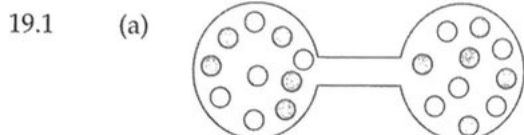


19 Chemical Thermodynamics

Visualizing Concepts



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

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

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

- 19.2 (a) Based on experience, the process is spontaneous. We know that 1,1-difluoroethane is a gas at atmospheric pressure, so the pressure inside the can must be much greater than atmospheric in order for the substance to be liquefied. When the nozzle is pressed and the system is open to the lower pressure of the atmosphere, the liquid vaporizes spontaneously. The 1,1-difluoroethane gas escapes the nozzle without external assistance.

- (b) We expect q_{sys} to be positive. We know that ΔH is positive for the vaporization of a gas. Because the change does not occur at constant pressure, q_{sys} and ΔH are not equal, but the sign of q_{sys} is still positive.

- (c) ΔS is definitely positive for this process. Because the process is spontaneous and ΔH is positive, ΔS must be positive and large so that ΔG is negative. It is also true that the system, the 1,1-difluoroethane molecules, occupy a larger volume and have greater motional freedom after vaporization.

- (d) The operation of the keyboard cleaner definitely depends more on entropy change than heat flow.

- 19.3 (a) The process depicted is a change of state from a solid to a gas. ΔS is positive because of the greater motional freedom of the particles. ΔH is positive because both melting and boiling are endothermic processes.

- (b) The sign of ΔS_{surr} is negative, and the magnitude is less than or equal to ΔS_{sys} . If the process is spontaneous, the second law states that $\Delta S_{\text{univ}} \geq 0$. Because ΔS_{sys} is positive, ΔS_{surr} must be negative. If the change occurs via a reversible pathway, $\Delta S_{\text{univ}} = 0$ and $\Delta S_{\text{surr}} = -\Delta S_{\text{sys}}$. If the pathway is irreversible, the magnitude of ΔS_{sys} is greater than the magnitude of ΔS_{surr} , but the sign of ΔS_{surr} is still negative.
- 19.4 Both ΔH and ΔS for this reaction are positive.
- The reaction involves breaking five blue–blue and twenty blue–red bonds and then forming twenty blue–red bonds. The net change is breaking five blue–blue bonds. Enthalpies for bond breaking (Section 8.8) are always positive.
- In the depicted reaction, both reactants and products are in the gas phase (they are far apart and randomly placed). There are twice as many molecules (or moles) of gas in the products, so ΔS is positive for this reaction.
- 19.5 *Analyze/Plan.* Consider the physical changes that occur when a substance is heated. How do these changes affect the entropy of the substance? *Solve.*
- (a) Both 1 and 2 represent changes in entropy at constant temperature; these are phase changes. Because 1 happens at a lower temperature, it represents melting (fusion), and 2 represents vaporization.
- (b) The substance changes from solid to liquid in 1, from liquid to gas in 2. The larger volume and greater motional freedom of the gas phase causes ΔS for vaporization to (always) be larger than ΔS for fusion.
- (c) For a perfect crystal at $T = 0$ K, the value of S is zero. This is the third law of thermodynamics.
- 19.6 (a) We expect the enthalpy of combustion of the two isomers to be very similar. The molecular formulas of the two molecules are the same, so the balanced chemical equations for the two combustion reactions are identical. In the calculation of combustion enthalpy from standard enthalpies of formation of products and reactants, the only difference will be in the standard enthalpies of formation of the two isomers.
- (b) We expect *n*-pentane to have the higher standard molar entropy. The rod-shaped *n*-pentane has more possible vibrational and rotational motions than the almost-spherical neopentane. That is, *n*-pentane has greater motional energy, which results in a higher standard molar entropy than that of neopentane.
- 19.7 (a) At 300 K, $\Delta H = T\Delta S$. Because $\Delta G = \Delta H - T\Delta S$, $\Delta G = 0$ at this point. When $\Delta G = 0$, the system is at equilibrium.
- (b) The reaction is spontaneous when ΔG is negative. This condition is met when $T\Delta S > \Delta H$. From the diagram, $T\Delta S > \Delta H$ when $T > 300$ K. The reaction is spontaneous at temperatures above 300 K.
- 19.8 (a) At equilibrium, $\Delta G = 0$. On the diagram, $\Delta G = 0$ at 250 K. The system is at equilibrium at 250 K.
- (b) A reaction is spontaneous when ΔG is negative. The reaction is spontaneous at temperatures greater than 250 K.

