

- 19.26 (a) Not necessarily. The only thing we know for sure is that the entropy of the universe increases for a spontaneous process.
- (b) ΔS_{surr} is positive and greater than the magnitude of the decrease in ΔS_{sys} .
- (c) $\Delta S_{\text{sys}} = 78 \text{ J/K}$.
- 19.27 *Analyze.* Consider ΔS for the isothermal expansion of 0.200 mol of an ideal gas at 27 °C and an initial volume of 10.0 L.
- (a) Whenever an ideal gas expands isothermally, we expect an increase in entropy, or positive ΔS , owing to the greater volume available for motion of the particles.
- (b) *Plan.* Use the relationship $\Delta S_{\text{sys}} = nR \ln(V_2/V_1)$, Equation 19.3.
Solve. $\Delta S_{\text{sys}} = 0.200 (8.314 \text{ J/mol-K})(\ln [18.5 \text{ L}/10.0 \text{ L}]) = 1.02 \text{ J/K}$.
Check. We expect ΔS to be positive when the motional freedom of a gas increases, and our calculation agrees with this prediction.
- (c) No. The temperature at which the expansion occurs is not needed to calculate the entropy change, as long as the process is isothermal.
- 19.28 (a) According to Boyle's law, pressure and volume are inversely proportional at constant amount and temperature. If the pressure of an ideal gas increases, volume decreases. We expect a decrease in entropy, or negative ΔS , for the isothermal compression of an ideal gas, owing to the smaller volume available for motion of the particles.
- (b) According to Boyle's law, $P_1V_1 = P_2V_2$ at constant n and T .
 $0.750 \text{ atm} \times V_1 = 1.20 \text{ atm} \times V_2$; $V_2/V_1 = 0.750 \text{ atm}/1.20 \text{ atm} = 0.62500 = 0.625$
 $\Delta S_{\text{sys}} = nR \ln(V_2/V_1) = 0.600 \text{ mol} (8.314 \text{ J/mol-K})(\ln 0.625) = -2.34 \text{ J/K}$
Check. An increase in pressure results in a decrease in volume at constant T , so we expect ΔS to be negative, and it is.
- (c) No. The temperature at which the compression (increase in pressure, decrease in volume) occurs is not needed to calculate the entropy change, as long as the process is isothermal.

The Molecular Interpretation of Entropy and the Third Law of Thermodynamics (Section 19.3)

- 19.29 (a) Yes, the expansion is spontaneous.
- (b) The ideal gas is the system, and everything else, including the vessel containing the vacuum, is the surroundings. There is literally nothing inside the vessel containing the vacuum, no gas molecules and no physical barriers. As the ideal gas expands into the vacuum, there is nothing for it to "push back," so no work is done. Mathematically, $w = -P_{\text{ext}}\Delta V$. Because the gas expands into a vacuum, $P_{\text{ext}} = 0$ and $w = 0$.
- (c) Entropy. The "driving force" for the expansion of the gas is the increase in entropy associated with greater volume, more motional freedom, and more possible positions for the gas particles.

- 19.30 (a) A thermodynamic *state* is a set of conditions, usually temperature and pressure, that defines the properties of a bulk material. A *microstate* is a single possibility for all the positions and kinetic energies of all the molecules in a sample; it is a snapshot of positions and speeds at a particular instant.
- (b) According to Equation 19.5 (Boltzmann law), the more possible microstates for a macroscopic state, the greater the entropy of the state. If S decreases going from A to B, then A has more microstates than B. Or, if ΔS is negative, the number of microstates decreases.
- (c) According to part (b), if the number of microstates available to a system decreases, ΔS_{sys} is negative. For a spontaneous process, ΔS_{univ} is positive, so ΔS_{surr} is positive (and the magnitude is greater than that of ΔS_{sys}).

- 19.31 (a) The higher the temperature, the broader the distribution of molecular speeds and kinetic energies available to the particles. At higher temperature, the wider range of accessible kinetic energies leads to more microstates for the system.
- (b) A decrease in volume reduces the number of possible positions for the particles and leads to fewer microstates for the system.
- (c) Going from liquid to gas, particles have greater translational motion, which increases the number of positions available to the particles and the number of microstates for the system.

