ$  and  $\Delta S^\circ$ , respectively; use these values to calculate  $\Delta G^\circ$  at various temperatures, using Equation [19.20]. The signs of  $\Delta H^\circ$  and  $\Delta S^\circ$  determine the variation of  $\Delta G^\circ$  with temperature. *Solve.*

(a) Calculate  $\Delta H^\circ$  and  $\Delta S^\circ$  to determine the sign of  $T\Delta S^\circ$ .

$\Delta H^\circ = 3\Delta H^\circ \text{NO}(\text{g}) - \Delta H^\circ \text{NO}_2(\text{g}) - \Delta H^\circ \text{N}_2\text{O}(\text{g})$

$= 3(90.37) - 33.84 - 81.6 = 155.7 \text{ kJ}$

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

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

$$\begin{aligned}\text{(b)} \quad \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ = 155.7 \text{ kJ} - (800 \text{ K})(0.1714 \text{ kJ/K}) \\ \Delta G^\circ &= 155.7 \text{ kJ} - 137 \text{ kJ} = 19 \text{ kJ}\end{aligned}$$

Since  $\Delta G^\circ$  is positive at 800 K, the reaction is not spontaneous at this temperature.

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

$\Delta G^\circ$  is negative at 1000 K and the reaction is spontaneous at this temperature.

$$\begin{aligned}\text{19.66 (a)} \quad \Delta H^\circ &= \Delta H_f^\circ \text{CH}_3\text{OH(g)} - \Delta H_f^\circ \text{CH}_4\text{(g)} - 1/2 \Delta H_f^\circ \text{O}_2\text{(g)} \\ &= -201.2 - (-74.8) - 0 = -126.4 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ \text{CH}_3\text{OH(g)} - S^\circ \text{CH}_4\text{(g)} - 1/2 S^\circ \text{O}_2\text{(g)} \\ &= 237.6 - 186.3 - 1/2(205.0) = -51.2 \text{ J/K} = -0.0512 \text{ kJ/K}\end{aligned}$$

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

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

The reaction is spontaneous at 298 K because  $\Delta G^\circ$  is negative at this temperature. In this case,  $\Delta G^\circ$  could have been calculated from  $\Delta G_f^\circ$  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.

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

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

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

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

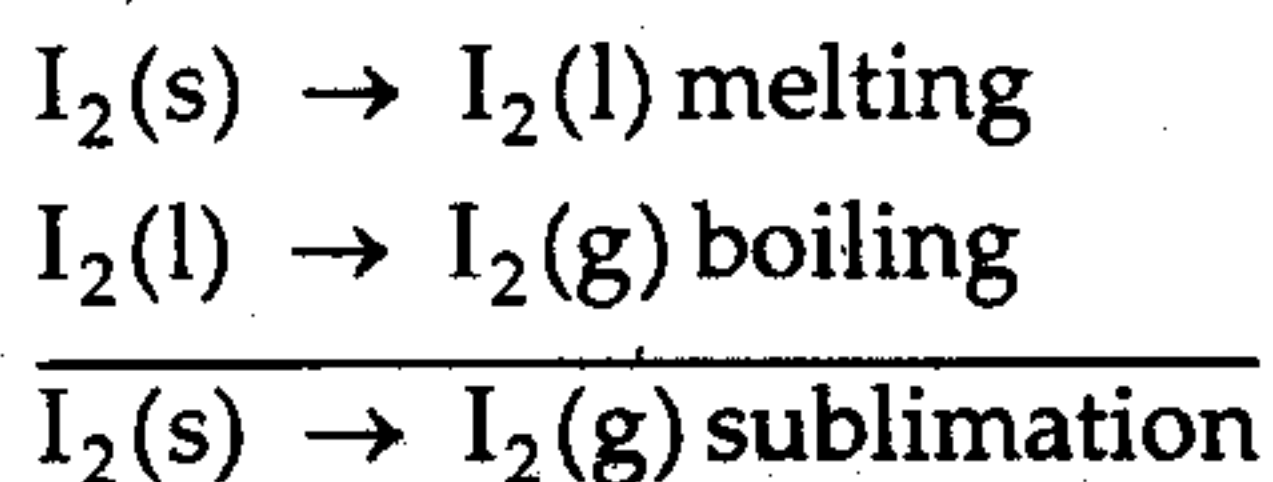
$$T_b = 33.9 \times 10^3 \text{ J} / 96.4 \text{ J/K} = 351.66 = 352 \text{ K} = 79^\circ\text{C}$$

(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  $\text{C}_6\text{H}_6\text{(g)}$  and experimental uncertainty in the boiling point measurement and the thermodynamic data.

$$\text{19.68 (a)} \quad \text{As in Sample Exercise 19.9, } T_{\text{sub}} = \Delta H_{\text{sub}}^\circ / \Delta S_{\text{sub}}^\circ$$

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





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

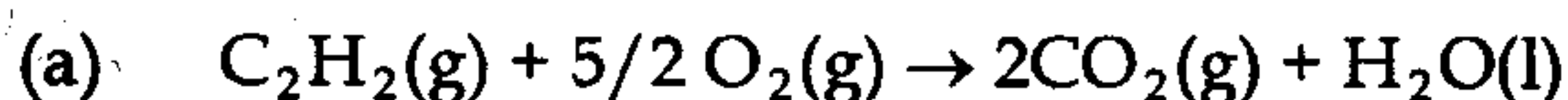
$$\Delta S_{\text{sub}}^{\circ} = S^{\circ} \text{I}_2(\text{g}) - S^{\circ} \text{I}_2(\text{s}) = 260.57 - 116.73 = 143.84 \text{ J/K} = 0.14384 \text{ kJ/K}$$

