

## CHAPTER 7

### THERMODYNAMICS: THE SECOND AND THIRD LAWS

7.1 (a) rate of entropy generation  $= \frac{\Delta S_{\text{surr}}}{\text{time}} = - \frac{q_{\text{rev}}}{\text{time} \cdot T}$   
 $= - \frac{\text{rate of heat generation}}{T}$   
 $= \frac{-(100. \text{ J} \cdot \text{s}^{-1})}{293 \text{ K}} = 0.341 \text{ J} \cdot \text{K}^{-1} \cdot \text{s}^{-1}$

(b)  $\Delta S_{\text{day}} = (0.341 \text{ J} \cdot \text{K}^{-1} \cdot \text{s}^{-1})(60 \text{ sec} \cdot \text{min}^{-1})(60 \text{ min} \cdot \text{hr}^{-1})(24 \text{ hr} \cdot \text{day}^{-1})$   
 $= 29.5 \text{ kJ} \cdot \text{K}^{-1} \cdot \text{day}^{-1}$

(c) Less, because in the equation  $\Delta S = \frac{-\Delta H}{T}$ , if  $T$  is larger,  $\Delta S$  is smaller.

7.3 (a)  $\Delta S = \frac{q_{\text{rev}}}{T} = \frac{65 \text{ J}}{298 \text{ K}} = 0.22 \text{ J} \cdot \text{K}^{-1}$

(b)  $\Delta S = \frac{65 \text{ J}}{373 \text{ K}} = 0.17 \text{ J} \cdot \text{K}^{-1}$

(c) The entropy change is smaller at higher temperatures, because the matter is already more chaotic. The same amount of heat has a greater effect on entropy changes when transferred at lower temperatures.

7.5 (a) The relationship to use is  $dS = \frac{dq}{T}$ . At constant pressure, we can

substitute

$$dq = n C_p dT :$$

$$dS = \frac{n C_p dT}{T}$$

Upon integration, this gives  $\Delta S = n C_p \ln \frac{T_2}{T_1}$ . The answer is calculated by

simply plugging in the known quantities. Remember that for an ideal monatomic gas

$$C_p = \frac{5}{2} R :$$

$$\Delta S = (1.00 \text{ mol}) \left( \frac{5}{2} \times 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \right) \ln \frac{431.0 \text{ K}}{310.8 \text{ K}} = 6.80 \text{ J} \cdot \text{K}^{-1}$$

(b) A similar analysis using  $C_v$  gives  $\Delta S = n C_v \ln \frac{T_2}{T_1}$ , where  $C_v$  for a monatomic ideal gas is  $\frac{3}{2} R$  :

$$\Delta S = (1.00 \text{ mol}) \left( \frac{3}{2} \times 8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \right) \ln \frac{431.0 \text{ K}}{310.8 \text{ K}} = 4.08 \text{ J} \cdot \text{K}^{-1}$$

**7.7** Because the process is isothermal and reversible, the relationship  $dS = \frac{dq}{T}$

can be used. Because the process is isothermal,  $\Delta U = 0$  and hence

$q = -w$ , where  $w = -PdV$ . Making this substitution, we obtain

$$dS = \frac{P dV}{T} = \frac{nRT}{TV} dV = \frac{nR}{V} dV$$

$$\therefore \Delta S = nR \ln \frac{V_2}{V_1}$$

Substituting the known quantities, we obtain

$$\begin{aligned} \Delta S &= (5.25 \text{ mol}) (8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \frac{34.058 \text{ L}}{24.252 \text{ L}} \\ &= 14.8 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

**7.9** The change in entropy for each block (block 1 and block 2) are:

$$\Delta S_1 = \frac{q_1}{T_1} \text{ and } \Delta S_2 = \frac{q_2}{T_2} \text{ energy is transferred, then the change in entropy}$$

for the system is:

$$\Delta S_{\text{sys}} = \Delta S_1 + \Delta S_2 = \frac{q_1}{T_1} + \frac{q_2}{T_2}$$

If 1 J of energy is transferred from block 2 to block 1  $q_1 = +1 \text{ J}$ ,

$$q_2 = -1 \text{ J, and } \Delta S_{\text{sys}} = \frac{1}{T_1} - \frac{1}{T_2}$$

For the transfer of heat from block 2 to block 1 to be spontaneous,

$\Delta S_{\text{sys}}$  must be positive and, therefore,  $T_2$  would have to be greater than  $T_1$ .

$$7.11 \quad (a) \quad \Delta S^\circ = \frac{q}{T} = \frac{\Delta H^\circ}{T} = \frac{1.00 \text{ mol} \times (-6.01 \text{ kJ} \cdot \text{mol}^{-1})}{273.2 \text{ K}} = -22.0 \text{ J} \cdot \text{K}^{-1}$$

$$(b) \quad \Delta S = \frac{q}{T} = \frac{\Delta H}{T} = \frac{\frac{50.0 \text{ g}}{46.07 \text{ g} \cdot \text{mol}^{-1}} \times 43.5 \text{ kJ} \cdot \text{mol}^{-1}}{351.5 \text{ K}} = +134 \text{ J} \cdot \text{K}^{-1}$$

7.13 (a) The boiling point of a liquid may be obtained from the relationship

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{B}}}, \text{ or } T_{\text{B}} = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}}. \text{ This relationship should be rigorously true}$$

if we have the actual enthalpy and entropy of vaporization. The data in the Appendix, however, are for 298 K. Thus, calculation of  $\Delta H_{\text{vap}}^\circ$  or  $\Delta S_{\text{vap}}^\circ$ , using the enthalpy and entropy differences between the gas and liquid forms at 298 K, give a good approximation of these quantities but the values are not exact. For ethanal(l)  $\longrightarrow$  ethanal(g), the data in the appendix give

$$\Delta H_{\text{vap}} \cong -166.19 \text{ kJ} \cdot \text{mol}^{-1} - (-192.30) \text{ kJ} \cdot \text{mol}^{-1} = 26.11 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S_{\text{vap}} \cong 250.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - 160.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 90.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$T_{\text{B}} = \frac{26.11 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{90.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = 290. \text{ K}$$

(b) The boiling point of ethanal is 20.8°C or 293.9 K.

(c) These numbers are in very good agreement.

(d) Differences arise partly because the enthalpy and entropy of vaporization are slightly different from the values calculated at 298 K, but the boiling point of ethanal is not 298 K.

- 7.15** (a) Trouton's rule indicates that the entropy of vaporization for a number of organic liquids is approximately  $85 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . Using this information and the relationship

$$T_B = \frac{\Delta H^\circ_{\text{vap}}}{\Delta S^\circ_{\text{vap}}} = \frac{21.51 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{85 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} = 253 \text{ K}.$$

- (b) The experimental boiling point of dimethyl ether is 248 K, which is in reasonably close agreement, given the nature of the approximation.

- 7.17** (a) The value can be estimated from

$$\Delta H^\circ_{\text{vap}} = T \Delta S^\circ_{\text{vap}}$$

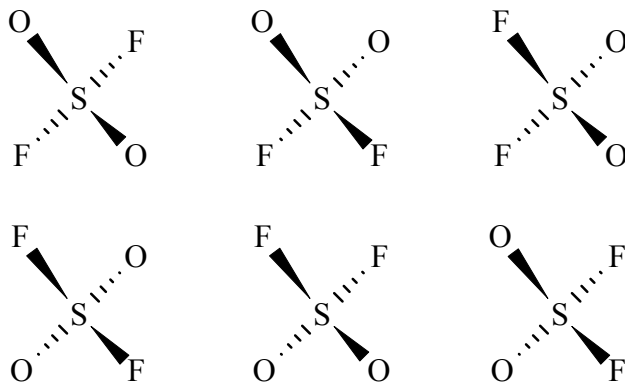
$$\begin{aligned} \Delta H^\circ_{\text{vap}} &= (353 \text{ K})(85 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\ &= +30. \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

(b) 
$$\Delta S^\circ_{\text{surr}} = -\frac{\Delta H^\circ_{\text{system}}}{T}$$

$$\Delta S_{\text{surr}} = -\left(\frac{10 \text{ g}}{78.11 \text{ g} \cdot \text{mol}^{-1}}\right)\left(\frac{30 \text{ kJ} \cdot \text{mol}^{-1}}{353 \text{ K}}\right) = -11 \text{ J} \cdot \text{K}^{-1}$$

- 7.19**  $\text{COF}_2$ .  $\text{COF}_2$  and  $\text{BF}_3$  are both trigonal planar molecules, but it would be possible for the molecule to be disordered with the fluorine and oxygen atoms occupying the same locations. Because all the groups attached to boron are identical, such disorder is not possible.