- 19.32 (a) ΔH_{vap} for H_2O at $25^\circ\text{C} = 44.02 \text{ kJ/mol}$; at $100^\circ\text{C} = 40.67 \text{ kJ/mol}$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{44.02 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1}{298 \text{ K}} = 148 \text{ J/mol-K}$$

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{40.67 \text{ kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{\text{kJ}} \times \frac{1}{373 \text{ K}} = 109 \text{ J/mol-K}$$

- (b) At both temperatures, the liquid \rightarrow gas phase transition is accompanied by an increase in entropy, as expected. That the magnitude of the increase is greater at the lower temperature requires some explanation.

In the liquid state, there are significant hydrogen bonding interactions between H_2O molecules. This reduces the number of possible molecular positions and the number of microstates. Liquid water at 100° has sufficient kinetic energy to have broken many hydrogen bonds, so the number of microstates for $\text{H}_2\text{O}(\text{l})$ at 100° is greater than the number of microstates for $\text{H}_2\text{O}(\text{l})$ at 25°C . The difference in the number of microstates upon vaporization at 100°C is smaller, and the magnitude of ΔS is smaller.

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

- (a) More gaseous particles means more possible arrangements and greater disorder; ΔS is positive.

- (b) S_{sys} increases when a banana ripens. Starches are polysaccharides, large molecules that break down into sugars, smaller monosaccharides and disaccharides, when ripening occurs. Formation of the sugars increases the number of molecules and the entropy.

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

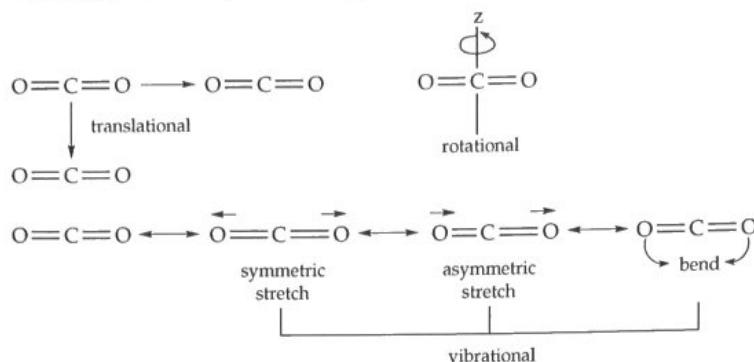
In 19.11 (c), the system goes from two moles of gaseous reactants to one mole of gaseous products, and S_{sys} decreases.

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

In 19.11 (e), the specified state is room temperature and 1 atm pressure. This means that H_2O is present as a liquid; there is then 1 mol of gaseous reactants (CO_2) and 3 mol of gaseous products (CH_4 and 2 O_2), so S_{sys} increases. (The reaction is not spontaneous because of the very large positive ΔH_{sys} for the reaction as written.)

- 19.34 (a) Solids are much more ordered than gases, so ΔS is negative.
- (b) The entropy of the system increases in Exercise 19.12 (a) and (e). There is more motional freedom for the system in both cases. In (b), (c), and (d), there is less motional freedom after the change and the entropy of the system decreases.
- 19.35 *Analyze/Plan.* Consider the conditions that lead to an increase in entropy: more mol gas in products than reactants, increase in volume of sample and, therefore, number of possible arrangements, more motional freedom of molecules, and so on. *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.
- 19.36 (a) When temperature increases, the range of accessible molecular speeds and kinetic energies increases. This produces more microstates and an increase in entropy.
- (b) When the volume of a gas increases (even at constant T), there are more possible positions for the particles, more microstates, and greater entropy.
- (c) When equal volumes of two miscible liquids are mixed, the volume of the sample and, therefore, the number of possible arrangements increases. This produces more microstates and an increase in entropy.
- 19.37 (a) False. The entropy of a pure crystalline substance at absolute zero is zero.
- (b) True.
- (c) False. Monoatomic gases have no rotational or vibrational states.
- (d) True.

- 19.38 (a) True. (From the Boltzmann relationship, $S = k \ln W$.)
- (b) False. The translational, rotational, and vibrational degrees of freedom of CO_2 (or any molecule) are determined by its structure. As long as heating does not change the basic molecular structure, it does not change the degrees of freedom. The additional kinetic energy due to heating is distributed as more translational, vibrational, and rotational motion. That is, number of microstates [see Solution 19.30 (a)] increases, but the degrees of freedom do not.