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

(b)  $T_{\text{m}}$  for  $\text{I}_2(\text{s}) = 386.85 \text{ K} = 113.7^{\circ}\text{C}$ ;  $T_{\text{b}} = 457.4 \text{ K} = 184.3^{\circ}\text{C}$   
(from WebElements™, 2005)

(c) The boiling point of  $\text{I}_2$  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  $\Delta H$  and  $\Delta S$ , so it is not surprising that the ratio of  $\Delta H/\Delta S$  is similar for sublimation and boiling.

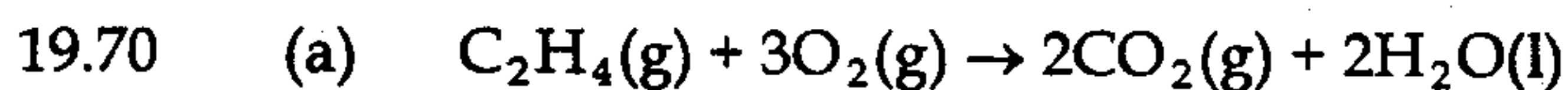
19.69 *Analyze/Plan.* We are asked to write a balanced equation for the combustion of acetylene, calculate  $\Delta H^{\circ}$  for this reaction and calculate maximum useful work possible by the system. Combustion is combination with  $\text{O}_2$  to produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Calculate  $\Delta H^{\circ}$  using data from Appendix C and Equation 5.31. The maximum obtainable work is  $\Delta G$  (Equation [19.19]), which can be calculated from data in Appendix C and Equation [19.13]. *Solve.*



(b) 
$$\begin{aligned} \Delta H^{\circ} &= 2\Delta H^{\circ} \text{CO}_2(\text{g}) + \Delta H^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H^{\circ} \text{C}_2\text{H}_2(\text{g}) - 5/2\Delta H^{\circ} \text{O}_2(\text{g}) \\ &= 2(-393.5) - 285.83 - 226.7 - 5/2(0) = -1299.5 \text{ kJ produced/mol C}_2\text{H}_2 \\ &\quad \text{burned} \end{aligned}$$

(c) 
$$\begin{aligned} w_{\text{max}} = \Delta G^{\circ} &= 2\Delta G^{\circ} \text{CO}_2(\text{g}) + \Delta G^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta G^{\circ} \text{C}_2\text{H}_2(\text{g}) - 5/2 \Delta G^{\circ} \text{O}_2(\text{g}) \\ &= 2(-394.4) - 237.13 - 209.2 - 5/2(0) = -1235.1 \text{ kJ} \end{aligned}$$

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.



$$\begin{aligned} \Delta H^{\circ} &= 2\Delta H_{\text{f}}^{\circ} \text{CO}_2(\text{g}) + 2\Delta H_{\text{f}}^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta H_{\text{f}}^{\circ} \text{C}_2\text{H}_4(\text{g}) - 3\Delta H_{\text{f}}^{\circ} \text{O}_2(\text{g}) \\ &= 2(-393.5) + 2(-285.83) - 52.30 - 3(0) = -1410.96 = -1411.0 \text{ kJ/mol C}_2\text{H}_4 \text{ burned} \end{aligned}$$

(b) 
$$\begin{aligned} w_{\text{max}} = \Delta G^{\circ} &= 2\Delta G_{\text{f}}^{\circ} \text{CO}_2(\text{g}) + 2\Delta H_{\text{f}}^{\circ} \text{H}_2\text{O}(\text{l}) - \Delta G_{\text{f}}^{\circ} \text{C}_2\text{H}_4(\text{g}) - 3\Delta G_{\text{f}}^{\circ} \text{O}_2(\text{g}) \\ &= 2(-394.4) + 2(-237.13) - 68.11 - 3(0) = -1331.2 \text{ kJ} \end{aligned}$$

The system can accomplish at most 1331.2 kJ of work per mole of  $\text{C}_2\text{H}_4$  on the surroundings.