- 7.21** There are six orientations of an  $\text{SO}_2\text{F}_2$  molecule as shown below:



The Boltzmann expression for one mole of  $\text{SO}_2\text{F}_2$  molecules having six possible orientations is

$$S = k \ln 6^{6.02 \times 10^{23}} = (1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}) \ln 6^{6.02 \times 10^{23}}$$
$$S = 14.9 \text{ J} \cdot \text{K}^{-1}$$

- 7.23** (a) HBr, because Br is more massive and contains more elementary particles than F in HF; (b)  $\text{NH}_3$ , because it has greater complexity, being a molecule rather than a single atom; (c)  $\text{I}_2(\text{l})$  because molecules in liquids are more randomly oriented than molecules in solids; (d) 1.0 mol  $\text{Ar}(\text{g})$  at 1.00 atm, because it will occupy a larger volume than 1.0 mol of  $\text{Ar}(\text{g})$  at 2.00 atm.
- 7.25** It is easy to order  $\text{H}_2\text{O}$  in its various phases because entropy will increase when going from a solid to a liquid to a gas. The main question concerns where to place  $\text{C}(\text{s})$  in this order, and that will essentially become a question of whether  $\text{C}(\text{s})$  should have more or less entropy than  $\text{H}_2\text{O}(\text{s})$ , because we would automatically expect  $\text{C}(\text{s})$  to have less entropy than any liquid. Because water is a molecular substance held together in the solid phase by weak hydrogen bonds, and in  $\text{C}(\text{s})$ , which we will take to be the standard state from graphite, the carbon is more rigidly held in place and will have less entropy.  $\text{C}(\text{s}) < \text{H}_2\text{O}(\text{s}) < \text{H}_2\text{O}(\text{l}) < \text{H}_2\text{O}(\text{g})$
- 7.27** (a) In the standard state, bromine is a liquid and iodine is a solid. If the two substances had the same state (i.e., both were gases or both liquids) we would expect iodine to have the higher entropy due to its larger mass and consequently larger number of fundamental particles. However, because the compounds are in different states, we would expect the liquid to have a higher entropy than the solid.
- (b) When we consider the two structures, it is clear that pentene will have more flexibility in its framework than cyclopentane, which will be

comparatively rigid. Therefore, we predict pentene to have a higher entropy.

(c) Ethene (or ethylene) is a gas and polyethylene is a solid, so we automatically expect ethene to have a higher entropy. Also, for the same mass, a sample of ethene will be composed of many small molecules, whereas polyethylene will be made up of fewer but larger molecules.

- 7.29** (a) Entropy should decrease because the number of moles of gas is less on the product side of the reaction.  
(b) Entropy should increase because the dissolution of the solid copper phosphate will increase the randomness of the copper and phosphate ions.  
(c) Entropy should decrease as the total number of moles decreases.

- 7.31**  $\Delta S_A > \Delta S_C > \Delta S_B$ . The change in entropy for container A is greater than that for container B or C due to the greater number of particles. The change in entropy in container C is greater than that of container B because of the disorder due to the vibrational motion of the molecules in container C.

- 7.33** (a)  $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{l})$

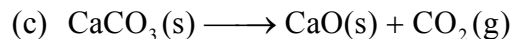
$$\begin{aligned}\Delta S^\circ_{\text{f}} &= \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}} \\ &= 69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + \frac{1}{2}(205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -163.34 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

The entropy change is negative because the number of moles of gas has decreased by 1.5. Note that the absolute entropies of the elements are not 0, and that the entropy change for the reaction in which a compound is formed from the elements is also not 0.

- (b)  $\text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$

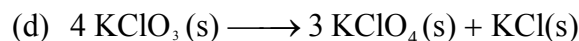
$$\begin{aligned}\Delta S^\circ_{\text{r}} &= 213.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad - [197.67 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + \frac{1}{2}(205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -86.50 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

The entropy change is negative because the number of moles of gas has decreased by 0.5.



$$\begin{aligned}\Delta S^\circ_r &= 39.75 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 213.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [+92.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\ &= +160.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

The entropy change is positive because the number of moles of gas has increased by 1.



$$\begin{aligned}\Delta S^\circ_r &= 3(151.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + 82.59 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad - [4(143.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -36.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

It is not immediately obvious, but the four moles of solid products are more ordered than the four moles of solid reactants.

**7.35**  $dS = \frac{dq_{rev}}{T} = \frac{C_{p,m} \cdot dT}{T}$  and, therefore,  $\Delta S = \int_{T_1}^{T_2} \frac{C_{p,m}}{T} dT$ .

if  $C_{p,m} = a + bT + c/T^2$  then

$$\begin{aligned}\Delta S &= \int_{T_1}^{T_2} \frac{a + bT + c/T^2}{T} dT \\ &= \int_{T_1}^{T_2} \left( \frac{a}{T} + b + \frac{c}{T^3} \right) dT = a \ln(T) + bT - \frac{c}{2T^2} \Big|_{T_1}^{T_2} \\ &= a \ln \left( \frac{T_2}{T_1} \right) + b(T_2 - T_1) - \frac{c}{2} \left( \frac{1}{T_2^2} - \frac{1}{T_1^2} \right)\end{aligned}$$

$\Delta S$  for heating graphite from 200 K to 500 K is

$$\begin{aligned}&= (16.86 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \left( \frac{500 \text{ K}}{200 \text{ K}} \right) + (0.00477 \text{ J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1}) \\ &\quad \times (500 \text{ K} - 200 \text{ K}) \\ &\quad - \frac{(-8.54 \times 10^5 \text{ J} \cdot \text{K} \cdot \text{mol}^{-1})}{2} \left( \frac{1}{(500 \text{ K})^2} - \frac{1}{(200 \text{ K})^2} \right) \\ &= 7.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

If we assume a constant heat capacity at the mean temperature of 350 K:

$$C_{p,m} = (16.86 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + (0.00477 \text{ J} \cdot \text{K}^{-2} \cdot \text{mol}^{-1})(350 \text{ K})$$

$$- \left( \frac{-8.54 \times 10^5 \text{ J} \cdot \text{K} \cdot \text{mol}^{-1}}{(500 \text{ K})^2} \right)$$

$$= 11.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

and

$$\Delta S = C_{p,m} \ln \frac{T_2}{T_1} = (11.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \left( \frac{500 \text{ K}}{200 \text{ K}} \right) = 10.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Not integrating the heat capacity leads to roughly a 34% error in  $\Delta S$ .

- 7.37** The entropy of vaporization of water at 75° may be carried out through a series of three reversible steps. Namely, reversibly heating the reactants to 100°C, Carrying out the phase change at this temperature, and finally cooling the products back to 75°C. The sum of the  $\Delta S$ 's for these three steps will be equivalent to vaporizing water at 75° in one irreversible step. Step 1, heating the reactants to 100°C:

$$\Delta S_1 = C_{p,m} \ln \left( \frac{T_2}{T_1} \right) = (75.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \left( \frac{373 \text{ K}}{348 \text{ K}} \right) = 5.22 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Step 2, the entropy of vaporization of H<sub>2</sub>O at 100°C is given to be 109.0 J · K<sup>-1</sup> · mol<sup>-1</sup>.