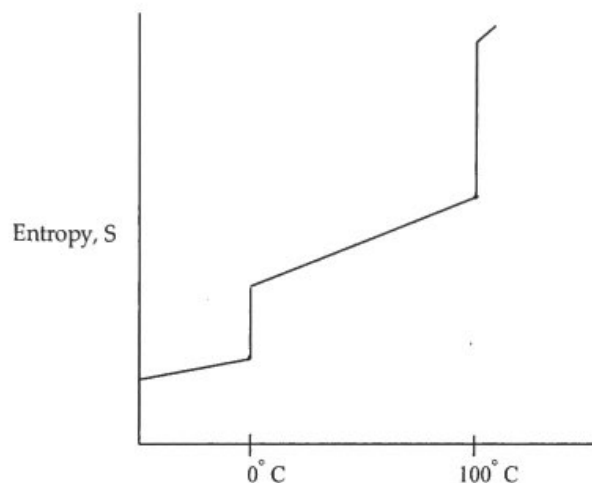


- (c) False. At a given temperature, $\text{CO}_2(\text{g})$ has more microstates and, thus, greater entropy than $\text{Ar}(\text{g})$. Because $\text{CO}_2(\text{g})$ is a triatomic molecule, it has multiple rotational and vibrational microstates not available to monatomic $\text{Ar}(\text{g})$.
- 19.39 *Analyze/Plan.* Consider the factors that lead to higher entropy: more mol gas in products than reactants, increase in volume of sample and, therefore, number of possible arrangements, more motional freedom of molecules, and so on. *Solve.*
- (a) $\text{Ar}(\text{g})$ (gases have higher entropy due primarily to much larger volume)
- (b) $\text{He}(\text{g})$ at 1.5 atm (larger volume and more motional freedom)
- (c) 1 mol of $\text{Ne}(\text{g})$ in 15.0 L (larger volume provides more motional freedom)
- (d) $\text{CO}_2(\text{g})$ (more motional freedom)
- 19.40 (a) One mole of $\text{O}_3(\text{g})$ at 300 °C, 0.01 atm ($\text{O}_3(\text{g})$ is a more complex molecule and has more vibrational degrees of freedom.)
- (b) 1 mol $\text{H}_2\text{O}(\text{g})$ at 100 °C, 1 atm [larger volume occupied by $\text{H}_2\text{O}(\text{g})$]
- (c) 0.5 mol $\text{CH}_4(\text{g})$ at 298 K, 20-L volume (more complex molecule, more rotational and vibrational degrees of freedom)
- (d) 100 g of $\text{Na}_2\text{SO}_4(\text{aq})$ at 30 °C (more motional freedom in aqueous solution)
- 19.41 *Analyze/Plan.* Consider the markers of an increase in entropy for a chemical reaction: liquids or solutions formed from solids, gases formed from either solids or liquids, increase in mol gas during reaction. *Solve.*
- (a) ΔS negative (moles of gas decrease)
- (b) ΔS positive (gas produced, increased disorder)
- (c) ΔS negative (moles of gas decrease)
- (d) ΔS is small and probably positive [moles of gas same in reactants and products, $\text{H}_2\text{O}(\text{g})$ is more structurally complex than $\text{H}_2(\text{g})$]

- 19.42 (a) $\text{Au(l)} \rightarrow \text{Au(s)}$; negative ΔS , less motional freedom in the solid
 (b) $\text{Cl}_2(\text{g}) \rightarrow 2 \text{Cl(g)}$; positive ΔS , moles of gas increase
 (c) $\text{CO(g)} + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_3\text{OH(l)}$; negative ΔS , moles of gas decrease
 (d) $3 \text{Ca(NO}_3)_2(\text{aq}) + 2 (\text{NH}_4)_3\text{PO}_4(\text{aq}) \rightarrow \text{Ca}_3(\text{PO}_4)_2(\text{s}) + 6 \text{NH}_4\text{NO}_3(\text{aq})$; ΔS is negative, less motional freedom, fewer moles of ions in aqueous solution