## Free Energy and Equilibrium

- 19.71 *Analyze/Plan.* We are given a chemical reaction and asked to predict the effect of the partial pressure of  $O_2(g)$  on the value of  $\Delta G$  for the system. Consider the relationship  $\Delta G = \Delta G^\circ + RT \ln Q$  where  $Q$  is the reaction quotient. *Solve.*
- $O_2(g)$  appears in the denominator of  $Q$  for this reaction. An increase in pressure of  $O_2$  decreases  $Q$  and  $\Delta G$  becomes smaller or more negative. Increasing the concentration of a reactant increases the tendency for a reaction to occur.
  - $O_2(g)$  appears in the numerator of  $Q$  for this reaction. Increasing the pressure of  $O_2$  increases  $Q$  and  $\Delta G$  becomes more positive. Increasing the concentration of a product decreases the tendency for the reaction to occur.
  - $O_2(g)$  appears in the numerator of  $Q$  for this reaction. An increase in pressure of  $O_2$  increases  $Q$  and  $\Delta G$  becomes more positive. Since pressure of  $O_2$  is raised to the third power in  $Q$ , an increase in pressure of  $O_2$  will have the largest effect on  $\Delta G$  for this reaction.
- 19.72 Consider the relationship  $\Delta G = \Delta G^\circ + RT \ln Q$ , where  $Q$  is the reaction quotient.
- $H_2(g)$  appears in the denominator of  $Q$  for this reaction. An increase in pressure of  $H_2$  decreases  $Q$  and  $\Delta G$  becomes smaller or more negative. Increasing the concentration of a reactant increases the tendency for a reaction to occur.
  - $H_2(g)$  appears in the numerator of  $Q$  for this reaction. Increasing the pressure of  $H_2$  increases  $Q$  and  $\Delta G$  becomes more positive. Increasing the concentration of a product decreases the tendency for the reaction to occur.
  - $H_2(g)$  appears in the denominator of  $Q$  for this reaction. An increase in pressure of  $H_2$  decreases  $Q$  and  $\Delta G$  becomes smaller or more negative.
- 19.73 *Analyze/Plan.* Given a chemical reaction, we are asked to calculate  $\Delta G^\circ$  from Appendix C data, and  $\Delta G$  for a given set of initial conditions. Use Equation [19.13] to calculate  $\Delta G^\circ$ , and Equation [19.21] to calculate  $\Delta G$ . Follow the logic in Sample Exercise 19.10 when calculating  $\Delta G$ . *Solve.*
- $\Delta G^\circ = \Delta G^\circ N_2O_4(g) - 2\Delta G^\circ NO_2(g) = 98.28 - 2(51.84) = -5.40 \text{ kJ}$
  - $$\Delta G = \Delta G^\circ + RT \ln P_{N_2O_4} / P_{NO_2}^2$$
$$= -5.40 \text{ kJ} + \frac{8.314 \times 10^{-3} \text{ kJ}}{\text{K} \cdot \text{mol}} \times 298 \text{ K} \times \ln[1.60/(0.40)^2] = 0.3048 = 0.3 \text{ kJ}$$
- 19.74
- $\Delta G^\circ = 2\Delta G^\circ HF(g) - [\Delta G^\circ H_2(g) + \Delta G^\circ F_2(g)] = 2(-270.70) - [0 + 0] = -541.40 \text{ kJ}$
  - $$\Delta G = \Delta G^\circ + RT \ln P_{HF}^2 / P_{H_2} \times P_{F_2}$$
$$= -541.40 + \frac{8.314 \times 10^{-3} \text{ kJ}}{\text{K} \cdot \text{mol}} \times 298 \text{ K} \ln[(0.36)^2 / 8.0 \times 4.5] = -555.34 = -555 \text{ kJ}$$
- 19.75 *Analyze/Plan.* Given a chemical reaction, we are asked to calculate  $K$  using  $\Delta G_f^\circ$  data from Appendix C. Follow the logic in Sample Exercise 19.13.  $\Delta G^\circ = -RT \ln K$ , Equation [19.22];  $\ln K = -\Delta G^\circ / RT$  *Solve.*

$$(a) \quad \Delta G^\circ = 2\Delta G^\circ \text{HI(g)} - \Delta G^\circ \text{H}_2\text{(g)} - \Delta G^\circ \text{I}_2\text{(g)}$$

$$= 2(1.30) - 0 - 19.37 = -16.77 \text{ kJ}$$

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

$$(b) \quad \Delta G^\circ = \Delta G^\circ \text{C}_2\text{H}_4\text{(g)} + \Delta G^\circ \text{H}_2\text{O(g)} - \Delta G^\circ \text{C}_2\text{H}_5\text{OH(g)}$$

$$= 68.11 - 228.57 - (-168.5) = 8.04 = 8.0 \text{ kJ}$$

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

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

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

$$19.76 \quad \Delta G^\circ = -RT \ln K; \quad \ln K = -\Delta G^\circ / RT; \quad \text{at } 298 \text{ K, } RT = 2.4776 = 2.478 \text{ kJ}$$

$$(a) \quad \Delta G^\circ = \Delta G^\circ \text{NaOH(s)} + \Delta G^\circ \text{CO}_2\text{(g)} - \Delta G^\circ \text{NaHCO}_3\text{(s)}$$

$$= -379.5 + (-394.4) - (-851.8) = +77.9 \text{ kJ}$$

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

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

$$(b) \quad \Delta G^\circ = 2\Delta G^\circ \text{HCl(g)} + \Delta G^\circ \text{Br}_2\text{(g)} - 2\Delta G^\circ \text{HBr(g)} - \Delta G^\circ \text{Cl}_2\text{(g)}$$

$$= 2(-95.27) + 3.14 - 2(-53.22) - 0 = -80.96 \text{ kJ}$$

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

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

$$(c) \quad \text{From Exercise 19.55(a), } \Delta G^\circ \text{ at } 298 \text{ K} = -140.0 \text{ kJ.}$$

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

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

19.77 *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  $\Delta G^\circ$  at the two temperatures using  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  and then calculate  $K$  and  $P_{\text{CO}_2}$ .  
*Solve.*