Step 3, cooling the products to 75°C:

$$\Delta S_3 = C_{p,m} \ln \left( \frac{T_2}{T_1} \right) = (33.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \left( \frac{348 \text{ K}}{373 \text{ K}} \right) = -2.33 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Therefore, the molar enthalpy of vaporization of H<sub>2</sub>O at 75°C is:

$$\Delta S_{v,m} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 111.9 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

- 7.39** To calculate the change in entropy for the hot and cold water, the amount of energy which flows from one to the other must first be calculated:



$$q(\text{H}_2\text{O})_{\text{cold}} = -q(\text{H}_2\text{O})_{\text{hot}}$$

$$= n_c \cdot C_{p,m}(\text{H}_2\text{O}) \cdot (T_f - T_{i,c}) = n_h \cdot C_{p,m}(\text{H}_2\text{O}) \cdot (T_f - T_{i,h})$$

where  $n_c$ , and  $n_h$  are the moles of cold and hot water, respectively, and  $T_{i,c}$ , and  $T_{i,h}$  are the temperatures of the cold and hot water, respectively.

Dividing both sides by  $C_{p,m}(\text{H}_2\text{O})$  we obtain:

$$n_c \cdot (T_f - T_{i,c}) = n_h \cdot (T_f - T_{i,h}).$$

Solving for  $T_f$  we find:

$$T_f = \frac{(n_c \cdot T_{i,c}) + (n_h \cdot T_{i,h})}{n_c + n_h}$$

The moles of hot and cold water are:

$$n_c = \frac{50 \text{ g}}{18.015 \text{ g} \cdot \text{mol}^{-1}} = 2.78 \text{ mol} \quad \text{and} \quad n_h = \frac{65 \text{ g}}{18.015 \text{ g} \cdot \text{mol}^{-1}} = 3.61 \text{ mol}.$$

and  $T_f$  is, therefore:

$$T_f = \frac{(2.78 \text{ mol} \cdot 293.15 \text{ K}) + (3.61 \text{ mol} \cdot 323.15 \text{ K})}{2.78 \text{ mol} + 3.61 \text{ mol}} = 310.1 \text{ K}$$

With  $T_f$ , we can calculate  $\Delta S$  for the hot and cold water, and the total  $\Delta S$  for the entire system:

$$\begin{aligned} \Delta S_c &= n_c \cdot C_{p,m} \ln \left( \frac{T_2}{T_1} \right) = (2.78 \text{ mol}) (75.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \left( \frac{310.1 \text{ K}}{293 \text{ K}} \right) \\ &= +11.9 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_h &= n_h \cdot C_{p,m} \ln \left( \frac{T_2}{T_1} \right) = (3.61 \text{ mol}) (75.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \left( \frac{310.1 \text{ K}}{323 \text{ K}} \right) \\ &= -11.1 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

Therefore,  $\Delta S_{\text{tot}}$  is:

$$\Delta S_{\text{tot}} = \Delta S_c + \Delta S_h = +0.8 \text{ J} \cdot \text{K}^{-1}$$

**7.41** (a) The change in entropy will be given by

$$\Delta S_{\text{surr}} = \frac{-\Delta H_{\text{system}}}{T} = \frac{-1.00 \text{ mol} \times 8.2 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{111.7 \text{ K}} = -73 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta S_{\text{system}} = \frac{\Delta H_{\text{system}}}{T} = \frac{1.00 \text{ mol} \times 8.2 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{111.7 \text{ K}} = +73 \text{ J} \cdot \text{K}^{-1}$$

$$(b) \Delta S_{\text{surr}} = \frac{-\Delta H_{\text{system}}}{T} = \frac{-1.00 \text{ mol} \times 4.60 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{158.7 \text{ K}} = -29.0 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta S_{\text{system}} = \frac{\Delta H_{\text{system}}}{T} = \frac{1.00 \text{ mol} \times 4.60 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{158.7 \text{ K}} = +29.0 \text{ J} \cdot \text{K}^{-1}$$

$$(c) \Delta S_{\text{surr}} = \frac{-\Delta H_{\text{system}}}{T} = \frac{-(1.00 \text{ mol} \times -4.60 \times 10^3 \text{ J} \cdot \text{mol}^{-1})}{158.7 \text{ K}} \\ = +29.0 \text{ J} \cdot \text{K}^{-1}$$

$$\Delta S_{\text{system}} = \frac{\Delta H_{\text{system}}}{T} = \frac{1.00 \text{ mol} \times -4.60 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{158.7 \text{ K}} = -29.0 \text{ J} \cdot \text{K}^{-1}$$

**7.43** (a) The total entropy change is given by  $\Delta S_{\text{tot}} = \Delta S_{\text{surr}} + \Delta S$ .  $\Delta S$  for an isothermal, reversible process is calculated from

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{-w_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1}. \text{ To do the calculation we need the value of}$$

$n$ , which is obtained by use of the ideal gas law:

$$(4.95 \text{ atm})(1.67 \text{ L}) = n(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(323 \text{ K}); n = 0.312 \text{ mol}.$$

$$\Delta S = (0.312 \text{ mol})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \ln \frac{7.33 \text{ L}}{1.67 \text{ L}} = +3.84 \text{ J} \cdot \text{K}^{-1}. \text{ Because the}$$

process is reversible,  $\Delta S_{\text{tot}} = 0$ , so  $\Delta S_{\text{surr}} = -\Delta S = -3.84 \text{ J} \cdot \text{K}^{-1}$ .

(b) For the irreversible process,  $\Delta S$  is the same,  $+3.84 \text{ J} \cdot \text{K}^{-1}$ . No work is done in free expansion (see Section 6.6) so  $w = 0$ . Because  $\Delta U = 0$ , it follows that  $q = 0$ . Therefore, no heat is transferred into the surroundings, and their entropy is unchanged:  $\Delta S_{\text{surr}} = 0$ . The total change in entropy is therefore  $\Delta S_{\text{tot}} = +3.84 \text{ J} \cdot \text{K}^{-1}$ .

**7.45** Exothermic reactions tend to be spontaneous because the result is an increase in the entropy of the surroundings. Using the mathematical relationship  $\Delta G_r = \Delta H_r - T\Delta S_r$ , it is clear that if  $\Delta H_r$  is large compared to  $\Delta S_r$ , then the reaction will generally be spontaneous.

$$\begin{aligned}
7.47 \quad (a) \quad \Delta H^\circ_r &= 3(-824.2 \text{ kJ} \cdot \text{mol}^{-1}) - [2(-1118.4 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= -235.8 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= 3(87.40 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) - [2(146.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\
&\quad + \frac{1}{2}(205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
&= -133.17 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
\Delta G^\circ_r &= 3(-742.2 \text{ kJ} \cdot \text{mol}^{-1}) - [2(-1015.4 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= -195.8 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

$\Delta G_r$  may also be calculated from  $\Delta H^\circ_r$  and  $\Delta S^\circ_r$  (the numbers calculated differ slightly from the two methods due to rounding differences):

$$\begin{aligned}
\Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r \\
&= -235.8 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-133.17 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(100 \text{ J} \cdot \text{kJ}^{-1}) \\
&= -196.1 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

$$\begin{aligned}
(b) \quad \Delta H^\circ_r &= -1208.09 \text{ kJ} \cdot \text{mol}^{-1} - [-1219.6 \text{ kJ} \cdot \text{mol}^{-1}] \\
&= 11.5 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= -80.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [68.87 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\
&= -149.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
\Delta G^\circ_r &= -1111.15 \text{ kJ} \cdot \text{mol}^{-1} - [-1167.3 \text{ kJ} \cdot \text{mol}^{-1}] \\
&= +56.2 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