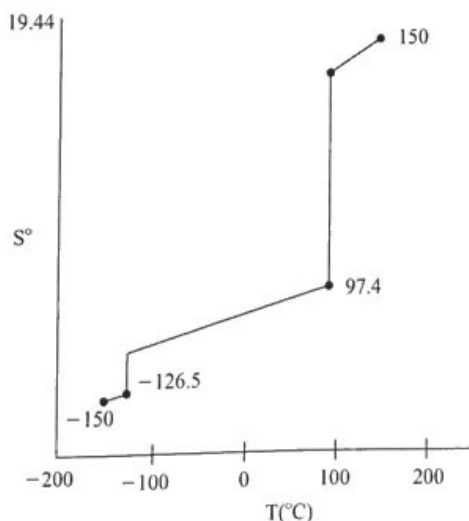
Entropy Changes in Chemical Reactions (Section 19.4)

- 19.43 (a)



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

- 19.44 Melting = -126.5 °C; boiling = 97.4 °C



- 19.45 *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° .
- $C_2H_6(g)$ has more degrees of freedom and larger S° .
 - $CO_2(g)$ has more degrees of freedom and larger S° .
- 19.46 Propylene will have a higher S° at 25 °C. At this temperature, both are gases, so there are no lattice effects. Because 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, whereas in cyclopropane the 3-membered ring severely limits rotation. The greater motional freedom of the propylene molecule leads to a higher absolute entropy.
- 19.47 *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, and so on. *Solve.*
- $Sc(g)$ will have the higher standard entropy at 25 °C. In general, the gas phase of a substance has a larger S° than the solid phase because of the greater volume and motional freedom of the molecules. $Sc(s)$, 34.6 J/mol-K; $Sc(g)$, 174.7 J/mol-K.
 - $NH_3(g)$ will have the higher standard entropy at 25 °C. Molecules in the gas phase have more motional freedom than molecules in solution. $NH_3(g)$, 192.5 J/mol-K; $NH_3(aq)$, 111.3 J/mol-K.
 - $O_3(g)$ will have the higher standard entropy at 25 °C. The triatomic molecule will have more vibrational degrees of freedom than the diatomic molecule. $O_2(g)$, 205.0 J/K; $O_3(g)$, 237.6 J/K.
 - $C(\text{graphite})$ will have the higher standard entropy at 25 °C. 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. $C(\text{diamond})$, 2.43 J/mol-K; $C(\text{graphite})$ 5.69 J/mol-K.
- 19.48
- $C_6H_6(g)$ will have the higher standard entropy at 25 °C. Molecules in the gas phase have larger volume and greater motional freedom than those in the liquid state. $C_6H_6(l)$, 172.8 J/K; $C_6H_6(g)$, 269.2 J/K.
 - $CO_2(g)$ will have the higher standard entropy at 25 °C. The more complex CO_2 molecule has more vibrational degrees of freedom and a slightly higher entropy. $CO(g)$, 197.9 J/mol-K; $CO_2(g)$, 213.6 J/mol-K.
 - Two moles of $NO_2(g)$ will have the higher standard entropy at 25 °C. More particles have a greater number of arrangements or microstates. 1 mol $N_2O_4(g)$, 304.3 J/K; 2 mol $NO_2(g)$, $2(240.45) = 480.90$ J/K.
 - $HCl(g)$ will have a greater standard entropy at 25 °C. The greater motional freedom of HCl molecules in the gas phase outweighs the greater number of particles in $HCl(aq)$. [$HCl(aq)$ is ionized into $H^+(aq)$ and $Cl^-(aq)$.] $HCl(g)$, 186.69 J/K; $HCl(aq)$, 56.5 J/K.