- (c) $\Delta G = \Delta H - T\Delta S$, in the form of $y = b + mx$. ΔH is the y intercept of the graph (where $T = 0$) and is positive.
- (d) The slope of the graph is $-\Delta S$. The slope is negative, so ΔS is positive. [Also, ΔG decreases as T increases, so the $T\Delta S$ term must become more negative and ΔS is positive.]
- 19.9 (a) *Analyze.* The boxes depict three different mixtures of reactants and products for the reaction $A_2 + B_2 \rightleftharpoons 2AB$.
- Plan.* $K_c = 1 = \frac{[AB]^2}{[A][B]}$. Calculate Q for each box, using number of molecules as a measure of concentration. If $Q = 1$, the system is at equilibrium. *Solve.*
- Box 1: $K = \frac{(3)^2}{(3)(3)} = 1$
- Box 2: $Q = \frac{(1)^2}{(4)(4)} = \frac{1}{16} = 0.0625 = 0.06$
- Box 3: $Q = \frac{(7)^2}{(1)(1)} = \frac{49}{1} = 49$
- Box 1 is at equilibrium.
- (b) Box 2.
- (c) Qualitatively, Box 3 is farthest from equilibrium, so it has the largest magnitude of ΔG (driving force to reach equilibrium), then Box 2, and then Box 1, where $\Delta G = 0$.
- Box 1 < Box 2 < Box 3
- Quantitatively, $\Delta G = \Delta G^\circ - RT \ln Q$. For Box 1, $\Delta G = 0$ and $K = 1$, so $\Delta G^\circ = 0$.
- Box 2: $\Delta G = 0 - RT \ln(0.0625) = 2.77 RT$
- Box 3: $\Delta G = 0 - RT \ln(49) = -3.89 RT$
- Quantitative treatment confirms the order for magnitude of ΔG as Box 1 < Box 2 < Box 3.
- 19.10 (a) True. When $\Delta G = 0$, the reaction is at equilibrium.
- (b) False. At equilibrium, there is a mixture of reactants and products.
- (c) False. There are fewer moles of gas in the products than the reactants, so ΔS is negative.
- (d) False. At the left and right extremes of the graph, reactants and products are gases at 1 atm pressure; they are in their standard states. The quantity "x" is the difference in free energy between reactants and products in their standard states, ΔG° .
- (e) True. ΔG is a measure of the driving force for a reaction to reach equilibrium.

Spontaneous Processes (Section 19.1)

- 19.11 *Analyze/Plan.* Follow the logic in Sample Exercise 19.1. *Solve.*
- (a) Spontaneous; at ambient temperature, ripening happens without intervention.
- (b) Spontaneous; sugar is soluble in water, and even more soluble in hot coffee.

- (c) Spontaneous; N_2 molecules are stable relative to isolated N atoms.
- (d) Spontaneous; under certain atmospheric conditions, lightning occurs.
- (e) Nonspontaneous; CO_2 and H_2O are in contact continuously at atmospheric conditions in nature and do not form CH_4 and O_2 .
- 19.12 (a) Nonspontaneous; at 1 atm, ice does not melt spontaneously at temperatures below its normal melting point.
- (b) Nonspontaneous; a mixture cannot be separated without outside intervention.
- (c) Spontaneous.
- (d) Spontaneous. The reaction is spontaneous but slow unless encouraged by a catalyst or spark.
- (e) Spontaneous; the very polar HCl molecules readily dissolve in water to form concentrated HCl(aq).
- 19.13 (a) True, assuming the conditions are the same for the forward and reverse reactions.
- (b) False. A spontaneous process occurs without outside intervention. This definition says nothing about how quickly the process occurs. Spontaneity is a thermodynamic property, while rate is a kinetic property.
- (c) False. All spontaneous processes are real processes and real processes are irreversible.
- (d) True.
- (e) False. The maximum amount of work can be accomplished by a reversible process.
- 19.14 (a) Yes. While most spontaneous processes are exothermic, some, such the melting of ice at room temperature, are endothermic.
- (b) Yes. Melting is an example of a process that is spontaneous at one temperature, the melting point, but nonspontaneous at other temperatures. Other phase changes are also examples of this behavior.
- (c) No. While the forward and reverse processes can be induced, the processes cannot be reversed with an infinitesimally small change in some property of the system.
- (d) Yes. The reversible pathway can accomplish the maximum amount of work on its surroundings because no entropy is lost to the universe. $\Delta S_{\text{universe}} = 0$.
- 19.15 *Analyze/Plan.* Define the system and surroundings. Use the appropriate definition to answer the specific questions. *Solve.*
- (a) Water is the system. Heat must be added to the system to evaporate the water. The process is endothermic.
- (b) At 1 atm, the reaction is spontaneous at temperatures above 100°C .
- (c) At 1 atm, the reaction is nonspontaneous at temperatures below 100°C .
- (d) The two phases are in equilibrium at 100°C .