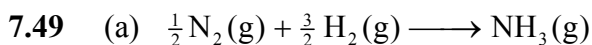
or

$$\begin{aligned}
\Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r \\
&= 11.5 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-149.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= 56.1 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

$$\begin{aligned}
(c) \quad \Delta H^\circ_r &= 9.16 \text{ kJ} \cdot \text{mol}^{-1} - [2(33.18 \text{ kJ} \cdot \text{mol}^{-1})] = -57.20 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= 304.29 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [2(240.06 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
&= -175.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
\Delta G^\circ_r &= 97.89 \text{ kJ} \cdot \text{mol}^{-1} - [2(51.31 \text{ kJ} \cdot \text{mol}^{-1})] = -4.73 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

or

$$\begin{aligned}
\Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r \\
&= -57.2 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-175.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= -4.80 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$



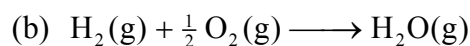
$$\Delta H^\circ_{\text{r}} = \Delta H^\circ_{\text{f}}(\text{NH}_3) = -46.11 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta S^\circ_{\text{r}} &= S^\circ_{\text{m}}(\text{NH}_3, \text{g}) - \left[ \frac{1}{2} S^\circ_{\text{m}}(\text{N}_2, \text{g}) + \frac{3}{2} S^\circ_{\text{m}}(\text{H}_2, \text{g}) \right] \\ &= 192.45 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - \left[ \frac{1}{2} (191.61 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \right. \\ &\quad \left. + \frac{3}{2} (130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \right] \\ &= -99.38 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_{\text{r}} &= -46.11 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-99.38 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= -16.49 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$S^\circ_{\text{m}}(\text{NH}_3) = 192.45 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$\Delta S^\circ_{\text{f}}(\text{NH}_3)$  is negative because several gas molecules combine to form 1  $\text{NH}_3$  molecule.



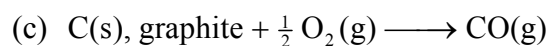
$$\Delta H^\circ_{\text{r}} = \Delta H^\circ_{\text{f}}(\text{H}_2\text{O}, \text{g}) = -241.82 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta S^\circ_{\text{r}} &= S^\circ_{\text{m}}(\text{H}_2\text{O}, \text{g}) - [S^\circ_{\text{m}}(\text{H}_2, \text{g}) + \frac{1}{2} S^\circ_{\text{m}}(\text{O}_2, \text{g})] \\ &= 188.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + \frac{1}{2} (205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= -44.42 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_{\text{r}} &= -241.82 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-44.42 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= -228.58 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$S^\circ_{\text{m}}(\text{H}_2\text{O}, \text{g}) = 188.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$\Delta S^\circ_{\text{f}}(\text{H}_2\text{O}, \text{g})$  is a negative number because there is a reduction in the number of gas molecules in the reaction when  $S^\circ_{\text{m}}$  is positive.



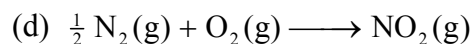
$$\Delta H^\circ_{\text{r}} = \Delta H^\circ_{\text{f}}(\text{CO}, \text{g}) = -110.53 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta S^\circ_{\text{r}} &= S^\circ_{\text{m}}(\text{CO}, \text{g}) - [S^\circ_{\text{m}}(\text{C}, \text{s}) + \frac{1}{2} S^\circ_{\text{m}}(\text{O}_2, \text{g})] \\ &= 197.67 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [5.740 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + \frac{1}{2} (205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= +89.36 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_{\text{r}} &= -110.53 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(89.36 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= -137.2 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$S^\circ_{\text{m}}(\text{CO}, \text{g}) = 197.67 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The  $S^\circ_{\text{m}}(\text{CO}, \text{g})$  is larger than  $\Delta S^\circ_{\text{f}}(\text{CO}, \text{g})$  because in the formation reaction the number of moles of gas is reduced.



$$\Delta H^\circ_{\text{r}} = \Delta H^\circ_{\text{f}}(\text{NO}_2) = +33.18 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\begin{aligned} \Delta S^\circ_{\text{r}} &= S^\circ_{\text{m}}(\text{NO}_2, \text{g}) - [\frac{1}{2} S^\circ_{\text{m}}(\text{N}_2, \text{g}) + S^\circ_{\text{m}}(\text{O}_2, \text{g})] \\ &= 240.06 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [\frac{1}{2}(191.61 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + 205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\ &= -60.89 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_{\text{r}} &= 33.18 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(-60.89 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= +51.33 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$S^\circ_{\text{m}}(\text{NO}_2, \text{g}) = 240.06 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The  $\Delta S^\circ_{\text{f}}(\text{NO}_2, \text{g})$  is somewhat negative due to the reduction in the number of gas molecules during the reaction. For all of these, the important point to gain is that the  $S^\circ_{\text{m}}$  value of a compound is not the same as the  $\Delta S^\circ_{\text{f}}$  for the formation of that compound.  $\Delta S^\circ_{\text{f}}$  is often negative because one is bringing together a number of elements to form that compound.

**7.51** Use the relationship  $\Delta G^\circ_{\text{r}} = \sum \Delta G^\circ_{\text{f}}(\text{products}) - \sum \Delta G^\circ_{\text{f}}(\text{reactants})$ :

$$\begin{aligned} \text{(a) } \Delta G^\circ_{\text{r}} &= 2\Delta G^\circ_{\text{f}}(\text{SO}_3, \text{g}) - [2\Delta G^\circ_{\text{f}}(\text{SO}_2, \text{g})] \\ &= 2(-371.06 \text{ kJ} \cdot \text{mol}^{-1}) - [2(-300.19 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -141.74 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The reaction is spontaneous.

$$\begin{aligned} \text{(b) } \Delta G^\circ_{\text{r}} &= \Delta G^\circ_{\text{f}}(\text{CaO}, \text{s}) + \Delta G^\circ_{\text{f}}(\text{CO}_2, \text{g}) - \Delta G^\circ_{\text{f}}(\text{CaCO}_3, \text{s}) \\ &= (-604.03 \text{ kJ} \cdot \text{mol}^{-1}) + (-394.36 \text{ kJ} \cdot \text{mol}^{-1}) \\ &\quad - (-1128.8 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= +130.41 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

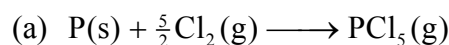
The reaction is not spontaneous.

$$\begin{aligned}
 \text{(c) } \Delta G^\circ_r &= 16\Delta G^\circ_f(\text{CO}_2, \text{g}) + 18\Delta G^\circ_f(\text{H}_2\text{O}, \text{l}) - [2\Delta G^\circ_f(\text{C}_8\text{H}_{18}, \text{l})] \\
 &= 16(-394.36 \text{ kJ} \cdot \text{mol}^{-1}) + 18(-237.13 \text{ kJ} \cdot \text{mol}^{-1}) \\
 &\quad - [2(6.4 \text{ kJ} \cdot \text{mol}^{-1})] \\
 &= -10\,590.9 \text{ kJ} \cdot \text{mol}^{-1}
 \end{aligned}$$

The reaction is spontaneous.

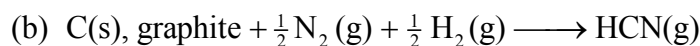
**7.53** The standard free energies of formation of the compounds are: (a)  $\text{PCl}_5(\text{g})$ ,  $-305.0 \text{ kJ} \cdot \text{mol}^{-1}$ ; (b)  $\text{HCN}(\text{g})$ ,  $+124.7 \text{ kJ} \cdot \text{mol}^{-1}$ ; (c)  $\text{NO}(\text{g})$ ,  $+86.55 \text{ kJ} \cdot \text{mol}^{-1}$ ; (d)  $\text{SO}_2(\text{g})$ ,  $-300.19 \text{ kJ} \cdot \text{mol}^{-1}$ . Those compounds with a positive free energy of formation are unstable with respect to the elements. Thus (a) and (d) are thermodynamically stable.