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

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

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

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

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

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

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

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

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

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

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

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

$$= -217.3 - 393.5 + 699.1 = 88.3 \text{ kJ}$$

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

$$= 68.70 + 213.6 - 131.0 = 151.3 \text{ J/K or } 0.1513 \text{ kJ/K}$$

$$(a) \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \text{ At } 393 \text{ K}, \Delta G^\circ = 88.3 \text{ kJ} - 393 \text{ K}(0.1513 \text{ kJ/K}) = 28.84$$

$$= 28.8 \text{ kJ}$$

$$\ln K = \frac{-\Delta G^\circ}{RT} = \frac{-28.84 \times 10^3 \text{ J}}{8.314 \text{ J/K} \times 393 \text{ K}} = -8.82631 = -8.83$$

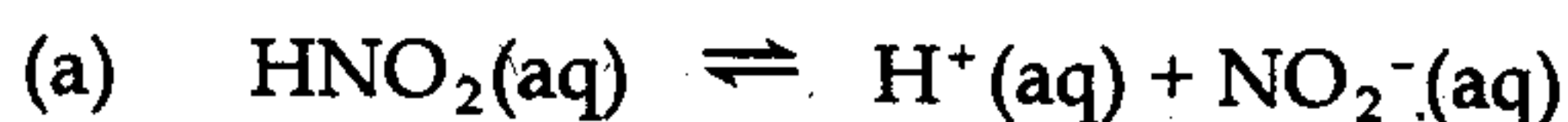
$$K = P_{\text{CO}_2} = 1.5 \times 10^{-4} \text{ atm}$$

$$(b) \quad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \text{ At } 753 \text{ K}, \Delta G^\circ = 88.3 \text{ kJ} - 753 \text{ K} (0.1513 \text{ kJ/K}) = -25.629$$

$$= -25.6 \text{ kJ}$$

$$\ln K = \frac{-(-25.629 \times 10^3 \text{ J})}{8.314 \text{ J/K} \times 753 \text{ K}} = 4.0938 = 4.09; \quad K = P_{\text{CO}_2} = 60 \text{ atm}$$

19.79 *Analyze/Plan.* Given an acid dissociation equilibrium and the corresponding  $K_a$  value, calculate  $\Delta G^\circ$  and  $\Delta G$  for a given set of concentrations. Use Equation [19.22] to calculate  $\Delta G^\circ$  and Equation [19.21] to calculate  $\Delta G$ . *Solve.*

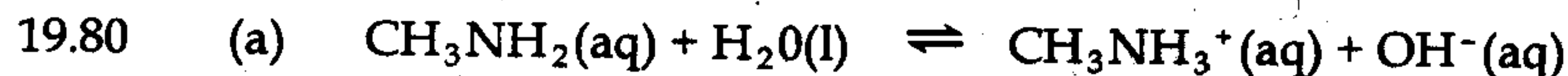


$$(b) \quad \Delta G^\circ = -RT \ln K_a = -(8.314 \times 10^{-3})(298) \ln (4.5 \times 10^{-4}) = 19.0928 = 19.1 \text{ kJ}$$

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

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

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



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

- (c)  $\Delta G = 0$  at equilibrium
- (d)  $\Delta G = \Delta G^\circ + RT \ln Q$ ;  $[\text{OH}^-] = 1 \times 10^{-14} / 1.5 \times 10^{-8} = 6.7 \times 10^{-7}$
- $$= 19.148 + (8.314 \times 10^{-3})(298) \ln \frac{(5.5 \times 10^{-4})(6.67 \times 10^{-7})}{0.120} = -29.43 = -29 \text{ kJ}$$

### Additional Exercises

- 19.81 (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  $\Delta H$  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.

19.82	Process	$\Delta H$	$\Delta S$
(a)		+	+
(b)		-	-
(c)		+	+
(d)		+	+
(e)		-	+

19.83 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.

19.84 If  $\text{NH}_4\text{NO}_3(\text{s})$  dissolves spontaneously in water,  $\Delta G = \Delta H - T\Delta S$ . If  $\Delta G$  is negative and  $\Delta H$  is positive, the sign of  $\Delta S$  must be positive. Furthermore,  $T\Delta S > \Delta H$  at room temperature.

19.85 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:

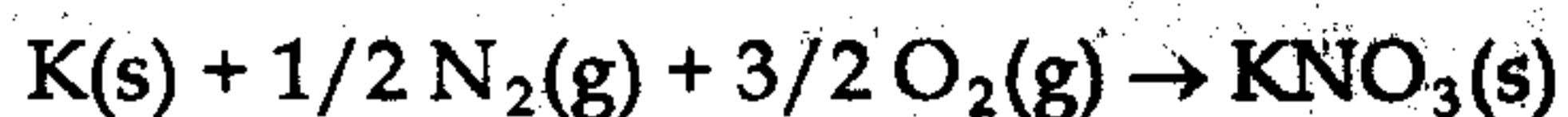
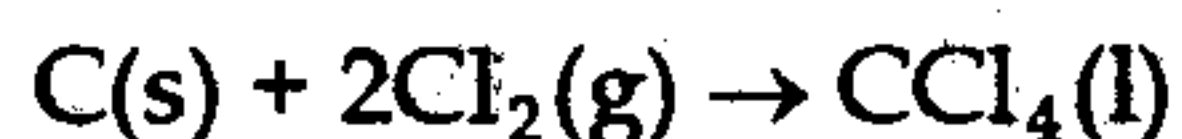
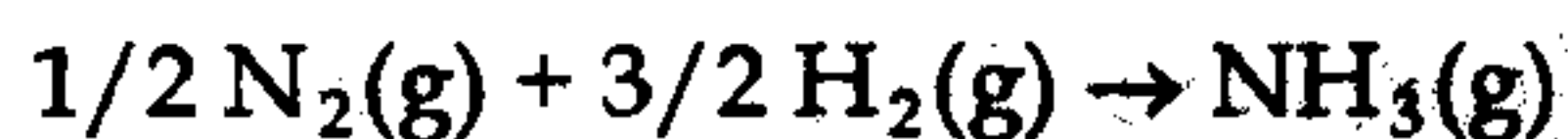