- 19.16 (a) Exothermic. If melting requires heat and is endothermic, freezing must be exothermic.
- (b) At 1 atm (indicated by the term *normal freezing point*), the freezing of *n*-octane is spontaneous at temperatures below $-57\text{ }^{\circ}\text{C}$.
- (c) At 1 atm, the freezing of *n*-octane is nonspontaneous at temperatures above $-57\text{ }^{\circ}\text{C}$.
- (d) At 1 atm and $-57\text{ }^{\circ}\text{C}$, the normal freezing point of *n*-octane, the solid and liquid phases are in equilibrium. That is, at the freezing point, *n*-octane molecules escape to the liquid phase at the same rate as liquid *n*-octane solidifies, assuming no heat is exchanged between *n*-octane and the surroundings.
- 19.17 *Analyze/Plan.* Consider the definitions of the terms *reversible*, *isothermal*, and *state function* to answer the questions. *Solve.*
- (a) No. Temperature is a state function, so a change in temperature does not depend on pathway. (As we are talking about an ideal gas, a reversible pathway may be possible for this change in state. An irreversible pathway is always possible.)
- (b) No. An isothermal process occurs at constant temperature.
- (c) No. ΔE is a state function. $\Delta E = q + w$; q and w are not state functions. Their values do depend on path, but their sum, ΔE , does not.
- 19.18 (a) Yes, because ΔE is a state function. $(1 \rightarrow 2) = -\Delta E (2 \rightarrow 1)$
- (b) No. We can say nothing about the values of q and w because we have no information about the paths.
- (c) The magnitudes of the work are equal, but the signs are opposite. 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.
- 19.19 *Analyze/Plan.* Define the system and surroundings. Use the appropriate definition to answer the specific questions. *Solve.*
- (a) An ice cube can melt reversibly at the conditions of temperature and pressure where the solid and liquid are in equilibrium. At 1 atm external pressure, the normal melting point of water is $0\text{ }^{\circ}\text{C}$.
- (b) No. We know that melting is endothermic, so ΔH for melting ice is a positive, nonzero value. Also, since ΔH is a state function, the nonzero value is independent of path. Whether the ice cube melts reversibly or irreversibly, ΔH for the process is not zero.
- 19.20 (a) The detonation of an explosive is definitely not reversible. The farflung debris from the explosion (system and surroundings) cannot be perfectly reconstructed, even with a large input of energy.
- (b) The quantity q is related to ΔH . As the detonation is highly exothermic, q is large and negative.
- If only P - V work is done and P is constant, $\Delta H = q$. Although these conditions probably do not apply to a detonation, we can still predict the sign of q , based on ΔH , if not its exact magnitude.

- (c) The sign (and magnitude) of w depend on the path of the process, the exact details of how the detonation is carried out. It seems clear, however, that work will be done by the system on the surroundings in almost all circumstances (buildings collapse, earth and air are moved), so the sign of w is probably negative.

Entropy and the Second Law of Thermodynamics (Section 19.2)

- 19.21 (a) True.
 (b) False. For a reversible process, the entropy change of the universe is zero.
 (c) True.
 (d) False. For a reversible process, the entropy change to the system need not be zero, but it must be matched by the entropy change to the surroundings.
- 19.22 (a) True.
 (b) False. For an irreversible process, the net entropy change of the system and surroundings must be positive.
 (c) False. For a spontaneous (and thus irreversible) process, the net entropy change of the system and surroundings must be positive. The entropy change of the system could be negative if the entropy change of the surroundings was large and positive.
 (d) True. For an isothermal process, $\Delta S = q_{\text{rev}}/T$.
- 19.23 (a) $\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$, entropy increases, more mol gas in products, greater motional freedom.
 (b)
$$\Delta S = \frac{\Delta H}{T} = \frac{29.6 \text{ kJ}}{\text{mol Br}_2(\text{l})} \times 1.00 \text{ mol Br}_2(\text{l}) \times \frac{1}{(273.15 + 58.8)\text{K}} \times \frac{1000 \text{ J}}{1 \text{ kJ}} = 89.2 \text{ J/K}$$
- 19.24 (a) $\text{Ga}(\text{l}) \rightarrow \text{Ga}(\text{s})$, ΔS is negative, less motional freedom
 (b)
$$\Delta H = 60.0 \text{ g Ga} \times \frac{1 \text{ mol Ga}}{69.723 \text{ g Ga}} \times \frac{-5.59 \text{ kJ}}{\text{mol Ga}} = -4.81046 = -4.81 \text{ kJ}$$

$$\Delta S = \frac{\Delta H}{T} = -4.81046 \text{ kJ} \times \frac{1000 \text{ J}}{1 \text{ kJ}} \times \frac{1}{(273.15 + 29.8)\text{K}} = -15.9 \text{ J/K}$$
- 19.25 (a) False. The second law states that entropy is conserved for a reversible process.
 (b) True. In a reversible process, $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$. If ΔS_{sys} is positive, ΔS_{surr} must be negative.
 (c) False. Because ΔS_{univ} must be positive for a spontaneous process, ΔS_{surr} must be greater than -4.2 J/K . Entropy is not conserved for a spontaneous process.