**7.55** To understand what happens to  $\Delta G^\circ_r$  as temperature is raised, we use the relationship  $\Delta G^\circ_r = \Delta H^\circ_r - T\Delta S^\circ_r$ . From this it is clear that the free energy of the reaction becomes less favorable (more positive) as temperature increases, only if  $\Delta S^\circ_r$  is a negative number. Therefore, we need only to find out whether the standard entropy of formation of the compound is a negative number. This is calculated for each compound as follows:



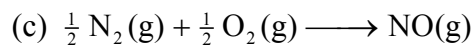
$$\begin{aligned}
 \Delta S^\circ_r &= S^\circ_m(\text{PCl}_5, \text{g}) - [S^\circ_m(\text{P}, \text{s}) + \frac{5}{2} S^\circ_m(\text{Cl}_2, \text{g})] \\
 &= 364.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [41.09 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + \frac{5}{2}(223.07 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
 &= -234.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
 \end{aligned}$$

The compound is less stable at higher temperatures.



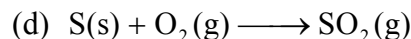
$$\begin{aligned}
 \Delta S^\circ_r &= S^\circ_m(\text{HCN}, \text{g}) - [S^\circ_m(\text{C}, \text{s}) + \frac{1}{2} S^\circ_m(\text{N}_2, \text{g}) + \frac{1}{2} S^\circ_m(\text{H}_2, \text{g})] \\
 &= 201.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [5.740 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
 &\quad + \frac{1}{2}(191.61 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + \frac{1}{2}(130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
 &= +34.90 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
 \end{aligned}$$

$\text{HCN}(\text{g})$  is more stable at higher  $T$ .



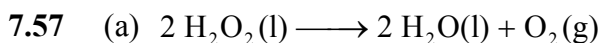
$$\begin{aligned}\Delta S^\circ_{\text{r}} &= S^\circ_{\text{m}}(\text{NO}, \text{g}) - [\tfrac{1}{2}S^\circ_{\text{m}}(\text{N}_2, \text{g}) + \tfrac{1}{2}S^\circ_{\text{m}}(\text{O}_2, \text{g})] \\ &= 210.76 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [\tfrac{1}{2}(191.61 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &\quad + \tfrac{1}{2}(205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= +12.38 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

NO(g) is more stable as  $T$  increases.



$$\begin{aligned}\Delta S^\circ_{\text{r}} &= S^\circ(\text{SO}_2, \text{g}) - [S^\circ(\text{S}, \text{s}) + S^\circ(\text{O}_2, \text{g})] \\ &= 248.22 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [31.80 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad + 205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\ &= +11.28 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

SO<sub>2</sub>(g) is more stable as  $T$  increases.



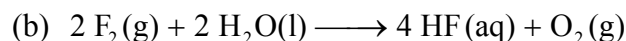
$$\begin{aligned}\Delta S^\circ_{\text{r}} &= 2S^\circ_{\text{m}}(\text{H}_2\text{O}, \text{l}) + S^\circ_{\text{m}}(\text{O}_2, \text{g}) - 2S^\circ_{\text{m}}(\text{H}_2\text{O}_2, \text{l}) \\ &= 2(69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + 205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad - 2(109.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\ &= +125.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{\text{r}} &= 2\Delta H^\circ_{\text{f}}(\text{H}_2\text{O}, \text{l}) - 2\Delta H^\circ_{\text{f}}(\text{H}_2\text{O}_2, \text{l}) \\ &= 2(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) - 2(-187.78 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -196.10 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ_{\text{r}} &= 2\Delta G^\circ_{\text{f}}(\text{H}_2\text{O}, \text{l}) - 2\Delta G^\circ_{\text{f}}(\text{H}_2\text{O}_2, \text{l}) \\ &= 2(-237.13 \text{ kJ} \cdot \text{mol}^{-1}) - 2(-120.35 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -233.56 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$\Delta G^\circ_{\text{r}}$  can also be calculated from  $\Delta S^\circ_{\text{r}}$  and  $\Delta H^\circ_{\text{r}}$  using the relationship:

$$\begin{aligned}\Delta G^\circ_{\text{r}} &= \Delta H^\circ_{\text{r}} - T\Delta S^\circ_{\text{r}} \\ &= -196.1 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(+125.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= -233.6 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$



$$\begin{aligned}
\Delta S^\circ_r &= 4S^\circ_m(\text{HF, aq}) + S^\circ_m(\text{O}_2, \text{g}) - [2S^\circ_m(\text{F}_2, \text{g}) + 2S^\circ_m(\text{H}_2\text{O, l})] \\
&= 4(-88.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + 205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
&\quad - [2(202.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + 2(69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
&= +14.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\end{aligned}$$

$$\begin{aligned}
\Delta H^\circ_r &= 4\Delta H^\circ_f(\text{HF, aq}) - [2\Delta H^\circ_f(\text{H}_2\text{O, l})] \\
&= 4(-330.08 \text{ kJ} \cdot \text{mol}^{-1}) - [2(-285.83 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= -748.66 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

$$\begin{aligned}
\Delta G^\circ_r &= 4 \times \Delta G^\circ_f(\text{HF, aq}) - [2 \times \Delta G^\circ_f(\text{H}_2\text{O, l})] \\
&= 4(-296.82 \text{ kJ} \cdot \text{mol}^{-1}) - [2(-237.13 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= -713.02 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

$\Delta G^\circ_r$  can also be calculated from  $\Delta S^\circ_r$  and  $\Delta H^\circ_r$  using the relationship:

$$\begin{aligned}
\Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r \\
&= -748.66 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(14.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= -753.01 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

**7.59** In order to find  $\Delta G^\circ_r$  at a temperature other than 298 K, we must first calculate  $\Delta H^\circ_r$  and  $\Delta S^\circ_r$  and then use the relationship

$$\Delta G^\circ_r = \Delta H^\circ_r + T\Delta S^\circ_r \text{ to calculate}$$

$$\Delta G^\circ_r.$$

$$\begin{aligned}
\Delta H^\circ_r &= 2\Delta H^\circ_f(\text{BF}_3, \text{g}) + 3\Delta H^\circ_f(\text{H}_2\text{O, l}) - [\Delta H^\circ_f(\text{B}_2\text{O}_3, \text{s}) \\
&\quad + 6\Delta H^\circ_f(\text{HF, g})] \\
&= 2(-1137.0 \text{ kJ} \cdot \text{mol}^{-1}) + 3(-285.83 \text{ kJ} \cdot \text{mol}^{-1}) \\
&\quad - [(-1272.8 \text{ kJ} \cdot \text{mol}^{-1}) + 6(-271.1 \text{ kJ} \cdot \text{mol}^{-1})] \\
&= -232.1 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

$$\begin{aligned}
\Delta S^\circ_r &= 2S^\circ_m(\text{BF}_3, \text{g}) + 3S^\circ_m(\text{H}_2\text{O, l}) \\
&\quad - [S^\circ_m(\text{B}_2\text{O}_3, \text{s}) + 6S^\circ_m(\text{HF, g})] \\
&= 2(254.12 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) + 3(69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\
&\quad - [53.97 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 6(173.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\
&= -378.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\end{aligned}$$

$$\begin{aligned}
\Delta G^\circ_r &= -232.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - (353 \text{ K})(-378.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= -98.42 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$