$$\Delta H_{\text{vap}} = \Delta H_f^\circ \text{Br}_2(\text{g}) - \Delta H_f^\circ \text{Br}_2(\text{l}) = 30.71 \text{ kJ} - 0 = 30.71 \text{ kJ}$$

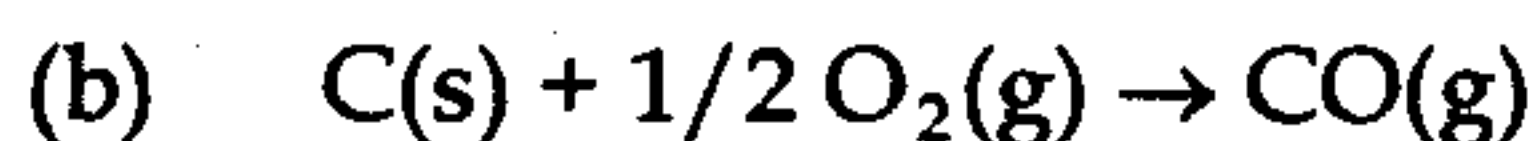
$$T_b = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} = \frac{30.71 \text{ kJ}}{88 \text{ J/mol}\cdot\text{K}} \times \frac{1000 \text{ J}}{\text{kJ}} = 349 = 3.5 \times 10^2 \text{ K}$$

- (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.

- 19.86 (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  $\Delta S^\circ$  to be negative. If  $\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ$  and  $\Delta S_f^\circ$  is negative,  $-T\Delta S_f^\circ$  is positive and  $\Delta G_f^\circ$  is more positive than  $\Delta H_f^\circ$ .



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

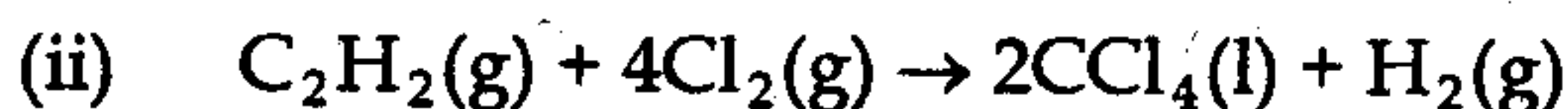


$$\Delta H^\circ = 2\Delta H^\circ \text{RbClO}_3(\text{s}) - 3\Delta H^\circ \text{O}_2(\text{g}) - 2\Delta H^\circ \text{RbCl}(\text{s})$$

$$= 2(-392.4) - 3(0) - 2(-430.5) = +76.2 \text{ kJ}$$

$$\Delta S^\circ = 2(152) - 3(205.0) - 2(92) = -495 \text{ J/K} = -0.495 \text{ kJ/K}$$

$$\Delta G^\circ = 2(-292.0) - 3(0) - 2(-412.0) = +240.0 \text{ kJ}$$

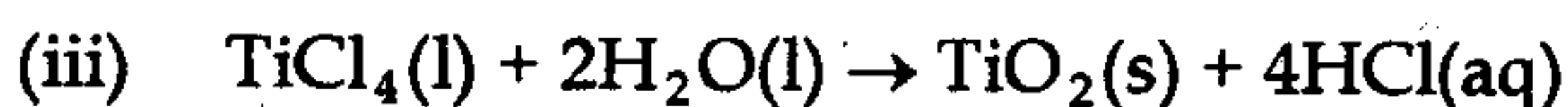


$$\Delta H^\circ = 2\Delta H^\circ \text{CCl}_4(\text{l}) + \Delta H^\circ \text{H}_2(\text{g}) - \Delta H^\circ \text{C}_2\text{H}_2(\text{g}) - 4\Delta H^\circ \text{Cl}_2(\text{g})$$

$$= 2(-139.3) + 0 - (226.7) - 4(0) = -505.3 \text{ kJ}$$

$$\Delta S^\circ = 2(214.4) + 130.58 - (200.8) - 4(222.96) = -533.3 \text{ J/K} = -0.5333 \text{ kJ/K}$$