- 19.49 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.
- 19.50 (a) C(diamond), $S^\circ = 2.43 \text{ J/mol-K}$; C(graphite), $S^\circ = 5.69 \text{ J/mol-K}$. 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 whereas there is very little translational or vibrational freedom within the covalent-network diamond lattice.
- (b) S° for buckminsterfullerene will be $\geq 10 \text{ J/mol-K}$. S° for graphite is twice S° for diamond, and S° for the fullerene should be higher than that of graphite. The 60-atom "bucky" balls have more flexibility than graphite sheets. Also, the balls have translational freedom in three dimensions, whereas 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.
- 19.51 *Analyze/Plan.* Follow the logic in Sample Exercise 19.5. *Solve.*
- (a) $\Delta S^\circ = S^\circ \text{C}_2\text{H}_6(\text{g}) - S^\circ \text{C}_2\text{H}_4(\text{g}) - S^\circ \text{H}_2(\text{g})$
 $= 229.5 - 219.4 - 130.58 = -120.5 \text{ J/K}$
 ΔS° is negative because there are fewer moles of gas in the products.
- (b) $\Delta S^\circ = 2S^\circ \text{NO}_2(\text{g}) - \Delta S^\circ \text{N}_2\text{O}_4(\text{g}) = 2(240.45) - 304.3 = +176.6 \text{ J/K}$
 ΔS° is positive because there are more moles of gas in the products.
- (c) $\Delta S^\circ = \Delta S^\circ \text{BeO}(\text{s}) + \Delta S^\circ \text{H}_2\text{O}(\text{g}) - \Delta S^\circ \text{Be}(\text{OH})_2(\text{s})$
 $= 13.77 + 188.83 - 50.21 = +152.39 \text{ J/K}$
 ΔS° is positive because the product contains more total particles and more moles of gas.
- (d) $\Delta S^\circ = 2S^\circ \text{CO}_2(\text{g}) + 4S^\circ \text{H}_2\text{O}(\text{g}) - 2S^\circ \text{CH}_3\text{OH}(\text{g}) - 3S^\circ \text{O}_2(\text{g})$
 $= 2(213.6) + 4(188.83) - 2(237.6) - 3(205.0) = +92.3 \text{ J/K}$
 ΔS° is positive because the product contains more total particles and more moles of gas.
- 19.52 (a) $\Delta S^\circ = S^\circ \text{NH}_4\text{NO}_3(\text{s}) - S^\circ \text{HNO}_3(\text{g}) - S^\circ \text{NH}_3(\text{g})$
 $= 151 - 266.4 - 192.5 = -307.9 = -308 \text{ J/K}$
 ΔS° is large and negative because all reactants are gases (2 moles) and the product is a solid.

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

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

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

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

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

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

Gibbs Free Energy (Sections 19.5 and 19.6)

- 19.53 (a) Yes. $\Delta G = \Delta H - T\Delta S$
 (b) No. If ΔG is positive, the process is nonspontaneous.
 (c) No. There is no relationship between ΔG and rate of reaction. A spontaneous reaction, one with a $-\Delta G$, may occur at a very slow rate. For example, $2 \text{H}_2(g) + \text{O}_2(g) \rightarrow 2 \text{H}_2\text{O}(g)$, $\Delta G = -457 \text{ kJ}$ is very slow if not initiated by a spark.
- 19.54 (a) No. $\Delta G = \Delta G^\circ + RT \ln Q$. The relative magnitudes of ΔG and ΔG° depend on the value of Q .
 (b) For a process that occurs at constant temperature and pressure, the system is at equilibrium when $\Delta G = 0$.
 (c) No. Activation energy is related to the rate constant, k . The sign and magnitude of ΔG give no information about rate.
- 19.55 *Analyze/Plan.* Consider the definitions of ΔH° , ΔS° , and ΔG° , along with sign conventions. $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. *Solve.*
 (a) ΔH° is negative; the reaction is exothermic.
 (b) ΔS° is negative; the reaction leads to decrease in disorder (increase in order) of the system.
 (c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -35.4 \text{ kJ} - 298 \text{ K} (-0.0855 \text{ kJ/K}) = -9.921 = -9.9 \text{ kJ}$
 (d) At 298 K, ΔG° is negative. If all reactants and products are present in their standard states, the reaction is spontaneous (in the forward direction) at this temperature.
- 19.56 (a) ΔH° is positive; the reaction is endothermic.
 (b) ΔS° is positive; the reaction leads to an increase in disorder.
 (c) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = 23.7 \text{ kJ} - 298 \text{ K} (0.0524 \text{ kJ/K}) = 8.0848 = 8.08 \text{ kJ}$