(a) In order to determine the range over which the reaction will be spontaneous, we consider the relative signs of  $\Delta H^\circ_r$  and  $\Delta S^\circ_r$  and their effect on  $\Delta G^\circ_r$ . Because  $\Delta H^\circ_r$  is negative and  $\Delta S^\circ_r$  is also negative, we expect the reaction to be spontaneous at low temperatures, where the term  $T\Delta S^\circ_r$  will be less than  $\Delta H^\circ_r$ . To find the temperature of the cutoff, we calculate the temperature at which  $\Delta G^\circ_r = 0$ . For this reaction, that temperature is

$$\Delta G^\circ_r = 0 = -232.1 \text{ kJ} \cdot \text{mol}^{-1} - (T)(-378.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$

$$T = 612.9 \text{ K}$$

The reaction should be spontaneous below 612.9 K.

$$\begin{aligned} \text{(b)} \quad \Delta H^\circ_r &= \Delta H^\circ_f(\text{CaCl}_2, \text{aq}) + \Delta H^\circ_f(\text{C}_2\text{H}_2, \text{g}) - [\Delta H^\circ_f(\text{CaC}_2, \text{s}) \\ &\quad + 2\Delta H^\circ_f(\text{HCl}, \text{aq})] \\ &= (-877.1 \text{ kJ} \cdot \text{mol}^{-1}) + 226.73 \text{ kJ} \cdot \text{mol}^{-1} \\ &\quad - [(-59.8 \text{ kJ} \cdot \text{mol}^{-1}) + 2(-167.16 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -256.3 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ_r &= S^\circ_m(\text{CaCl}_2, \text{aq}) + S^\circ_m(\text{C}_2\text{H}_2, \text{g}) \\ &\quad - [S^\circ_m(\text{CaC}_2, \text{s}) + 2S^\circ_m(\text{HCl}, \text{aq})] \\ &= 59.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 200.94 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad - [69.96 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 2(56.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})] \\ &= +77.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\Delta G^\circ_r = -256.2 \text{ kJ} \cdot \text{mol}^{-1} - (353 \text{ K})(+77.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$

Because  $\Delta H^\circ_r$  is negative and  $\Delta S^\circ_r$  is positive, the reaction will be

spontaneous at all temperatures.

(c)

$$\begin{aligned} \Delta H^\circ_r &= \Delta H^\circ_f(\text{C (s), diamond}) = +1.895 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta S^\circ_r &= S^\circ_m(\text{C (s), diamond}) - S^\circ_m(\text{C (s), graphite}) \\ &= +2.377 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - 5.740 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &= -3.363 \text{ J} \cdot \text{K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_r &= +1.895 \text{ kJ} \cdot \text{mol}^{-1} - (353 \text{ K})(-3.363 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= +3.082 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Because  $\Delta H_r^\circ$  is positive and  $\Delta S_r^\circ$  is negative, the reaction will be nonspontaneous at all temperatures. Note: This calculation is for atmospheric pressure. Diamond can be produced from graphite at elevated pressures and high temperatures.

- 7.61** Assuming standard state conditions,  $\Delta G_r^\circ$  for  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\text{l})$  is:

$$\begin{aligned}\Delta G_r^\circ &= (-174.8 \text{ kJ} \cdot \text{mol}^{-1}) - (68.15 \text{ kJ} \cdot \text{mol}^{-1}) - (-228.57 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -14.4 \text{ kJ} \cdot \text{mol}^{-1} \quad \text{Negative } \Delta G_r^\circ \text{ indicates a spontaneous reaction.}\end{aligned}$$

$\Delta G_r^\circ$  for  $\text{C}_2\text{H}_6(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\text{l}) + \text{H}_2(\text{g})$  is:

$$\begin{aligned}\Delta G_r^\circ &= (-174.8 \text{ kJ} \cdot \text{mol}^{-1}) - (-32.82 \text{ kJ} \cdot \text{mol}^{-1}) - (-228.57 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= +86.6 \text{ kJ} \cdot \text{mol}^{-1} \quad \text{Positive } \Delta G_r^\circ \text{ indicates a nonspontaneous reaction.}\end{aligned}$$

Reaction A is spontaneous but reaction B is not spontaneous

- 7.63** (a) 1-propanol ( $\text{C}_3\text{H}_8\text{O}$ ) and 2-propanone ( $\text{C}_3\text{H}_6\text{O}$ ) have similar numbers of electrons so that we would expect the molar entropies to be similar. Because 1-propanol exhibits hydrogen bonding, however, we might expect the liquid phase to be more ordered than for 2-propanone. This is observed. The standard molar entropy for 2-propanone is  $200 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  while that of 1-propanol is  $193 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ . (b) In the gas phase, hydrogen bonding will not be important because the molecules are too far apart, so the standard molar entropies should be more similar.

- 7.65** For the cis compound there will be 12 different orientations:  
For the trans compound there will only be 3 different orientations.  
Comparing the Boltzmann entropy calculations for the cis and trans forms:  
cis:

$$S = k \ln 12^{6.02 \times 10^{23}} = (1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}) \ln 12^{6.02 \times 10^{23}}$$

$$S = 20.6 \text{ J} \cdot \text{K}^{-1}$$

trans:

$$S = k \ln 3^{6.02 \times 10^{23}} = (1.38 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}) \ln 3^{6.02 \times 10^{23}}$$

$$S = 9.13 \text{ J} \cdot \text{K}^{-1}$$

The cis form should have the higher residual entropy.

- 7.67** According to Trouton's rule, the entropy of vaporization of an organic liquid is a constant of approximately  $85 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ . The relationship between entropy of fusion, enthalpy of fusion, and melting point is given

$$\text{by } \Delta S_{\text{fus}}^{\circ} = \frac{\Delta H_{\text{fus}}^{\circ}}{T_{\text{fus}}}.$$

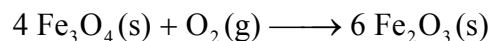
$$\text{For Pb: } \Delta S_{\text{fus}}^{\circ} = \frac{5100 \text{ J}}{600 \text{ K}} = 8.50 \text{ J} \cdot \text{K}^{-1}$$

$$\text{For Hg: } \Delta S_{\text{fus}}^{\circ} = \frac{2290 \text{ J}}{234 \text{ K}} = 9.79 \cdot \text{K}^{-1}$$

$$\text{For Na: } \Delta S_{\text{fus}}^{\circ} = \frac{2640 \text{ J}}{371 \text{ K}} = 7.12 \text{ J} \cdot \text{K}^{-1}$$

These numbers are reasonably close but clearly much smaller than the value associated with Trouton's rule.

- 7.69** This is best answered by considering the reaction that interconverts the two compounds



We calculate  $\Delta G_{\text{r}}^{\circ}$  using data from Appendix 2A:

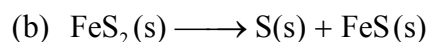
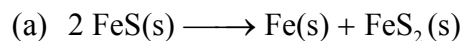
$$\Delta G_{\text{r}}^{\circ} = 6\Delta G_{\text{f}}^{\circ}(\text{Fe}_2\text{O}_3, \text{s}) - [4\Delta G_{\text{f}}^{\circ}(\text{Fe}_3\text{O}_4, \text{s})]$$

$$\begin{aligned} \Delta G_{\text{r}}^{\circ} &= 6(-742.2 \text{ kJ} \cdot \text{mol}^{-1}) - [4(-1015.4 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -391.6 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Because  $\Delta G_{\text{r}}^{\circ}$  is negative, the process is spontaneous at  $25^{\circ}\text{C}$ .

Therefore,  $\text{Fe}_2\text{O}_3$  is thermodynamically more stable.

**7.71** We can calculate the free energy changes associated with the conversions:



For (a),

$$\Delta G^\circ_r = -166.9 \text{ kJ} \cdot \text{mol}^{-1} - 2(-100.4 \text{ kJ} \cdot \text{mol}^{-1}) = +33.9 \text{ kJ} \cdot \text{mol}^{-1}$$

This process is predicted to be nonspontaneous.