$$\Delta G^\circ = 2(-68.6) + 0 - (209.2) - 4(0) = -346.4 \text{ kJ}$$

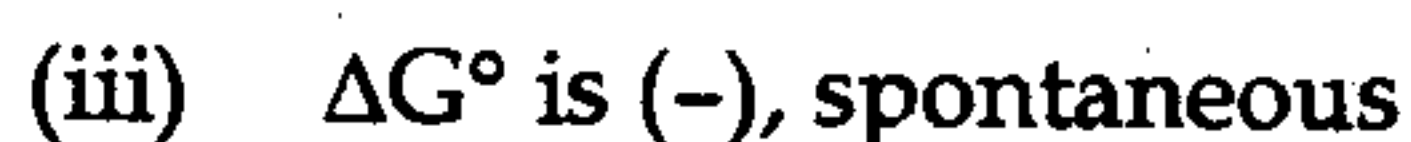
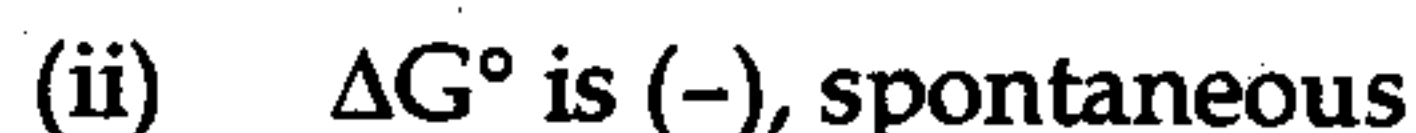
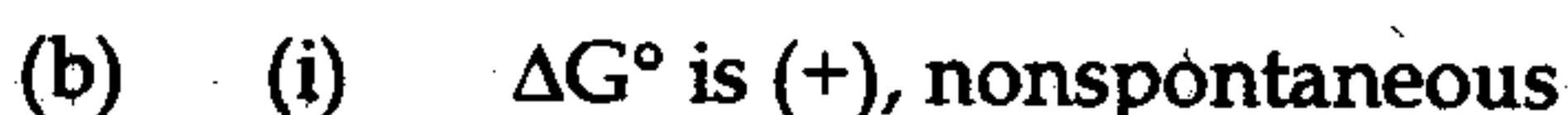


$$\Delta H^\circ = \Delta H^\circ \text{TiO}_2(\text{s}) + 4\Delta H^\circ \text{HCl}(\text{aq}) - \Delta H^\circ \text{TiCl}_4(\text{l}) - 2\Delta H^\circ \text{H}_2\text{O}(\text{l})$$

$$= -944.7 + 4(-167.2) - (-804.2) - 2(-285.83) = -237.6 \text{ kJ}$$

$$\Delta S^\circ = 50.29 + 4(56.5) - 221.9 - 2(69.91) = -85.43 \text{ J/K} = -0.0854 \text{ kJ/K}$$

$$\Delta G^\circ = -889.4 + 4(-131.2) - (-728.1) - 2(-237.13) = -211.8 \text{ kJ}$$



- (c) In each case the manner in which free energy change varies with temperature depends mainly on  $\Delta S$ :  $\Delta G = \Delta H - T\Delta S$ . When  $\Delta S$  is substantially positive,  $\Delta G$  becomes more negative as temperature increases. When  $\Delta S$  is substantially negative,  $\Delta G$  becomes more positive as temperature increases.

- (i)  $\Delta S^\circ$  is negative,  $\Delta G^\circ$  becomes more positive with increasing temperature.
- (ii)  $\Delta S^\circ$  is negative,  $\Delta G^\circ$  becomes more positive with increasing temperature.  
(The reaction will become nonspontaneous at some temperature.)
- (iii)  $\Delta S^\circ$  is negative,  $\Delta G^\circ$  becomes more positive with increasing temperature.  
(The reaction will become nonspontaneous at some temperature.)

19.88  $\Delta G = \Delta G^\circ + RT \ln Q$

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

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

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

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

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

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

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

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

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

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

19.89	Reaction	(a) Sign of $\Delta H^\circ$	(a) Sign of $\Delta S^\circ$	(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  $\Delta H^\circ$  leads to a smaller value of  $K$ , while positive  $\Delta S^\circ$  increases the value of  $K$ .

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

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

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

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

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

The reaction is exothermic, so the value of  $K$  will decrease with increasing temperature, and the mole fraction of  $\text{CH}_3\text{COOH}$  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.

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

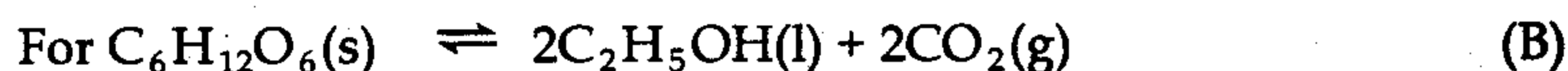
$$-137.9 \text{ kJ} = T(-0.1649 \text{ kJ/K}), T = 836.3 \text{ K}$$

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

19.91 (a) First calculate  $\Delta G^\circ$  for each reaction:



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



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

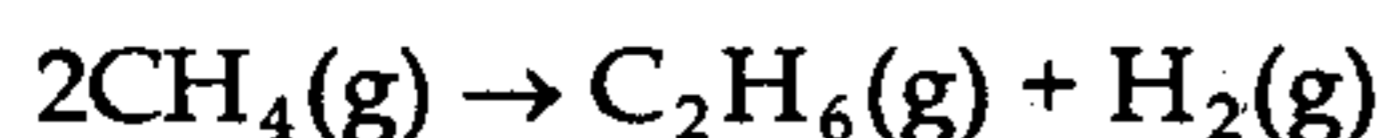
$$\text{For (A), } \ln K = 2879 \times 10^3 / (8.314)(298) = 1162; K = 5 \times 10^{504}$$

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

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

19.92 (a)  $\Delta G^\circ = -RT \ln K$  (Equation [19.22]);  $\ln K = -\Delta G^\circ / RT$