For (b),  $\Delta G^\circ_r = -100.4 \text{ kJ} \cdot \text{mol}^{-1} - (-166.9 \text{ kJ} \cdot \text{mol}^{-1}) = +66.5 \text{ kJ} \cdot \text{mol}^{-1}$

This process is predicted to be nonspontaneous.

(c) The presence of added sulfur or iron should not affect these answers.

**7.73** (a) Because the enthalpy change for dissolution is positive, the entropy change of the surroundings must be a negative number

$$\left( \Delta S^\circ_{\text{surr}} = - \frac{\Delta H^\circ_{\text{system}}}{T} \right). \text{ Because spontaneous processes are accompanied}$$

by an increase in entropy, the change in enthalpy does not favor the

dissolution process. (b) In order for the process to be spontaneous

(because it occurs readily, we know it is spontaneous), the entropy change

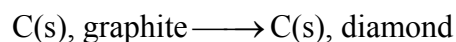
of the system must be positive. (c) Locational disorder is dominant.

(d) Because the surroundings participate in the solution process only as a source of heat, the entropy change of the surroundings is primarily a result

of the dispersal of thermal motion. (e) The driving force for the

dissolution is the dispersal of matter, resulting in an overall positive  $\Delta S$ .

**7.75** The values are calculated simply from the Hess's law relationship that the sums of the various energy quantities for the products minus the similar sum for the reactants will give the overall change in the state function desired:



$$\begin{aligned}
\Delta H^\circ &= \Delta H^\circ_f(\text{C(s), diamond}) = +1.895 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ &= \Delta S^\circ_m(\text{C(s), diamond}) - \Delta S^\circ_m(\text{C(s), graphite}) \\
&= 2.377 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - 5.740 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
&= -3.363 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
\Delta G^\circ &= \Delta G^\circ_f(\text{C(s), diamond}) = +2.900 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

Notice that the values used for the entropy calculation are absolute entropies, not  $\Delta S^\circ$  values and that the  $S^\circ_m$  value for C(s), graphite, is not 0. Graphite has a delocalized structure similar to that of benzene, whereas in diamond, all the carbon atom are bonded to four other carbon atoms in a very rigid lattice. It is not surprising that the change in entropy upon going from graphite to diamond would decrease, because we would expect graphite to have a higher molar entropy than diamond. Similarly, one can compare the bond formation and breaking that accompanies a change from graphite to diamond. Given the actual numbers, the change is clearly small however. In graphite, the carbon atom is bonded to three other carbon atoms with delocalized bonds (we can approximate this very roughly, using the values of  $518 \text{ kJ} \cdot \text{mol}^{-1}$  of delocalized C—C bonds, as given in Table 6.7). In diamond, the carbon atom is bonded to four other carbon atoms by single C—C bonds (approximately by  $348 \text{ kJ} \cdot \text{mol}^{-1}$ ). Even though these approximations overestimate the effect of delocalization on the C—C bond strength in graphite, the trend is expected—the three delocalized bonds in C(s) graphite are actually slightly more exothermic than the four C—C single bonds in diamond, making the standard enthalpy change a positive number. (Notice that if one considered the C—C bonds in graphite to be localized, the opposite prediction would have been made.) The standard free energy change for this reaction is positive as follows, from a positive standard enthalpy change and a negative standard entropy change for the reaction.

**7.77** The entries all correspond to aqueous ions. The fact that they are negative is due to the reference point that has been established. Because ions cannot

actually be separated and measured independently, a reference point that defines  $S^\circ_{\text{m}}(\text{H}^+, \text{aq}) = 0$  has been established. This definition is then used to calculate the standard entropies for the other ions. The fact that they are negative will arise in part because the solvated ion  $\text{M}(\text{H}_2\text{O})_x^{n+}$  will be more ordered than the isolated ion and solvent molecules ( $\text{M}^{n+} + x \text{H}_2\text{O}$ ).

**7.79**  $\Delta G = \Delta H - T\Delta S$ , therefore,

$$\Delta S_r = \frac{\Delta H_r - \Delta G_r}{T}$$

Given the reaction  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$  and 0.50 g of  $\text{H}_2(\text{g})$  consumed:

$$\Delta G_r = (-273.25 \text{ kJ} \cdot \text{mol}^{-1}) \left( \frac{0.50 \text{ g}}{18.015 \text{ g} \cdot \text{mol}^{-1}} \right) = -6.58 \text{ kJ}$$

Therefore,

$$\Delta S_r = \frac{-70.9 \text{ kJ} - (-6.58 \text{ kJ})}{298 \text{ K}} = 216 \text{ J} \cdot \text{K}^{-1}$$

**7.81** (a) In order to calculate the free energy at different temperatures, we need to know  $\Delta H^\circ$  and  $\Delta S^\circ$  for the process:  $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{g})$

$$\begin{aligned} \Delta H^\circ_r &= \Delta H^\circ_f(\text{H}_2\text{O}, \text{g}) - \Delta H^\circ_f(\text{H}_2\text{O}, \text{l}) \\ &= (-241.82 \text{ kJ} \cdot \text{mol}^{-1}) - [-285.83 \text{ kJ} \cdot \text{mol}^{-1}] \\ &= 44.01 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S^\circ_r &= S^\circ_{\text{m}}(\text{H}_2\text{O}, \text{g}) - S^\circ_{\text{m}}(\text{H}_2\text{O}, \text{l}) \\ &= 188.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\ &= 118.92 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r \\ &= 44.01 \text{ kJ} \cdot \text{mol}^{-1} - T(118.92 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \end{aligned}$$

$$T(\text{K}) \Delta G^\circ_r (\text{kJ})$$

$$298 \quad 8.57 \text{ kJ}$$

$$373 \quad -0.35 \text{ kJ}$$

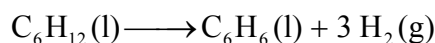
$$423 \quad -6.29 \text{ kJ}$$

The reaction goes from being nonspontaneous near room temperature to being spontaneous above 100°C.

(b) The value at 100°C should be exactly 0, because this is the normal boiling point of water.

(c) The discrepancy arises because the enthalpy and entropy values calculated from the tables are not rigorously constant with temperature. Better values would be obtained using the actual enthalpy and entropy of vaporization measured at the boiling point.

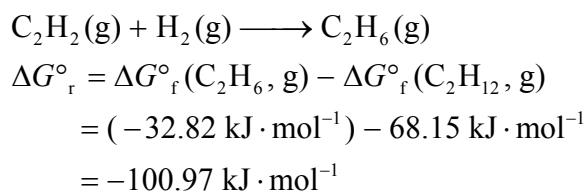
**7.83** The dehydrogenation of cyclohexane to benzene follows the following equation:



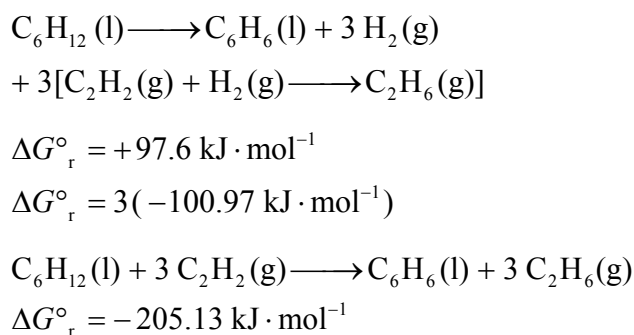
We can confirm that this process is nonspontaneous by calculating the  $\Delta G^\circ_{\text{r}}$  for the process, using data in Appendix 2A:

$$\begin{aligned}\Delta G^\circ_{\text{r}} &= \Delta G^\circ_{\text{f}}(\text{C}_6\text{H}_6, \text{l}) - \Delta G^\circ_{\text{f}}(\text{C}_6\text{H}_{12}, \text{l}) \\ &= 124.3 \text{ kJ} \cdot \text{mol}^{-1} - 26.7 \text{ kJ} \cdot \text{mol}^{-1} \\ &= +97.6 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

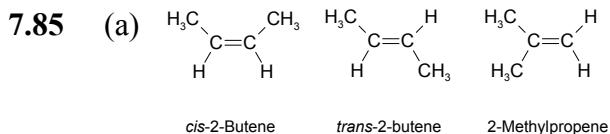
The reaction of ethane with hydrogen can be examined similarly:



We can now combine these two reactions so that  $\text{C}_2\text{H}_2(\text{g})$  accepts the hydrogen that is formed in the dehydrogenation reaction:



We can see that by combining these two reactions, the overall process becomes spontaneous. Essentially, we are using the energy of the favorable reaction to drive the nonfavorable process.