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



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



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

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

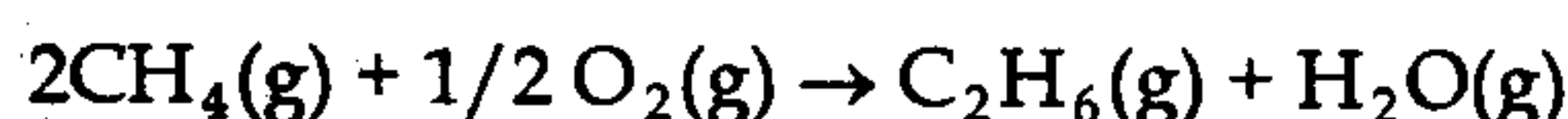
$$\text{at } 298 \text{ K, } \Delta G = 64.92 \text{ kJ} - 298 \text{ K}(-12.52 \times 10^{-3} \text{ kJ/K}) = 68.65 = 68.7 \text{ kJ}$$

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

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

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

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



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

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

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

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

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

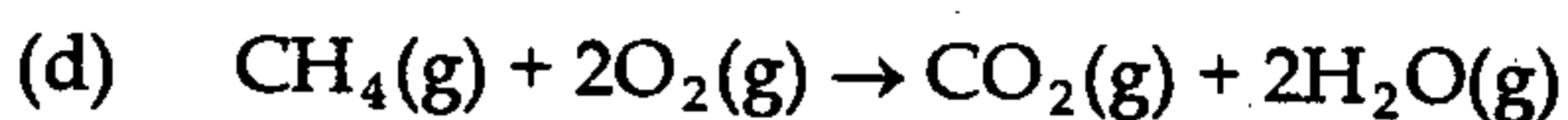
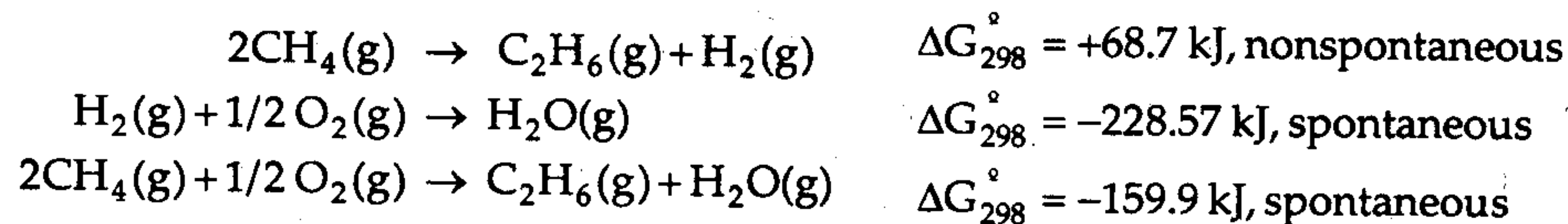
$$\ln K = \frac{-(-159.98 \text{ kJ})}{(8.314 \times 10^{-3} \text{ kJ/K})(298 \text{ K})} = 64.571 = 64.57; K = 1.1 \times 10^{28}$$

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

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

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

- (b) The difference in  $\Delta G^\circ$  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.



19.93  $\Delta G^\circ$  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  $\Delta G$  values that reflect actual concentration, partial pressure, and pH in a cell.

- 19.94 (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,  $\Delta G$  is not zero because the concentrations are not the same on both sides of the membrane. Use Equation [19.21] to calculate  $\Delta G$ :

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

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

- 19.95 (a) To obtain  $\Delta H^\circ$  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,  $\Delta H^\circ$  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  $\Delta S^\circ/R$ .

- 19.96  $S = k \ln W$  (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.)

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

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

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

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

- 19.97 Absolute entropy is a fundamental property of matter at a specified set of conditions, that is, a state. In order to lower the entropy of the fuel, either the structure of the molecules or the conditions (temperature, pressure, amount) must be changed. Any of these changes would require energy, which would reduce the amount of energy available to drive the car, not increase it.

### Integrative Exercises

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

$$\text{acetone: } \Delta S_{\text{vap}}^{\circ} = \Delta H_{\text{vap}}^{\circ} / T = (29.1 \text{ kJ/mol}) / 329.25 \text{ K} = 88.4 \text{ J/mol}\cdot\text{K}$$

$$\text{dimethyl ether: } \Delta S_{\text{vap}}^{\circ} = (21.5 \text{ kJ/mol}) / 248.35 \text{ K} = 86.6 \text{ J/mol}\cdot\text{K}$$

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

$$\text{octane: } \Delta S_{\text{vap}}^{\circ} = (34.4 \text{ kJ/mol}) / 398.75 \text{ K} = 86.3 \text{ J/mol}\cdot\text{K}$$

$$\text{pyridine: } \Delta S_{\text{vap}}^{\circ} = (35.1 \text{ kJ/mol}) / 388.45 \text{ K} = 90.4 \text{ J/mol}\cdot\text{K}$$