(b) For the three reactions, the calculation of  $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$  are as follows:

$$\begin{aligned}\Delta G_r^\circ &= \Delta G_f^\circ(2) - \Delta G_f^\circ(1) \\ &= 62.97 \text{ kJ} \cdot \text{mol}^{-1} - 65.86 \text{ kJ} \cdot \text{mol}^{-1} \\ &= -2.89 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta H_r^\circ &= \Delta H_f^\circ(2) - \Delta H_f^\circ(1) \\ &= (-11.17 \text{ kJ} \cdot \text{mol}^{-1}) - (-6.99 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -4.18 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta G_r^\circ &= \Delta H_r^\circ - T\Delta S_r^\circ \\ -2.89 \text{ kJ} \cdot \text{mol}^{-1} &= -4.18 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(\Delta S_r^\circ)/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ \Delta S_r^\circ &= -4.33 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ \Delta G_r^\circ &= \Delta G_f^\circ(3) - \Delta G_f^\circ(1) \\ &= 58.07 \text{ kJ} \cdot \text{mol}^{-1} - 65.86 \text{ kJ} \cdot \text{mol}^{-1} \\ &= -7.79 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta H_r^\circ &= \Delta H_f^\circ(3) - \Delta H_f^\circ(1) \\ &= (-16.90 \text{ kJ} \cdot \text{mol}^{-1}) - (-6.99 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= -9.91 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta G_r^\circ &= \Delta H_r^\circ - T\Delta S_r^\circ \\ -7.79 \text{ kJ} \cdot \text{mol}^{-1} &= -9.91 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(\Delta S_r^\circ)/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ \Delta S_r^\circ &= -7.11 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

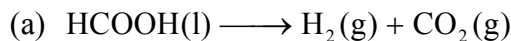


$$\begin{aligned}
\Delta G^\circ_r &= \Delta G^\circ_f(3) - \Delta G^\circ_f(2) \\
&= 58.07 \text{ kJ} \cdot \text{mol}^{-1} - 62.97 \text{ kJ} \cdot \text{mol}^{-1} \\
&= -4.90 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta H^\circ_r &= \Delta H^\circ_f(3) - \Delta H^\circ_f(2) \\
&= (-16.90 \text{ kJ} \cdot \text{mol}^{-1}) - (-11.17 \text{ kJ} \cdot \text{mol}^{-1}) \\
&= -5.73 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta G^\circ_r &= \Delta H^\circ_r - T\Delta S^\circ_r \\
-4.90 \text{ kJ} \cdot \text{mol}^{-1} &= -5.73 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(\Delta S^\circ_r)/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
\Delta S^\circ_r &= -2.78 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\end{aligned}$$

The most stable of the three compounds is 2-methylpropene.

(c) Because  $\Delta S^\circ$  is also equal to the difference in the  $S^\circ_m$  values for the compounds, we can examine those values to place the three compounds in order of their relative absolute entropies. The ordering is  $S^\circ_m(1) > S^\circ_m(2) > S^\circ_m(3)$ .

**7.87** We need to calculate  $\Delta H^\circ_r$  and  $\Delta S^\circ_r$  for each process.



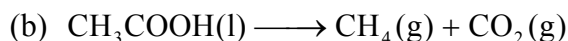
$$\begin{aligned}
\Delta H^\circ_r &= \Delta H^\circ_f(\text{CO}_2, \text{g}) - \Delta H^\circ_f(\text{HCOOH, l}) \\
&= (-393.51 \text{ kJ} \cdot \text{mol}^{-1}) - (-424.72 \text{ kJ} \cdot \text{mol}^{-1}) \\
&= +31.21 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= S^\circ_m(\text{H}_2, \text{g}) + S^\circ_m(\text{CO}_2, \text{g}) - [S^\circ_m(\text{HCOOH, l})] \\
&= 130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 213.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
&\quad - [128.95 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\
&= +215.47 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\end{aligned}$$

The reaction will become spontaneous above the temperature at which

$$\Delta G^\circ_r = 0:$$

$$0 = 31.21 \text{ kJ} \cdot \text{mol}^{-1} - T(215.47 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$

$$T = 144.8 \text{ K}$$



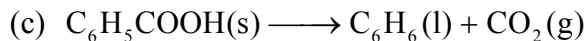
$$\begin{aligned}
\Delta H^\circ_r &= \Delta H^\circ_f(\text{CH}_4, \text{g}) + \Delta H^\circ_f(\text{CO}_2, \text{g}) - \Delta H^\circ_f(\text{CH}_3\text{COOH}, \text{l}) \\
&= (-74.81 \text{ kJ} \cdot \text{mol}^{-1}) + (-393.51 \text{ kJ} \cdot \text{mol}^{-1}) - (-484.5 \text{ kJ} \cdot \text{mol}^{-1}) \\
&= +16.18 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= S^\circ_m(\text{CH}_4, \text{g}) + S^\circ_m(\text{CO}_2, \text{g}) - [S^\circ_m(\text{CH}_3\text{COOH}, \text{l})] \\
&= 186.26 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 213.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [159.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\
&= +240.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\end{aligned}$$

The reaction will become spontaneous above the temperature at which

$$\Delta G^\circ_r = 0 :$$

$$0 = 16.18 \text{ kJ} \cdot \text{mol}^{-1} - T(240.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$

$$T = 67.36 \text{ K}$$



$$\begin{aligned}
\Delta H^\circ_r &= \Delta H^\circ_f(\text{C}_6\text{H}_6, \text{l}) + \Delta H^\circ_f(\text{CO}_2, \text{g}) - [\Delta H^\circ_f(\text{C}_6\text{H}_5\text{COOH}, \text{s})] \\
&= +49.0 \text{ kJ} \cdot \text{mol}^{-1} + (-393.51 \text{ kJ} \cdot \text{mol}^{-1}) - [-385.1 \text{ kJ} \cdot \text{mol}^{-1}] \\
&= +40.6 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= S^\circ_m(\text{C}_6\text{H}_6, \text{l}) + S^\circ_m(\text{CO}_2, \text{g}) - [S^\circ_m(\text{C}_6\text{H}_5\text{COOH}, \text{s})] \\
&= +173.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 213.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
&\quad - (167.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) \\
&= +219.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\end{aligned}$$

The reaction will become spontaneous above the temperature at which

$$\Delta G^\circ_r = 0 :$$

$$0 = 40.58 \text{ kJ} \cdot \text{mol}^{-1} - T(219.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$

$$T = 185.0 \text{ K}$$

It is clear from these calculations that all of these carboxylic acids are thermodynamically unstable with respect to decomposition to produce  $\text{CO}_2(\text{g})$ . A consideration of the parameters shows that this is driven by the entropy increase in the production of the gas, because the enthalpy of the reaction in all cases is endothermic.