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

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

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

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

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

- 19.99 (a) Polymerization is the process of joining many small molecules (monomers) into a few very large molecules (polymers). Polyethylene in particular can have extremely high molecular weights. In general, reducing the number of particles in a system reduces entropy, so  $\Delta S_{\text{poly}}$  is expected to be negative.
- (b)  $\Delta G_{\text{poly}} = \Delta H_{\text{poly}} - T\Delta S_{\text{poly}}$ . If the polymerization of ethylene is spontaneous,  $\Delta G_{\text{poly}}$  is negative. If  $\Delta S_{\text{poly}}$  is negative,  $-T\Delta S_{\text{poly}}$  is positive, so  $\Delta H_{\text{poly}}$  must be negative for  $\Delta G_{\text{poly}}$  to be negative. The enthalpy of polymerization must be exothermic.
- (c) According to Equation [12.1], polymerization of ethylene requires breaking one  $\text{C}=\text{C}$  and forming  $2\text{C}-\text{C}$  per monomer ( $1\text{C}-\text{C}$  between the C-atoms of the monomer and  $2 \times 1/2 \text{C}-\text{C}$  to two other monomers).

$$\Delta H = D(\text{C}=\text{C}) - 2D(\text{C}-\text{C}) = 614 - 2(348) = -82 \text{ kJ/mol C}_2\text{H}_4$$

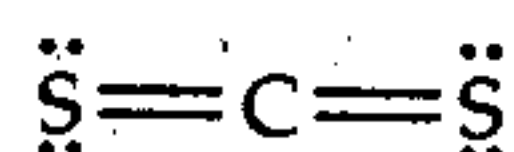
$$\frac{-82 \text{ kJ}}{\text{mol C}_2\text{H}_4} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ molecules}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 1.36 \times 10^{-19} \text{ J/C}_2\text{H}_4 \text{ monomer}$$

- (d) The products of a condensation polymerization are the polymer and a small molecule, typically  $\text{H}_2\text{O}$ ; there is usually one small molecule formed per monomer unit. Unlike addition polymerization, the total number of particles is not reduced. A condensation polymer does impose more order on the monomer or monomers than an addition polymer. If there is a single monomer, it has different functional groups at the two ends and only one end can react to join the polymer, so orientation is required. If there are two different monomers, as in nylon, the monomers alternate in the polymer, so only the correct monomer can react to join the polymer. In terms of structure, the condensation polymer imposes more order on the monomer(s) than an addition polymer. But, condensation polymerization does not lead to a reduction in the number of particles in the system, so  $\Delta S_{\text{poly}}$  will be less negative than for addition polymerization.

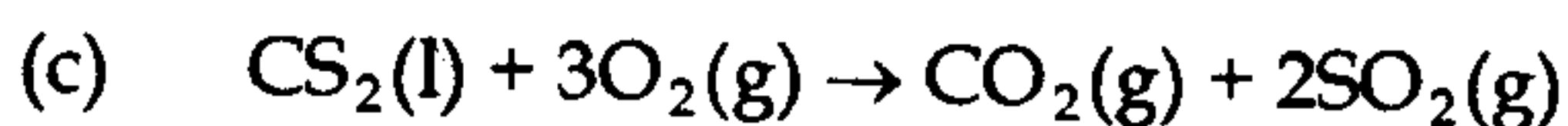
19.100 The activated complex in Figure 14.13 is a single "particle" or entity that contains four atoms. It is formed from an atom A and a triatomic molecule, ABC, that must collide with exactly the correct energy and orientation to form the single entity. There are many fewer degrees of freedom for the activated complex than the separate reactant particles, so the *entropy of activation* is negative.

- 19.101 (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)  $\text{NaCl}(\text{aq}) \rightarrow \text{NaCl}(\text{s}) + \text{H}_2\text{O}(\text{l})$ ;  $\Delta S$  decreases as the mixture (seawater, greater disorder) is separated into pure substances (fewer possible arrangements, more order).

19.102 (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



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

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

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

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

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

$\Delta S_{\text{vap}}$  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
- $\Delta H_{\text{vap}} = T_b \Delta S_{\text{vap}}$
- .

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

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

- 19.103 (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)
- $\Delta G_f^{\circ} = \Delta H_f^{\circ} - T\Delta S_f^{\circ}$
- ;
- $\Delta S_f^{\circ} = (\Delta G_f^{\circ} - \Delta H_f^{\circ})/(-T) = (\Delta H_f^{\circ} - \Delta G_f^{\circ})/T$

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

$\Delta S_f^{\circ}$  is relatively large and negative, as anticipated from part (a).

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

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

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

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

- (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
- $\text{AgNO}_3$
- (
- $\Delta S^{\circ} = +78.9 \text{ J/K}$
- ). 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
- $\text{MgSO}_4$
- solution has a van't Hoff factor of 1.21. That is, for each mole of
- $\text{MgSO}_4$
- 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  $\text{H}_2\text{O}$  molecules lead to a decrease in entropy for  $\text{MgSO}_4(\text{aq})$  relative to  $\text{MgSO}_4(\text{s})$ .

19.104 (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,  $P_{\text{NO}_2} = P_{\text{N}_2\text{O}_4} = 1.0 \text{ atm}$ ,  $P_T = 2.0 \text{ atm}$ .

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

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

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

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

(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  $T$ .

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

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

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

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

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

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

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

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

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

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

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

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

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

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

- 19.106 (a) When the rubber band is stretched, the molecules become more ordered, so the entropy of the system decreases,  $\Delta S_{\text{sys}}$  is negative.
- (b)  $\Delta S_{\text{sys}} = q_{\text{rev}}/T$ . Since  $\Delta S_{\text{sys}}$  is negative,  $q_{\text{rev}}$  is negative and heat is evolved by the system.